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DIAGENESIS OF THE OLIGOCENE-MIOCENE BLUFF FORMATION OF THE CAYMAN ISLANDS – A PETROGRAPHIC AND HYDROGEOCHEMICAL APPROACH

by

KWOK-CHOI SAMUEL NG

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF GEOLOGY

EDMONTON, ALBERTA
SPRING, 1990

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled DIAGENESIS OF THE OLIGOCENE-MIOCENE BLUFF FORMATION OF THE CAYMAN ISLANDS - A PETROGRAPHIC AND HYDROGEOCHEMICAL APPROACH submitted by KWOK-CHOI SAMUEL NG in partial fulfilment of the requirements for the degree of DOCTOR OF PHILOSOPHY in GEOLOGY.

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Date December 18, 1989

ABSTRACT

Dolostones of the Oligocene-Miocene Bluff Formation on the Cayman Islands serve as host for major fresh water lenses (4-15 km^2) that are less than 20 m thick. Although the lenses are all developed under similar conditions, they show distinct temporal and spatial variations in hydrochemistry and stable isotopes. These variations result from variable extrinsic controls, mixing effects, water-rock interactions, and development of subenvironments due to jointing and karsting.

Detailed analysis of the ground water indicates that saturation states with respect to calcite and dolomite generally increase with increasing salinity. Carbonate cement distribution relating to present day hydrochemistry suggests a progressive decrease in fluid salinity from dolomite to calcite precipitation. This relationship is in agreement with $\delta^{18}O$ fractionation calculations between the carbonate minerals and ground water. The Lower Valley and East End lenses have similar salinity; however, most of the water in the Lower Valley lens is saturated with respect to calcite whereas that in East End lens is saturated with respect to calcite and dolomite. These characteristics can be correlated with the cementation patterns.

Based on evidence from aragonite dissolution, mineralogy, petrography and isotopic geochemistry, dolomitization of the Bluff Formation probably occurred at two separate times. The two phases of dolomitization replaced the metastable carbonates of the Oligocene Cayman Member and Miocene Pedro Castle Member shortly after the deposition of their respective sediments. Dolomitizing fluids of mixed marine-fresh water were delivered by gravitational flow, downward reflux, upward convection and tidal pumping.

The Bluff Formation has been affected by at least three phases of karstification. The extent of karsting is controlled by past sea levels, paleoclimatic regimes and antecedent tectonic fracturing.

Moldic cavities, caves and joints are commonly filled by numerous phases of dolomite and calcite cements, dolomitized caymanite, dolomitized skeletal grainstone, speleothemic calcite and terra rossa. The complex distribution of diagenetic fabrics is attributed to successive cycles of regressions and transgressions, variation in hydrochemistry, and activity of micro-organisms. A paragenetic sequence of cements suggesting increase in the degree of meteoric influence is clear or zoned dolomite, alternating calcite and dolomite, and clear or zoned sparry calcite.

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I wish to express my sincere thanks to Dr. Brian Jones for his friendship, guidance, advice, supervision and encouragement throughout the course of the research. This thesis has improved immensely by his careful and critical editing. Dr. Jones has also generously provided some of his geochemical data for my discussion sections.

During my three years with the Water Authority of the Cayman Islands, Mr. Richard Beswick, the Director, has been supportive of my research and has encouraged my participation in various conferences pertaining to the Caribbean region. I wish to express my gratitude for the experience of working with him and for his trust and confidence in me and my work.

The research was supported by the Government of the Cayman Islands and the Natural Science and Engineering Research Council of Canada (NSERC Grant A6090 to Jones). Financial support was provided by the Government of the Cayman Islands, the University of Alberta and the Government of the Province of Alberta. Grants were generously provided by the United Nations (UNDP and UNESCO), Caribbean Development Bank (CBWMP), the Government of the Cayman Islands, NSERC (Grant A6090 to Jones) and the University of Alberta for attending various conferences and workshops. To all these organizations, I offer my sincere thanks.

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I. INTRODUCTION

An effective prediction of reservoir porosity and permeability distribution in carbonate sequences requires an understanding of the diagenesis of the sediments and rocks themselves. Many studies on carbonate diagenesis are based solely on textural criteria (e.g. Land, 1967, 1983a; Bricker, 1971; Folk, 1974; Folk and Land, 1975; Bathurst, 1975; Longman, 1980; Kaldi and Gilman, 1982; Jones *et al.*, 1984). This is largely due to the fact that studies of ancient carbonate sequences rarely, if ever, allow the concomitant investigation of the pore solutions that were responsible for the post-depositional modifications of the rock fabrics. This is further complicated by the fact that the rocks were commonly subjected to later burial and/or tectonic events which mask the original diagenetic fabrics. As a result, it is commonly difficult to ascertain the paleogeography and the paleohydrogeological regime which controlled the chemistry of the diagenetic fluids.

Geochemical equilibrium models allow most geochemical interactions between pore solutions and sediments/rocks to be evaluated by thermodynamic calculation of the dissolved species in the pore fluids (e.g. Ball *et al.*, 1979; Harvie and Weare, 1980; Parkhurst *et al.*, 1980). The accuracy of these calculations, however, relies on the correct use of thermodynamic constants, the accurate analysis of all the dissolved species, and the physico-chemical parameters. Moreover, too little attention has been devoted to petrographic studies to verify the precipitation and dissolution phenomenon indicated by the chemical modelling.

Recent studies in hydrology and sedimentary geology have shown that stable isotope analyses can contribute significantly to deciphering the origin of ground water composition and sedimentological conditions (e.g. Fritz and Fontes, 1980a; Anderson and Arthur, 1983; Land, 1983b; Longstaffe, 1987). There is, however, little coordinated effort to investigate the relationship between the diagenetic carbonate minerals and the host rocks to that of the associated ground waters. Furthermore, it is commonly difficult to sample and assess the pore fluids that were responsible for the diagenetic alteration.

In this connection, it is apparent that the study of diagenesis should be interdisciplinary, encompassing hydrogeology, aqueous and stable isotope geochemistry and detailed petrography. This approach to diagenetic studies should shed some light on the understanding of diagenetic phenomena operative in ancient carbonate sequences.

A. OBJECTIVES

The Tertiary Bluff Formation of the Cayman Islands (Fig. I.1) is ideal for studying carbonate diagenesis because (1) it is relatively young in age (Oligocene-Miocene), (2) it has not been subjected to intense tectonic activity or deep burial since deposition, (3) the paleohydrogeological regime can be inferred with confidence, (4) the source of pore fluids can be determined, and (5) the present day water-rock interactions can be assessed.

In this connection, it should be possible to unravel the diagenetic history of the Bluff Formation by approaching the detailed diagenetic studies petrographically and geochemically. The objectives of this study are (1) to examine the present day hydrogeological and hydrochemical regime in the aquifers, (2) to establish the relationship between the present day hydrochemical characteristics in the aquifers and cementation patterns in the rocks, (3) to assess the salinity of the fluids from which the minerals were precipitated using isotope geochemistry, and (4) to use the above information to decipher the diagenetic history of the Bluff Formation; in particular, the causes of pervasive dolomitization and karstification, an [illegible] tions leading to post-dolomitization diagenesis.

B. METHOD OF STUDY

This study deals with the Tertiary Bluff Formation on Grand Cayman and Cayman Brac because (1) it contains the major fresh ground water lens; consequently, ground water data collection for this study can be incorporated in the water resources investigation, (2) it encompasses the complete spectrum of hydrochemical zones, (3) ground water in the Bluff Formation is less likely to mix with that from the Pleistocene Ironshore Formation because

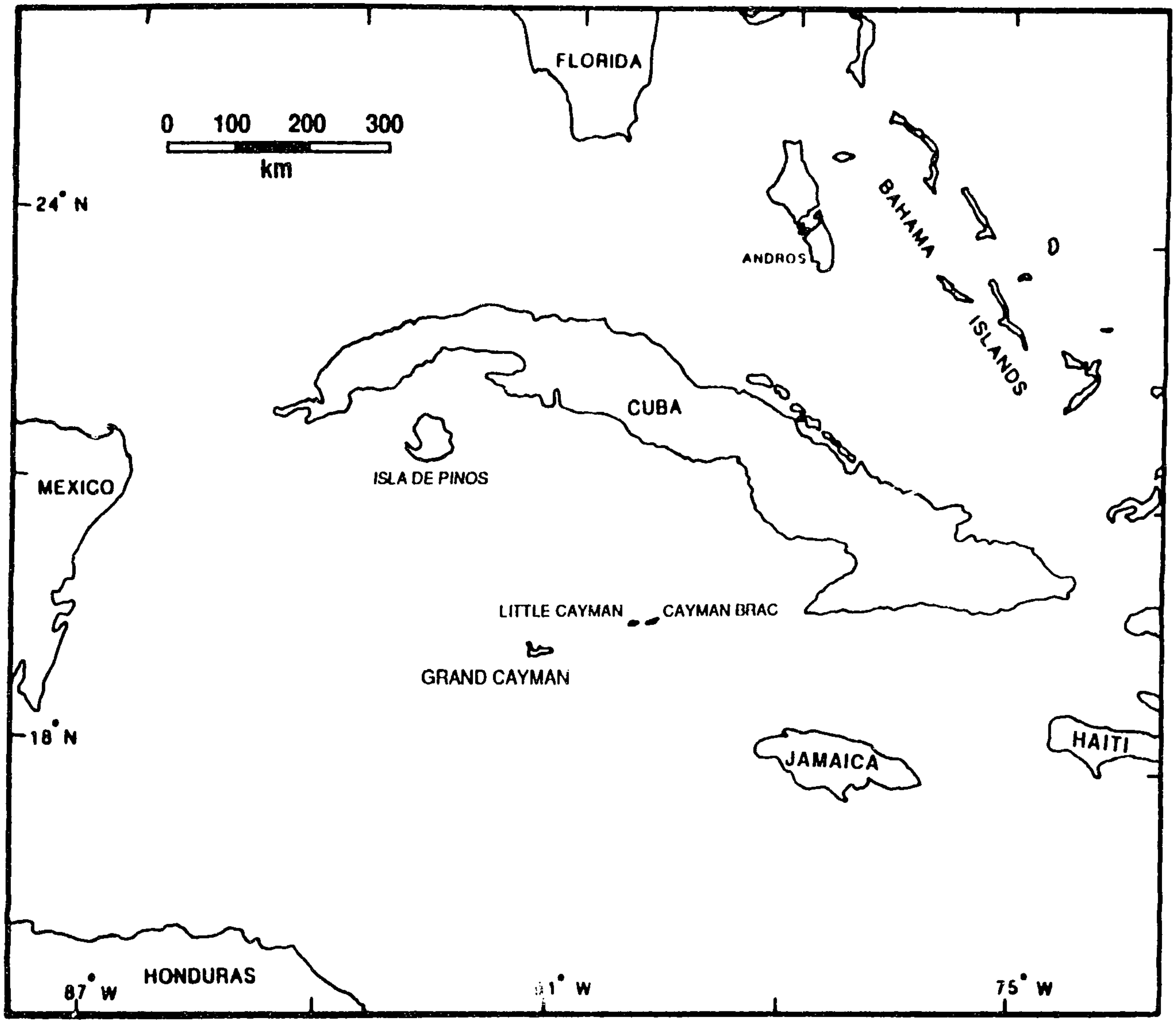


Fig. I.1 Geographic location of the Cayman Islands in the Caribbean region (modified after the National Geographic Map of the Caribbean, 1975).

of the prevalent flow path, and (4) it contains both calcite and dolomite cements, differing from the Ironshore Formation which contains only calcite and aragonite cements (Jones *et al.*, 1984).

Little Cayman, the smallest of the three Cayman Islands (Fig. I.1), is not included in this study because no ground water study has been conducted on that island. Nevertheless, the similarity in geological setting and physiography to that of Grand Cayman suggests that the ground water behaviour may be similar to that on Grand Cayman.

The present day hydrogeological regime was identified by employing geological field studies, collection of hydrological data, monitoring of observation boreholes and piezometers and interpretation of aerial photographs. The collection of hydrological data and sampling of waters for chemical analyses were carried out over a three year period from June 1985 to July 1988. The data and samples were collected on a weekly to biweekly schedule. This hydrogeological information, together with the physiographical and geological characteristics, is used to outline the paleohydrogeological setting which provides the fundamental framework on which the project is based.

Water samples were collected from different hydrochemical strata ranging from unsaturated water, saturated fresh water, brackish water and saline water zone, as well as rain, sea and pond water. Some 350 water samples were analysed for the major cations and anions. The major ions generally included Cl^-, SO_4^{2-}, HCO_3^-/CO_3^{2-}, Na^+, K^+, Mg^{2+}, and Ca^{2+}. Chemical analyses were carried out at the Water Chemistry Laboratory of the Water Authority of the Cayman Islands. Charge balance of ±5% was used as the limits for acceptable results. All analyses were performed within 24 hours of collection and in accordance with the Standard Methods for the Examination of Water and Wastewater (Standard Methods, 1981). Thermodynamic equilibrium calculation of the aqueous species was carried out using PHREEQE (Parkhurst *et al.*, 1980; Crowe and Longstaffe, 1987) with particular emphasis on the saturation indices of calcite and dolomite.

Fifty-seven water samples were analysed for $\delta^{18}O$ and $\delta^{2}H$ at the Isotope Laboratory of the University of Waterloo. These water samples were selected from the samples collected for chemical analyses, and included waters from all hydrological and hydochemical zones. Stable oxygen isotopes of carbonate cements and host rocks determined from previous studies (Pleydell, 1987; Smith, 1987; Jones *et al.*, 1989) were incorporated in the present study. These data permitted the calculation of equilibrium fractionation effects between the carbonates and the ground water.

Rock samples, mostly from cores or cuttings obtained from well drilling, were collected from various locations and depths on Grand Cayman and Cayman Brac. These, together with the samples obtained from outcrops, provide both vertical and lateral controls on the distribution of cement types and patterns in different hydrochemical zones. The diagenetic signatures present in the rocks are documented in detail using petrographic microscopy supplemented by scanning electron microscopy. Some 160 thin sections were prepared for microscopic examination. The thin sections were impregnated with blue epoxy to enhance the identification of pores and stained with Alizarin Red-S to facilitate the differentiation of calcite and dolomite. Scanning electron microscopy was used on seven rock samples.

Porosity and permeability analyses were performed on 18 pieces of rock core obtained during ground water exploratory studies on the East End and Lower Valley lens of Grand Cayman. The analyses were carried out at the Department of Mineral Engineering of the University of Alberta.

The integration of diagenetic fabrics with the knowledge from hydrogeological, hydrochemistry, and stable isotopes permits the detailed investigation of the water-rock reactions in the aquifer system of the Bluff Formation. Of particular importance is the late-phase cements that are in contact with the present day pore solutions. This connection forms the backbone in the interpretation of the diagenetic history of the Bluff Formation.

II. GROUND WATER FLOW REGIME

The occurrence of fresh ground water on the Cayman Islands is influenced by the physiography, geology, soil and vegetation cover, hydrology, tectonic setting, and the paleohydrogeological regime.

A. GEOGRAPHIC LOCATION

The Cayman Islands are comprised of three small islands which are situated in the western part of the Caribbean (Fig. I.1). The islands lie between 19° 15' and 19° 45' North and 79° 44' and 81° 27' West. The largest island, Grand Cayman, is located 280 km west-north-west of Jamaica and 240 km south of Isla de Pinos of Cuba. The two smaller islands, Little Cayman and Cayman Brac, are approximately 120 km and 140 km, respectively, northeast of George Town, Grand Cayman.

B. GEOLOGICAL FRAMEWORK

The fact that the Cayman Islands are sited on the Cayman Ridge (Uchupi, 1975; Rigby and Roberts, 1976; MacDonald and Holcombe, 1978) suggests that tectonism should have played an important role in the formation of the islands. The marked difference in elevation among the islands attests to the possibility of independent vertical movements of each island prior to late Pleistocene (Stoddart, 1980; Woodroffe, 1988). Furthermore, uniformity of the joint sets and intense jointing (Rigby and Roberts, 1976) present in the Bluff Formation of Grand Cayman and Cayman Brac are probably related to past tectonism of the Cayman Trench.

The Cayman Islands are formed of the Bluff and Ironshore formations (Figs. II.1, 2; Matley, 1926; Mather, 1972; Brunt *et al.*, 1973; Rigby and Roberts, 1976; Jones *et al.*, 1984; Jones and Hunter, 1989). From the point of view of ground water resources , the Bluff Formation is of particular importance because it contains the major fresh water

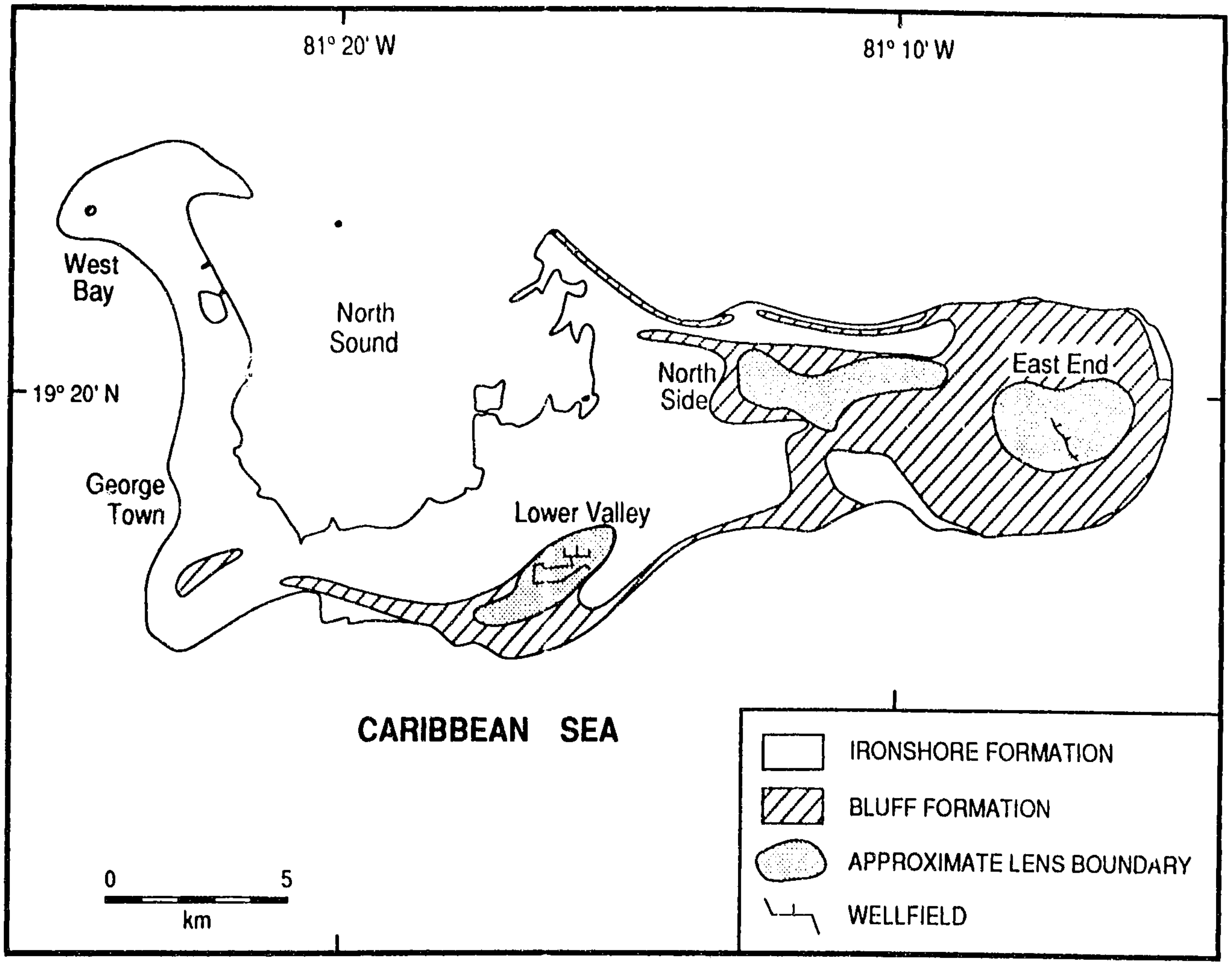


Fig. II.1 Hydrogeological setting of the three major fresh water lenses on Grand Cayman. Geological sketch map modified from Brunt *et al.* (1973) by I. Hunter (1989, unpublished).

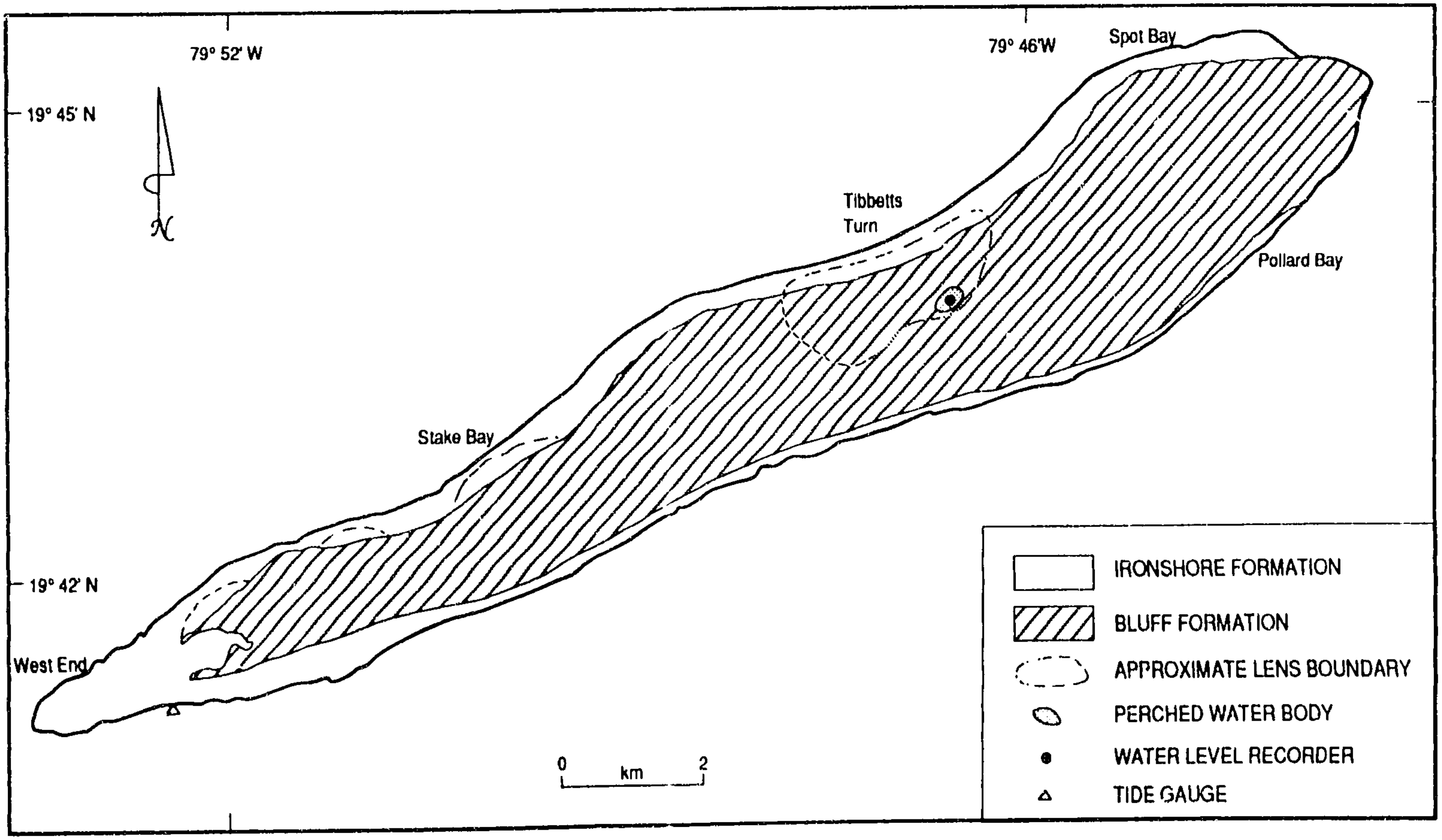


Fig. II.2 Hydrogeological setting of the fresh ground water occurrences on Cayman Brac. Geological sketch map modified from Brunt *et al.*, 1973.

resources (Figs. II.1, 2; Mather, 1972). Some small fresh water bodies occur in the Ironshore Formation (Mather, 1972).

Paleontological data suggest that the Bluff Formation is Oligocene-Miocene in age (Matley, 1926; Vaughan, 1926; Richards, 1955; Emery and Milliman, 1980; Jones and Hunter, 1989). The lithology is typically a dense, white to light tan, finely crystalline dolostone. Molluscs and coral fragments are common, but are preferentially leached out and preserved as molds (Folk *et al.*, 1973; Jones *et al.*, 1984; Pleydell and Jones, 1988; Jones and Hunter, 1989). The dolostone is massive but intensely jointed. The Pleistocene Ironshore Formation, which unconformably overlies the Bluff Formation, is predominantly formed of poorly consolidated limestone (Brunt *et al.*, 1973; Hunter and Jones, 1989).

Jones and Hunter (1989) recognized a major disconformity which divides the Bluff Formation into the lower Cayman Member and the upper Pedro Castle Member. On the basis of coral assemblages, Jones and Hunter (1989) suggested that the upper part of the Cayman Member is of early late Oligocene age whereas the Pedro Castle is of middle Miocene age. The presence of the disconformity, together with the sedimentological and diagenetic evidence, suggests that the Cayman Member was subaerially exposed and subjected to karst development prior to deposition of the Pedro Castle Member (Jones and Hunter, 1989).

C. PHYSIOGRAPHY

Grand Cayman has a land surface area of about 196 km^2. It is 35 km long from east to west and has an average width of 8 km. The eastern portion of the island is relatively high, with elevation up to 17 m; the remainder of the island is generally less than 4 m above mean sea level.

Little Cayman and Cayman Brac are both elongated in a northeast to southwest orientation with a land surface area of about 29 and 39 km^2 respectively. Cayman Brac is characterized by high cliffs with an elevation up to 50 m at the eastern end of the island. By comparison, Little Cayman is low lying with the highest elevation at about 12 m.

The three islands have a rugged karst terrain with underlying solution caverns (Doran, 1954; Folk *et al.*, 1973; Rigby and Roberts, 1976; Bugg and Lloyd, 1976; Jones *et al.*, 1984; Jones and Smith, 1988). Karst terrains are well developed on the Bluff Formation (Doran, 1954; Folk *et al.*, 1973; Rigby and Roberts, 1976; Bugg and Lloyd, 1976; Jones *et al.*, 1984; Jones and Smith, 1988; Squair, 1988); flat, featureless topography with calcrete crusts is common on the Ironshore Formation (Brunt *et al.*, 1973; Rigby and Roberts, 1976).

The high permeability of the rock formations precludes the development of surface water streams. However, several large ponds are present on the periphery of the islands. These ponds may have been formed by beach-ridge damming associated with fluctuation in sea level in late Pleistocene times (Doran, 1954; Rigby and Roberts, 1976). The salinity of the pond waters ranges from brackish to saline.

D. SOIL AND VEGETATION

The soils of the Cayman Islands vary in colour, structure and depth. Where present, the soils are typically thin and patchy, although deep soil pockets up to 3 m deep occur locally (Baker, 1974; Bugg and Lloyd, 1976; Squair, 1988). Different soils have developed on the two rock formations. Reddish soils of bauxitic nature are developed on the Bluff formation whereas dark to dark brown vertisolic soils occur above the Ironshore Formation (Ahmad and Jones, 1969; Baker, 1974).

Although the soil development on the islands is generally patchy, it supports a moderately dense vegetation. According to the Beard system, the vegetation of the Cayman Islands falls into the dry evergreen, the seasonal swamp, and the swamp series (Proctor, 1984). Approximately 50% of the land surface area in Grand Cayman is covered by brackish water mangrove (red, black and white) swamp and fresh water (buttonwood) swamp (Mather, 1972; Bugg and Lloyd, 1976; Proctor, 1984).

E. HYDROGEOLOGICAL MONITORING PROGRAMME

A comprehensive monitoring programme was initiated in mid-1985 to collect all relevant hydrological and hydrogeological data. In Lower Valley and East End (Fig. II.1), where government well fields are in operation, hydrogeological networks comprise observation wells, piezometers, water level recorders, and a tide gauge (Figs. II.3, 4). The lens at Tibbetts Turn on Cayman Brac is monitored by observation wells, a water level recorder and a tide gauge (Fig. II.2). Most of the hydro-meteorological data in Grand Cayman are provided by two meteorological stations, which are supplemented by an island wide network of primary rain gauge stations (Fig. II.5).

F. HYDROLOGICAL REGIME

Water evaporating from the surrounding ocean is carried landward by prevailing easterly wind during most of the year. Once the water vapour condenses, the rain falls on the land surface. A portion of the rainfall then returns back to the atmosphere through evapotranspiration and the remaining portion is lost by overland runoff and submarine discharge. This circulation of water between ocean, atmosphere, and land completes the hydrologic cycle (Fig. II.6). In areas where the geological conditions favour storage and there is net recharge, accumulation of fresh water occurs.

Rainfall

The average annual rainfall registered at the Owen Roberts International Airport, Grand Cayman between 1920-1965 was 1740 mm (Beswick, 1980). When this period was extended to 1987, the average annual rainfall dropped to 1513 mm, demonstrating a declining trend in the rainfall on the island. Precipitation is primarily convectional rain with

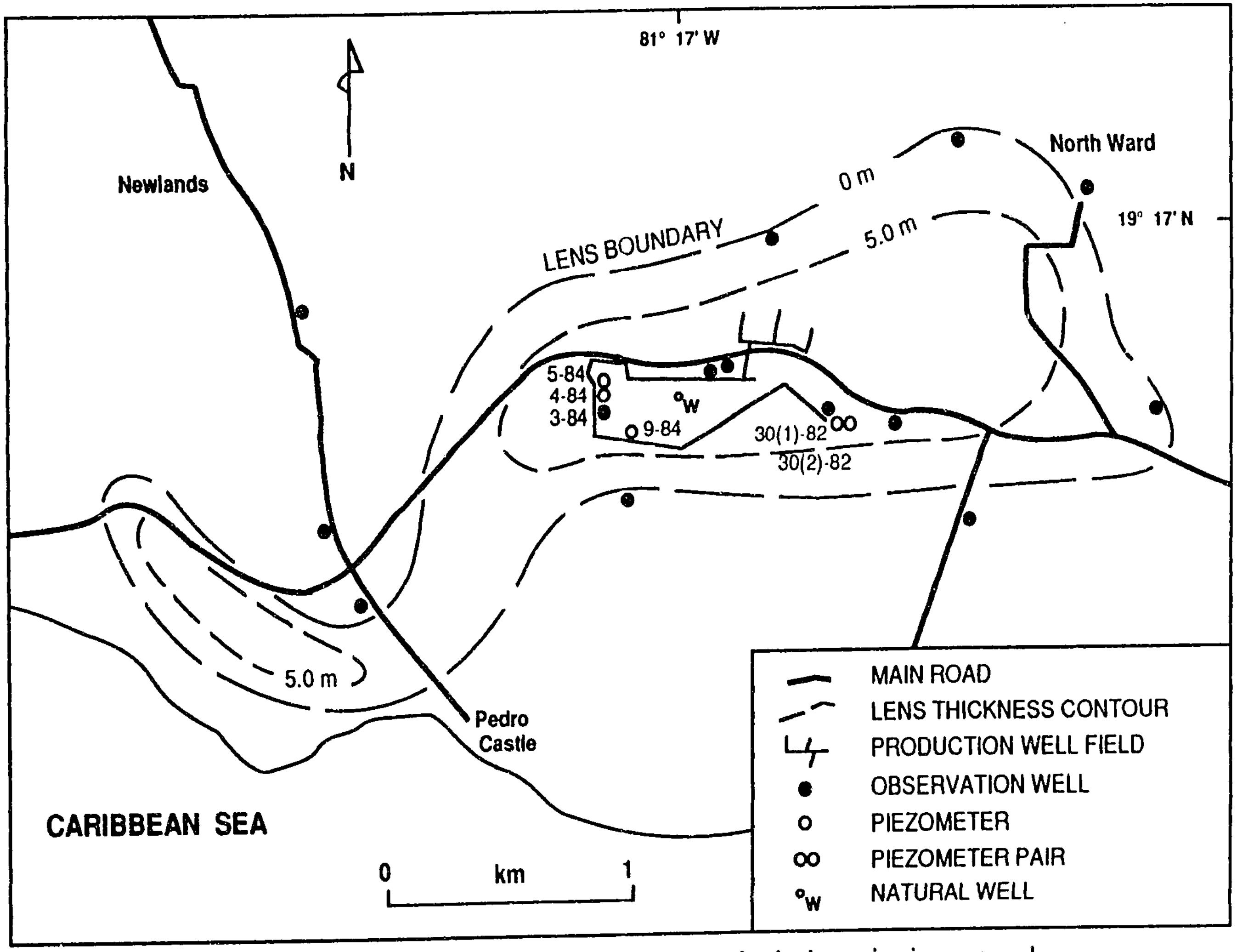


Fig. II.3 Lower Valley lens configuration and hydrogeological monitoring network. Fresh water lens boundary defines by 600 ppm chloride.

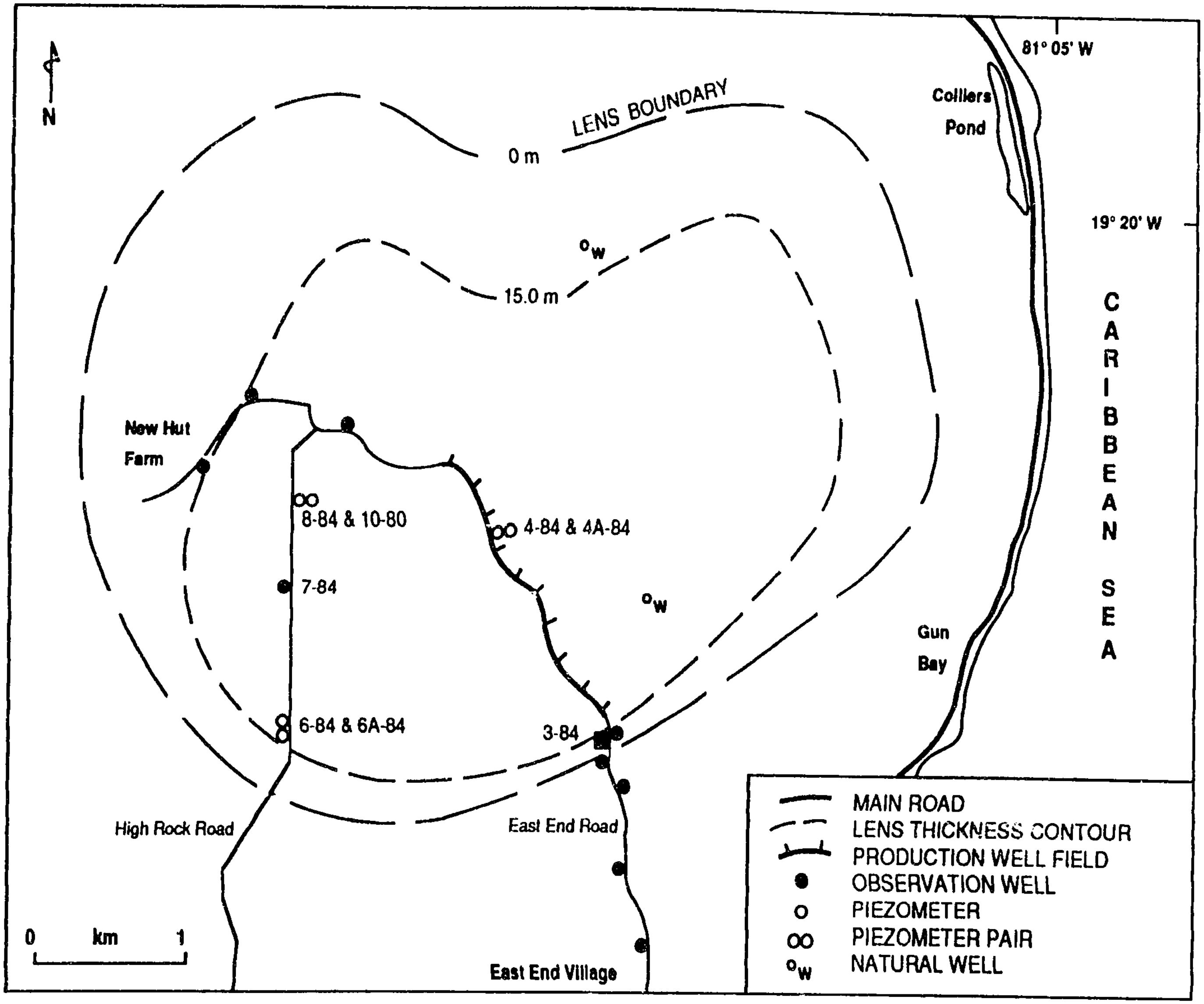


Fig. II.4 East End lens configuration and hydrogeological monitoring network. Fresh water lens boundary defines by 600 ppm chloride.

■ 3-84 denotes the well location where continuous rock coring (12 m) was made.

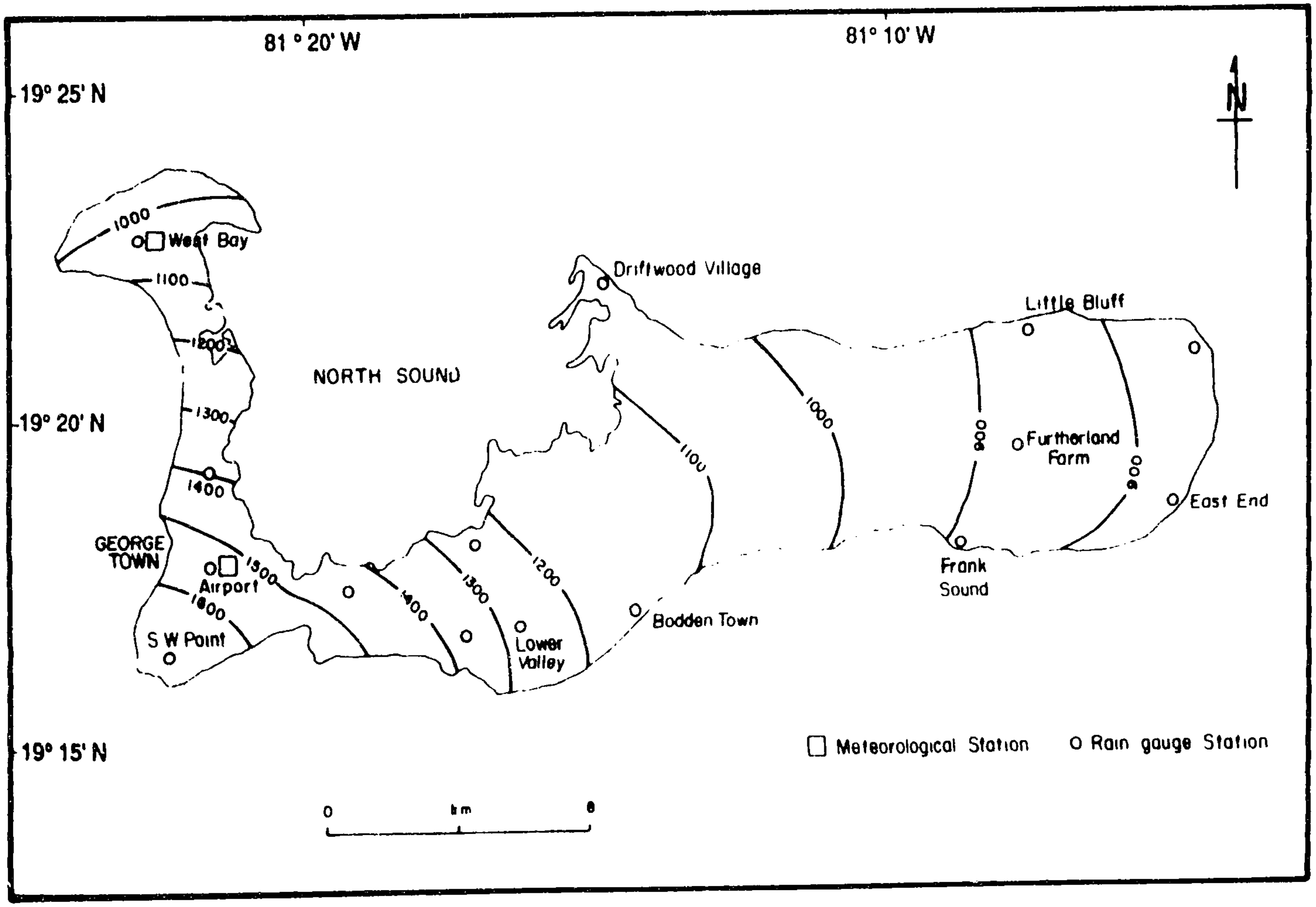


Fig. II.5 Sketch map of Grand Cayman showing the hydro-meteorological network and isohyets (mm) in 1987. Rainfall records courtesy of the Water Authority, Civil Aviation Authority, and Mosquito Research and Control Unit of Grand Cayman.

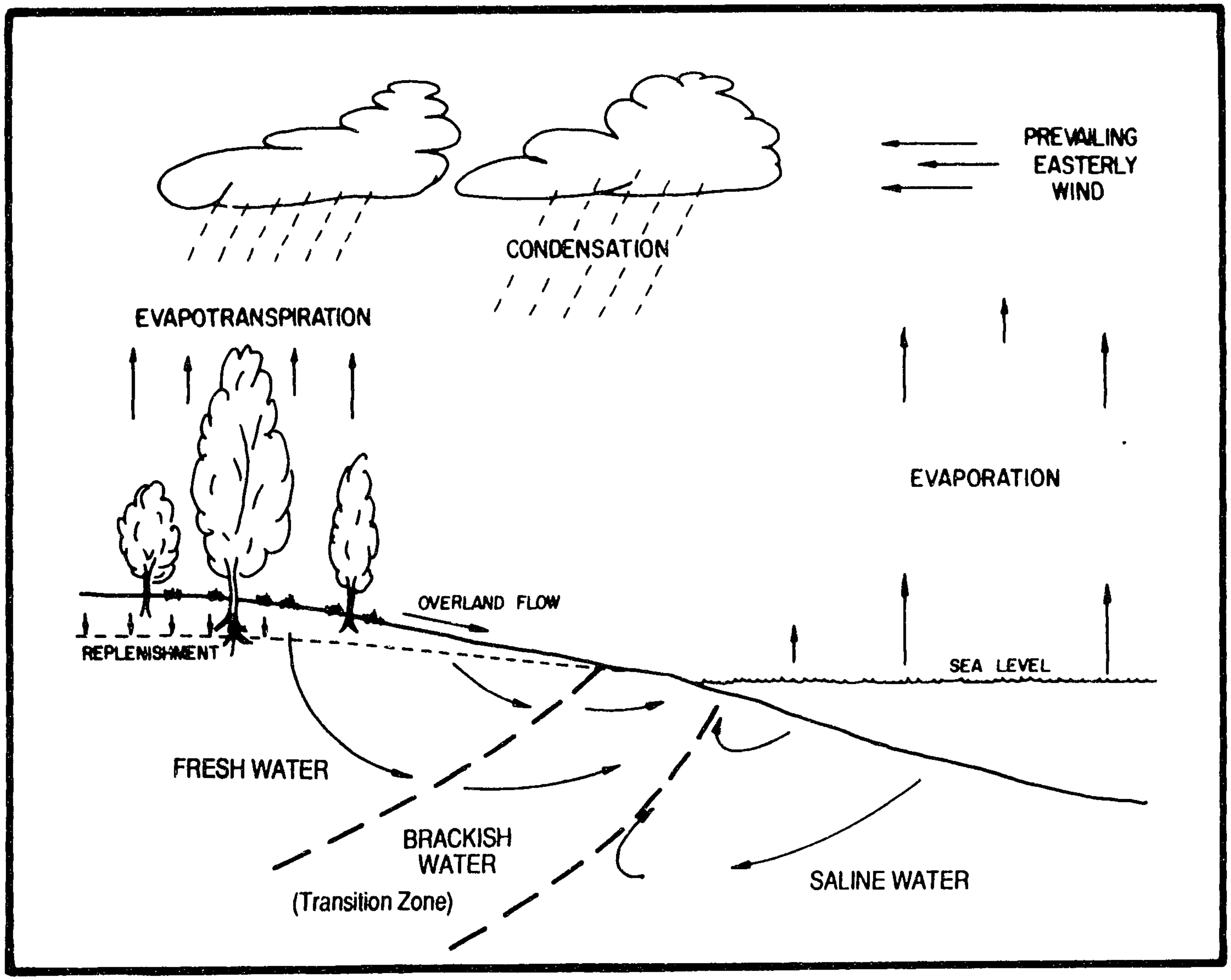


Fig. II.6 Schematic representation of the hydrologic cycle and ground water flow lines under a seaward hydraulic gradient.

minimal orographic effects due to the flatness of Grand Cayman. Rainfall is, however, irregularly distributed over Grand Cayman with the eastern part of the island generally having the driest regime (Fig. II.5).

On a yearly basis, rainfall varies widely (Fig. II.7A). The rainfall pattern is attributed to the prevailing easterly trade wind during the wet summer months from May to October (Fig. II.7B); however, the monthly rainfall varies widely from year to year (Fig. II.7B). Summer hurricanes, characterized by high intensity heavy rainfall, are common in the Caribbean region. During the winter months, rainfall is occasionally brought in by northwesterly winds.

On Cayman Brac, the rainfall distribution is controlled by the prevailing easterly winds and the high land (locally known as 'Bluff') at the centre of the island. These factors are probably responsible for the highly irregular variation of the annual rainfall recorded at Stake Bay, on the north coast of Cayman Brac. Annual rainfall ranges from a high of 1472 mm in 1979 to a record low of 587 mm in 1986 over the last 10 years.

Infiltration and Recharge

Recharge is one of the most important hydrological parameters in terms both of ground water resource evaluation and diagenetic studies. The fresh ground waters are recharged entirely by infiltration of precipitation not lost to evapotranspiration or surface runoff. A study of the annual cumulative departure from the mean from 1967 to 1987 (Fig. II.7A) shows that there is a considerable fluctuation in rainfall surplus or deficiency, and hence, in the quantity of recharge from year to year. Observation of ground water levels generally yields little information about the recharge in the aquifers because small individual recharge events are masked by tidal effects, and because the aquifer, on the whole, is too transmissive to experience changes on the water table.

The patchy soil cover together with the intense jointing and karsting suggest that the Bluff Formation should have a high infiltration capacity. This phenomenon was indicated

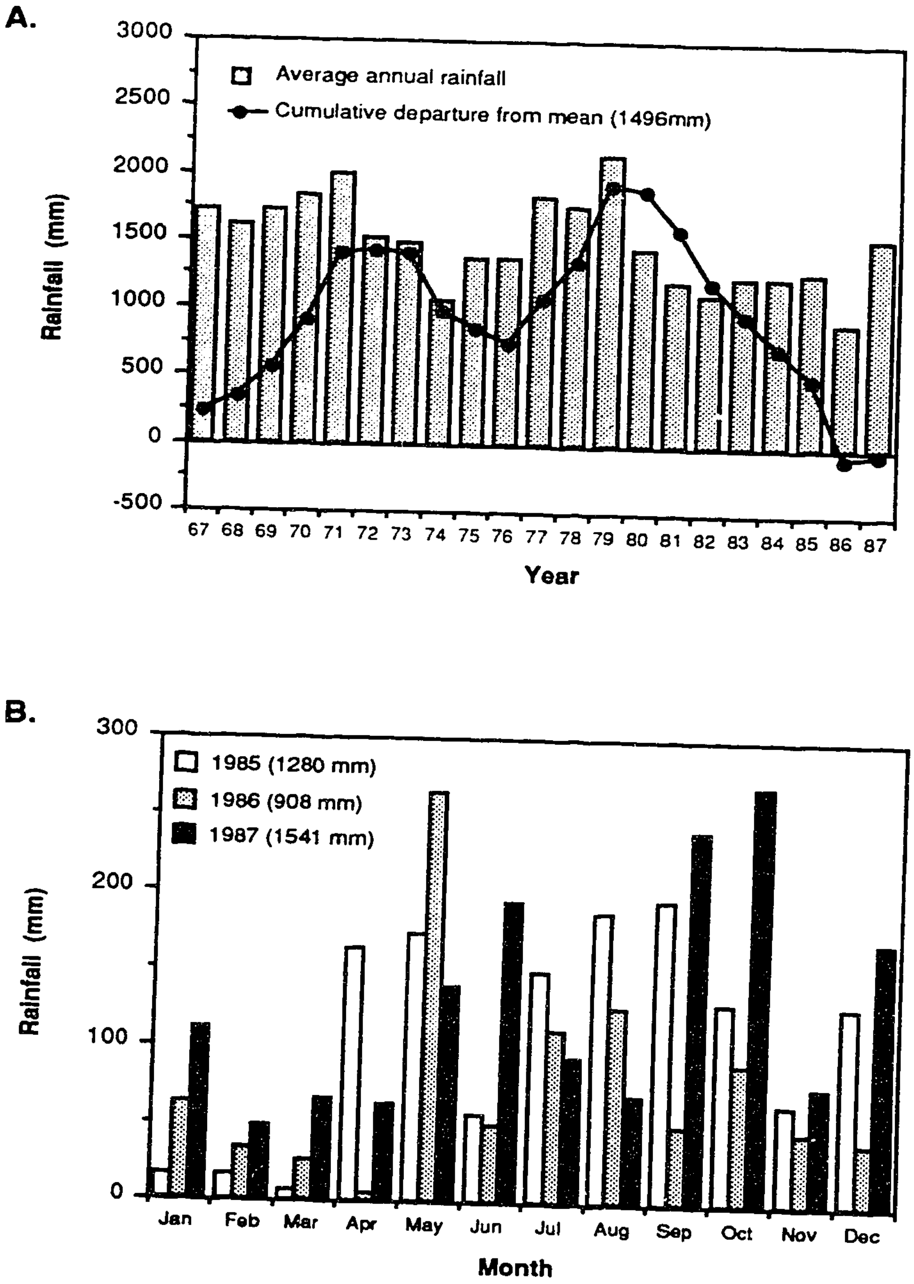


Fig. II.7A Bar chart showing the annual rainfall of Grand Cayman from 1967-1987 and the cumulative departure from the 20 years average.

II.7B Bar chart showing monthly rainfall of Grand Cayman 1985-1987. Note the large variations from on monthly and yearly basis. All rainfall data are from U.S. meteorological station at the Owen Roberts International Airport, Grand Cayman.

by the hydrograph of well 7-84 at East End (Figs. II.4, 8). Fox and Rushton (1976) suggested that rapid recharge takes place through the fissure system in the Lincolnshire Limestone, England. Rapid recharge through sinkholes and swallow holes were also noted by Thrailkill (1968) and Rushton and Redshaw (1979) respectively. Rapid recharge, in response to each individual rainfall event, probably occurs when rain water infiltrates through the fissures or caverns to form an ephemeral ground water mound which dissipates quickly but at a decreasing rate (Fig. II.8). This rapid decline of the water table demonstrates the efficient transmission of the ground water in the aquifer. The fact that the water table does not respond to ocean tides suggests that some fissures and solution caverns probably create semi-confined conditions in the unconfined aquifer.

In deeper wells (greater than 2 m below the water table) where the water table fluctuates in response to ocean tides, rainfalls of low intensity are commonly masked by the ground water tides and are difficult to interpret from the water table hydrographs. Measurable effects on the water table occur when the rainfall intensity exceeds 50 mm per day. Shallower wells, which are less influenced by ocean tides, require an intensity of about 25 mm per day. Similar rainfall-water table relationship was recorded by Viswanathan (1984) for the Tomago Sandbeds, in Newcastle, Australia.

Rapid improvement of water quality in the wells also indicates recharge. Borehole salinity profiles (Fig. II.9) measured before and immediately after a rain storm (1.5 hours apart) show significant drops in electrical conductivity (salinity) throughout the whole water column. This suggests that the rain water probably causes dilution of water salinity in the shallow aquifer during rapid recharge. Rushton (1980) and Ravenscroft (1984) argued that the salinity distribution of water in open boreholes may be different from that present in the aquifer due to non-steady state conditions. However, using depth specific piezometers to monitor changes of water quality with time shows that this phenomenon appears to be of minor impact in the aquifers of the Cayman Islands. The sharp decrease

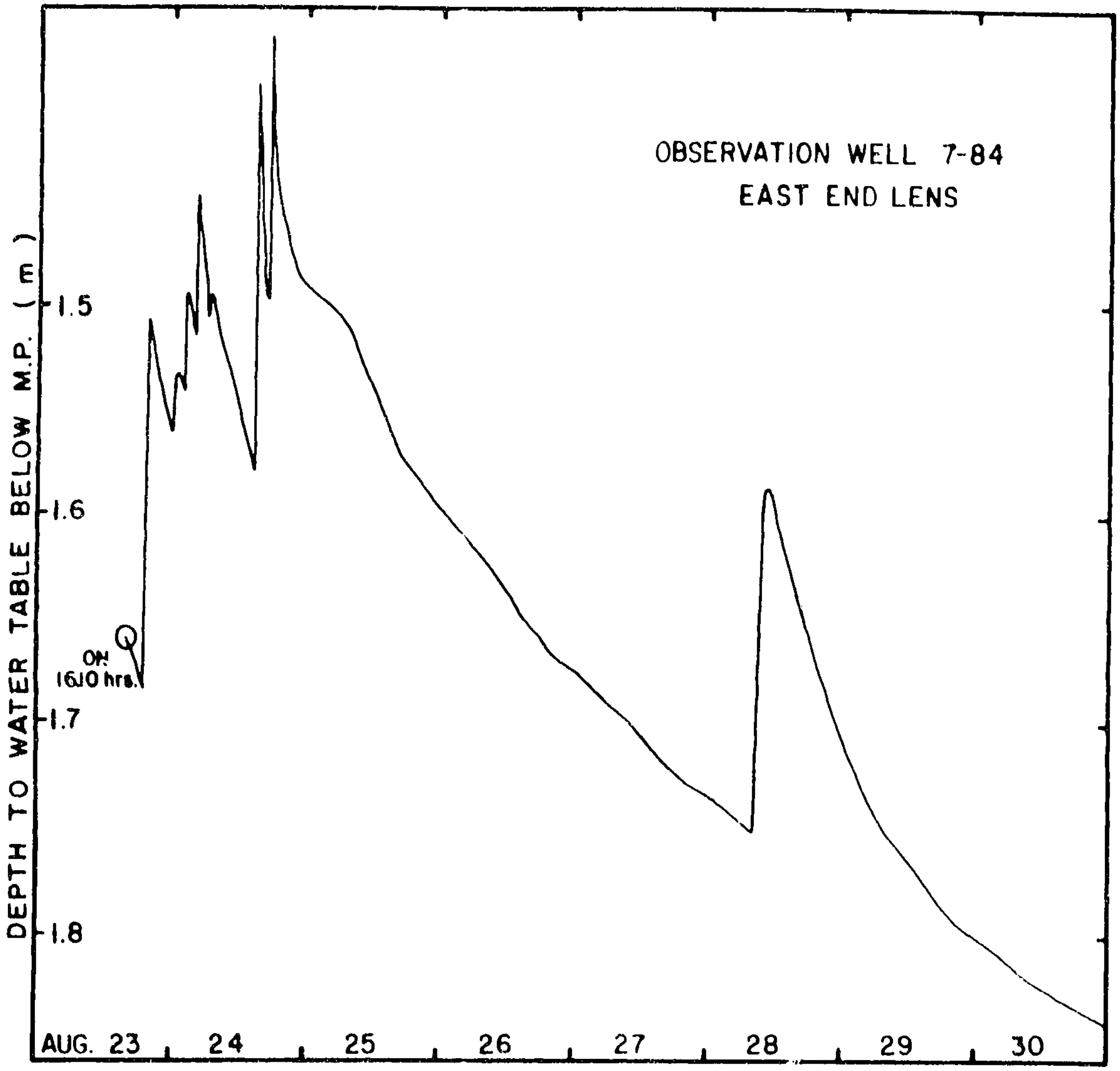


Fig. II.8 Water table hydrograph showing rapid infiltration and discharge of rain water in response to rainfall events (well location shown on Fig. II.4). M.P. refers to measuring point which is top of the well casing.

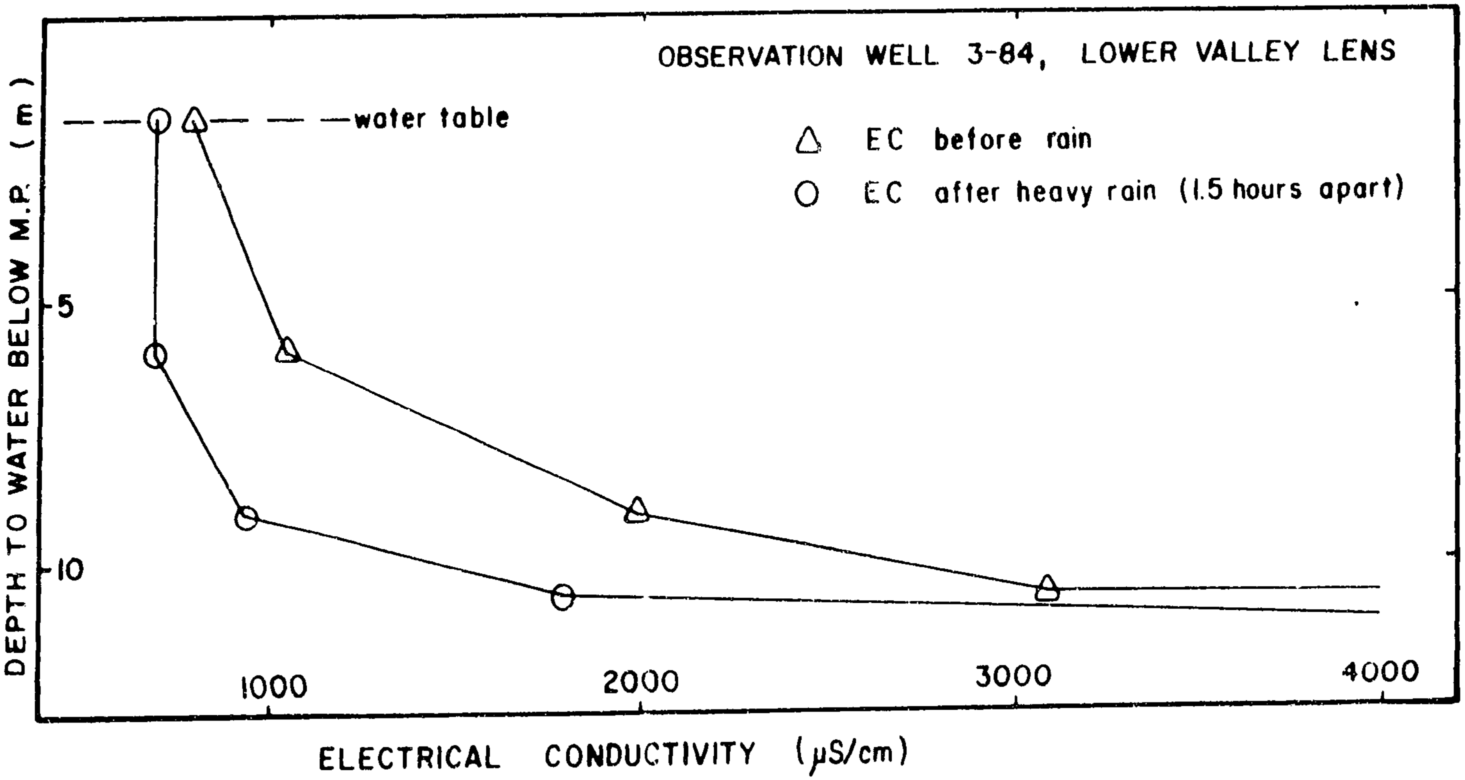


Fig. II.9 Borehole salinity profiles showing significant improvement of water quality after a rainstorm (well location shown on Fig. II.3). M.P. refers to measuring point which is top of the well casing, EC is the electrical conductivity.

in salinity at the end of May, 1986 (Fig. II.10) was in response to a storm that lasted for 12 days with a total rainfall of 245.5 mm.

Wells located in local topographic depressions generally show a greater improvement in the water quality after rainfall (Ng, 1985). This suggests that the depressions probably act as focal points for ground water recharge in a manner similar to that described by Meyboom (1966) and Lissey (1971) in hummocky terrains.

Stringfield and LeGrand (1969) noted that some large lakes occupying solution basins in Tallahassee, Florida are drained from time to time. Sinkholes which are partially clogged by washed-in debris of soils and weathered materials may also drain periodically. In one closely monitored sinkhole (10 m by 10 m) in Lower Valley on Grand Cayman, most of the water trapped in the sinkhole drains away after a period of very heavy rain. In such a case, the recharge water is a mixture of rain and rain water modified by evaporation.

Evapotranspiration

A significant part of the precipitation generally returns to the atmosphere through evapotranspiration which includes the sum of water loss by both evaporation and transpiration processes (Gray *et al.*, 1970). On the Cayman Islands, where the temperature averages about 30°C during the wet summer season and 25°C in the dry winter season, evapotranspiration is an active process. Furthermore, in recent years (1970-1986) there has been a gradual rise in the average annual temperature (Fig. II.11A) and an increasing number of clear days (Fig. II.11B). In the 20 years prior to 1971, the average annual temperature was 26.2°C; in the 20 year interval prior to 1986, the average annual temperature was 26.8°C. Thus, the rise in average annual temperature, coupled with the decrease in cloudiness, suggests an increase in evapotranspiration loss over the last 20 years. During this period, the average annual rainfall has declined. The increased rate of evapotranspiration and the corresponding decrease in rainfall suggests that the net recharge

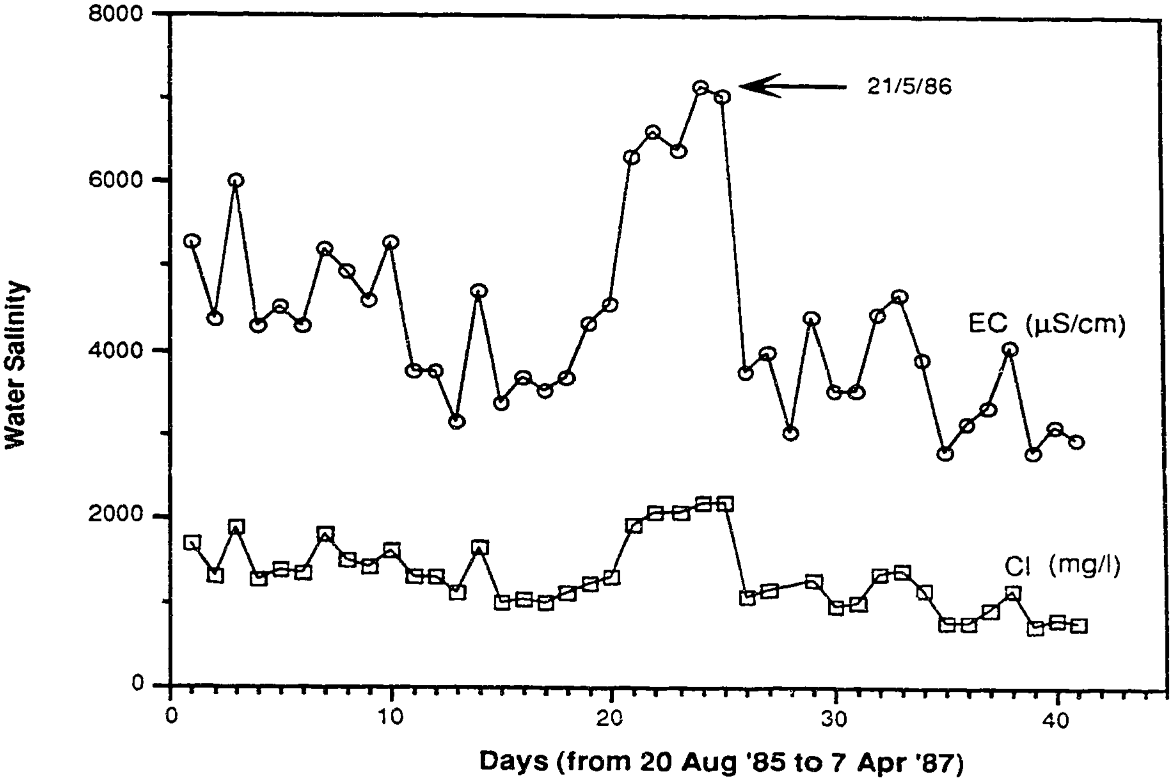
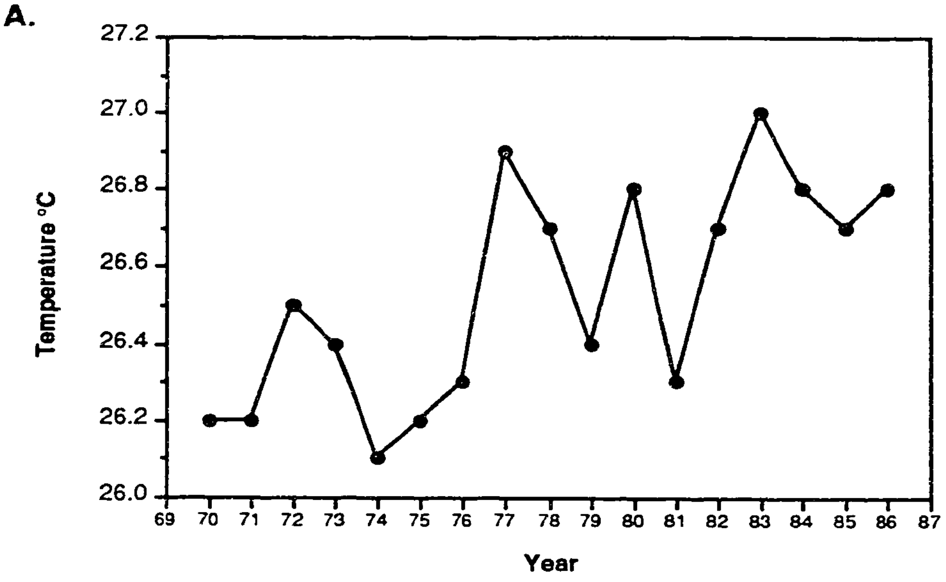


Fig. II.10 Temporal variation of water salinity in the Lower Valley Lens recorded by piezometer 4-84LV installed in the lightly brackish water zone (piezometer location shown on Fig. II.3). Note rapid improvement of water quality after a prolonged heavy rainstorm at the end of May 1986.



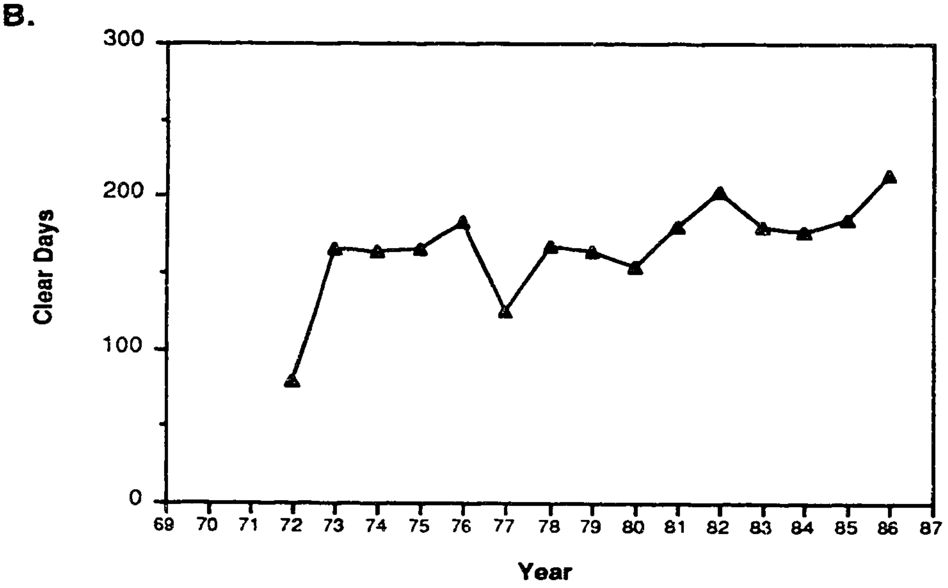


Fig. II.11A Average annual temperature on Grand Cayman from 1970-1986. Data from U.S. meteorological station at the Owen Roberts International Airport, Grand Cayman.

II.11B Number of clear days per annum on Grand Cayman during the period from 1972-1986. Data from U.S. meteorological station.

to the fresh water lens has been gradually reduced, and hence, the size of the fresh water lenses probably has diminished.

Processes operational on the Cayman Islands include (1) evaporation from open bodies of water in sinkholes which may or may not be connected to the ground water system, (2) evaporation from large open bodies of water in mangrove swamps and large ponds, (3) evaporation from soil moisture, (4) evaporation of precipitation intercepted by vegetation cover, (5) direct evaporation of ground water where the water table is close to the land surface as in local depressions, (6) transpiration from soil by plants, and (7) direct withdrawals from the ground water by phreatophytes where plant roots reach the water table.

Besides accounting for the major loss of precipitation that falls on the land surface, evapotranspiration also has a significant impact on the chemical quality of the ground water. The fluctuation of water salinity with time, recorded by piezometer 4-84LV (Fig. II.10), is caused by the interplay between the rain water recharge and evapotranspiration. Furthermore, the various processes outlined above affect both the local and regional ground water flow regime. Evaporation of water from the mangrove swamps acts as a natural pumping mechanism which creates a seaward hydraulic gradient for the regional flow regime.

A correct estimate of the evapotranspiration loss is commonly difficult to determine because of insufficient data (Gray *et al.*, 1970; Chidley and Lloyd, 1977a). This is further compounded by the effect of various forms of recharge phenomena. Vacher and Ayers (1980) proposed the utility of chloride content, which is concentrated by evapotranspiration, as a tracer for such an assessment. Following the method of Vacher and Ayers (1980), evaporative losses of about 75-85% and 90% are estimated for Grand Cayman and Cayman Brac respectively. These estimates are comparable to those suggested for other small tropical to subtropical oceanic islands (Thomson and Foster, 1986; Cant and Weech, 1986). The relatively high loss on Cayman Brac probably indicates evaporation of infiltrating rain water in the thick (up to 50 m) unsaturated zone.

Runoff and Discharge

Overland runoff accounts for a minor portion of the outflow, as indicated by the absence of surface streams. Ponding occurs only locally, on limestone and dolostone surfaces, after prolonged heavy rain. Under normal conditions, a seaward hydraulic gradient exists in the aquifer (Fig. II.6) and fresh water drains into the sea. The submarine discharge is particularly enhanced due to the solubility of the carbonate rocks.

G. AQUIFER CHARACTERISTICS

Aquifer porosity of the Bluff Formation, which is primarily secondary, is in the form of open joints, fissures, solution channels, and caverns (Fig. II.12). Most of the primary intergranular porosity was obliterated through pervasive volume to volume dolomite replacement with preservation of allochem textures (Jones *et al.*, 1984; Pleydell, 1987; Jones and Hunter, 1989). As a result, matrix porosity is low. However, on Cayman Brac there are some beds, such as the rubble facies (Jones, 1989a), with retention of high original porosity. In the East End lens, bailing of one well volume of water from a piezometer caused a drop of 7.5 m in the water level (i.e. the well was dry) and took about 6 months to recover. This indicates that certain parts of the dolostone aquifer are essentially impermeable.

Skeletal Moldic Porosity

Secondary intergranular and intragranular pores, formed by the selective leaching of aragonitic molluscs and coral fragments, were commonly filled or partly filled by multi-phase calcite and dolomite cements, flowstone, and internal sediments (Jones *et al.*, 1984; Lockhart, 1986; Jones and Smith, 1988; Jones and Hunter, 1989). Porosity and

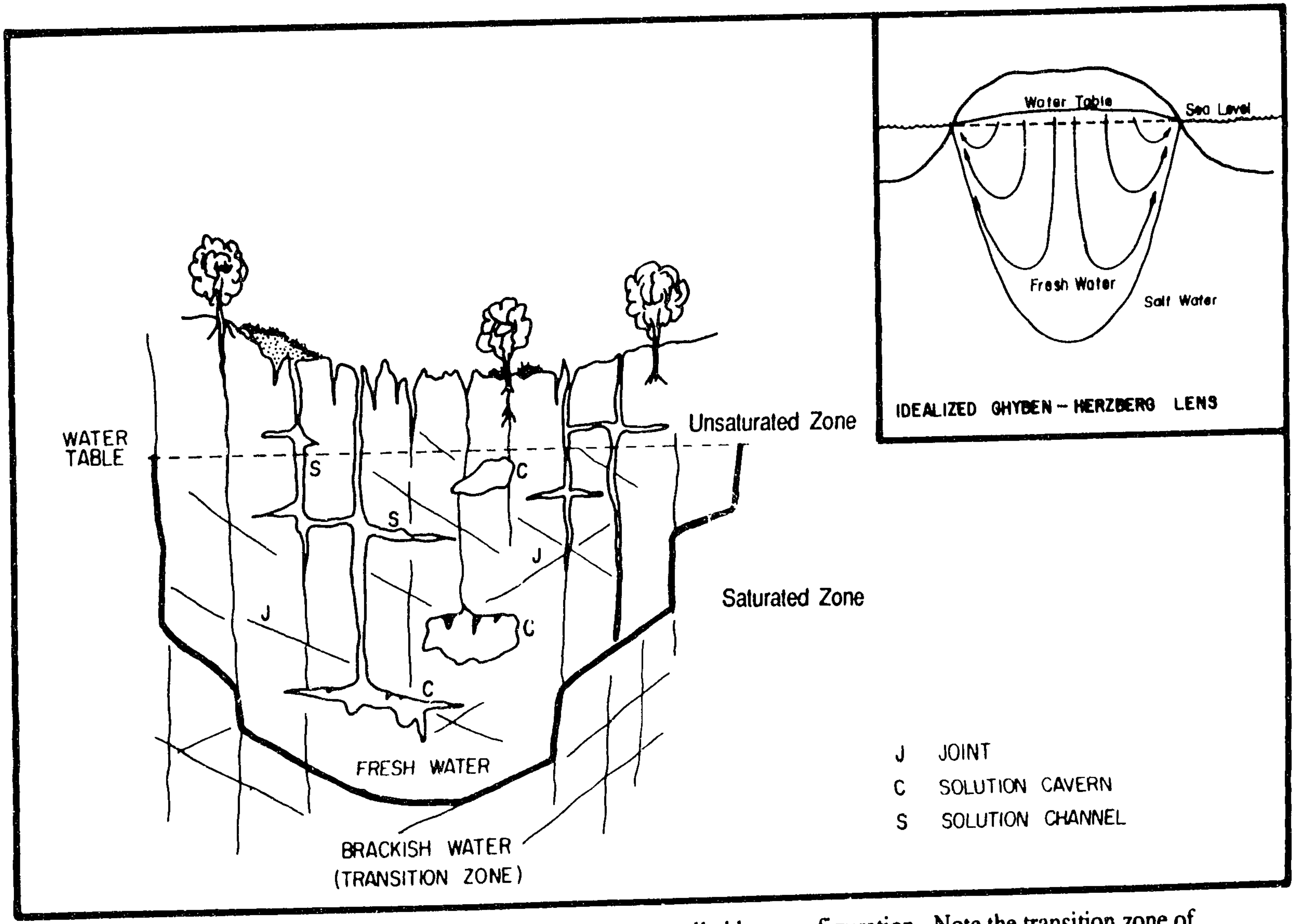


Fig. II.12 Schematic representation of joint and karst controlled lens configuration. Note the transition zone of brackish water underneath the fresh water zone. Inset map shows an idealized Ghyben-Herzberg lens with a sharp interface between the fresh and sea water.

permeability analyses of dolostone cores from East End and Lower Valley of Grand Cayman show that rock porosity and permeability vary both laterally and vertically (Table II.1).

Porosity distribution with depth from cores of well 3-84EE indicates three distinct porosity zones (Fig. II.13). An examination of the rock cores shows that the porosity in zone A probably resulted from active ground water circulation at the water table. Thrailkill (1968), Stringfield and Rapp (1977), and Esteban and Klappa (1983) also suggested that the shallow phreatic zone is characterized by active dissolution due to mixing corrosion and high hydraulic erosion. The differences in porosity between zone B and C (Fig. II.13) appear to be facies controlled. Zone C has a high coral content; zone B has only scattered mollusc fragments.

The irregularity in permeability distribution is well exemplified by the K_{max} and K_{min} values, which denote the two permeability measurements taken at 90° intervals (Table II.1). Permeability analyses of rock cores from well 3-84EE show that permeability increases with increasing depth (Table II.1). The porosity and permeability of cores from different parts of Lower Valley lens (Table II.1) also indicate their lateral variations over a small geographic area (< 1 km^2).

Fissures and Joints

Detailed joint measurement on the coastal exposures of Bluff Formation on Grand Cayman showed three major joint sets trending at about 020°, 090° and 160° (Rigby and Roberts, 1976). Development of open fractures and joints, apparently formed under tectonic stress, is an important porosity and permeability creation mechanism in the Bluff Formation. In surface outcrops, the joints appear continuous, planar, rough and open, and commonly occur in conjugate sets (Figs. II.14, 15, 16). The depth extent of these joints and fissures are not known. Parizek (1976) and LeGrand (1979) noted that fractures tend to be larger and most pronounced near the land surface than at deep levels. Therefore, it is

Table II.1 Results of porosity and permeability analyses of Bluff dolostone rock cores.

Well #	**Core #**	**Depth** m (below land surface)		**Porosity** %	K_{max} darcy	K_{min} darcy
3-84EE	2.3	6.0	– water table	12.4	23.2	0.5
3-84EE	2.8	6.4		15.8	1.3	0.2
3-84EE	3.2	7.5		15.9	3.1	1.8
3-84EE	3.6	8.2		14.8	8.7	0.9
3-84EE	4.2	9.4		7.0	3.2	0.7
3-84EE	5.2	10.5		2.4	4.8	4.0
3-84EE	5.5	11.1		7.5	22.7	2.4
3-84EE	5.11	11.5		3.6	1.9	1.7
3-84EE	6.3	12.3		3.4	3.1	0.9
3-84EE	7.8	14.5		11.7	17.1	8.3
3-84EE	8.2	15.6		26.1	29.2	12.5
3-84EE	8.6	16.1		15.3	34.9	12.4
3-84EE	8.9	16.4		22.6	45.9	18.8
1-82LV		3.0		4.6	3.1	2.1
3-82LV		6.1		13.0	8.6	2.0
3-82LV		7.6		24.9	5.5	4.2
11-82LV		2.4		12.4	1.0	0.2
13-82LV		1.8		23.0	1.4	0.6

Note: 1 darcy = $0.987*10^{-8}$ cm^2; 1 darcy = $9.66*10^{-6}$ m/s (for water flow).
EE and LV refer to East End and Lower Valley lens respectively.
K_{max} and K_{min} are the respective maximum and minimum permeability of the rock cores measured at 90° intervals.

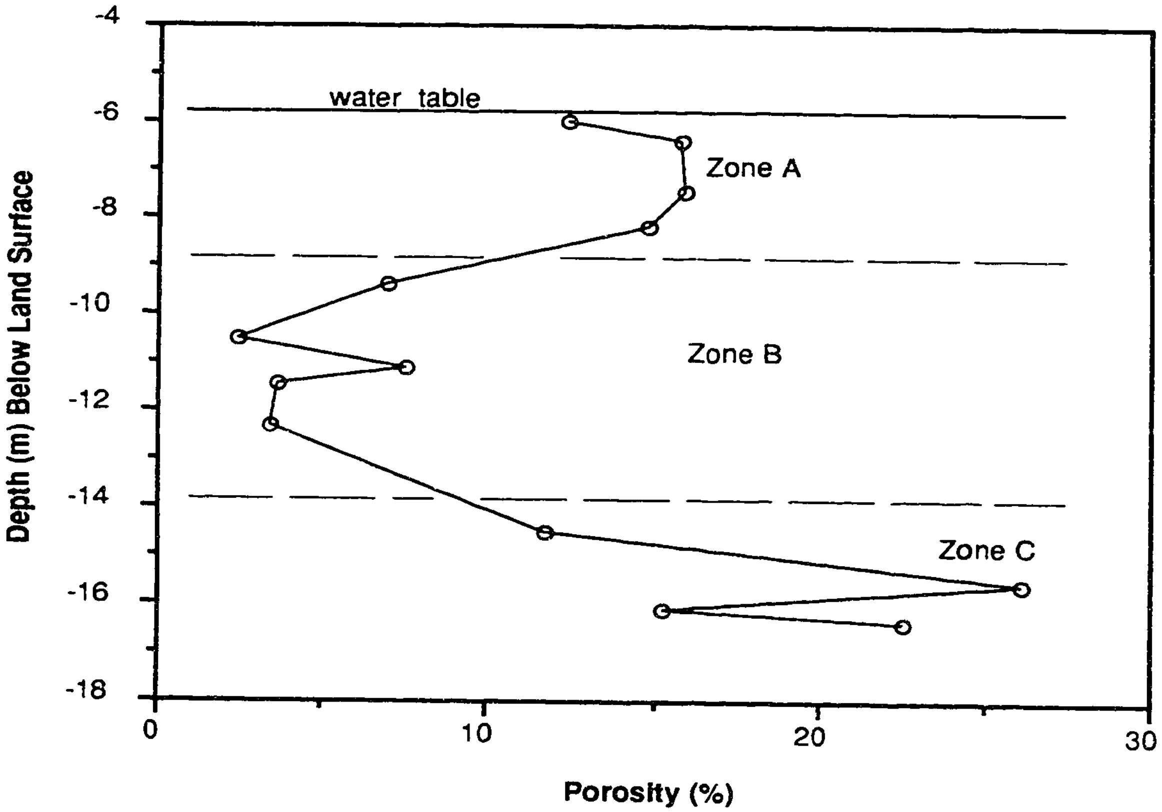


Fig. II.13 Porosity distribution with depth. Data obtained from analysis of rock cores from well 3-84EE.

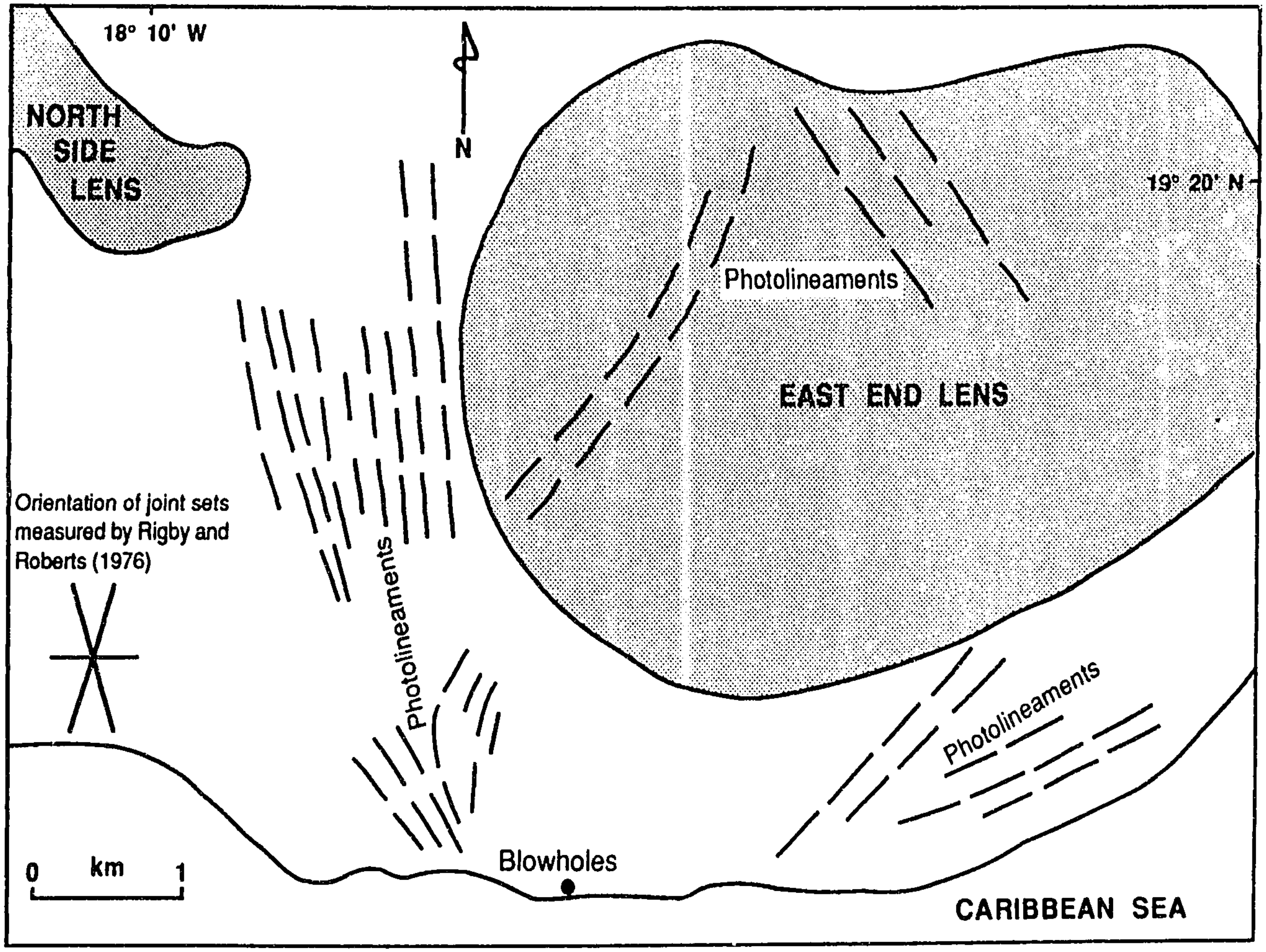


Fig. II.14 Structural photolineaments near the East End lens on Grand Cayman.

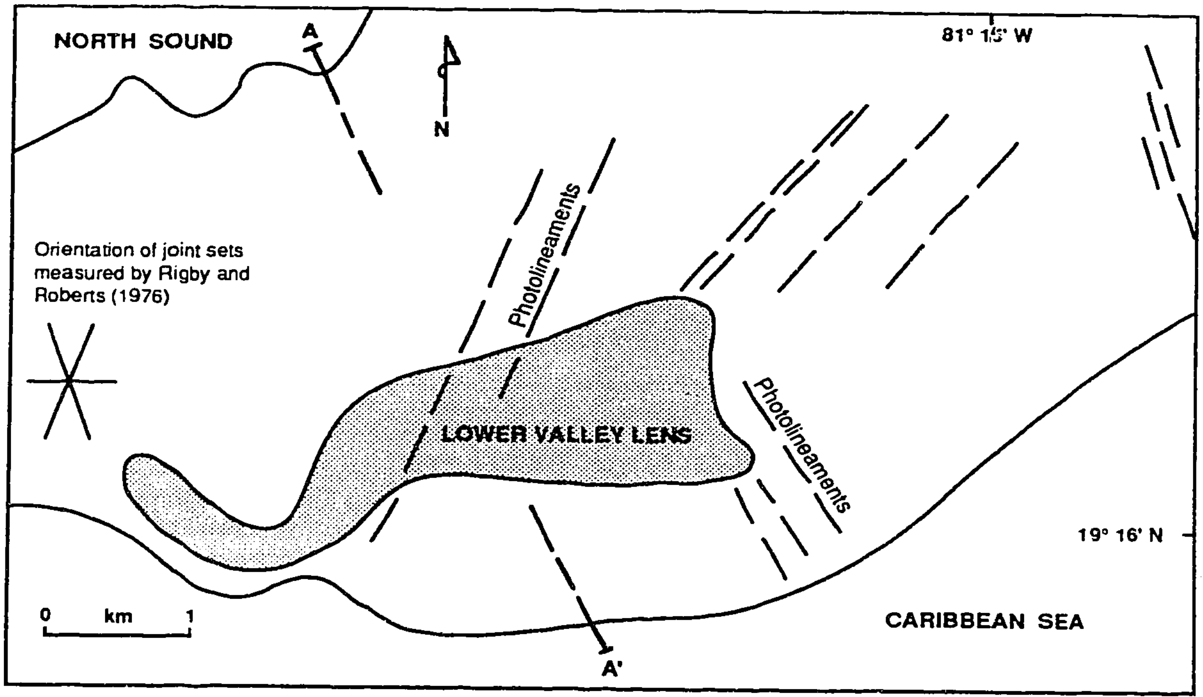


Fig. II.15 Structural photolineaments near the Lower Valley lens on Grand Cayman. AA' indicates line of X-section shown on Fig. II.19.

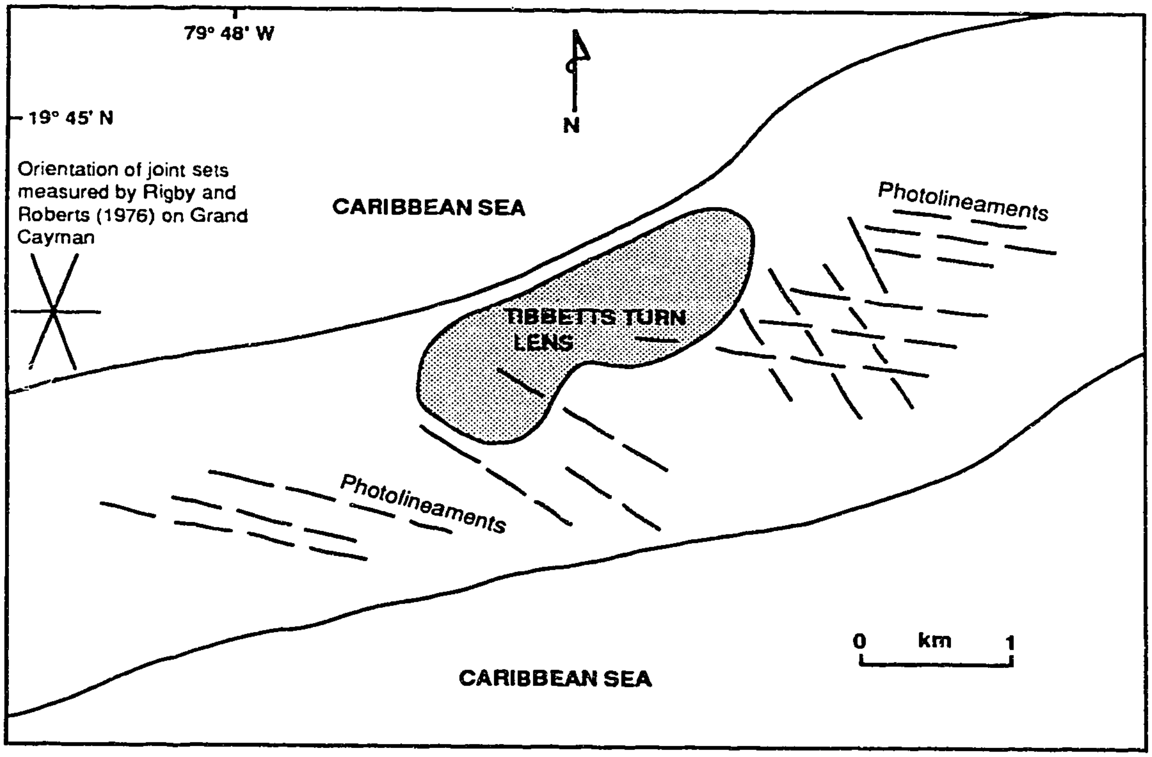


Fig. II.16 Structural photolineaments at the eastern part of Cayman Brac.

probable that some of the fissures and joints do not reach the present water table, particularly on Cayman Brac where the unsaturated zone is thick (up to 50 m at the east end of the island). A few of the fissures exposed on the high land of Cayman Brac were examined. None of them penetrate down to the water table.

Structural lineaments, readily discernible on aerial photographs, reflect joints and fissures in the subsurface. Thus, aerial photographs allow examination of joint orientation and frequency in the interior of the islands. The structural lineaments are particularly pronounced in the eastern half of Grand Cayman where the Bluff Formation is exposed. Near the East End lens, two vertical conjugate photolineaments striking 030-040° (near the westernmost portion of the East End lens, Fig. II.14) and 175° (in area between the North Side and East End lens, Fig. II.14) are particularly well developed. Southward to the coast, besides the east-west trending joint set, two joint groups trending 050° and 160° are present (Fig. II.14). Around the Lower Valley lens, dominant photolineaments, commonly indicated by the alignment of small ponds, trend at 020° and 150° (Fig. II.15). The general agreement on the orientation of the joints measured on outcrops (Figs. II.14, 15; Rigby and Roberts, 1976) and of the photolineaments mapped in this study further supports the suggestion that the lineaments are surface expressions of subsurface joints and fissures.

On Cayman Brac, photolineaments are also more prominent on the eastern part of the island. Most strike in a northwest-southeast orientation at 100°, 120-130°, and 150° (Fig. II.16). At the western portion of the island, a minor set trends at 020°. The difference in the orientation of the photolineaments on Grand Cayman and Cayman Brac suggests that the tectonic history of the two islands might be different.

Lattman and Parizek (1964), Parizek (1976), LaRiccia and Rauch (1977) and LeGrand (1979) demonstrated that wells penetrating fractures generally have high flow rates. In the case of the Cayman Islands, the joints and fissures probably affect the ground water flow regime in the following ways:

(1) They provide direct hydraulic connection between the aquifer and the surrounding ocean. Ng (1985) noted that wells located along the 020° photolineaments in the Lower Valley lens (Fig. II.15) show significant water quality deterioration in response to pumping. This suggests that the fissures provide direct access for the sea water or deep saline water to enter the aquifer.

(2) They may create semi-confined conditions in an unconfined aquifer as shown by wells not responding to the ocean tide (Fig. II.8).

(3) They provide avenues for mixing of water from different hydrochemical zones (Ng, 1985). This mixing process is particularly effective due to the absence of lateral and vertical geological barriers to the ground water flow.

(4) They allow rapid recharge of rain water into the aquifer. The slightly higher water table elevation in the vicinity of the joint set striking 030°-040° at the East End lens (Fig. II.14) appears to indicate that the joints serve such a role.

(5) To a certain extent they define the lens geometry. This is shown by the irregular lens geometry and sharp lens boundary (Figs. II.12, 14, 15, 16). The photolineament set (striking at 175°) between the North Side and East End lens (Fig. II.14) may be responsible for the intrusion of the saline water which divides and prevents linkage of the two lenses.

(6) They facilitate the leaching process by providing adequate pathways for fluid flow. Differential enlargement of fissures by solution resulted in concentrated flow, which increased dissolution rates and further enlarged the incipient caverns and channels.

In places, the dolostone of the Bluff Formation is slightly weathered to a dolomitic limestone (Ng, 1985) which was formed by partial replacement of dolomite by calcite (Jones *et al.*, 1989). Chalky dolostone, recovered from drilling returns, probably formed by preferential weathering along fissures. This chalky dolostone conforms to the description of crushed dolomite from the Dinaric Karst of Yugoslavia (Zogovic, 1966) and pulverulite from the Cretaceous Edwards Formation of central Texas (Chafetz and Butler, 1980). Weathering phenomena in carbonate rocks related to fissures have also been described by Parizek (1976) and Williams (1983).

Karst Porosity

Karst porosity is readily seen on exposed surfaces. At depth, caverns and solution channels (Fig. II.12) are commonly indicated during well drilling by the sudden drop of drilling tools, loss of circulation, and the lack of cutting returns.

Following the hydrologic classification of carbonate aquifers by White (1977), the ground water movement in the dolostone aquifer is essentially by diffuse flow. Free or concentrated flow occurs in areas where cave systems are well developed and jointing is intense.

Cave development tends to proceed preferentially along closed joints or partings in carbonate rocks even when open joints are present (Davies, 1966; Powell, 1977; Thrailkill, 1968). The most distinctive feature of karst is that permeability is self-engendered (LeGrand, 1983). Where ground water is in continual motion through pores, it dissolves and carries away soluble material, which in turn increases ground water circulation and permeability in the rock. This dissolution phenomenon leads to the development of a permeable zone which acts like fissures by (1) providing direct avenues for hydraulic connection with the surrounding ocean, (2) facilitating mixing, (3) facilitating recharge, (4) forming semi-confined zones, (5) defining lens boundary, and (6) facilitating leaching and subterranean erosion.

The zone of greatest permeability tends to develop in the zone of greatest circulation, which is commonly just below the water table (Thrailkill, 1968; Stringfield and Rapp, 1977; LeGrand, 1983). At the discharge zone, permeability also increases as a result of concentrated flow, and hence, higher flow rate and rate of solution (Chidley and

Lloyd, 1977b; Lloyd, 1980). In the brackish water transition zone which develops between fresh and sea water, Runnells (1969), Hanshaw *et al.* (1971), Badiozamani (1973), and Plummer (1975) suggest that undersaturation with respect to calcite occurs as a result of mixing. Jones and Smith (1988) also suggested that the cave development in Grand Cayman probably occurred in the mixing zone.

H. HYDROGEOLOGICAL REGIME

On Grand Cayman, fresh water lenses of exploitable significance, namely, Lower Valley, North Side and East End lens (Fig. II.1), were first identified by Mather (1972). Their configuration and geometry were further delineated using surface resistivity measurement, drilling, and borehole salinity profiling (Bugg and Lloyd, 1976; Beswick, 1980). Similar techniques were employed by the Water Authority of the Cayman Islands in defining the ground water resources of Cayman Brac.

Hydrodynamic Dispersion

The sea around the Cayman Islands generally experiences an average semi-diurnal tide range of 0.2 m (Fig. II.17) and a seasonal fluctuation of about 0.4 m (Figs. II.18A, 18B). The ground water table fluctuates in response to the sea tides (Figs. II.17, 18A, 18B) because the aquifers are hydraulically linked to the surrounding ocean.

On average, the deeper wells have shorter time lags and higher tidal efficiencies than the shallow wells. A similar phenomenon occurs in the Bahamas (Mather and Buckley, 1973), Bermuda (Vacher, 1978), Enjebi Island, Enewetak (Wheatcraft and Buddemeier, 1981), and Majuro atoll, Marshall Islands (Anthony *et al.*, 1989). Tidal efficiency generally decreases with increasing distance from the coast, if the geological setting remains constant. Therefore, tidal effects on different lenses are not the same (Figs. II.18A, 18B; Table II.2).

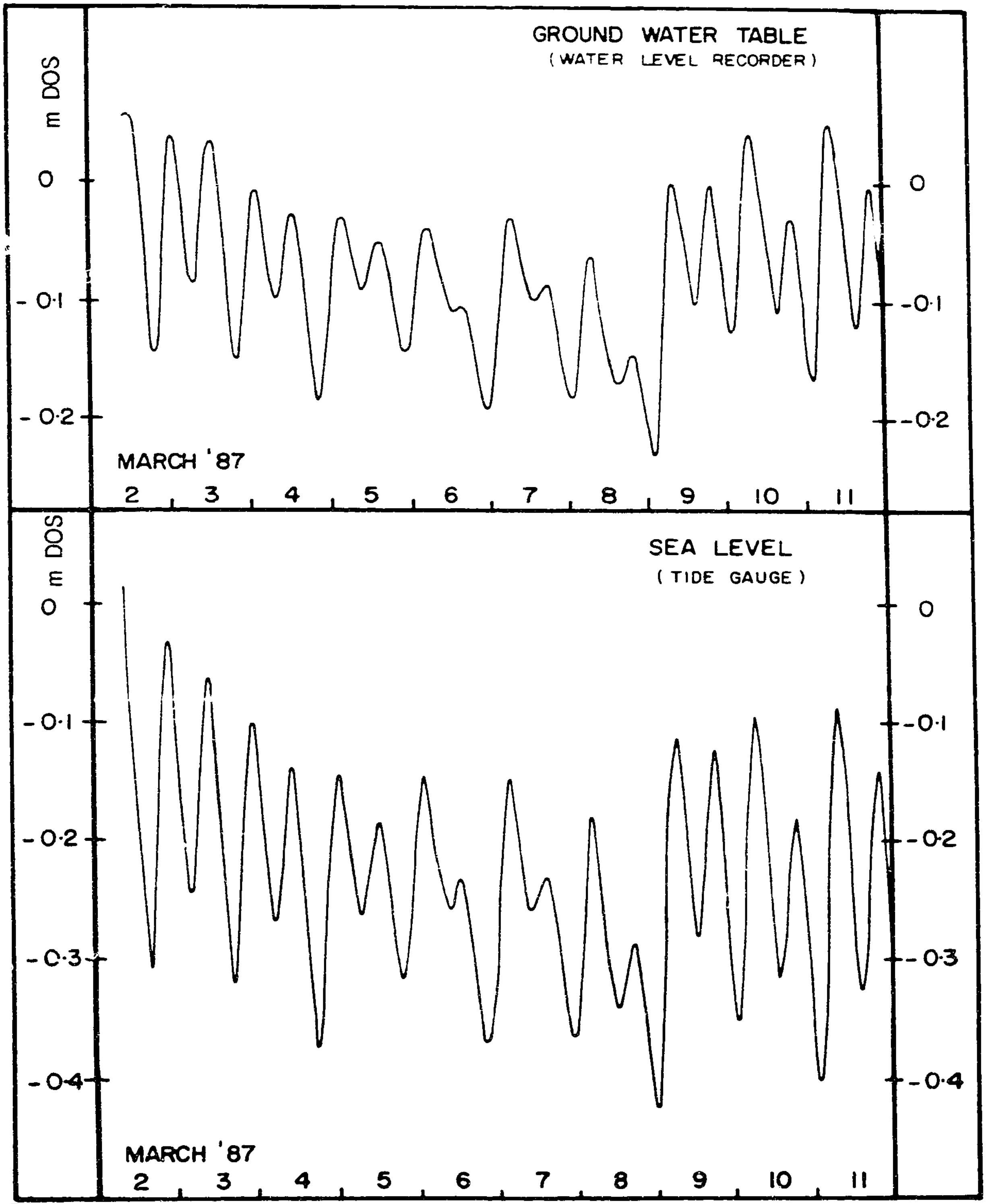
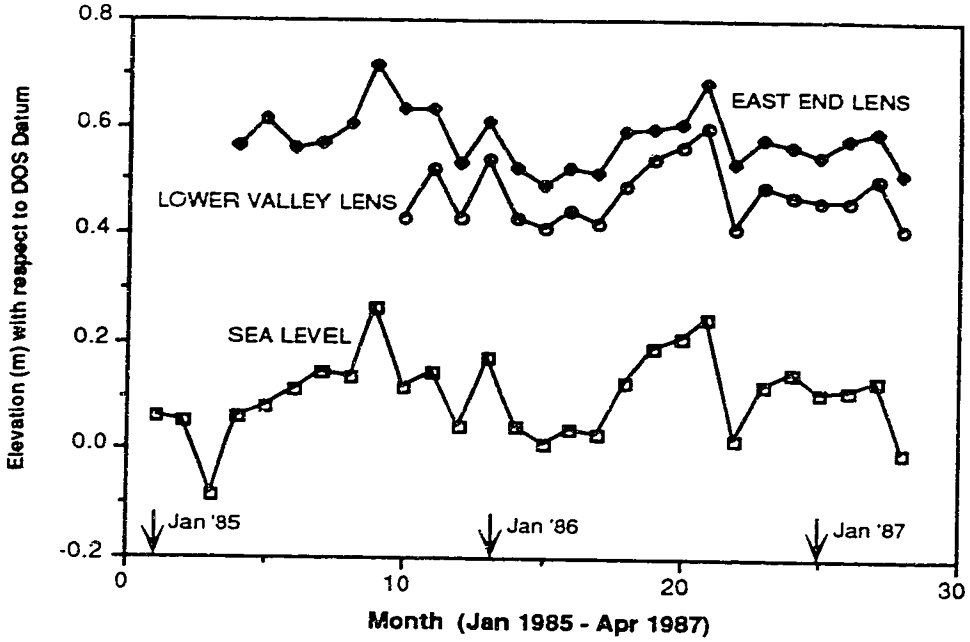


Fig. II.17 Charts comparing water table and sea level fluctuation recorded on Cayman Brac (location of observation well and tide gauge shown on Fig. II.2). DOS refers to Directorate Overseas Survey datum used for land survey.

A.



B.

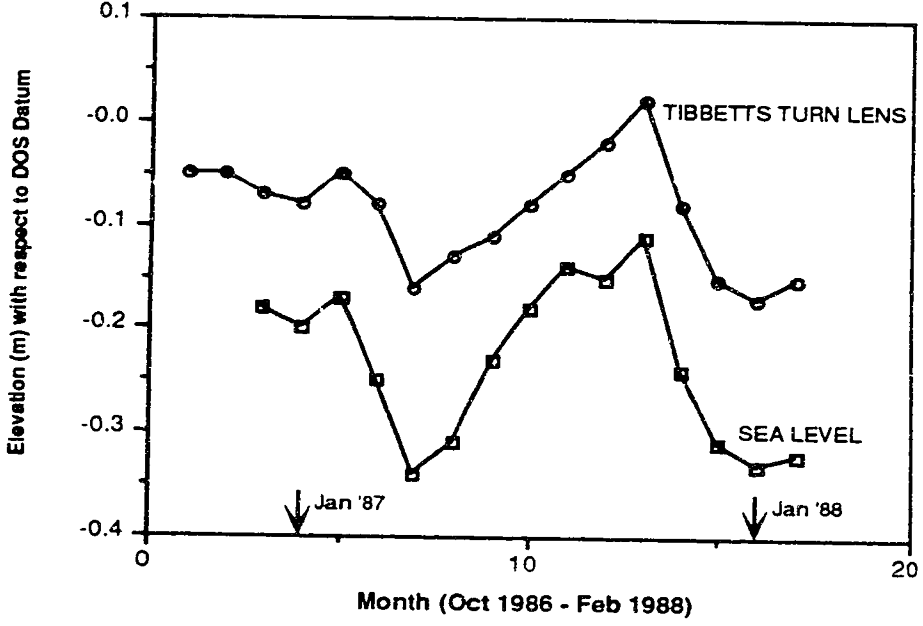


Fig. II.18A Average monthly sea level around Grand Cayman and water table elevation of Lower Valley and East End lens.
II.18B Average monthly sea level around Cayman Brac and water table elevation of Tibbetts Turn lens.
DOS refers to Directorate Overseas Survey datum used for land survey on the Cayman Islands. Note the DOS datum is different between the two islands.

Table II.2 Aquifer properties of the three lenses calculated from continuous sea level and water table records (time lag and tidal efficiency) and from pumping test results (specific capacity).

Location	Well #	Time Lag (hours)	Tidal Efficiency (%)	Specific Capacity (m^3/h/m)
Lower Valley, Grand Cayman	6-80LV	1.5	73	11.0
East End, Grand Cayman	13-80EE	3.0	34	40.0
Tibbetts Turn, Cayman Brac	B1	2.0	70	14.0

Mixing of fresh ground water and the underlying saline water is generated by tidal oscillations. As a result, a thick transition zone of brackish water develops between the fresh and sea water (Figs. II.6, 12) in response to tide-generated hydrodynamic dispersion. Schwartz (1984) noted that dispersion phenomenon is caused by variability in the velocity field. Therefore, Ng (1985) suggested that turbulent free flow occurring in the cavernous sections of the aquifer and the subtle increase in average linear velocity along fissures would enhance the hydrodynamic dispersion or mixing effect. The enhanced mixing is well exemplified by fluctuation in water quality in wells that penetrated the cavernous zone during each semi-diurnal tidal cycle (Ng, 1985).

Cooper (1964) suggested the cyclic flow of sea water, in which sea water flows landward from the sea floor into the transition zone and then discharges seaward (Fig. II.6). Cooper (1964) further suggested that the dispersion effect varies directly with the amplitude but inversely with the period of the ground water tide. Studies of the Biscayne aquifer of the Miami area (Kohout, 1964) showed that seaward flow occurs through portions of the aquifer that are up to 75% sea water. Using 500 parts per million (ppm) chloride limit in defining fresh water, Bugg and Lloyd (1976) found that the thickness of the fresh ground water lens on Grand Cayman has been reduced to 1:20 versus the theoretical Ghyben-Herzberg 1:40 relationship. However, the highly variable permeability of the aquifers argues that a constant 1:20 ratio is essentially meaningless.

Aquifer System

Fresh water accumulations on the Cayman Islands are typically lens shaped and entirely land locked (Figs. II.1, 2), features that are common on small limestone oceanic islands (Mather and Buckley, 1973; Vacher, 1978; Lloyd, 1980; Ayers and Vacher, 1986). The major fresh water lenses on Grand Cayman are developed in an unconfined condition in the Bluff Formation (Fig. II.12), where the land surface elevations are highest. The lens size is, however, restricted by the physiography, hydrological environment and geological setting of the islands.

Fresh water lenses developed on the Cayman Islands typically have an irregular configuration (Figs. II.1, 2, 12) which reflects the attitude and orientation of the joint and fissure system. Commonly, they are not in agreement with the general theories of the Ghyben-Herzberg principle and dynamic equilibrium (Fig. II.12). This is probably due to the continual changes in the ground water compositions, the mixing effect of the fresh and underlying saline water, and the heterogeneity and anisotropy of the aquifers.

The highly permeable nature of the karstic bedrocks prevents the development of surface streams and thick soil cover. The high transmissivity of the aquifer, which results in limited storage of fresh water in the aquifer, is well exemplified by the low ground water table elevations. On Grand Cayman, the average water table elevation of the fresh water zone is generally 0.5 m (Fig. II.18A) above mean sea level; on Cayman Brac, it is only 0.2 m (Figs. II.17, 18B).

As a result of the small size of the islands, their elongated dimensions and low topographic elevations, the abundance of brackish water swamp, the high permeability of the aquifer, and low effective recharge versus high evapotranspiration losses, the fresh water lenses are generally fairly small. The thickness of the fresh water part of the lens is generally less than 1% of the lateral dimension (Fig. II.19). On Grand Cayman, the three major fresh water lenses cover a total area of about 28.5 sq km (Fig. II.1) which is approximately 14.5% of the land surface area. The fairly high specific capacities (Table II.2), therefore, do not translate to high storage capacity for the lenses. Thus, most of the aquifers are bathed in brackish and saline water. Mandel (1964) suggested that as solution proceeds at the point of discharge, ground water heads will be lowered and will eventually cause sea water to intrude into the aquifer. Subsequently, the lens geometry will undergo continual modification due to the soluble nature of the aquifer.

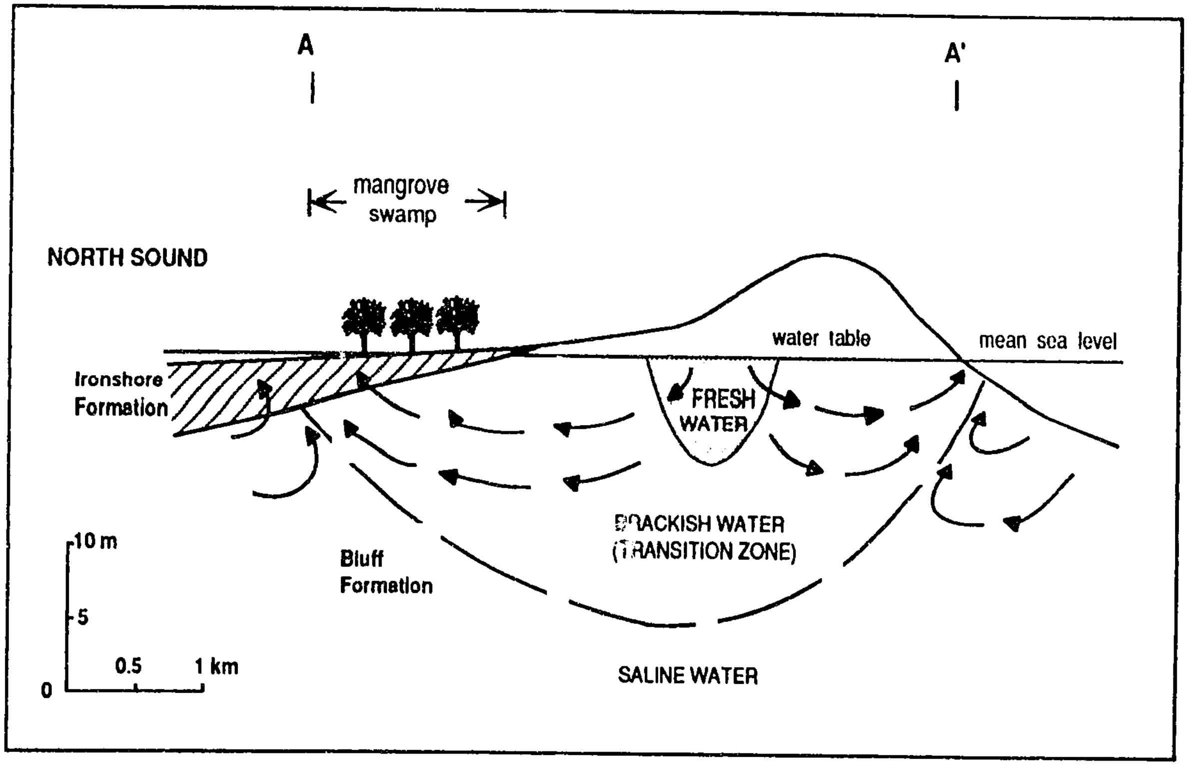


Fig. II.19 Schematic cross section of the Lower Valley lens (section location shown on Fig. II.15). Note the small thickness of the lens relative to the lateral dimension, and the mangrove swamp and Ironshore Formation fringing the northeastern margin of the lens. Arrows indicate ground water flow path. Note different vertical and horizontal scales.

Hydrogeological Zones

On the basis of ground water movement, the karst profile of the Cayman Islands can be divided into unsaturated, shallow saturated, and deep saturated hydrogeological zones (Figs. II.6, 12). In general, the ground water behaviour in each zone is similar to that described for intergranular aquifers (cf. Freeze and Cherry 1979; Sokolov, 1967; Brown *et al.*, 1983).

(1) Unsaturated (vadose) zone: This is the zone of downward infiltration of rain water from the land surface. The water percolates through the pores, fissures, joints, solution caverns and channels.

The unsaturated zone on Cayman Brac, up to 50 m thick in the eastern half of the island, led to the formation of perched water lenses. Their development is caused by the non-uniform permeability of the rocks. One such lens (Fig. II.2) occurred about 10.7 m above the true water table and bottomed at about 3.5 m above the true water table. The fact that the perched water table fell from 10.7 m to 6.7 m above the true water table before the drilling reached the lens base indicates that the lens was of limited lateral extent. However, the occurrence of perched water lenses may be fairly common and would be important in the diagenetic modifications of the rocks.

(2) Shallow saturated (phreatic) zone: Water movement in the upper zone, above the sea level, is gravitational. In contrast, the lower zone below sea level is characterized by siphonal circulation (Milanovic, 1981). This zone is also characterized by numerous subhorizontal caves formed by hydraulic erosion and mixing corrosion (Thrailkill, 1968; LeGrand, 1983; Esteban and Klappa, 1983). On the Cayman Islands, the waters in the saturated zone range from fresh, to brackish or saline.

(3) Deep saturated (phreatic) zone: This zone is characterized by saline water of about sea water composition and slow water circulation. On the Cayman Islands, deep

ground water commonly contains hydrogen sulfide gas (1-3 mg/l), suggesting that sulfate reduction or organic decomposition is common in this zone. Dissolution of the rocks is rare because of the low water exchange and stable chemical composition.

I. PALEOHYDROGEOLOGICAL REGIME

In order to unravel the diagenetic history of the Bluff Formation, it is imperative to reconstruct the paleohydrogeology which controlled the diagenetic regime. It is possible to deduce the hydrogeological setting with a fair degree of confidence because the Bluff Formation has not been subjected to intense tectonic activity. Past tectonic activity caused differential uplift or down faulting of the islands prior to late Pleistocene (Stoddart, 1980; Woodroffe, 1988), and development of joints and fissures (Rigby and Roberts, 1976).

Eustatic sea level changes have initiated great interest since the application of seismostratigraphy by Vail *et al.* (1977) in identifying past sea levels. For the Tertiary period, the most significant sea level fall of nearly 400 m took place in late Oligocene (Vail *et al.*, 1977; Vail and Mitchum, 1979). Olsson *et al.* (1980), however, argued that a rapid sea level drop of up to 150 m occurred in the early Oligocene. The major regression near the end of the Miocene is well documented (Adams *et al.*, 1977; Vail *et al.*, 1977; Loutit and Keigwin, 1982; Cita and McKenzie, 1984; Haq *et al.*, 1987). Jones and Hunter (1989) suggested that the stratigraphic record in the Bluff Formation is in agreement with the global pattern of sea level changes (Vail *et al.*, 1977; Haq *et al.*, 1987). Thus, according to Jones and Hunter (1989), the Cayman Member of the Bluff Formation was subaerially exposed in the late Oligocene. Subsequent to the major transgression in Miocene times when the Pedro Castle Member was being deposited, the sequence again emerged in the late Miocene as a result of the late Miocene regression (Jones and Hunter, 1989).

The glacial-interglacial fluctuation from late Pliocene to the present was described in great detail by Shackleton *et al.* (1984). A detailed history of sea level changes for the last 150,000 years was obtained from studying coral terraces on Barbados (Mesolella *et al.*, 1969; Bender *et al.*, 1973; Steinen *et al.*, 1973). The sea level curve interpreted from Pleistocene coral reef terraces on Huon Peninsula, New Guinea (Bloom *et al.*, 1974) is in agreement with that recognised on Barbados. Although the records of Pleistocene sea level fluctuation on the Cayman Islands are less complete than those for Barbados, there are several lines of evidence to suggest that the islands have been subjected to changing levels of the Caribbean Sea during the Quaternary, and/or to vertical tectonic movement. This evidence includes:

(1) well defined wave-cut notches at the north coast of Grand Cayman and around Cayman Brac at about 6 m above present sea level (Woodroffe *et al.*, 1983; Jones and Ng, 1988a). These probably developed at the time the Ironshore Formation (125,000 years old) was being deposited (Jones and Ng, 1988a; Jones and Smith, 1988);

(2) a wave-cut notch at about 2.5 m above present sea level, noted by Woodroffe *et al.* (1983), on the southeastern coast of Grand Cayman;

(3) two levels of caves along the cliff face on Cayman Brac at about 18 m and 30 m above present sea level, probably related to past sea levels as suggested by their horizontal orientation;

(4) submerged wave-cut notches around Grand Cayman at about 19 m below present sea level (B. Jones, 1988, pers. comm.) and possibly at about 150 m below present sea level (reported by pilots of the research submersible submarine); and

(5) low marine terraces (six levels at 2 m, 4 m, 6 m, 8 m, 11 m and 15 m) above present sea level (Emery, 1981) and submerged terraces (5-10 m and 20 m) around Grand Cayman (Rigby and Roberts, 1976).

The sea level records attest that the Bluff Formation was subjected to more than one cycle of subaerial exposure since late Oligocene times as a result of sea level falls.

Past climates are primarily deduced from indirect evidence of depositional environments and paleoecological considerations (Frakes, 1979). The skeletal components of corals, green algae, red algae, and foraminifera, present in the Bluff Formation, suggest that the surface temperatures in the past were probably similar to those at the present time. Based on stable oxygen isotopic composition of low latitude planktonic foraminifera, Savin and Yeh (1981) suggested that surface temperatures at low latitude since the Tertiary have been fairly constant except for a few low values in Oligocene time. Since the beginning of the Pleistocene epoch, the isotopic composition of the oceans has undergone rapid alterations primarily in relation to ice volume fluctuation (Emiliani and Shackleton, 1974; van Donk, 1976; Shackleton and Opdyke, 1977). However, McIntyre *et al.* (1976) demonstrated that the central Atlantic and Caribbean regions cooled only slightly during the last glaciation, about 18,000 years ago.

Meteorological data, such as temperature and rainfall recorded on Grand Cayman over the last 50 years, show distinct variations. A small but steady increase in temperature is apparent for the last 20 years (Fig. II.7A). A gradual decrease in rainfall is also indicated by the records of the last 68 years. Hurricanes, storms with winds more than 119 km/hr (Holford, 1972), appear to have been more frequent and of greater intensity in the 1800's and early 1900's (Williams, 1970) than in the recent years.

Major diminution of land-snails shell size occurred about 2000 years ago in Jamaica. This led Goodfriend (1987) to suggest that some time in the last 2000 years there was a major decrease in precipitation on Jamaica. It is probable that this major decrease in precipitation also affected the Cayman Islands because the rainfalls on the Cayman Islands and Jamaica are brought in by the same easterly trade wind. The karsting and speleothemic deposits on the Cayman Islands also suggest that they did not develop under present day climatic regime, but were probably developed in the past when the rainfall was much higher. Thus, it appears that the climatic conditions on the Cayman Islands were probably quite variable.

On the basis of the present day hydrological and hydrogeological regime, the following paleohydrogeological conditions are suggested:

(1) Initially, the ground water flow in the carbonate sediments was primarily intergranular.

(2) Fissures and joints, developed in response to tectonic activities, gradually became important avenues for ground water flow in the aquifers.

(3) Preferential movement along joints and fissures led to development of solution channels and caves.

(4) Karst development became more significant with time as the rocks were subjected to numerous cycles of subaerial exposure as a result of variations in sea level.

(5) The extent of karstification with respect to each individual sea level drop was probably related to the climatic conditions, particularly the rainfall intensity, quantity, and duration.

(6) The hydrogeological system and zonation were similar to that of the present day, but the fresh water lenses were probably more extensive both laterally and vertically because the rock mass was less permeable than that of the present day.

(7) Sea level caves and wave cut notches corresponded to established past sea levels, and hence, were associated with established ground water circulation systems.

(8) Ground water movement in the aquifers changed from diffuse to concentrated flow.

(9) Perched ground water lenses were probably more common and more extensive during the low stands of sea level.

(10) Strata that were in the phreatic zone were later exposed to vadose condition or vice versa; therefore, cave deposits were either eroded or re-deposited.

(11) Rocks were subjected to various diagenetic regimes and fluids in response to emergence and/or submergence.

J. SYNOPSIS

Detailed study of the hydrological and hydrogeological regime of the Cayman Islands permits the following conclusions:

(1) Rainfall distribution is irregular over the islands and varies widely from year to year.

(2) Recharge occurs in several ways, such as (i) rapid recharge through fissures and sinkholes, (ii) slow recharge through percolation of the unsaturated zone, (iii) depression-focused recharge in local depressions and partially clogged sinkholes, and (iv) rapid recharge by draining of water trapped in partially clogged sinkholes from time to time. These different types of recharge water would have a profound effect on the diagenetic modification of the rocks (aquifers) because they have variable chemical properties.

(3) Evapotranspiration accounts for the major loss of precipitation (75 to 90%) that falls on the land surface. This process affects both the ground water chemistry and the flow regime.

(4) The dolostone aquifer in the Bluff Formation is characterized by secondary porosity in the form of open joints, fissures, solution channels and caverns. Solution processes in the aquifer are a function of the (i) rate of ground water flow, (ii) chemical characteristics of the water, (iii) lithological and chemical characteristics of the rock, (iv) initial distribution of porosity in the rock, and (v) availability of transmissive avenues such as fissures and joints.

(5) The jointing and karsting lead to the development of permeable zones which (i) provide direct avenues for hydraulic connection with the surrounding ocean, (ii) facilitate mixing, (iii) facilitate recharge, (iv) create semi-confined zones, (v) define lens boundaries, and (vi) facilitate leaching and subterranean erosion.

(6) The ground water table fluctuates in response to the daily, semi-diurnal and seasonal tidal oscillations because the aquifers are hydraulically connected to the

surrounding ocean. The tidal fluctuation also causes hydrodynamic mixing of the fresh ground water and the underlying saline water.

(7) The major fresh water lenses are developed in unconfined conditions. They are characterized by (i) small size, (ii) irregular lens geometry, (iii) lens thickness not in agreement with the Ghyben-Herzberg principle, (iv) limited storage capacity, (v) low water table elevations, and (vi) rapid recharge and discharge.

(8) Based on the ground water movement, the hydrogeological regime can be divided into unsaturated, shallow saturated, and deep saturated zones.

(9) The Bluff Formation has been affected by numerous cycles of sea level changes since the deposition of the Cayman Member in Oligocene times. Each stage of karstification probably modified the previously formed karst features, making it difficult to determine the precise age of each karst development.

(10) Paleohydrological conditions such as temperature and rainfall were probably different from those of the present day, based on the meteorological data over the last 50 years. The extensive cave system and speleothemic deposition are incompatible with the present day climatic regime.

(11) The aquifer of the Bluff Formation has become more anisotropic and heterogeneous with time as a result of tectonic fracturing and karst development.

(12) The rocks of the Bluff Formation have been subjected to various diagenetic regimes in response to successive cycles of emergence and submergence.

III. HYDROCHEMISTRY

Hydraulic information on the aquifers on the Cayman Islands is difficult to interpret because ground water flow in the karstic dolostone is heterogeneous. Moving ground water is in continual interaction with the bedrock (Hanshaw and Back, 1979; Freeze and Cherry, 1979; Toth, 1984). In carbonate terrains where water-rock interactions are significant, chemical characteristics of the ground water have implications for both the lithology of the bedrock and the ground water flow path.

In order to decipher the role of ground water in the diagenetic modification of the host rock, it is necessary to ensure that the water samples are representative of subsurface aquifer conditions. This is of fundamental importance to hydrochemical and diagenetic studies of the aquifer systems. Such information then allows (1) interpretation of the origin of the water chemistry, (2) differentiation of the hydrochemical zones in the aquifers, (3) identification of the hydrochemical facies, and (4) assessment of the variation in water chemistry.

A. WATER SAMPLING

An understanding of the origin of the ground water requires analyses of water from the complete spectrum of the hydrological cycle, because the ground water is the end product of the various hydrological, hydrogeological, and geochemical processes. On Grand Cayman, the Lower Valley and East End lenses are monitored by networks of production wells, observation wells, and piezometers (Figs. II. 3, 4). Most water samples came from the production wells and piezometers. Observation wells, which are essentially open boreholes, were used to record fluctuations in the water table and to measure the salinity profile of the water column.

The aquifers of the Cayman Islands are characterized by highly permeable zones, such as fractures, joints and solution caverns, and by the lack of lateral and vertical geological barriers. Therefore, salt water intrusion from the surrounding ocean and upconing of underlying brackish and saline ground water occurs where the piezometric head is depressed below sea level for steady state conditions. The open fractures and solution features have also enhanced this phenomenon by providing a direct hydraulic connection between the various hydrochemical zones.

Water from production wells is an integrated water from all permeable horizons in the cone of influence (Freeze and Cherry, 1979; Hunt and Wilson, 1986). Consequently, it is possible to have a near steady state hydraulic condition but a temporal chemical variation (Gaona-Vizcayno *et al.*, 1985). On Grand Cayman, all production wells are non-screened and have about 3 m open section below the water table regardless of land surface elevations. In the Lower Valley well field, all production wells are equipped with 0.13 litres per second (l/s) flow restrictors to prevent excessive drawdowns of the water table. All the pumps installed in the East End well field are of positive displacement type such that pumping capacity, which ranges from 0.13 to 0.63 l/s, is controlled by the pump speed. Even though the wells were pumped at a low rate, temporal variation in water quality is evident (Figs. III.1A, 1B). This is due to a combination of factors, such as abstraction, recharge, evapotranspiration, and tide induced dispersion. Furthermore, fluctuation in ground water chemistry may result from seasonal recharge and aquifer type (Shuster and White, 1971) or be caused by the introduction of oxygen into the hydrogeochemical environment during pumping (Blaszyk and Gorski, 1981). It cannot be overemphasized that representative samples are difficult to obtain from production wells. On Grand Cayman, the production wells were sampled on a weekly basis for about three years to monitor the temporal effect. In order to avoid the effect of upconing caused by well field abstraction, all production wells were sampled prior to being put into operation. This sampling method ensured that the water samples represented the original ground water chemistry of the lenses prior to any human disturbances.

In this connection, small bore (51 mm diameter PVC) piezometers, which largely eliminate the vertical component of flow, were installed in both the Lower Valley and East

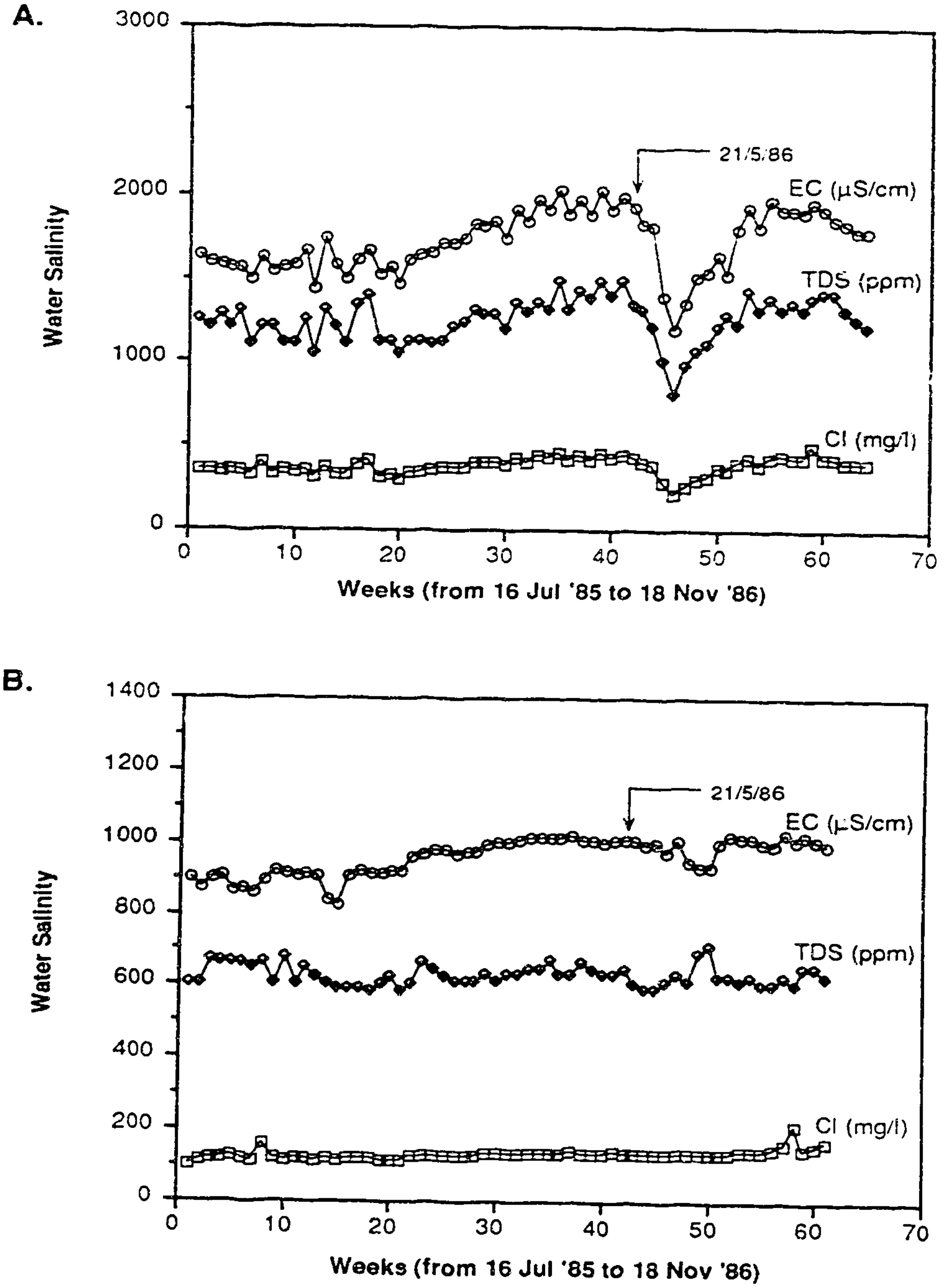


Fig. III.1 Temporal variation of water salinity in (A) Lower Valley and (B) East End lenses.

End lenses (Figs. II.3, 4) to collect depth specific water samples. The piezometers had about 1 m saw-slotted open sections. They were commonly installed in pairs (Table III.1); the shallower one opened into the fresh water zone whereas the deeper one opened into the brackish water zone. The annulus above the open sections was sealed by bentonite and cement mix to prevent cross flow. Water samples were collected from these piezometers on a fortnightly or monthly schedule.

Deep wells (15-50 m deep), which were drilled for abstraction, drainage or injection purposes, are all located in the western part of Grand Cayman (Fig. III.2). The abstraction wells were drilled to obtain saline ground water for desalination and the injection wells to take in treated effluents. Water samples from these wells were obtained prior to them being put into operation.

On Cayman Brac, all water samples were collected during the ground water investigation program carried out in July and August, 1986. When practical, drilling equipment was withdrawn from the boreholes when the water table was reached and before water samples were collected. Other samples were collected after the completion of the drilling. Only one perched water lens (Fig. II.2) was encountered during drilling and water samples were collected from the lens.

Except for production wells which were fitted with electric pumps, all well samples were collected by an ISO Model 2600 well sampler. The sampler, with an outside diameter of 44.5 mm, is operated by compressed air which does not come in contact with the water sample. The inflation and deflation of the rubber bladder displaced water through the ball check valve and delivered it to the surface at about 0.05-0.14 l/s depending on the lift. Prior to sampling, at least 3-5 well volumes of water were bailed to ensure that the sample was representative of the aquifer. All samples were collected in 1 litre sized polyethylene bottles.

Rain water was collected in standard Castella rain gauges installed at various locations on Grand Cayman (Fig. III.3). The rain water was transferred to 125 ml sized

Table III.1 Installation details of the piezometers in the Lower Valley and East End lens. All elevations measured in metres with respect to mean sea level. Location of piezometers shown on Figs. II.3 and II.4.

Piezometer #	**Land Surface Elevation**	**Water Table Elevation**	**Elevation of the Open Section**
LOWER VALLEY:			
4-84LV	+2.23	+0.56	-8.5 to -9.5
5-84LV	+2.23	+0.56	-4.5 to -5.5
9-84LV	+3.32	+0.55	-3.0 to -4.0
30(1)-82LV	+6.18	+0.55	-3.5 to -4.5
30(2)-82LV	+6.18	+0.55	-7.0 to -8.0
EAST END:			
4-84EE	+3.61	+0.65	-15.5 to -16.5
4A-84EE	+3.81	+0.65	-13.2 to -14.2
6-84EE	+1.36	+0.61	-16.7 to -17.7
6A-84EE	+1.45	+0.64	-13.0 to -14.0
8-84EE	+3.30	+3.43	-17.3 to -18.3
10-80EE	+3.20	+3.34	-14.0 to -15.0

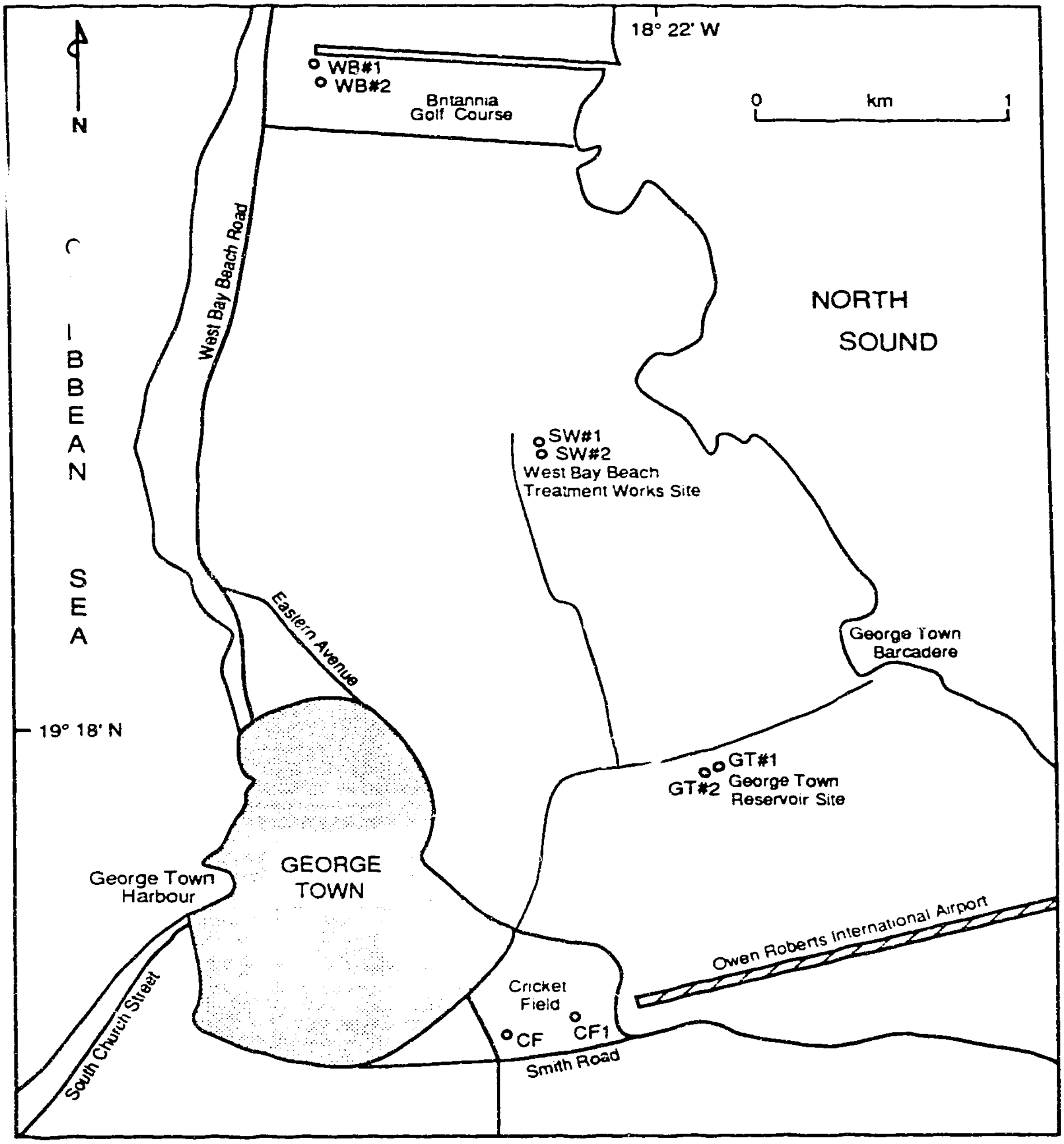


Fig. III.2 Sketch map of western part of Grand Cayman showing location of deep wells. Well cuttings were collected from CF, CF1, WB#1, and WB#2.

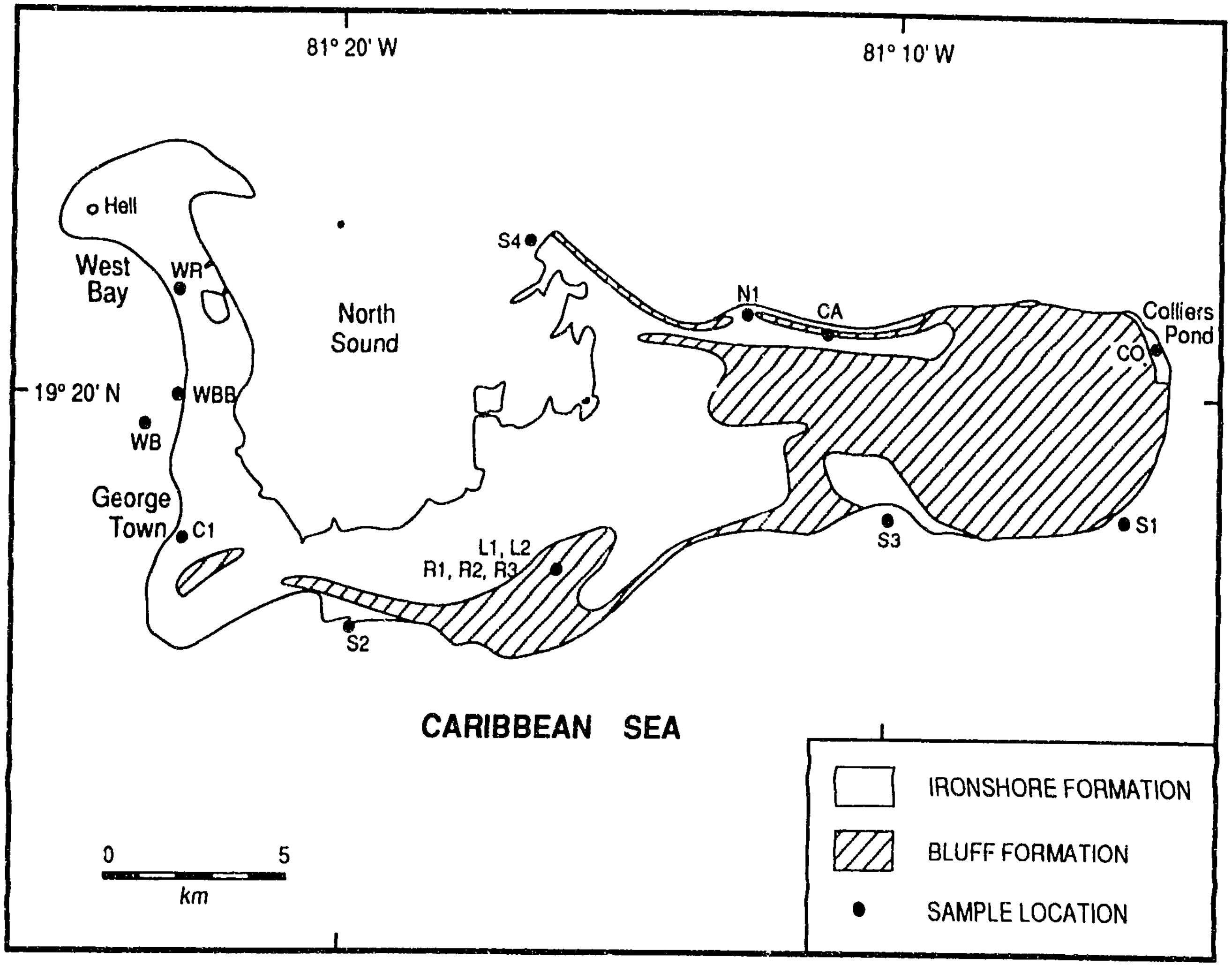


Fig. III.3 Sketch map of Grand Cayman showing location of surface water samples. Geological sketch map modified from Brunt *et al.* (1973) by I. Hunter (1989, unpublished).

polyethylene bottles and delivered to the laboratory within 24 hours of the rainfall. Only rainfalls that were greater than 50 mm provided adequate quantity for complete chemical or isotope analysis. Therefore, it was necessary to use different rain water samples for different types of analytical examination. Evaporation might affect the composition of the rain water samples, both chemically and isotopically, when the samples were collected from rainfalls of low intensity.

Surface waters such as sea water, pond water and cave pool water are a part of the regional hydrogeological system; therefore, it is necessary to collect and analyse the surface waters. Sea water was collected from various localities around Grand Cayman (Fig. III.3) for chemical and stable isotope analysis to ensure that there is no regional variation in sea water composition. Water samples were collected from Colliers Pond and a cave pool in Old Man Bay Cave (Fig. III.3).

B. WATER CHEMICAL ANALYSIS

Water samples collected from the full spectrum of the hydrological cycle of the Cayman Islands were analysed for their major chemical constituents (Cl^-, SO_4^{2-}, HCO_3^- /CO_3^{2-}, Na^+, K^+, Mg^{2+} and Ca^{2+}). Except for a few saline ground water samples, which were analysed by the Environmental Quality Laboratory of Florida, all water testing was performed at the Water Chemistry Laboratory of the Water Authority of the Cayman Islands.

Some of the water samples were analysed twice to ensure the reproducibility of the tests. The results of the total water analysis comprising all the major species were checked by charge balance between the cations and anions to identify any incomplete analysis or analytical errors, a common checking procedure used in chemical analysis of water (Freeze and Cherry, 1979; Standard Methods, 1981).

Field versus Laboratory Measurement

The main source of error in geochemical studies of carbonate ground water is due to thermodynamic calculations that are based on laboratory results rather than field pH measurements (Back, 1961a; Hem, 1970; Langmuir, 1971; Freeze and Cherry, 1979). The difference between the two measurements is caused by the escape of carbon dioxide from the water when the samples were exposed to atmospheric condition. Langmuir (1971) and Shuster and White (1971) also noted that temperature differences between field and laboratory measurement may cause inaccuracy in evaluating the actual ground water conditions.

Field Measurements

pH and temperature were measured in the field. Measurement of the pH was made with a portable Orion meter with a universal glass pH electrode. The meter was calibrated in Fisher standard buffers of pH 7 and 10. Measurements were reproducible with an accuracy of ±0.05. The temperature dependent electrical conductivity (EC), which measures the capability of the water to conduct an applied electrical current (Freeze and Cherry, 1979), was also measured in the field.

Temperature and electrical conductivity were measured by a YSI Model 33 or LF91 conductivity meter. The former was used for down-well salinity and temperature profiling and the latter for measuring water samples.

Total dissolved solids (TDS) and dissolved oxygen (DO) were measured by a Myron 3.2 TDS meter and a YSI Model 51 portable oxygen meter respectively. Water samples with TDS exceeding 5000 ppm, the upper limit of the TDS meter, were measured by the evaporation method in the laboratory (Standard Methods, 1981). Where the presence of hydrogen sulfide gas (H_2S) was suspected by its distinct rotten egg smell, the amount of hydrogen sulfide in water was measured by a Chemitrex sulfide adsorption kit.

Laboratory Analyses

Water samples were usually analysed within 24 hours of collection, particularly for bicarbonate (HCO_3^-) and nitrate (NO_3^-) species. Standard Methods (1981) were followed as closely as possible for the chemical tests. In order to avoid the risk that suspended calcium carbonate ($CaCO_3$) might be present in carbonate saturated well waters, a number of the samples were filtered through Whatman 40 paper and acidified as suggested by Langmuir (1971). Subsequent tests showed that such steps were not necessary for the ground water of the Cayman Islands.

Alkalinity and HCO_3^- were determined by titration with standard 0.02N sulfuric acid to the inflection point indicated by methyl orange. The end point was accurately determined using a Fisher Accument Model 750 selective ion analyser with a standard glass-body combination electrode. The meter was calibrated in Fisher buffer solutions of pH 4, 7, and 10 with an accuracy of ±0.01 pH. A gran plot approach (Stumm and Morgan, 1981; Standard Methods, 1981) was used to calculate the HCO_3^- concentration. Carbonate (CO_3^{2-}) concentration was determined using phenolpthalein indicator when pH was greater than 8.3.

Analyses for total hardness (sum of all divalent metals present in water) and calcium (Ca^{2+}) ion concentration were done by titration with standard EDTA (ethylene-diamine-tetraacetic acid) solution using Erichrome Black T and Calcon indicators respectively. Magnesium (Mg^{2+}) ion concentration was determined by the difference between total hardness and calcium. The analytical procedure and calculation were described in Standard Methods (1981).

The sodium (Na^+), potassium (K^+), strontium (Sr^{2+}) and NO_3^- contents were analysed by a Fisher Accument Model 750 selective ion analyser with respective Orion ion-selective electrodes. This instrument is capable of measuring the cations down to second decimal points of mg/l.

The chloride concentration was determined by silver nitrate titration using potassium chromate as an indicator (Standard Methods, 1981). Analysis for sulfate (SO_4^{2-}) ion concentration was determined by mixing the sample with barium chloride reagent and then measuring with an UV spectrophotometer.

Determination of TDS for water of high salinity (TDS >5000 ppm) was made using the evaporation technique. A temperature of 180°C was used as the drying temperature (Standard Methods, 1981). Correct drying temperature is important as different drying temperatures give correspondingly different TDS values as a result of oxidation, loss of water of crystallization, and volatilization (Sokoloff, 1933; Howard, 1933; Standard Methods, 1981).

C. ORIGIN OF WATER CHEMISTRY

The major ionic species of all water types on the Cayman Islands are Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^-, and SO_4^{2-}. Surface water encompasses (1) rain water, (2) brackish water in ponds and swamps, (3) saline to hypersaline pond water, and (4) sea water. Similarly, ground water salinity ranges from fresh to brackish to saline. The low salinity ground water (EC <1000 µS/cm) is typically part of the shallow, undisturbed fresh water from the ground water lenses; the high salinity (EC >50,000 µS/cm) water is typically drawn from underlying saline water on which the water lenses float.

Rain Water

Rainfall on Grand Cayman is basic (pH >7.0) with EC between 29 and 133 µS/cm (Table III.2). This variation appears to reflect the effects of geographic location (Fig. III.3), particularly the distance from the coast, as well as seasonal control. In general, rain water from near shore has a higher salinity than that from further inland (Fig. III.3, Table III.2).

Table III.2 Chemical characteristics of the surface waters (rain, sea and pond) on Grand Cayman.

Sample #	Location	pH	EC	TDS	Ca^{2+}	Mg^{2+}	Na^+	K^+	Sr^{2+}	Cl^-	HCO_3^-	SO_4^{2-}
RAIN WATER:												
N1	North Side	7.8	133	-	20.4	1.2	4	0	-	7	61	4
L1	Lower Valley	7.5	97	57	13.6	1.7	8	0	-	13.5	38.5	7
L2	Lower Valley	7.3	59	34	8	1.5	4.5	0	-	7.7	24.2	5
R1 *	Lower Valley	-	75	-	-	-	-	-	-	-	-	-
R2 *	Lower Valley	-	29	-	-	-	-	-	-	-	-	-
R3 *	Lower Valley	-	65	-	-	-	-	-	-	-	-	-
C1 *	George Town	7.4	83	55	10	0	7	0	-	12	28.1	0
WR	West Bay Beach	7.0	104	-	13.6	2.2	-	-	-	8.4	45	-
SEA WATER:												
WB	West Bay	8.2	49800	37200	413	1294	10760	387	8.0	19353	142	2712
WBB	West Bay Beach	8.27	52000	38000	383	1450	11400	372	7.1	20200	109	2700
S1 *	Gun Bay	-	50000	-	-	-	-	-	-	-	-	-
S2 *	Prospect Beach	-	51000	-	-	-	-	-	-	-	-	-
S3 *	Frank Sound	-	49800	-	-	-	-	-	-	-	-	-
S4 *	North Sound	-	50200	-	-	-	-	-	-	-	-	-
POND WATER:												
CO	Colliers Pond	8.5	58400	45000	1962	976	15600	280	-	28743	177	2700
CA	Old Man Bay Cave	7.8	48500	3650	130	115	810	14	-	1605	296	84

Note: ' * ' denotes samples sent for stable isotope analyses; ' - ' denotes species which were not analyzed.

Seasonal effect is best illustrated by data obtained from the Lower Valley rain water (Table III.2). Sample L1, collected from the first major rainfall event after a long dry winter of 1986, had an EC of 97 µS/cm. Precipitation collected on the following day (Sample L2) had an EC of 59 µS/cm. An even lower salinity of 29 µS/cm was brought by tropical rain storm Floyd (Sample R2) in October, 1987.

The chloride content of 7-13.5 mg/l is similar to that of precipitation in Hawaii (Eriksson, 1957) and Bermuda (Plummer *et al.*, 1976). The chloride ion probably comes from airborne sea spray. Ion separation at sea-atmosphere interface was also suggested by Plummer *et al.* (1976), Dethier (1979), Dalal (1979), and Nativ *et al.* (1983) as the means of providing the salt contents of the rain water. Similarly, sea salts are probably the main contributors of sodium and sulfate ions.

Of particular interest is the alkaline pH of the rainfall on Grand Cayman. Acidic pH commonly occurs in rainfall of other oceanic islands such as Bermuda (Plummer *et al.*, 1976), Trinidad (Dalal, 1979), and Hawaii (Eriksson, 1957). In those cases, the acidic character of the rain water can be related to the acidic bedrocks and their weathering products, and/or industrial and agricultural activities. On Grand Cayman, these factors are absent. Instead, the carbonate bedrock and calcitic soil are probably the source of the alkaline pH, HCO_3^-, Ca^{2+} and Mg^{2+}. Nativ *et al.* (1983) has suggested that the alkaline pH of the rainfall in Negev Desert, Israel was produced by the limy dust that neutralized the hydrogen ions in the atmosphere.

Sea Water

The chemical composition of the sea water around Grand Cayman (Table III.2) is similar to that cited by Badiozamani (1973) and Back *et al.* (1986) from the Caribbean Sea and Berner (1966) from sea around Bermuda. Indeed, open sea water salinity around the globe is similar with mean salinity between 45,000-55,000 µS/cm (Custodio, 1987), and can be calculated according to TDS (ppm) = 34.6 + 0.0175 (E-P), where E and P are respectively the annual evaporation rate and rainfall measured in mm (Gilcher, 1965).

Rigby and Roberts (1976) noted that salinity of the water in the sounds around Grand Cayman varies widely because of (1) wind circulation, (2) the influx of fresh and brackish water from swamps in the interior of the islands, and (3) the influx of brackish water from offshore springs. The slight variation in salinity among the samples collected in this study (Fig. III.3, Table III.2) suggests that the main controlling factors are probably rainfall and evaporation effect rather than the influx of water from land.

In general, the sea water (Table III.2) is characterized by (1) a predominance of the chloride and sodium ions, (2) alkaline pH, and (3) high molar Mg/Ca ratio of about 5.2:1. The relative increase in Na^+ and Cl^- concentrations in beach water (Sample WBB) compared with those of the open sea water (Sample WB) suggests that the beach water was probably modified by evaporation. Conversely, the relative decrease in the Ca^{2+} content of the beach water may result from the precipitation of calcite cement, a common phenomenon in carbonate beach settings (Moore, 1973; Hanor, 1978; Jones and Goodbody, 1984). Such precipitation was probably initiated by evaporation and caused an increase in the molar Mg/Ca ratio.

Surface Pond Water

Surface ponds, located on the periphery of the islands, are hydraulically connected to the sounds on the seaward side and to the brackish water swamps on the landward sides. Thus, water levels in the ponds fluctuate in accordance with the ocean tides. During the dry winter months, many ponds dry out completely. Such a condition occurs when the dry periods coincide with the seasonal low tides. In this context, the water chemistry of these ponds is controlled by rain, sea and subterranean water, and subsequent modification by surface evaporation. As a result, salinity varies from lightly brackish after heavy rainfall in summer months to hypersaline at the end of dry periods.

The effect of evaporation is well exemplified by the hypersaline condition of water from Colliers Pond (Fig. III.3), where water salinity, Na^+ and Cl^- concentrations are well in excess of the sea water (Table III.2). The molar Mg/Ca ratio of 0.82 is, however, substantially lower than that of the sea water (Table III.2). This may be due to the (1) influx of calcium enriched water, (2) precipitation of magnesium carbonate, and/or (3) dissolution of calcium carbonate. It seems possible that the first process may be operating, because Colliers Pond is surrounded by Pleistocene limestones of the Ironshore Formation (Fig. III.3). Thus, calcium enriched ground water from the limestone aquifer probably enters the pond periodically depending on the water levels in the pond at different times of the year. The second possibility is discounted because examination of the sediments from Colliers Pond using a scanning electron microscope did not indicate the presence of any form of magnesium carbonate. Thirdly, the high concentration of calcium carbonate in the pond water suggests that calcium carbonate is more likely to have been precipitated from the water instead of dissolving in the water.

Cave Pool Water

Water ponding in caves is rare on the Cayman Islands. However, the caves have not been thoroughly explored due to narrow constrictions between chambers and inaccessibility. As a result, only a small chamber in the Old Man Bay Cave was found to contain standing water. The water from the cave pool is lightly brackish with a TDS content of 3650 ppm (Table III.2). Unfortunately, it cannot be determined if this water is connected to the ground water system or if it is an isolated water body. Nevertheless, its water quality appears to be similar to other brackish water in the dolostone aquifers (e.g. Piez. 6-84 and 8-84 of the East End Jens, Table III.3). This implies that this cave pool water is a part of the hydrogeological regime. Jones and Smith (1988), however, noted that caves on Grand Cayman are not active in precipitating speleothems at present. This means that the cave pool water is probably not related to the speleothems formed in the Old Man Bay Cave.

Ground Water

The chemical constituents, added to the rain water from atmospheric (e.g. CO_2, O_2), marine (e.g. Na^+, Cl^-, SO_4^{2-}), and terrestrial (e.g. Ca^{2+}, Mg^{2+}, HCO_3^-) sources, are the antecedents of the ground water quality on the Cayman Islands. As soon as the rain falls on land, water-rock/soil interactions begin to modify its composition. This is particularly significant in a carbonate terrain like that of the Cayman Islands, where bedrock is readily dissolved in water having a low pH. The lack of geological barriers together with the fractured and karstic nature of the aquifers also suggests that sea water is another important modifier of the ground water chemistry.

Rain water on Grand Cayman contains 7-13.5 mg/l of chloride ion (Table III.2). Using the chloride method (Vacher and Ayers, 1980), it can be calculated that a 75-90% volume loss of the rain water through evapotranspiration will give a chloride ion concentration of about 60-120 mg/l. However, this chloride source alone is inadequate to explain the high content (>200 mg/l) present in most ground water (Tables III.3-8). Kreitler and Browning (1983) noted that the ground water in populated districts of Grand Cayman has been contaminated by sewage. In general, sewage contamination is indicated by high nitrate content and corresponding increase in chloride concentration; however, the lack of a positive correlation between the chloride and nitrate ion concentration suggests that sewage contamination is not an important contributor of chloride. Thus, it appears that most of the chloride ions are derived from the upward migration of the underlying saline water due to hydrodynamic dispersion in response to tidal oscillation. This mixing (dispersion) phenomenon is well illustrated by the thick transition zone developed between the fresh and saline ground water (Figs. II.6, 12, 19).

Table III.3 Concentration of major species in the ground water from piezometers at Lower Valley and East End lens. Samples collected on 7 April, 1987.

Well #	**pH**	**Ca^{2+}** (mg/l)	**Mg^{2+}** (mg/l)	**Na^{+}** (mg/l)	**K^{+}** (mg/l)	**Cl^{-}** (mg/l)	**HCO_3^{-}** (mg/l)	**SO_4^{2-}** (mg/l)	**Molar** **(Mg/Ca)**
Lower Valley									
4-84	7.66	84	63	420	1.5	772	257	60	1.23
5-84	7.74	52	34	109	0.5	208	238	19	1.08
9-84	7.48	72	46	260	1.0	459	310	36	1.05
30(1)-82	9.59	64	9.7	260	1.0	463	(12.0)	40	0.26
30(2)-82	9.83	88	7.3	401	1.5	724	(18.0)	48	0.14
East End									
4-84	7.70	64	61	369	1.0	652	285	57	1.57
4A-84	7.69	60	49	210	0.5	377	281	38	1.34
6-84	7.44	124	160	1310	3.0	2250	272	75	2.12
6A-84	7.46	68	39	192	0.5	338	276	43	0.94
8-84	8.10	108	63	790	1.5	1470	(92)	100	0.96
10-80	8.42	12	46	93	0.3	169	(190)	25	6.31

Note: Round bracketed HCO_3^{-} values indicate CO_3^{2-} makes up a portion of the total alkalinity.

Table III.4 Concentration of major species in the Lower Valley ground water. All samples were collected from production wells (3 m open section) in September 1983 prior to well field operation.

Well #	pH	EC (μS/cm)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	Na^{+} (mg/l)	K^{+} (mg/l)	Cl^{-} (mg/l)	HCO_3^{-} (mg/l)	SO_4^{2-} (mg/l)	Molar (Mg/Ca)
1	7.33	987	103	14	95	1.5	173	314	22	0.22
2	7.50	612	64	20	43	1.5	78	267	10	0.51
3	7.48	772	65	27	68	3	123	294	11	0.68
4	7.32	955	67	28	98	5	179	285	18	0.69
5	7.40	525	63	22	28	0.9	45	290	7	0.57
6	7.38	677	77	15	49	3	90	257	26	0.32
7	7.53	603	36	15	31	4	56	169	6	0.69
8	7.20	878	83	30	58	4.5	106	356	21	0.59
9	7.47	775	82	16	46	2	84	290	16	0.32
10	7.38	716	78	35	37	0.9	67	380	12	0.74
11	7.43	947	75	32	86	5	157	327	25	0.70
12	7.25	607	79	20	31	0.9	56	322	5	0.42
13	7.39	638	78	20	31	0.8	56	322	5	0.42
14	7.50	809	66	25	67	5	123	279	19	0.62
15	7.59	525	58	18	30	[illegible]	45	261	12	0.51
16	7.51	933	72	26	92	2	168	287	16	0.59
17	7.44	1464	77	35	181	8	330	279	48	0.75
18	7.44	771	87	24	40	8	73	336	36	0.45
23	7.50	1175	64	29	148	5	269	245	29	0.75
24	7.50	1175	62	28	141	4.5	257	234	29	0.74
25	7.50	914	75	24	89	3	162	284	21	0.53
26	7.66	1046	67	22	64	5	117	261	23	0.54
27	7.58	1039	73	28	110	4	201	288	23	0.63
28	7.52	1116	74	33	129	5	235	305	26	0.73
29	7.45	1165	83	35	129	5.5	235	337	25	0.69
30	7.50	1200	75	35	129	6.8	235	320	28	0.77
31	7.65	1121	68	35	117	5	213	300	28	0.85
32	7.52	992	72	29	98	3	179	296	22	0.66
33	7.65	670	58	29	34	0.9	62	297	8	0.82
34	7.52	978	80	30	83	2.5	151	335	19	0.62
TW	7.60	930	120	15	65	1.0	145	333	28	0.21

Table III.5 Concentration of major species in the East End ground water. (A) refers to East End well field where samples collected in April 1985, and (B) refers to irrigation well field at New Hut Farm where samples collected in February 1987. All samples collected from production well (3 m open section) prior to well field operation.

(A)

Well #	**pH**	**EC** (µS/cm)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	Na^{+} (mg/l)	K^{+} (mg/l)	Cl^{-} (mg/l)	HCO_3^{-} (mg/l)	SO_4^{2-} (mg/l)	**Molar** (Mg/Ca)
PW1	7.5	1016	77	41	79	1	141	395	12	0.88
PW2	7.5	871	88	34	50	0.5	92	398	13	0.64
PW3	7.5	1016	91	40	69	1	131	420	15	0.72
PW4	7.5	762	77	33	42	0.5	83	354	13	0.71
PW5	7.5	1102	99	45	69	1	141	451	16	0.75
PW7	7.5	872	[illegible]	37	42	0.5	79	440	11	0.63
PW8	7.5	90	[illegible]	34	56	0.5	100	410	12	0.61
PW9	7.5	897	64	32	78	1	143	296	17	0.82
PW10	7.5	986	64	34	92	1	173	293	16	0.87

(B)

Well #	**pH**	**EC** (µS/cm)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	Na^{+} (mg/l)	K^{+} (mg/l)	Cl^{-} (mg/l)	HCO_3^{-} (mg/l)	SO_4^{2-} (mg/l)	**Molar** (Mg/Ca)
EE11	7.7	1121	100	41	70	1	154	397	29	0.67
EE12	7.6	1252	72	44	123	1.5	261	278	32	1.01
EE12A	7.4	1230	76	34	142	1.5	261	294	30	0.74
EE12B	7.5	950	72	34	83	1	159	312	20	0.78
EE13	7.7	1060	88	39	50	0.5	203	233	20	0.73
EE14	7.4	1387	92	44	108	[illegible]	270	305	31	0.79
EE15	7.5	1326	88	41	110	1	270	289	33	0.77
EE16	7.5	1361	80	41	140	1.5	290	285	30	0.84
EE17	7.6	745	72	34	37	0.5	97	298	19	0.78
EE18	7.5	587	72	29	19	0	34	353	5	0.66
EE19	7.5	1092	116	34	48	0.5	154	356	24	0.48

Table III.6 Concentration of major species in the Cayman Brac ground water. All samples were collected from the exploration wells drilled in July/August, 1986.

Sample#	Well #	pH	EC (µS/cm)	TDS (ppm)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	Na^+ (mg/l)	K^+ (mg/l)	Cl^- (mg/l)	HCO_3^- (mg/l)	SO_4^{2-} (mg/l)	NO_3^- (mg/l)	Molar (Mg/Ca)
CB1(pw)	B1	7.9	912	580	60	45	57	0.9	150	266	29	40	1.23
CB2(pw)	B1	7.9	917	580	57	47	55	0.9	135	280	25	34	1.36
CB3(pw)	B1	7.9	948	600	57	49	57	0.9	145	284	29	26	1.41
CB4	B1	7.5	1430	900	92	41	147	5	273	361	42	4	0.74
CB5	B2	7.7	4300	3000	109	101	559	18.8	1020	437	127	30	1.52
CB7(wt)	B3	8.1	880	500	37	62	51	2	94	376	41	5	2.76
CB8	B3	7.8	940	580	75	38	65	2.7	118	351	32	5	0.83
CB9	B3	7.6	1218	750	85	40	112	4.5	203	371	38	8	0.77
CB10	B4	7.8	3260	2600	104	85	520	[illegible]	[illegible]	374	114	26	1.34
CB11(wt)	B5	7.9	963	650	72	61	77	2.4	[illegible]	456	52	3	1.39
CB12	B5	7.7	1555	1050	105	54	160	4.8	[illegible]	467	44	-	0.85
CB13	B6	7.9	4060	3400	104	114	690	23.2	[illegible]	377	147	-	1.80
CB14	B6	7.9	3870	3300	92	108	660	22.4	1165	250	138	-	1.93
CB16	K1	7.8	6250	-	105	167	1134	39	1979	362	222	-	2.62
CB17	K2	7.6	10170	-	336	163	2080	75	3549	386	407	-	0.80
CB18	CR	7.7	2900	1920	89	61	357	13.1	628	321	78	-	1.13
CB19	AR	8.0	8500	-	132	175	1368	48.4	2414	272	308	-	2.18

Note: (pw) refers to perched water samples, (wt) refers to samples collected at water table.

Table III.7 Concentration of major species in the highly brackish (>15% sea water salinity) to saline ground water. Samples WB collected in September 1985; samples CF, GT and SW collected in November 1987.

Sample #	pH	EC (µS/cm)	TDS (ppm)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	Na^+ (mg/l)	K^+ (mg/l)	Sr^{2+} (mg/l)	Fe^{2+} (mg/l)	Cl^- (mg/l)	HCO_3^- (mg/l)	SO_4^{2-} (mg/l)	NO_3^- (mg/l)	F^- (mg/l)	Molar (Mg/Ca)
CF1	7.20	20600	20600	300	437	3660	94	-	-	6625	215	940	9.5	-	2.40
WB1	6.79	32400	19600	228	696	6510	208	5.4	1.83	11000	233	1690	7.71	0.77	5.04
GT1	7.30	34300	25933	380	886	7390	113	5.5	-	13366	362	1900	7.7	-	3.85
WB2	7.01	39500	28100	548	877	8400	250	6.1	-	15300	282	1900	-	0.84	2.64
GT2	7.30	44700	33533	660	1044	9290	125	-	-	16794	322	2380	-	-	2.61
SW2	7.40	51400	38400	500	1469	10010	134	8.0	-	18103	188	2570	-	-	4.85
SW1	7.50	50900	38000	460	1882	10860	136	-	-	19644	201	2790	-	-	6.75
WB3	7.21	-	36800	396	559	11700	372	8.1	0.19	20500	287	2890	0.63	0.86	2.33
WB4	7.41	-	37600	422	573	12100	382	8.5	0.04	20500	210	3020	0.01	0.87	2.24
WB5	7.11	52800	38000	449	1390	13300	382	8.9	-	20600	265	2770	-	0.89	5.11
WB6	6.87	50200	37000	604	1060	11000	382	7.7	-	20700	292	2350	-	0.82	2.90
WB7	7.25	-	37900	417	573	12000	401	8.0	0.53	20800	259	2890	-	0.89	2.27
WB8	7.31	-	38400	441	573	12000	382	8.8	1.88	21000	262	2960	0.01	0.90	2.14
WB9	6.93	51800	36900	655	1360	11000	382	8.1	0.05	21400	254	4210	-	0.84	3.42

Note: 1. All concentration of the ionic species are measured in mg/l; EC is in µS/cm; TDS is in ppm.
2. ' - ' indicates species which were not analyzed.

Table III.8 Concentration of major species in the saline ground water. Samples collected from a deep well (30 m) at the Cricket Field of Grand Cayman (well CF). During the sampling period, the well was pumped continuously at about 13 l/s.

Date	EC µmhos	TDS (ppm)	Cl^- (mg/l)	pH	HCO_3^- (mg/l)	K^+ (mg/l)	Mg^{2+} (mg/l)	Ca^{2+} (mg/l)	Molar (Mg)/(Ca)
18.11.85	49800	37500	21010	7.46	231	454	1348	480	4.63
18.11.85	49700	37200	21156	7.49	238	454	1319	488	4.46
19.11.85	50300	36800	20670	7.49	235	450	1367	488	4.62
19.11.85	50200	38400	21253	7.33	233	450	1389	472	4.86
20.11.85	50700	38400	21250	7.47	233	456	1409	480	4.84
21.11.85	50700	37400	20573	7.31	235	448	1350	476	4.68
22.11.85	51000	37500	21691	7.52	233	450	1406	484	4.79
25.11.85	51000	37100	20816	7.45	240	457	1367	488	4.62
26.11.85	51200	36300	20500	7.24	242	459	1377	472	4.81
27.11.85	51100	36100	20475	7.25	237	464	1360	480	4.68
28.11.85	50700	36500	20718	7.24	250	461	1338	476	4.64
29.11.85	50400	36600	20913	7.42	235	468	1330	480	4.57
2.12.85	50200	36700	20670	7.42	238	463	1367	488	4.62
3.12.85	50300	36600	19576	7.39	238	471	1397	480	4.80
4.12.85	50900	36300	21983	7.11	233	466	1404	488	4.74

The high bicarbonate ion concentrations (Tables III.3-8) and pH (>7.0) are indicative of carbonate dissolution. Rain water dissolves carbon dioxide (CO_2) from the atmosphere as well as from the soil and root zones. Subsequent dissociation of carbon dioxide releases the hydrogen ion which results in water particularly suited for mineral dissolution or weathering. This process has been well documented by many workers (e.g. Thrailkill, 1968; Hem, 1970; Langmuir, 1971; Freeze and Cherry, 1979; Langmuir and Mahoney, 1984). The abundance of dolomite and calcite cements partly or completely filling many cavities in the dolostone of the Bluff Formation (Folk *et al.*, 1973; Jones *et al.*, 1984; Pleydell, 1987; Jones and Smith, 1988) suggests that precipitation of carbonate minerals also occurs in the aquifer.

Although the Lower Valley (Fig. II.1, Tables III.3, 4) and East End lens (Fig. II.1, Tables III.3, 5) on Grand Cayman and Tibbetts Turn lens (Fig. II.2, Table III.6) on Cayman Brac are developed in dolostone, the respective fresh ground water (<600 mg/l Cl^-) have different molar Mg/Ca ratios. Some of the Lower Valley waters have a Mg/Ca ratio less than 0.5 (Table III.4). In a dolostone aquifer, a molar ratio close to 1.0 is expected (Hsu, 1963; Langmuir, 1971). Therefore, the low ratios (<0.5) in the fresh ground water of the Lower Valley lens are possible only if waters with high calcium content are mixing with the ground water in the Lower Valley aquifer. Perhaps the ground water in the limestone aquifer of the Ironshore Formation, which is rich in calcium ions, has intruded the dolostone aquifer of the Bluff Formation. This is possible because the Ironshore Formation borders the northern and eastern margin of the Lower Valley lens (Fig. II.1). A minor source of calcium ion may be provided by dissolution of the porous dolomitic limestone, which is a weathering product of dolomite (Ng, 1985; Jones *et al.*, 1989).

The saline ground water, which commonly occurs at about 20 m below the water table, has a chloride and strontium ion concentration similar to that of the surrounding ocean water (Tables III.2, 7, 8). Hem (1970) noted that because chloride ions do not significantly enter into chemical or biochemical processes, the chloride content in ground water provides an indirect history of the ground water circulation. Similarly, strontium ions do not become involved in most chemical reactions other than entering the aragonite crystal structure as trace elements in a marine environment (Bathurst, 1975; Hanshaw and Back, 1979). Therefore, the similarity in chloride and strontium content of the saline ground water and sea water suggests that the saline ground water was essentially derived from sea water. There are, however, some significant differences in other chemical species between the saline ground water and sea water, such as the pH, Ca^{2+}, Mg^{2+} and HCO_3^- content (Tables III.2, 7, 8). These variations probably resulted from ground water circulation and water-rock interactions.

Dissolved oxygen (DO) of the shallow ground water (<10 m) on the Cayman Islands generally lies between 1.5 and 7.5 mg/l, indicating an oxidizing environment. Although hydrogen sulfide (H_2S) is not exclusive to the highly brackish and saline ground water, concentrations of up to 3.0 mg/l are common in the deep ground water. The H_2S probably resulted from the reduction of sulfate by sulfate-reducing bacteria, a common phenomenon in a reducing environment (Stumm and Morgan, 1981).

The temperature of the ground water on the Cayman Islands ranges from 25 to 30 °C. The main source of heat in the ground water is solar radiation. Thus, the ground water temperature fluctuates with respect to climatic conditions. In general, the shallow ground water temperature is similar to that of the atmospheric temperature and the temperature decreases to about 25 °C at a depth of 20-25 m.

D. HYDROCHEMICAL ZONES

The karst profile of the Cayman Islands has been divided into unsaturated, shallow saturated, and deep saturated hydrogeological zones on the basis of ground water movement. The shallow saturated hydrogeological zone is divided into the fresh, brackish and saline water zones (Figs. II.6, 12, 19). This zonation has been described in many coastal and/or oceanic carbonate aquifers, such as Florida (Cooper, 1964), Yucatan (Back and Hanshaw, 1970), Grand Cayman (Mather, 1972), Bahamas (Mather and Buckley, 1973), Jamaica (Land, 1973a), Barbados (Steinen *et al.*, 1978), Bermuda (Vacher, 1979), and Majuro atoll, Marshall Islands (Anthony *et al.*, 1989).

For ground water geologists, the main concern is the potability of the water. The most commonly used standards for drinking water (fresh water) were recommended by the World Health Organization (1971) and the U.S. Environmental Protection Agency (1975) who suggested a chloride ion concentration limit of 200-250 mg/l (500 ppm TDS equivalent) and an acceptable limit of 600 mg/l (1500 ppm TDS). In North America and Europe, a level of 250 mg/l Cl^- is the fresh water standard. However, many national standards are different and tend to approach the upper limit, particularly in countries where water is scarce (Custodio, 1987). In the Bahamas, the fresh water limit is 400-500 mg/l chloride (Cant and Weech, 1986) whereas in Bermuda, it is 1000 ppm total dissolved solids (Thomson and Foster, 1986). Conversely, Bugg and Lloyd (1976) and Chidley and Lloyd (1977a) suggested a chloride concentration of 500 mg/l on Grand Cayman because this level was easily detected in the surface resistivity studies. Thus, the upper limit for fresh water zone has been defined between 200 and 600 mg/l Cl^-.

Hydrogeologists are commonly not interested in the brackish water quality other than defining the concentration limits for watering livestock (U.S. Environmental Protection Agency, 1973). Cant and Weech (1986) used a 1200 mg/l Cl^- content to define the boundary between the transition and saline zones. Conversely, Freeze and Cherry (1979) gave a TDS range of 1000-10,000 ppm for brackish water and of 10,000-100,000 ppm for saline water. It is therefore apparent that there is little conformity in defining the salinity and quality of the brackish water zone.

Regardless of the lack of consensus in the usage of the actual compositions of the fresh (meteoric) and brackish (mixed) water, both meteoric and mixed waters have been cited in many diagenetic studies of carbonates (e.g. Land, 1970, 1973a, 1973b; Steinen and Matthews, 1973; Folk, 1974; Folk and Land, 1975; Magaritz *et al.*, 1980; Kaldi and Gilman, 1982; Morrow, 1982b; James and Choquette, 1984; Jones *et al.*, 1984). Equally, workers who questioned the ability of mixed meteoric-marine water for dolomitizing thick sequence of limestone (Land, 1985; Machel and Mountjoy, 1986; Hardie, 1987) failed to address the question of what is considered fresh and brackish (mixed) water.

Badiozamani (1973) argued that mixing of Yucatan ground waters with up to 30% sea water (which is actually 50% according to his Text-Figure 4) could cause replacement of calcite by dolomite. Hanshaw *et al.* (1971) suggested that the brackish water zone in the Yucatan and Floridan aquifer has a Mg/Ca ratio greater than 1. It is imperative to note that these properties cannot be universally adopted without considering the ground water flow system, both locally and regionally, and the aquifer conditions. Indeed, the chemical composition of the ground water is controlled by (1) the antecedent water composition prior to entering the carbonate aquifer, (2) the residence time of the water in the aquifer, (3) the mineralogical compositions of the aquifer, (4) the aquifer characteristics, and (5) the interaction between the water and the aquifer. Therefore, mixed water in different geological and hydrogeological settings would possess different chemical characteristics.

In view of the lack of a criteria to define the various hydrochemical zones and the confusion caused by such a deficiency, particularly in relation to diagenetic realms, the following scheme (Table III.9) is recommended.

(1) Perched water zone: refers to ground water in the unsaturated zone and above the zone of saturation. The chemical composition of the water in this zone is affected by evapotranspiration and water-rock interaction.

(2) Fresh water zone: defined by an upper limit of 600 mg/l Cl$^-$ (1500 ppm TDS or 2300 µS/cm EC). This value is suggested because it is the limit of potable water quality recommended by the World Health Organization (1971) and is well known among hydrologists and hydrogeologists.

Table III.9 Classification of hydrogeological and hydrochemical zones on the Cayman Islands.

Hydrogeological Zone	**Hydrochemical Zone**	**Salinity Range**
Unsaturated (vadose) - downward percolation	Perched Water	Variable water chemistry (generally <600 mg/l Cl^-)
Shallow Saturated (phreatic) - gravitational and siphonal circulation	Fresh Water	<600 mg/l Cl^- (or <1500 ppm TDS, <2300 µS/cm EC)
	Brackish Water	>600 - <19,000 mg/l Cl^- (or >1500 - <38,000 ppm TDS, > 2300- <50,000 µS/cm EC)
	Saline Water	Type I: >19,000 mg/l Cl^- (variable water chemistry)
Deep Saturated (phreatic) - very slow flow rate	Saline Water	Type II: >19 000 mg/l Cl^- (almost constant water chemistry)

(3) Brackish water zone: defined by an upper limit of 19,000 mg/l Cl^- (approximately 38,000 ppm TDS or 50,000 µS/cm), which is equivalent to that of the sea water of the Cayman Islands. The chloride content of sea water in the open sea commonly falls close to this value (Custodio, 1987). Thus, the brackish water zone comprises ground water having Cl^- concentration from >600 to <19,000 mg/l (>1500 - <38,000 ppm TDS or >2300 - <50,000 µS/cm). This zone can be further subdivided to lightly, moderately and highly brackish or by means of percentage of sea water as was used by Badiozamani (1973) and Ward and Halley (1985).

(4) Saline water zone: contains water having a Cl^- content of 19,000 mg/l or above. This zone encompasses two types of saline water Type I saline water is in the ground water circulation system, and hence, has a variable chemical composition (Table III.7). Type II saline water has very slow flow rate and has an almost constant chemical composition (Table III.8). The Type II saline water was sampled from a 30 m deep well at the Cricket Field, George Town (Fig. III.2). The well was pumped at 13 l/s (200 US gpm) continuously for 16 days. The daily sampling shows that the water chemistry remained essentially constant (Table III.8). Type I saline water is in the shallow saturated hydrogeological zone while type II saline water is in the deep saturated hydrogeological zone (Table III.9).

E. HYDROCHEMICAL FACIES

Back (1960, 1961b) introduced the concept of hydrochemical facies to denote the diagnostic chemical aspects of ground water solutions in the aquifers. The major cations (Ca^{2+}, Mg^{2+}, and Na^{+}+K^{+}) and major anions (Cl^-, HCO_3^-+CO_3^{2-}, and SO_4^{2-}) are plotted as percentages of their equivalents per million on a trilinear diagram (Piper, 1944). Ground water composition is then interpreted in accordance with the hydrochemical facies (Fig. III.4) which reflects the effect of solution-mineral reactions and the ground water flow patterns (Back 1960, 1961b; Seaber, 1962).

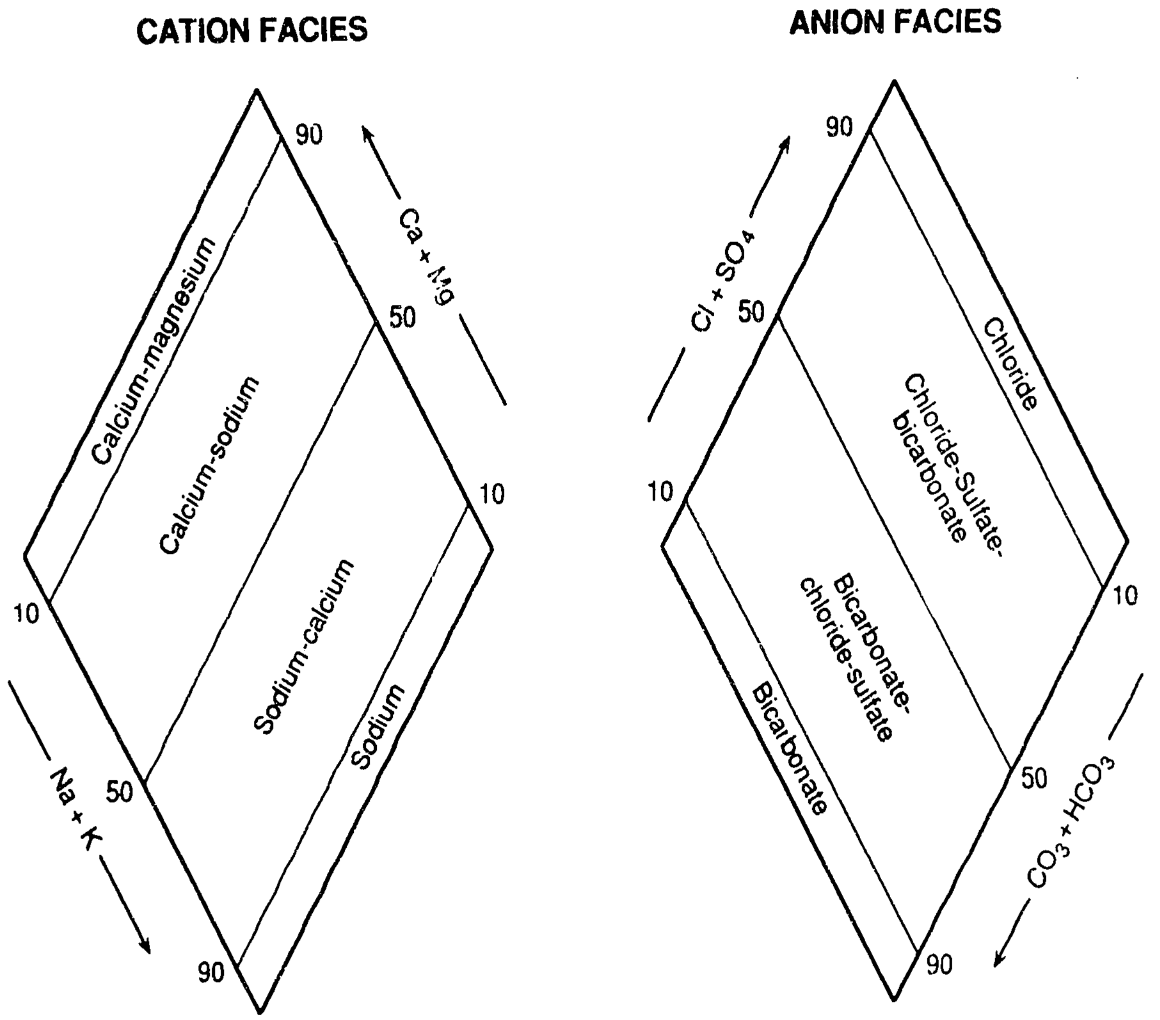


Fig. III.4 Hydrochemical facies diagram (adapted from Back, 1961a). Percentage of chemical constituents in equivalent per million.

The ground water on the Cayman Islands belongs to two different hydrochemical facies. On Grand Cayman, the fresh ground water in the East End and Lower Valley lens is of calcium-magnesium bicarbonate type water (Fig. III.5, Tables III.4, 5). Sodium chloride type water (Fig. III.5) is an indication of upconing of the underlying brackish water or of sea water intrusion even though the water is in the fresh water zone. Although the fresh ground waters of the East End and Lower Valley lenses appear to have the same hydrochemical facies (Fig. III.5), the molar Mg/Ca ratio of the two waters are different (Tables III.4, 5). The Lower Valley fresh ground water's molar Mg/Ca ratios range from 0.21 to 0.85 whereas the East End fresh ground water's ratios range between 0.61 and 0.88. The low ratio (<0.5) is indicative of influx of calcium-bearing water into the dolostone aquifer from the limestone aquifer.

On Cayman Brac, the fresh ground water from both the perched and phreatic aquifer is of calcium-magnesium bicarbonate type (Fig. III.6, Table III.6). There are, however, distinct differences between them (Fig. III.6). First, the molar Na/Cl ratios of the perched water (0.59-0.63) are significantly lower than those of the phreatic water (0.75-0.85). Second, the molar Mg/Ca ratios of the perched water (CB1, CB2, CB3, Table III.6) are greater than 1 whereas the ratios of the fresh water from the saturated zone (CB4, CB8, CB9, CB12, Table III.6) are less than 1. The molar ratios suggest that the chemical constituents of the perched water originated from water-rock interactions.

Another interesting feature is shown by samples CB7 and CB11 (Table III.6) collected at the water table (fresh water zone) of the Tibbetts Turn lens. Both have a significantly higher molar Mg/Ca ratio (2.76 for CB7 and 1.39 for CB11) than the fresh water (0.74-0.83) immediately below them. The high molar ratios, which cannot be derived from the underlying brackish water, may have resulted from incongruent dissolution of dolomite similar to that described by Langmuir (1971) and Freeze and Cherry (1979).

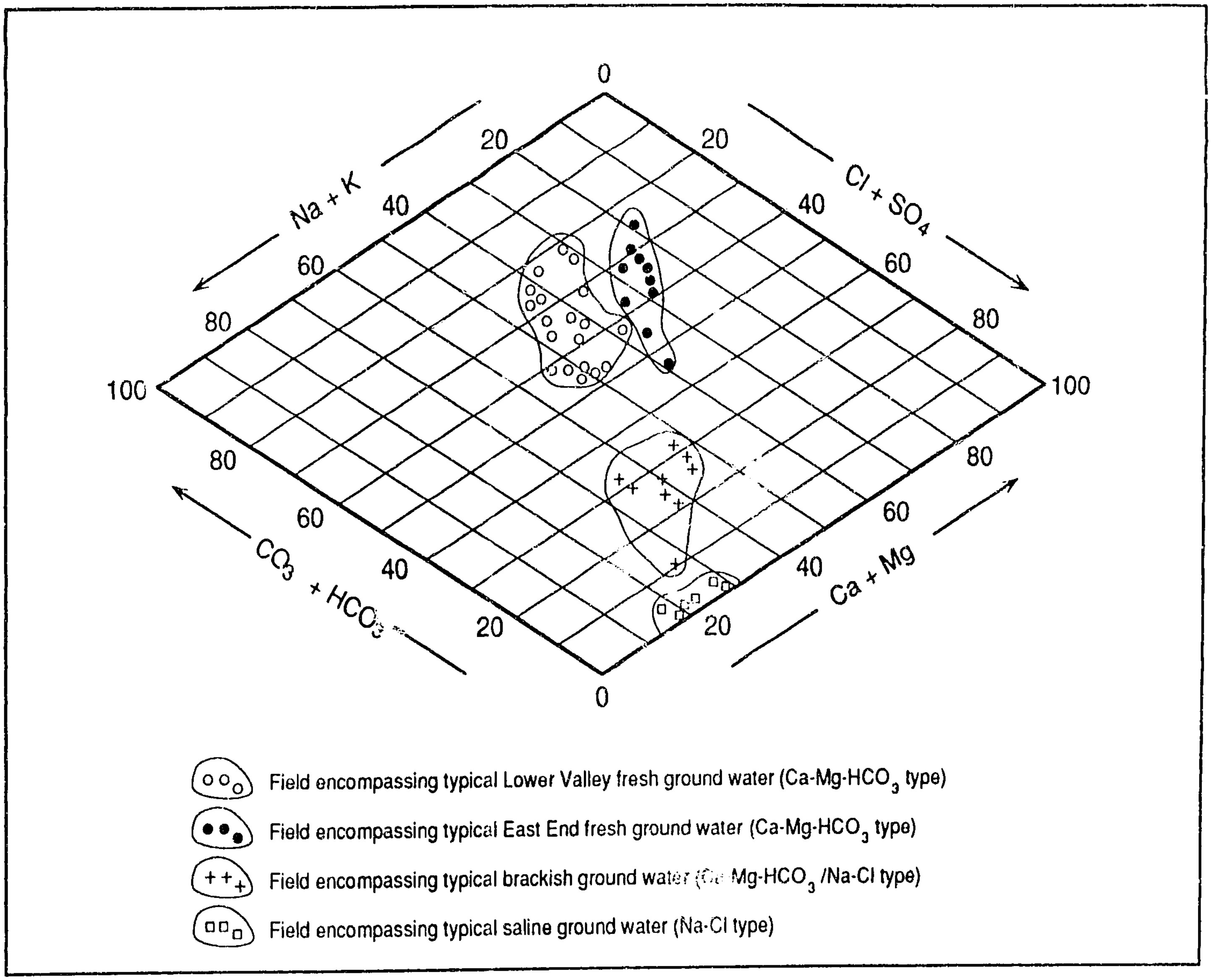


Fig. III.5 Facies diagram showing hydrochemical characters of the ground water on Grand Cayman.

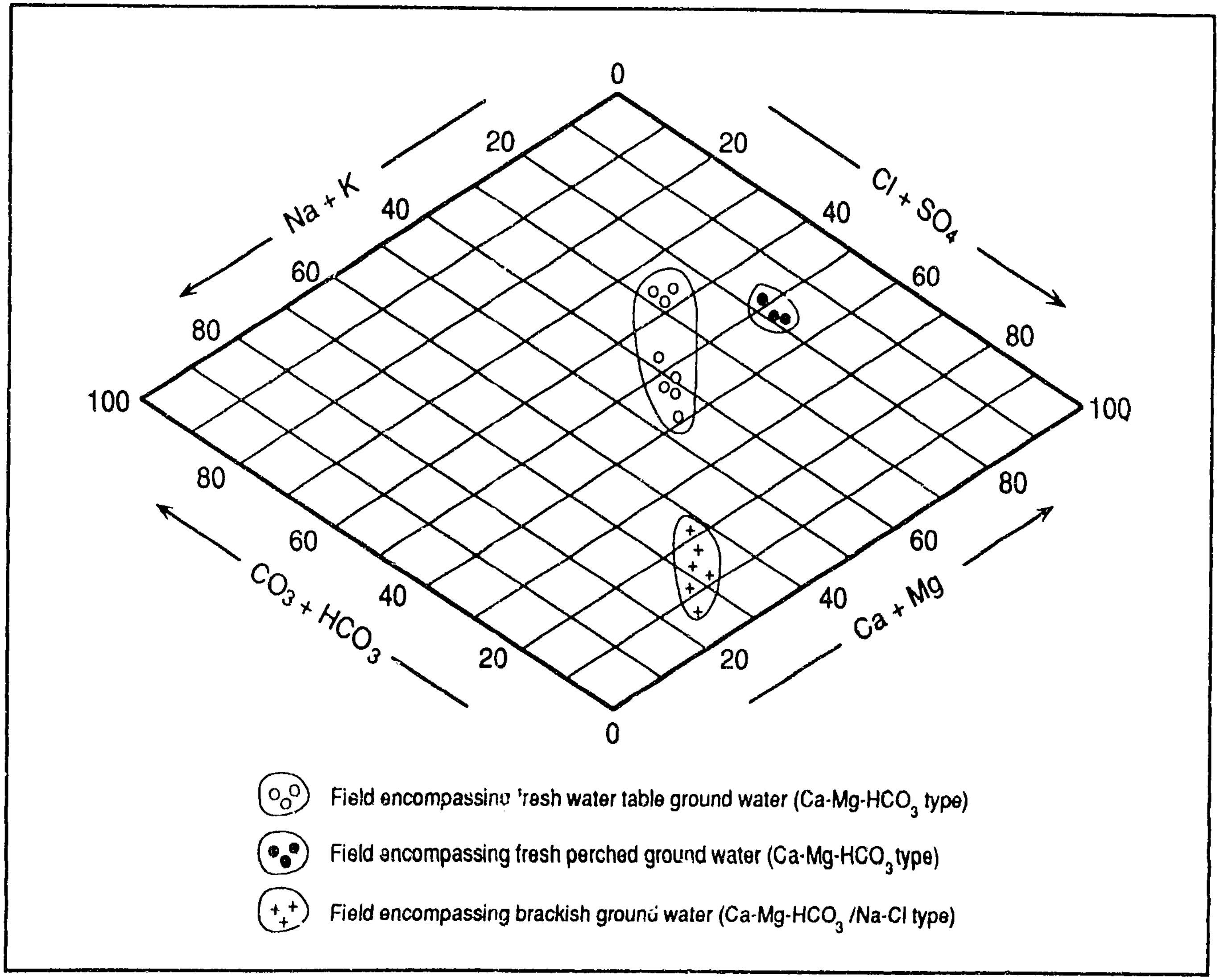


Fig. III.6 Facies diagram showing hydrochemical characters of the ground water on Cayman Brac.

The brackish and saline ground water, which generally has a highly variable salt content, is of the sodium chloride type (Figs. III.5, 6). Although the Cl^- concentration of the Type I saline water is fairly constant, the HCO_3^- content and Mg/Ca ratio varies considerably (Table III.7).

There is a distinct variation in water chemistry between the three fresh water lenses (Figs. III.5, 6), even though they are all developed in the dolostone aquifers of the Bluff Formation. Although the hydrochemical facies is useful in defining the water from different geographic locations and hydrochemical zones, it lacks some important features: (1) waters of different salinity but similar percentage of equivalents per million cannot be differentiated on the diagram, and (2) the molar Na/Cl and Mg/Ca ratios, which are important in identifying the flow pattern, cannot be presented on the facies diagram.

F. VARIATION IN WATER CHEMISTRY

Studies on the temporal and spatial variation of the water chemistry were carried out on the Lower Valley and East End lens of Grand Cayman (Figs. II.3, 4) over the three year period from 1985 to 1988. Spatial variation in the ground water chemistry of the aquifers of the Cayman Islands is well illustrated by the distribution of hydrochemical facies (Figs. III.5, 6) and the molar Na/Cl and Mg/Ca ratios (Tables III.3-8). Temporal variation in the water chemistry was determined by monitoring the production wells and piezometers over a period of about 2 years.

Lower Valley Lens

The fresh water zone of the Lower Valley lens is about 3.8 km^2 in size and less than 12 m thick (Figs. II.3, 19). The small size of the lens together with the low land surface elevation means that the lens is particularly susceptible to the effects of evapotranspiration, precipitation, tides, and abstraction. During the dry season, when evapotranspiration exceeds precipitation, salinity of the ground water increases due to the invasion of the underlying and surrounding brackish water into the fresh water zone. During wet seasons, the high salinity water is flushed out by the rainfall recharge (Figs. III.1A, 7). The composite water (from 25 production wells) of the Lower Valley lens showed a sharp decline in salinity after a prolonged heavy rainfall (>200 mm in 1 week) at the end of May, 1986. Changes in the water chemistry are also indicated by the depth-specific piezometers (Figs. III.7, 8).

Monitoring of piezometer 9-84LV (Fig. II.3, Tables III.1, 3), which was installed in the fresh water zone (308-488 mg/l Cl^-), indicates the following (Fig. III.7): (1) Cl^- and SO_4^{2-} concentration increased during the dry periods and decreased after heavy rainfall. such as the one at the end of May, 1986 (on day 260 in Fig. III.7), and (2) Ca^{2+}, Mg^{2+} and HCO_3^- content showed a gradual increase with time over the monitoring period of about 600 days The changes in salinity can be explained by convection circulation (Kohout, 1964) in response to changes of the water table elevation. The second phenomenon may have resulted from solution of the dolostone bedrock.

A different scenario (Fig. III.8) is indicated by the monitoring of piezometer 30(2)-82LV (Fig. II.3, Tables III.1, 3), which was installed at the base of the fresh water zone (600 mg/l Cl^-). The features include: (1) fairly constant Cl^- and SO_4^{2-} concentration with time, (2) high pH (8-10) and correspondingly low HCO_3^- content, and (3) fluctuation of Ca^{2+} and Mg^{2+} concentration with time. The anomaly of high HCO_3^- content on day 377 was probably due to the relatively low pH of 7.80. The lack of response to heavy rainfall and the high pH suggests that the water occurs in a closed or partially closed aquifer. The cause of the continual variation in Mg^{2+} and Ca^{2+} content is not clear, perhaps both dissolution and precipitation of carbonates were taken place at different times.

East End Lens

The fresh water zone of the East End lens is much larger than the Lower Valley lens (Figs. II.3, 4). It covers a surface area of about 15.0 km^2 and has a maximum thickness of

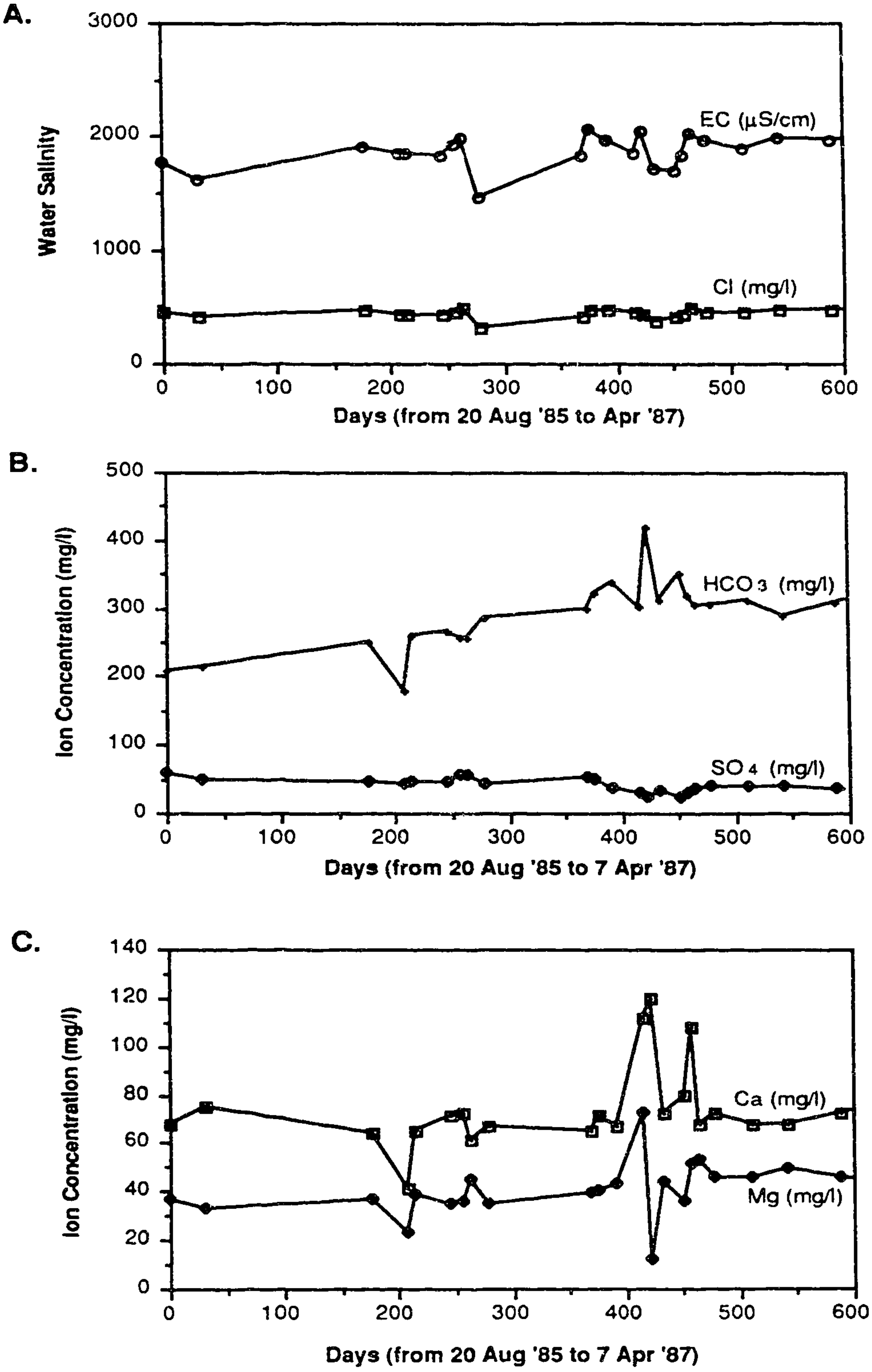


Fig. III.7 Temporal variation of (A)water salinity and chloride (B) bicarbonate and sulfate, and (C) calcium and magnesium ion concentrations recorded by piezometer 9-84LV, Lower Valley Lens.

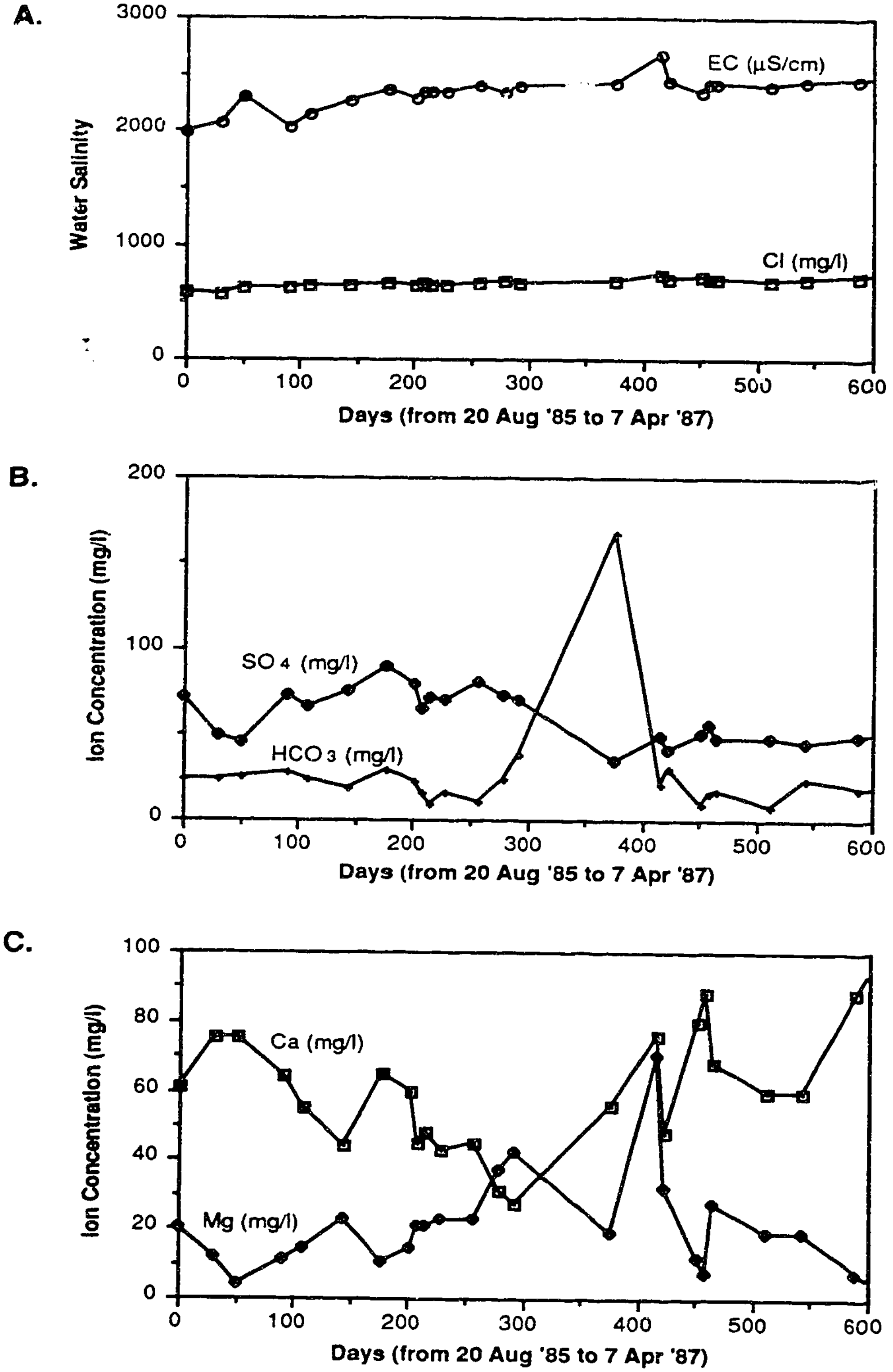


Fig. III.8 Temoral variation of (A) water salinity and chloride, (B) bicarbonate and sulfate, and (C) calcium and magnesium ion concentrations recorded by piezometer 30(2)-82LV, Lower Valley Lens.

about 20 m. The large volume of water in the lens provides an appreciable buffer to external influence as demonstrated by the unchanged water salinity after the heavy rainfall at the end of May, 1986 (Fig. III.1B). However, sampling of depth-specific piezometers indicated some fine details.

The following temporal variations (Fig. III.9) were identified from the monitoring of piezometer 6-84EE (Fig. II.4, Tables III.1, 3): (1) Cl^- concentration was fairly constant with time at about 2000 mg/l , (2) Ca^{2+}, Mg^{2+} and HCO_3^- content were fairly constant with a molar Mg/Ca ratio of about 2, and (3) SO_4^{2-} concentration showed a sharp decline after day 200 before it reached a steady value on day 415. The last phenomenon is of geochemical significance because the water commonly contained about 1 mg/l of H_2S. In this connection, the decrease in sulfate probably resulted from sulfate reduction in a reducing environment as described by Stumm and Morgan (1981).

Data from the monitoring of piezometer 6A-84EE (Fig. II.4, Tables III.1, 3), which was installed in the fresh water zone (300 mg/l Cl^-), showed a rather different picture (Fig. III.10): (1) Cl^- and SO_4^{2-} concentrations were fairly constant, and (2) other than an initial rise in the HCO_3^- content, the overall HCO_3^-, Ca^{2+} and Mg^{2+} concentrations were fairly constant with an average molar Mg/Ca ratio of about 0.9.

The above examples (Figs. III.5-10) clearly indicate the temporal and spatial variation of water chemistry in the dolostone aquifers of the Cayman Islands. The spatial variation is largely due to the fractured and karstic nature of the aquifers which provide many possible subenvironments in the unconfined aquifer, such as open, closed, and partially closed. The temporal variation of water quality is partly the result of seasonal effect, such as heavy rainfall, and is partly due to chemical processes occurring in the ground water system.

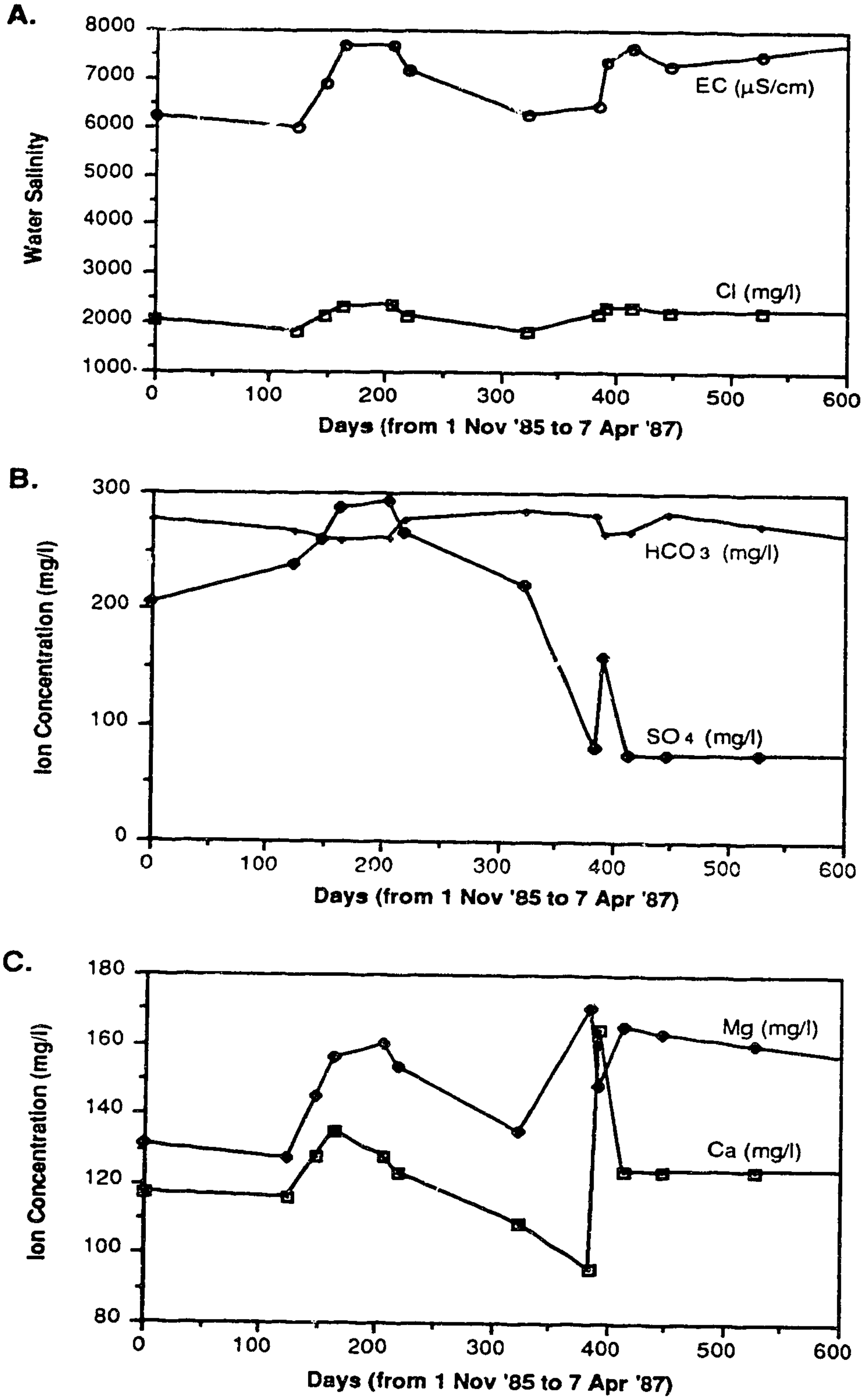


Fig. III.9 Temporal variation of (A) water salinity and chloride, (B) bicarbonate and sulfate, and (C) calcium and magnesium ionconcentrations recorded by piezometer 6-84EE, East End Lens.

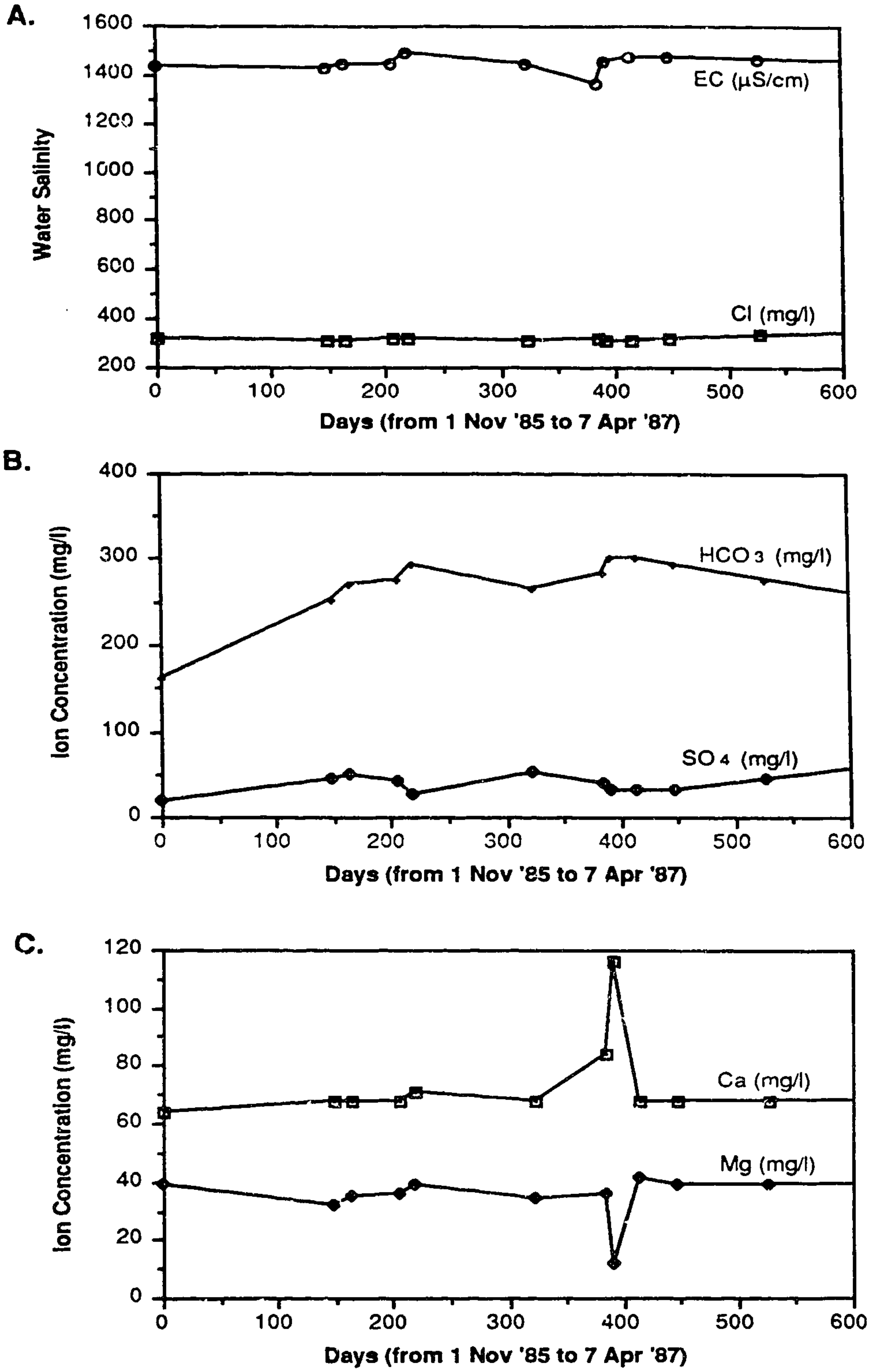


Fig. III.10 Temporal variation of (A) water salinity and chloride, (B) bicarbonate and sulfate, and (C) calcium and magnesium ion concentrations recorded by piezometer 6A-84EE, East End Lens.

G. SYNOPSIS

Hydraulic information on the dolostone aquifers of the Bluff Formation is difficult to interpret; however, systematic study of the chemical characteristics of the ground water permits the following conclusions.

(1) Chemical constituents of the rain water are derived from (i) atmospheric (CO_2 and O_2), (ii) marine (air borne sea spray), and (iii) terrestrial (calcitic soil and dust) sources.

(2) Chemical constituents of the ground water are derived from (i) salts from rain water which are subsequently concentrated by evaporation, (ii) influx of calcium enriched ground water from the limestone aquifer of the Ironshore Formation, (iii) periodic influx of waters of varying composition, which are trapped in sinkholes, (iv) dissolution of carbonate minerals, (v) precipitation of carbonate minerals, (vi) sulfate reduction in a reducing environment, and (vii) salts derived from the underlying saline water which is a derivative of the surrounding sea water.

(3) On the basis of the water salinity and chemical properties, the ground water is divided into perched water, fresh water (<600 mg/l Cl^-), brackish water (>600 to <19,000 mg/l Cl^-), Type I saline water (>19,000 mg/l Cl^-, variable chemical compositions) and Type II saline water (>19,000 mg/l Cl^-, almost constant chemical compositions) hydrochemical zones.

(4) The ground water can be differentiated into three hydrochemical facies: (i) Ca-Mg-HCO_3 type for the fresh ground water, (ii) Na-Cl type for the brackish and saline ground water, and (iii) mixed Ca-Mg-HCO_3/Na-Cl type for fresh ground water affected by minor quantities of saline water.

(5) Even though all the major fresh water lenses are in the Bluff Formation, they show distinct variation in the water chemistry due to different degrees of external influence and water-rock interaction.

(6) Spatial and temporal variations in the water chemistry are also caused by the joint and karst controlled nature of the dolostone, which provides many possible subenvironments such as open, closed, or partially closed conditions within the unconfined aquifer.

IV. THERMODYNAMIC EQUILIBRIUM CONSIDERATIONS

Chemical processes in the dolostone aquifer of the Bluff Formation encompass a variety of reactions leading to the addition or removal of dissolved species from the ground water. Dissolution of the bedrock results in an increase in the porosity and permeability; precipitation of carbonate minerals causes a decrease in the porosity and permeability. These reactions are governed by various chemical equilibrium and kinetic concepts. Thus, in order to decipher the equilibrium water-rock interactions that might occur in the aquifer, it is necessary to consider (1) chemical equilibrium versus chemical kinetics, (2) chemical equilibrium concepts, (3) the equilibrium speciation model, (4) the mixed water model, (5) the equilibrium speciation calculation, and (6) factors controlling the validity of speciation calculation.

A. CHEMICAL EQUILIBRIUM VERSUS CHEMICAL KINETICS

The maximum and minimum concentration of the aqueous species present in ground water is defined by the chemical equilibrium concept (Langmuir and Mahoney, 1984). Chemical kinetics define the reaction pathways and the time it takes to reach equilibrium (Langmuir and Mahoney, 1984). Hoffman (1981), Rubin (1983), and Langmuir and Mahoney (1984) noted that the applicability of using chemical equilibrium concepts to describe ground water chemistry depends on rates of reaction and the ground water residence times in a particular water-rock system.

Hoffman (1981) suggested the use of the half-life of a reaction ($T_{1/2}$) and the residence time of the ground water (T_R) to determine if an equilibrium or kinetic model is required to describe the state of the reaction. When the reaction rates are much faster than the residence time of the ground water ($T_{1/2} \ll T_R$), only equilibrium models are needed. Conversely, when the rate of reactions are comparable or less than the hydraulic residence time ($T_{1/2} \gg T_R$), kinetic models are required. Thus, equilibrium concepts are applicable to ground water studies in deep sedimentary basin where ground water flow is very slow (Langmuir and Mahoney, 1984; Crowe and Longstaffe, 1987).

In the ground water systems of the Cayman Islands, it appears that the chemical equilibrium approach is only applicable to the Type II saline water hydrochemical zone where water movement is slow and chemical compositions of the water are relatively constant (Table III.8). For the other hydrochemical zones, the temporal and spatial variation in the water chemistry (Fig. III.1, III.4-9) suggests that the reactions involving those species have not reached thermodynamic equilibrium. Therefore, both equilibrium and kinetic concepts are probably needed to study the chemical reactions that take place in the shallow unconfined aquifer of the Bluff Formation.

A comprehensive three level scheme was presented by Rubin (1983) for classifying the water chemistry reactions that occur in a ground water system. In the first level, the reactions were divided into sufficiently fast and reversible (chemical equilibrium controlled), or insufficiently fast and/or irreversible (kinetics controlled). Secondly, the reactions were divided into homogeneous (occurs in a single phase) or heterogeneous (occurs between two phases) reaction. Thirdly, the heterogeneous reaction was further divided into surface or classical reactions.

In accordance with Rubin's classification (1983) and the approximate half lives of reactions given by Langmuir and Mahoney (1984), the major geochemical reactions in the dolostone aquifer of the Bluff Formation can be grouped as follows:

(1) Sufficiently fast and reversible homogeneous reactions –

Hydration

$$CO_{2(aq)} + H_2O = H_2CO_3$$

Dissociation

$$H_2CO_3 = H^+ + HCO_3^-$$

$$HCO_3^- = H^+ + CO_3^{2-}$$

Ion complexation

$$Ca^{2+} + CO_3^{2-} = CaCO_3^{\circ}$$

$$Ca^{2+} + HCO_3^{-} = CaHCO_3^{-}$$

(2) Sufficiently fast and reversible heterogeneous classical reactions –

Gas solution and exsolution

$$CO_{2(g)} = CO_{2(aq)}$$

Carbonate dissolution and precipitation (in Type II saline zone)

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^-$$

$$CaMg(CO_3)_2 + 2H^+ = Ca^{2+} + Mg^{2+} + 2HCO_3^-$$

(3) Insufficiently fast heterogeneous classical reactions –

Carbonate dissolution and precipitation (in shallow hydrochemical zones)

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^-$$

$$CaMg(CO_3)_2 + 2H^+ = Ca^{2+} + Mg^{2+} + 2HCO_3^-$$

(4) Insufficiently fast and irreversible heterogeneous classical reactions –

Sulfate reduction and organic oxidation

$$2CH_2O + SO_4^{2-} = H_2S + 2HCO_3^-$$

In the shallow unconfined aquifer of the Bluff Formation, ground water is in active circulation through the well developed joint and karst system. Furthermore, the ground water system is under continual external influences because of tidal oscillation, rainfall recharge, evapotranspiration, influx of surface water and ground water, and tide induced mixing. Thermodynamic equilibrium of the water-rock reactions are difficult to achieve in such a hydrogeological setting because dissolution-precipitation reactions of carbonates have half lives ($T_{1/2}$) of weeks or more (Langmuir and Mahoney, 1984). Therefore, it is apparent that kinetic concepts are needed to understand the diagenetic processes operative in such an environment.

Despite the improved understanding of the kinetics regarding dissolution and precipitation of carbonate minerals (e.g. Plummer *et al.*, 1978, 1979; Berner, 1978, 1981; Busenberg and Plummer, 1982; Dreybrodt, 1981a, 1981b; Morse, 1983; Sjöberg and Rickard, 1984), the application of kinetic concepts to such reactions remains difficult because the (1) reactions are strongly dependent on the surface characteristics of the mineral grains (Berner, 1978, 1981) and the effect of foreign ions (Plummer *et al.*, 1978, 1979), (2) kinetic reactions are poorly characterized (Crowe and Longstaffe, 1987), and (3) the resulting differential equations are mathematically complex to solve (Schwartz, 1984).

Plummer (1984) noted that there are probably no ground water systems that are in overall chemical equilibrium with their host mineralogy, because temperature and pressure variations cause shifts in the equilibrium composition of the system. As a result, a partial equilibrium system may develop (Plummer, 1984). Equilibrium considerations can, however, provide useful information on the possible saturation states of the carbonate minerals in the ground water. However, the reaction mechanisms are probably dictated by chemical kinetics. Thus, a cautious approach in interpreting the water-rock interactions based on results derived from chemical equilibrium concepts is needed.

B. CHEMICAL EQUILIBRIUM CONCEPTS

Chemical equilibrium concepts, which are based on the systematics of thermodynamics, are fairly well defined and can be used to characterized a wide variety of geochemical reactions that occur in the ground water system. The mathematical derivations that lead to the determination of the relative extent of equilibration of the carbonate minerals in the ground water-rock system are well documented (Garrels and Christ, 1965; Krauskopf, 1967; Langmuir, 1971, 1984; Freeze and Cherry, 1979; Stumm and Morgan, 1981; Morel, 1983).

Activities of Dissolved Species

The extent of reaction among species in solution or between solutes, gases or minerals is a function of the activities of the species or substances involved (Garrels and Christ, 1965). Activity and molality are related by:

$$[Si] = \gamma i\ (Si)$$

where [Si] and (Si) are the activity and molality of solute species Si respectively, and γi is the activity coefficient that is commonly less than 1 for ionic species. The activity of a given solute, which changes with the ionic strength (I) of the solution, is defined by:

$$I = \frac{1}{2} \sum (Si)(Zi)^2$$

where Zi is the valence or charge of ionic species Si.

For ionic strength below 0.1 molal (mol/kg), the Debye-Huckel equation is commonly used to compute the activity coefficients of dissolved ionic species. The equation is:

$$\log \gamma i = \frac{-A(Zi)^2\sqrt{I}}{1 + Bai\sqrt{I}} \quad \cdots\cdots\cdots\cdots\cdots\cdots (1)$$

where A and B are functions of temperature (Truesdell and Jones, 1974; Stumm and Morgan, 1981), ai is the 'effective size' of the hydrated ion in Angstroms (Garrels and Christ, 1965; Stumm and Morgan, 1981). To extend the Debye-Huckel equation to a higher ionic strength (0.5 molal), the equation (Helgeson and Kirkham, 1974) becomes:

$$\log \gamma i = \frac{-A(Zi)^2\sqrt{I}}{1 + Bai\sqrt{I}} + biI \quad \cdots\cdots\cdots\cdots\cdots (2)$$

where bi is an adjustable parameter (Truesdell and Jones, 1974) which accounts for the changes to the ion in solution of high salinity. For ions that do not have the ion parameters (ai), the Davies equation (Davies, 1962) is used:

$$\log \gamma i = -A(Zi)^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - cI \right) \cdots\cdots\cdots\cdots (3)$$

where c is an empirical parameter set as 0.3 (Parkhurst *et al.*, 1980). For saline ground water having ionic strength above that of sea water, the Pitzer equation is required (Pitzer, 1973; Crowe and Longstaffe, 1987). For the Cayman Islands, the Pitzer equation is not used, because the surface and ground water are less than, or close to, sea water salinity.

The activity coefficients of uncharged solute species such as CO_2 and O_2 are computed according to the empirical expression (Garrels and Christ, 1965):

$$\log \gamma_i = K_m I \cdots\cdots\cdots\cdots\cdots\cdots (4)$$

where Km is the molal salting coefficient which is commonly close to 0.1 (Morel, 1983). Km is equal to 0.09 for aqueous carbon dioxide at 25°C and 1 atm total pressure (Langmuir, 1984).

For neutral ion pairs, activity coefficients are expressed by the empirical equation (Reardon and Langmuir, 1974):

$$\log \gamma_i = -BI \cdots\cdots\cdots\cdots\cdots\cdots (5)$$

where at 25°C, when $I < 1$, B equals to 0.1 for monovalent ion pair and 0.5 for divalent ion pairs (Reardon and Langmuir, 1974).

Equilibrium Constants and Saturation States

For a given chemical reaction where the constituents A and B react to produce C and D: $aA + bB = cC + dD$, where a, b, c, and d denote the number of moles of the chemical constituents A, B, C, and D respectively, the law of mass action gives:

$$K = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

where K is the temperature dependent equilibrium constant and square brackets refer to activities of respective species.

Limestone and dolostone dissolve when attacked by acids. Besides the atmospheric carbon dioxide that dissolves in the rainfall, the other source of carbon dioxide comes from the root and soil zone (Russell, 1973; Trainer and Heath, 1976). Furthermore, carbon dioxide may be generated by oxidation of organic matter as suggested by James (1977). The aggressiveness of the ground water is governed by the partial pressure of carbon dioxide and the equilibrium expressions. The series of chemical reactions are:

$$CO_{2(g)} + H_2O = H_2CO_3^*$$

$$K_{CO_2} = \frac{[H_2CO_3^*]}{P_{CO_2}}$$

The aqueous concentration of carbon dioxide (P_{CO_2}) and carbonic acid are commonly added and expressed by $H_2CO_3^*$ (Plummer *et al.*, 1976; Morel, 1983).

For the first dissociation of $H_2CO_3^*$

$$H_2CO_3^* = H^+ + HCO_3^-$$

$$K_1 = \frac{[H^+]\,[HCO_3^-]}{[H_2CO_3^*]}$$

For the second step of dissociation

$$HCO_3^- = H^+ + CO_3^{2-}$$

$$K_2 = \frac{[H^+]\,[CO_3^{2-}]}{[HCO_3^-]}$$

where $[H^+]$ = -log pH, at pH <8.3, HCO_3^- is the dominant species, while at pH >8.3, CO_3^{2-} is the dominant species in solution (Freeze and Cherry, 1979; Stumm and Morgan, 1981; Morel, 1983).

For the dissociation of ion pairs, e.g.

$$CaHCO_3^+ = Ca^{2+} + HCO_3^-$$

$$K_{CaHCO_3^+} = \frac{[Ca^{2+}]\,[HCO_3^-]}{[CaHCO_3^+]}$$

$$CaCO_3^\circ = Ca^{2+} + CO_3^{2-}$$

$$K_{CaCO_3^\circ} = \frac{[Ca^{2+}]\,[CO_3^{2-}]}{[CaCO_3^\circ]}$$

For the dissolution of calcite and dolomite

$$CaCO_3 = Ca^{2+} + CO_3{}^{2-}$$

$$Kc = [Ca^{2+}]\ [CO_3{}^{2-}]$$

$$CaMg(CO_3)_2 = Ca^{2+} + Mg^{2+} + 2CO_3{}^{2-}$$

$$Kd = [Ca^{2+}]\ [Mg^{2+}]\ [CO_3{}^{2-}]^2$$

where Kc and Kd are the equilibrium constants (activity product or thermodynamic solubility product constants) of calcite and dolomite respectively. The thermodynamic data base for most common occurring species is available from many sources (e.g. Ball *et al.*, 1979; Kharaka and Barnes, 1973; Parkhurst *et al.*, 1980). Although there is a general concensus on the Kd value (Hsu, 1963; Langmuir, 1971; Hanshaw *et al.*, 1971), the inability to precipitate dolomite in earth surface condition means that the exact value of Kd remains debatable.

The saturation states of a ground water with respect to calcite or dolomite depends on the ion activity product of calcite (IAPc) and dolomite (IAPd) in the solution.

$$IAPc = [Ca^{2+}]\ [CO_3{}^{2-}]$$

$$IAPd = [Ca^{2+}]\ [Mg^{2+}]\ [CO_3{}^{2-}]^2$$

The saturation indices (Langmuir, 1971) of calcite (SIc) and dolomite (SId) are:

$$SIc = \log \frac{IAPc}{Kc}$$

$$SId = \log \frac{IAPd}{Kd}$$

When SIc or SId equals zero, the ground water is saturated with respect to calcite or dolomite. Negative SI indicates undersaturation; positive SI denotes supersaturation. Langmuir (1971, 1984) suggested that the saturation indices within ±0.3 units of zero are saturated with the carbonate minerals due to possible errors in the (1) measurements of pH values, (2) analyses of Ca^{2+}, Mg^{2+} and $HCO_3{}^-$, (3) calculations of ionic strength and ion activity products, and (4) values of calcite and dolomite equilibrium constants. Plummer

(1984), however, noted that an uncertainty of ±0.2 may be needed for the saturation index of dolomite.

According to the equations (1 to 3, and 5) for computing the activity coefficients of the dissolved species (ions and ion pairs), when I increases, γ decreases, and hence, IAP decreases. Therefore, it appears that the solubility of carbonate minerals increases with increasing ionic strength of the solution. However, if the increase in ionic strength results from influx of water containing Ca^{2+}, Mg^{2+} or HCO_3^-, carbonate precipitation may occur, a phenomenon known as the common ion effect (Freeze and Cherry, 1979). In contrast, for uncharged solute species such as CO_2, O_2 and H_2S, solubility decreases with increasing ionic strength (equation 4). Morel (1983) suggested that the effective increase in the activity coefficient of the neutral species is due to the interaction between the neutral species and the ionic species through modification of the dielectric constant of the water. This phenomenon is known as the salting out effect (Freeze and Cherry, 1979; Morel, 1983).

Ion pairing involving Ca^{2+}, Mg^{2+}, HCO_3^- and CO_3^{2-} ions reduces the concentration of the free ions in the water, and hence, the saturation states of the water with respect to the carbonate minerals. Such effects become significant in water of high salinity such as sea water. Formation of $MgCO_3^\circ$, $CaCO_3^\circ$, and $NaCO_3^-$ ion pairs reduces the free CO_3^{2-} concentration by 85.5% (Reardon and Langmuir, 1974), and approximately 50% of Ca^{2+} and Mg^{2+} in the sea water is paired with Cl^- (Johnson and Pyktowicz, 1978).

C. EQUILIBRIUM SPECIATION MODEL

The prime application of speciation calculations is to determine if a particular mineral in the water-rock system tends to dissolve or precipitate. These calculations are based on a chemical equilibrium model of the aqueous solution and thermodynamic data for the mineral-water reactions in questions (Nordstrom *et al.*, 1979; Plummer, 1984). Invariably, computerized geochemical models are used in the calculation of multicomponent, multiphase equilibria. Nordstrom *et al.* (1979) reviewed and compared results from more than 30 computerized chemical models using type sea water and river water. The results generally show a better agreement in the river water test case than the sea water because of the more reliable activity coefficients and the smaller amount of ion complexing at low ionic strength (Nordstrom *et al.*, 1979).

In this study, a modified version of the PHREEQE geochemical model (Parkhurst *et al.*, 1980) called PHREEQEX (Crowe and Longstaffe, 1987) was used for equilibrium speciation calculations. The PHREEQE model is based on the ion-association theory using an equilibrium constant approach with considerations for both free ions and ion pairs (complexes). The model is based on solving a set of simultaneous equations (Parkhurst *et al.*, 1980) which included (1) charge balance for the solution, (2) conservation of electron for the water-rock system, (3) mass balance for each element, (4) mineral equilibrium for each mineral phase, and (5) mass action for each aqueous species other than master species. Activity coefficients are calculated by the extended Debye-Huckel or Davies equation (Parkhurst *et al.*, 1980). The results obtained are the ion concentrations, the activity coefficients, and the activities and saturation states of the aqueous phase with respect to various mineral phases.

Crowe and Longstaffe (1987) modified the PHREEQE model by: (1) compiling the program with VS FORTRAN, (2) altering the code to reduce execution time, (3) increasing the temperature limit on the data base, and (4) expanding the data base of thermodynamic properties for the aqueous species. The PHREEQEX data base (Crowe and Longstaffe, 1987) included approximately 250 aqueous species, 50 minerals and 6 gases, whereas the PHREEQE data base (Parkhurst *et al.*, 1980) included only 120 aqueous species and 24 minerals including P_{CO_2}. The additional data base of PHREEQEX was largely adopted from that of Kharaka and Barnes (1973) in the equilibrium model SOLMNEQ (A.S. Crowe, 1987, pers. comm.).

PHREEQE has been extensively tested and successfully validated through application to many geochemical problems (Parkhurst *et al.*, 1980; Plummer, 1984; Crowe and Longstaffe, 1987). In order to ensure that the modified version (PHREEQEX) provides comparable results, the program was tested by carrying out equilibrium computation for the sea water test data of Nordstrom *et al.* (1979). The results on the activity coefficients (Table IV.1) and molality (Table IV.2) of selected major species and saturation indices of the carbonate minerals (Table IV.2) are similar to those computed by seven other models studied by Nordstrom *et al.* (1979). The differences in the saturation indices of the carbonate minerals obtained from the different models are within the uncertainty limits suggested by Langmuir (1971, 1984) and Plummer (1984).

The slight differences in the results between PHREEQEX and the other geochemical models (Tables IV.1, 2) probably resulted from the limitations suggested by Nordstrom *et al.* (1979), which are caused by differences in the (1) thermodynamic data, (2) calculation of activity coefficients, (3) assumption of redox states, (4) total number of complexes considered, (5) correction of alkalinity for non-carbonate components, and (6) correction of temperature dependent equilibrium constants. This comparative study demonstrates that the PHREEQEX model gives comparable results even for water of sea-water salinity; therefore, this model is employed for the speciation calculation and simulation study of the ground water of Cayman Islands.

D. MIXED WATER MODEL

Runnells (1969) showed that mixing of aqueous solutions produces non-linear chemical effects which include changes in the concentration and electrical properties of a solution and shifts in homogeneous equilibria, which causes precipitation or dissolution of a solid phase. Since then, geochemical models have been used to investigate the non-linear behaviour in the mixture of fresh calcium carbonate ground water and sea water (Badiozamani, 1973; Plummer, 1975; Palmer, 1984; Back *et al.*, 1986) and of carbonate

Table IV.1 Activity coefficients of selected major species in sea water calculated by different geochemical models.

MODEL	EQUIL	EQ3	MIRE	SEAWAT	SOLMNEQ	WATEQF	WATEQ2	PHREEQEX
γCa^{2+}	0.245	0.245	0.231	0.245	0.244	0.249	0.249	0.251
$\gamma CaSO_4^{\circ}$	1.172	1.000	0.507	1.150	1.180	1.170	1.170	1.157
$\gamma CaHCO_3^{+}$	0.714	0.714	0.589	0.669	0.737	0.747	0.747	0.742
$\gamma CaCO_3^{\circ}$	1.172	1.000	1.123	1.150	1.180	1.170	1.170	1.157
γMg^{2+}	0.315	0.315	0.296	0.314	0.263	0.288	0.288	0.288
$\gamma MgSO_4^{\circ}$	1.172	1.000	1.123	1.150	1.180	1.170	1.170	1.157
$\gamma MgHCO_3^{+}$	0.671	0.670	0.589	0.669	0.670	0.747	0.747	0.742
$\gamma MgCO_3^{\circ}$	1.172	1.000	0.387	1.150	1.180	1.170	1.170	1.157
γNa^{+}	0.671	0.670	0.631	0.688	0.670	0.706	0.706	0.706
$\gamma NaSO_4^{-}$	0.683	0.682	0.589	0.669	0.720	0.747	0.747	0.742
$\gamma NaHCO_3^{\circ}$	1.172	-	1.123	1.150	1.180	1.170	1.170	1 157
γK^{+}	0.626	0.626	0.589	0.625	0.626	0.622	0.622	0.627
γKSO_4^{-}	0.650	0.647	0.589	0.669	0.720	0.747	0.747	0.742
γCl^{-}	0.627	0.626	0.589	0.625	0.626	0.622	0.622	0.627
γSO_4^{2-}	0.618	0.167	0.158	0.167	0.167	0.181	0.181	0.156
γHCO_3^{-}	0.690	0.690	0.631	0.669	0.720	0.675	0.747	0.678
γCO_3^{2-}	0.188	0.187	0.195	0.190	0.222	0.207	0.311	0.212
γSr^{2+}	0.207	-	-	-	0.207	0.311	0.311	0.304
γH^{+}	0.804	0.805	-	0.750	0.804	0.747	0.747	0.742
γOH^{-}	0.650	0.649	0.589	0.685	0.649	0.747	0.747	0.742

Table IV.2 -Log molality of selected major species and saturation indices of selected minerals in sea water calculated by different geochemical models.

MODEL	EQUIL	EQ3	MIRE	SEAWAT	SOLMNEQ	WATEQF	WATEQ2	PHREEQEX
-log (Ca^{2+})	2.013	2.027	2.074	2.053	2.013	2.024	2.025	2.020
-log (Mg^{2+})	1.304	1.319	1.322	1.347	1.299	1.311	1.312	1.619
-log (Na^{+})	0.336	0.320	0.335	0.321	0.336	0.320	0.320	0.333
-log (K^{+})	1.982	1.983	2.000	1.981	1.982	1.983	1.983	1.974
-log (Sr^{2+})	4.016	-	-	-	4.045	4.016	4.016	4.056
-log (Cl^{-})	0.257	0.247	0.265	0.247	0.256	0.247	0.247	0.248
-log (SO_4^{2-})	1.906	1.823	1.836	2.009	1.881	1.811	1.808	1.840
-log (HCO_3^{-})	2.884	2.816	2.815	2.808	2.885	2.825	2.836	2.772
-log (CO_3^{2-})	4.419	4.371	4.415	4.369	4.484	4.422	4.566	4.380
-log (H^{+})	8.125	8.126	-	-	8.125	8.093	8.093	8.091
-log (OH^{-})	5.603	5.606	5.552	5.613	5.601	5.660	5.660	5.662
Ionic Strength	0.663	0.677	0.655	0.660	0.666	0.680	0.680	0.633
Total Carbon	-	-	-	-	-	-	$2.142*10^{-3}$	$2.257*10^{-3}$
Saturation Index:								
Calcite	+0.60	+0.806	+0.621	+0.631	+0.597	+0.742	+0.774	+0.802
Dolomite	+2.30	+3.439	+2.277	+2.305	+2.219	+2.330	+2.394	+2.109
Siderite	-2.65	-10.276	-	-	-6.691	-9.006	-8.973	-8.846
Rhodochrosite	-3.57	-4.444	-4.077	-	-3.709	-3.727	-3.695	-4.401

waters of different compositions (Wigley and Plummer, 1976). These mathematical manipulations are complicated by (1) whether the mixing is in a closed or open system, (2) determination of the chemical compositions of the original solutions, and (3) the changes in the physico-chemical conditions in which mixing occurs. The modelling approach also depends on the limitations imposed by the chemical models (Nordstrom *et al.*, 1979). The geochemical properties of the mixed water obtained from the aqueous models do not necessarily represent the actual chemical characteristics in aquifer conditions. Therefore, these results cannot be applied to carbonate diagenetic studies without addressing the hydrogeological setting and the actual hydrochemical properties.

On the Cayman Islands, the joint and karst controlled aquifer system results in the development of subenvironments (open, closed, or partially closed conditions) in a single aquifer. This situation is well illustrated by the spatial and temporal variation of the ground water chemistry (Figs. III.5-10). The chemical composition of the fresh ground water is variable and it is not possible to assign an average value that can be used in the mixing models.

The validity of using sea water as the other end member in the mixing models is questionable. Using sea water as one of the end member ignores the fact that once sea water enters the carbonate rock system, water-rock interactions occur. It has been shown that although the Type II saline ground water has a fairly constant chemical composition (Table III.8) and has a salinity similar to that of the sea water (Table III.3), the chemical constituents of the two waters are quite different (Tables III.3, 8). Furthermore, there are at least seven possible forms of mixing in the dolostone aquifer of the Bluff Formation:

(1) rain water (infiltrated through the unsaturated zone) and ground water at the water table,

(2) rain water (infiltrated through open joints) and ground water at the water table,

(3) rain water and perched ground water in the unsaturated zone,

(4) fresh ground water and the underlying saline water,

(5) fresh ground water and sea water at coastal discharge zone,

(6) ground water of the dolostone aquifer and the calcium enriched ground water from the limestone aquifer of the Ironshore Formation, and

(7) ground water and surface water from sinkholes, large ponds, and swamps.

These are the mixing phenomena that are actively occurring in the dolostone aquifer of the Bluff Formation. Thus, it is unrealistic to use the simple mixed ground water-sea water model to describe the chemical equilibrium conditions of the complicated natural water-rock system on the Cayman Islands.

In view of the difficulties in determining (1) the chemical compositions of the end members of the various mixing processes, (2) the pH of the mixed waters, and (3) the aquifer conditions of the mixed waters, this study deals with the actual chemical compositions of the ground waters sampled from different hydrochemical zones. This method of study allows the investigation of the saturation states of the carbonate minerals in different hydrochemical zones and their constancy or fluctuation with respect to time.

E. EQUILIBRIUM SPECIATION CALCULATIONS

Speciation calculations were used to examine the saturation states of the ground water with respect to calcite and dolomite in different hydrochemical zones, and hence, determine if dissolution or precipitation would occur. These calculations were done assuming that equilibrium exists throughout the water-rock system. It is imperative to note that the computations did not take into consideration the kinetics of the reactions. Thus, it is possible that the reactions calculated from chemical equilibrium concepts may not be occurring in the subsurface environment due to kinetic factors.

The saturation indices of calcite (SIc) and dolomite (SId) were computed with consideration of the effects of ionic strength and ion complexation. Confidence limits of ±0.1 for SIc and SId were used to define the saturation states of the ground water with respect to calcite and dolomite.

Rain Water

Rain water of the Cayman Islands is undersaturated with respect to both calcite and dolomite (Table IV.3) because of its low concentration of calcium, magnesium and bicarbonate ion. Partial pressure of carbon dioxide (P_{CO_2}) in the water (Table IV.3) is similar to that of the atmosphere (0.0003 atm). This suggests that the carbon dioxide in the rain water is in equilibrium with the atmospheric carbon dioxide. The undersaturation of the rain water with respect to the carbonate minerals indicates that the rain water is capable of dissolving bedrock when it falls on the land surface.

Ground Water – Perched Water Zone

The perched waters collected from Cayman Brac (Table III.6) are supersaturated with respect to calcite and dolomite (CB1, CB2, CB3, Table IV.4), indicating that precipitation of carbonate cements could occur in that zone. P_{CO_2} of the perched water is about three times that in the atmosphere. The increase in P_{CO_2} indicates that carbon dioxide was added to the ground water when the rain water infiltrated through the soil and root zone.

Ground Water – Fresh Water Zone

Fresh ground water of the Lower Valley lens (Figs. II.1,3) is saturated or supersaturated with respect to calcite (SI_{cI}, Table IV.5). However, only 14 of the 31 wells sampled have ground water which is supersaturated with respect to dolomite (SI_{dI}, Table IV.5). Most of the water samples collected from wells located further to the south (well # 26-34) are supersaturated with respect to dolomite (Table IV.5). This distribution suggests that there may be a geographic effect on the chemical properties of the ground water. The ground water located near the northern and eastern margin of the fresh water lens (Fig. IV.1) is probably influenced by the influx of (1) calcium-enriched ground water from the Ironshore Formation, and (2) water from the mangrove swamps which has a pH range of

Table IV.3 Saturation states of rain water with respect to calcite and dolomite on Grand Cayman.

Location	**pH**	**pe**	**I**	**(Mg/Ca)**	**$(Mg/Ca)_I$**	**$[Mg/Ca]_I$**	**SIc**	**SId**	**P_{CO_2}**
North Side (NS)	7.8	12.0	0.0017	0.098	0.047	0.047	-0.5144	-1.1405	0.00028
Lower Valley (L1)	7.5	12.0	0.0015	0.210	0.130	0.130	-1.1808	-1.5815	0.00036
Lower Valley (L2)	7.3	12.0	0.0010	0.310	0.230	0.230	-1.7925	-2.0768	0.00036
George Town (C1)	7.4	12.0	0.0010	0.000	0.000	0.000	-1.5296	N/A	0.00033

Note: (Mg/Ca) refers to molar ratio, $(Mg/Ca)_I$ refers to molar ratio with ion complexation, $[Mg/Ca]_I$ refers to activity ratio with ion complexation.

Table IV.4 Saturation states of fresh ground water with respect to calcite and dolomite in the Tibbetts Turn Lens on Cayman Brac.

Sample #	**pH**	**I**	**(Mg/Ca)**	**$(Mg/Ca)_I$**	**$[Mg/Ca]_I$**	**SIc**	**SId**	**P_{CO_2}**
CB1(pw)	7.9	0.0106	1.24	0.59	0.59	0.5406	0.4639	0.00090
CB2(pw)	7.9	0.0104	1.36	0.65	0.65	0.5439	0.4870	0.00095
CB3(pw)	7.9	0.0107	1.42	0.68	0.68	0.5476	0.5005	0.00096
CB4(fw)	7.5	0.0170	0.73	0.52	0.53	0.4120	0.3079	0.00300
CB7(wt)	8.1	0.0099	2.76	1.03	1.04	0.6711	0.7144	0.00080
CB8(fw)	7.8	0.0115	0.84	0.45	0.45	0.6481	0.5122	0.00150
CB9(fw)	7.6	0.0148	0.78	0.51	0.51	0.5034	0.3942	0.00250
CB11(wt)	7.9	0.0137	1.40	0.69	0.70	0.8124	0.7693	0.00151
CB12(fw)	7.7	0.0194	0.85	0.52	0.53	0.7573	0.6535	0.00240

Note: (pw) refers to perched water, (wt) refers to fresh water collected at the water table, (fw) refers to fresh water collected below the water table.

Table IV.5 Effect of ion complexation on the fresh ground water of the Lower Valley lens on Grand Cayman. Subscript I refers to calculation with ion complexing.

Well #	pH	I	(Mg/Ca)	$(Mg/Ca)_I$	SIc	SIc_I	SId	SId_I
P1	7.33	0.0128	0.22	0.17	0.3818	0.2691	0.0957	-0.0742
P2	7.50	0.0083	0.52	0.35	0.2747	0.2073	0.1694	0.0185
P3	7.48	0.0102	0.69	0.48	0.3032	0.2161	0.2598	0.0940
P4	7.32	0.0120	0.69	0.53	0.1429	0.0404	0.1007	-0.0585
P5	7.40	0.0078	0.58	0.42	0.2037	0.1430	0.1225	-0.0079
P6	7.38	0.0092	0.32	0.24	0.2184	0.1388	0.0105	-0.1350
P7	7.53	0.0054	0.69	0.45	-0.1438	-0.1688	-0.1866	-0.3043
P8	7.20	0.0115	0.60	0.49	0.2125	0.1095	0.1388	-0.0091
P9	7.47	0.0093	0.32	0.23	0.3882	0.3071	0.1806	0.0218
P10	7.38	0.0105	0.74	0.55	0.3939	0.2997	0.3671	0.2086
P11	7.43	0.0123	0.70	0.51	0.3616	0.2507	0.3239	0.1435
P12	7.25	0.0089	0.42	0.33	0.1975	0.1248	0.0465	-0.0775
P13	7.39	0.0087	0.42	0.31	0.3319	0.2593	0.1837	0.0438
P14	7.50	0.0101	0.62	0.43	0.3071	0.2187	0.2436	0.0736
P15	7.59	0.0071	0.51	0.33	0.3121	0.2561	0.2053	0.0495
P16	7.51	0.0116	0.60	0.41	0.3672	0.2659	0.2933	0.1101
P17	7.44	0.0172	0.75	0.55	0.3141	0.1658	0.2902	0.0738
P18	7.44	0.0104	0.45	0.33	0.4478	0.3484	0.3155	0.1439
P23	7.50	0.0140	0.75	0.52	0.2373	0.1165	0.2127	0.0132
P24	7.50	0.0135	0.75	0.52	0.2036	0.0874	0.1783	-0.0170
P25	7.50	0.0116	0.53	0.37	0.3704	0.2684	0.2702	0.0879
P26	7.66	0.0097	0.54	0.33	0.4447	0.3575	0.3502	0.1535
P27	7.58	0.0127	0.63	0.42	0.4447	0.3317	0.3839	0.1789
P28	7.52	0.0142	0.74	0.51	0.4155	0.2907	0.3874	0.1814
P29	7.45	0.0150	0.70	0.51	0.4387	0.3072	0.3985	0.1965
P30	7.50	0.0145	0.77	0.54	0.4222	0.2939	0.4040	0.1979
P31	7.65	0.0133	0.85	0.53	0.5016	0.3810	0.5047	0.2805
P32	7.52	0.0122	0.66	0.46	0.3906	0.2820	0.3404	0.1491
P33	7.65	0.0082	0.82	0.50	0.4282	0.3589	0.4249	0.2462
P34	7.52	0.0121	0.62	0.43	0.4901	0.3807	0.4244	0.2324
TW	7.62	0.0127	0.21	0.13	0.7436	0.6440	0.4393	0.2412

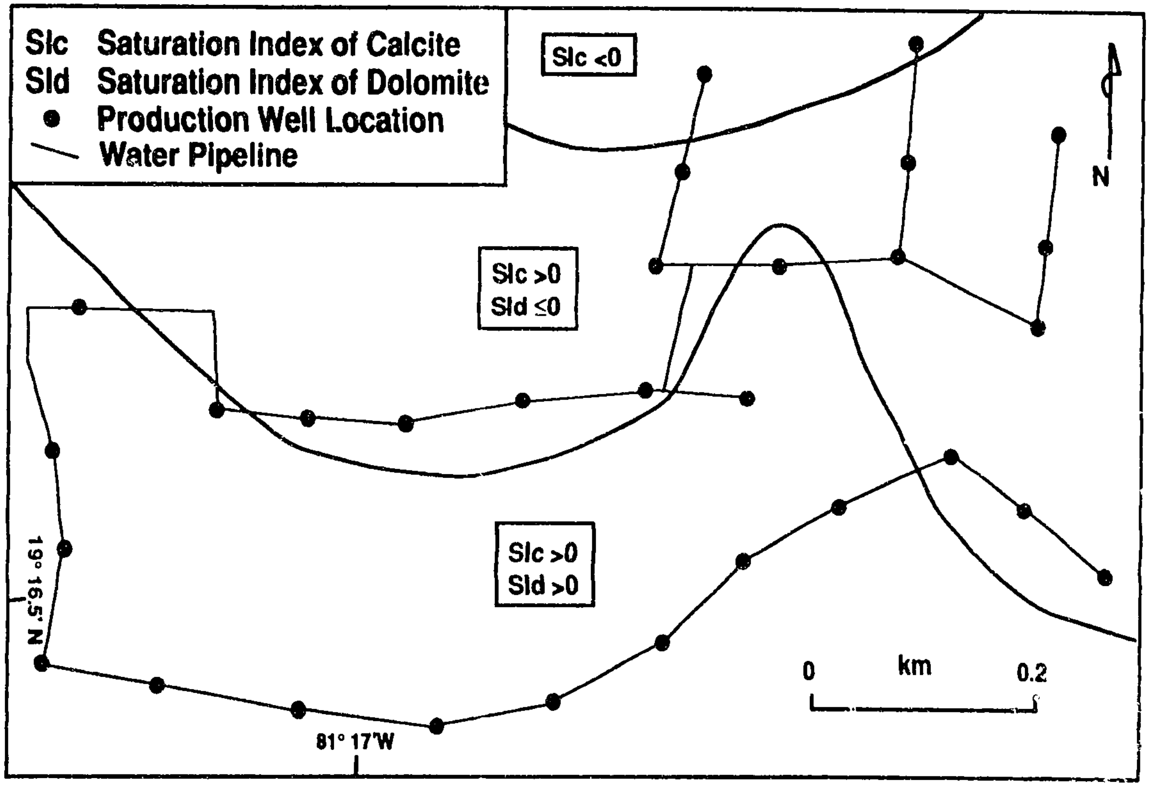


Fig. IV.1 Regions of calcite and dolomite saturation around Lower Valley well field. Location of Lower Valley well field shown on Fig. II.3. Caribbean coast is about 1.5 km form the centre of the well field.

6-7.5. Both factors would cause a decrease in the saturation state of the ground water with respect to dolomite. Plummer *et al.* (1976) suggested that undersaturation of the ground water with respect to the carbonate minerals in the aquifers of Bermuda is caused by the influx of CO_2 from neighbouring peat marshes. Anthony *et al.* (1989) also noted that elevated P_{CO_2} values in the ground water on Majuro atoll are commonly associated with taro pits where CO_2 is generated by respiration of plant roots and decay of organic matter. Conversely, fresh ground water located near the southern boundary of the Lower Valley lens (Fig. IV.1) is influenced by mixing with saline water. The saline water (a sea water derivative) provides the Mg^{2+} that causes an increase in the ion activity product of dolomite in the ground water. Despite the low molar Mg/Ca ratio (<1.0), the water is saturated with respect to dolomite.

The East End lens, which is located in the interior of the eastern portion of Grand Cayman (Fig II.1), has fairly constant saturation states with respect to calcite and dolomite (Table IV.6). The fairly constant chemical properties of the ground water suggests that the lens is less susceptible to external influence than the Lower valley lens due to its (1) geographic location, (2) higher topographic relief, and (3) larger lens size. The molar Mg/Ca ratios of less than 1.0 probably result from leaching of the calcium rich terra rossa during the rainy seasons. The fresh ground water is supersaturated with respect to both calcite and dolomite and has P_{CO_2} about 6-12 times that in the atmosphere. The moderate-to-dense vegetation cover above the East End lens is probably the main source of CO_2.

For the Tibbetts Turn lens of Cayman Brac (Fig. II.2), the fresh ground water is supersaturated with respect to calcite and dolomite (Table IV.4). The P_{CO_2} of the Tibbetts Turn lens is lower than that of the East End lens (Tables IV.4), although the vegetation covers above both lenses are similar. The lower CO_2 content in the Tibbetts Turn lens is probably caused by exsolution of CO_2 when the water moves through the thick unsaturated zone. Similarly, the lower P_{CO_2} of the waters at the water table than those immediately

Table IV.6 Saturation states of fresh ground water with respect to calcite and dolomite in the East End lens on Grand Cayman.

Well #	pH	pe	I	(Mg/Ca)	$(Mg/Ca)_I$	$[Mg/Ca]_I$	SIc	SId	P_{CO_2}
PW1	7.5	12.0	0.0127	0.88	0.61	0.62	0.4101	0.3417	0.00335
PW2	7.5	12.0	0.0115	0.64	0.44	0.45	0.4800	0.3411	0.00339
PW3	7.5	12.0	0.0132	0.72	0.51	0.51	0.5032	0.3936	0.00355
PW4	7.5	12.0	0.0104	0.71	0.49	0.49	0.3839	0.2662	0.00303
PW5	7.5	12.0	0.0142	0.75	0.53	0.53	0.5608	0.4594	0.00379
PW7	7.5	12.0	0.0120	0.64	0.44	0.45	0.5558	0.4169	0.00373
PW8	7.5	12.0	0.0120	0.62	0.43	0.43	0.5035	0.3577	0.00348
PW9	7.5	12.0	0.0110	0.82	0.57	0.58	0.2234	0.1395	0.00254
PW10	7.5	12.0	0.0118	0.88	0.61	0.61	0.2120	0.1418	0.00250
EE11	7.7	12.0	0.0138	0.68	0.41	0.41	0.7076	0.5494	0.00209
EE12	7.6	12.0	0.0147	1.01	0.66	0.66	0.3125	0.2591	0.00186
EE12A	7.4	12.0	0.0150	0.74	0.55	0.56	0.1611	0.0695	0.00312
EE12B	7.5	12.0	0.0120	0.78	0.54	0.55	0.2865	0.1910	0.00266
EE13	7.7	12.0	0.0122	0.73	0.43	0.44	0.4439	0.2993	0.00124
EE14	7.4	12.0	0.0159	0.79	0.59	0.60	0.2519	0.1753	0.00321
EE15	7.4	12.0	0.0155	0.77	0.57	0.58	0.2125	0.1300	0.00306
EE16	7.5	12.0	0.0159	0.85	0.59	0.60	0.2828	0.1877	0.00239
EE17	7.6	12.0	0.0099	0.78	0.50	0.50	0.3838	0.2701	0.00203
EE18	7.5	12.0	0.0086	0.66	0.46	0.46	0.3732	0.2403	0.00306
EE19	7.5	12.0	0.0136	0.48	0.34	0.34	0.5322	0.3346	0.00299

Note: PW refers to production wells at the East End well field, EE refers to Irrigation wells at the New Hut Farm well field.
(Mg/Ca) refers to molar ratio, $(Mg/Ca)_I$ refers to molar ratio with ion complexation, $[Mg/Ca]_I$ refers to activity ratio with ion complexation.

below the water table (cf. CB7 and CB8, CB11 and CB12, Table IV.4) is probably the result of exsolution of CO_2 at the water table.

Ground Water – Lightly Brackish Water Zone

In all cases, the lightly brackish water (<15% sea water) on the Cayman Islands is supersaturated with respect to calcite and dolomite (Table IV.7). The molar Mg/Ca ratios are all close to or greater than 1.0 except for CB17 (Table IV.7), which suggests that the water is formed by mixing of fresh carbonate ground water and the underlying saline water. For sample CB17, the low Mg/Ca ratio (0.8) probably results from the influx of calcium enriched water from the Ironshore Formation which is less than 0.5 km north of the sampling well. This inflow of ground water from the coastal limestone aquifer may occur during periods of seasonal high tide which raise the potentiometric head of the ground water in the limestone aquifer.

Ground Water – Highly Brackish to Type I Saline Water Zone

In general, the highly brackish ground water (CF, GT1, W2, GT2, SW2) and the Type I saline ground water (SW1, W3-5, W7-8) are saturated to supersaturated with respect to calcite and dolomite (Table IV.8). The water samples (W1, W6, W9) that are undersaturated with respect to calcite and/or dolomite have pH values less than 7.0. The low pH may be due to the influx of CO_2 from the brackish water swamps because the brackish water swamps are a part of the regional hydrogeological flow regime. A similar phenomenon was suggested for aquifers in Bermuda (Plummer *et al.*, 1976). Hanshaw and Back (1979) also suggested that in the zone of dispersion, CO_2 flux may result from root respiration, or decomposition of organic material in intruding ocean water.

There appears to be no direct relationship between the ionic strength of the solutions and the molar Mg/Ca ratios (Fig. IV.2A), and the saturation states (Fig. IV.2B). These results do not agree with the simple mixing of fresh carbonate ground water and sea water

Table IV.7 Saturation states of lightly brackish ground water (<15% sea water) with respect to calcite and dolomite.

Sample	**pH**	**I**	**(Mg/Ca)**	**$(Mg/Ca)_I$**	**$[Mg/Ca]_I$**	**SIc**	**SId**	**P_{CO_2}**
Lower Valley, Grand Cayman (samples from piezometers):								
4-84	7.66	0.0304	1.24	0.80	0.81	0.3164	0.3065	0.00142
9-84	7.48	0.0211	1.05	0.76	0.77	0.2009	0.1796	0.00268
East End, Grand Cayman (samples from piezometers):								
4-84	7.70	0.0265	1.57	0.97	0.99	0.2995	0.3328	0.00146
6-84	7.44	0.0797	2.13	1.65	1.71	0.1498	0.3021	0.00229
8-84	8.10	0.0482	0.96	0.40	0.41	0.3435	0.1858	0.00017
Tibbetts Turn, Cayman Brac (samples from observation wells):								
CB5	7.7	0.0424	1.53	0.98	1.00	0.6363	0.6723	0.00214
CB10	7.8	0.0383	1.35	0.79	0.80	0.6640	0.6518	0.00146
CB13	7.8	0.0485	1.81	1.07	1.10	0.6306	0.6866	0.00144
CB14	7.9	0.0447	1.94	1.03	1.05	0.5134	0.5605	0.00076
CB16	7.8	0.0727	2.62	1.60	1.65	0.5513	0.6960	0.00133
CB17	7.6	0.1297	0.80	0.58	0.61	0.7829	0.7119	0.00211
CB18	7.7	0.0278	1.13	0.71	0.72	0.4818	0.4448	0.00163
CB19	8.0	0.0854	2.19	1.11	1.15	0.6892	0.7555	0.00061

Note: Round bracket refers to molar ratio, square bracket refers to activity ratio, Subscript I refers to ion complexation.

Table IV.8 Saturation states of highly brackish to saline ground water and sea water with respect to calcite and dolomite on Grand Cayman.

Sample #	**pH**	**I**	**Cl^-**	**Mg^{2+}**	**Ca^{2+}**	**(Mg/Ca)**	**$(Mg/Ca)_I$**	**SIc**	**SId**
CF	7.20	0.2298	6625	437	300	2.40	2.08	-0.0229	0.1872
WB1	6.79	0.3779	11000	696	228	5.03	4.68	-0.6313	-0.2529
GT1	7.30	0.4492	13366	886	380	3.84	3.26	0.2892	0.6058
WB2	7.01	0.5110	15300	877	548	2.64	2.42	0.0078	0.2472
GT2	7.30	0.5661	16794	1044	660	2.61	2.22	0.4429	0.6796
SW2	7.40	0.6205	18103	1469	500	4.84	4.01	0.1700	0.5369
SW1	7.50	0.6856	19644	1882	460	6.75	5.40	0.2427	0.6760
WB3	7.21	0.6315	20500	559	396	2.33	2.06	0.0548	0.2635
WB4	7.41	0.6410	20500	573	422	2.24	1.88	0.1405	0.3301
WB5	7.11	0.7275	20600	1390	449	5.10	4.64	-0.0562	0.3315
WB6	6.87	0.6644	20700	1060	604	2.89	2.72	-0.1054	0.3285
WB7	7.25	0.6440	20800	573	417	2.27	1.99	0.0704	0.2720
WB8	7.31	0.6479	21000	573	441	2.14	1.86	0.1581	0.3446
WB9	6.93	0.7051	21400	1360	656	3.42	3.13	-0.1024	0.1993
Sea Water	8.20	0.6187	19350	1294	413	5.17	2.47	0.8006	1.0621
Beach Water	8.27	0.6471	20200	1450	383	6.24	2.87	0.6016	0.8824

Note: (Mg/Ca) refers to molar ratio of Mg/Ca,
$(Mg/Ca)_I$ refers to molar ratio of Mg/Ca with ion complexation.
All ion concentrations in mg/l.

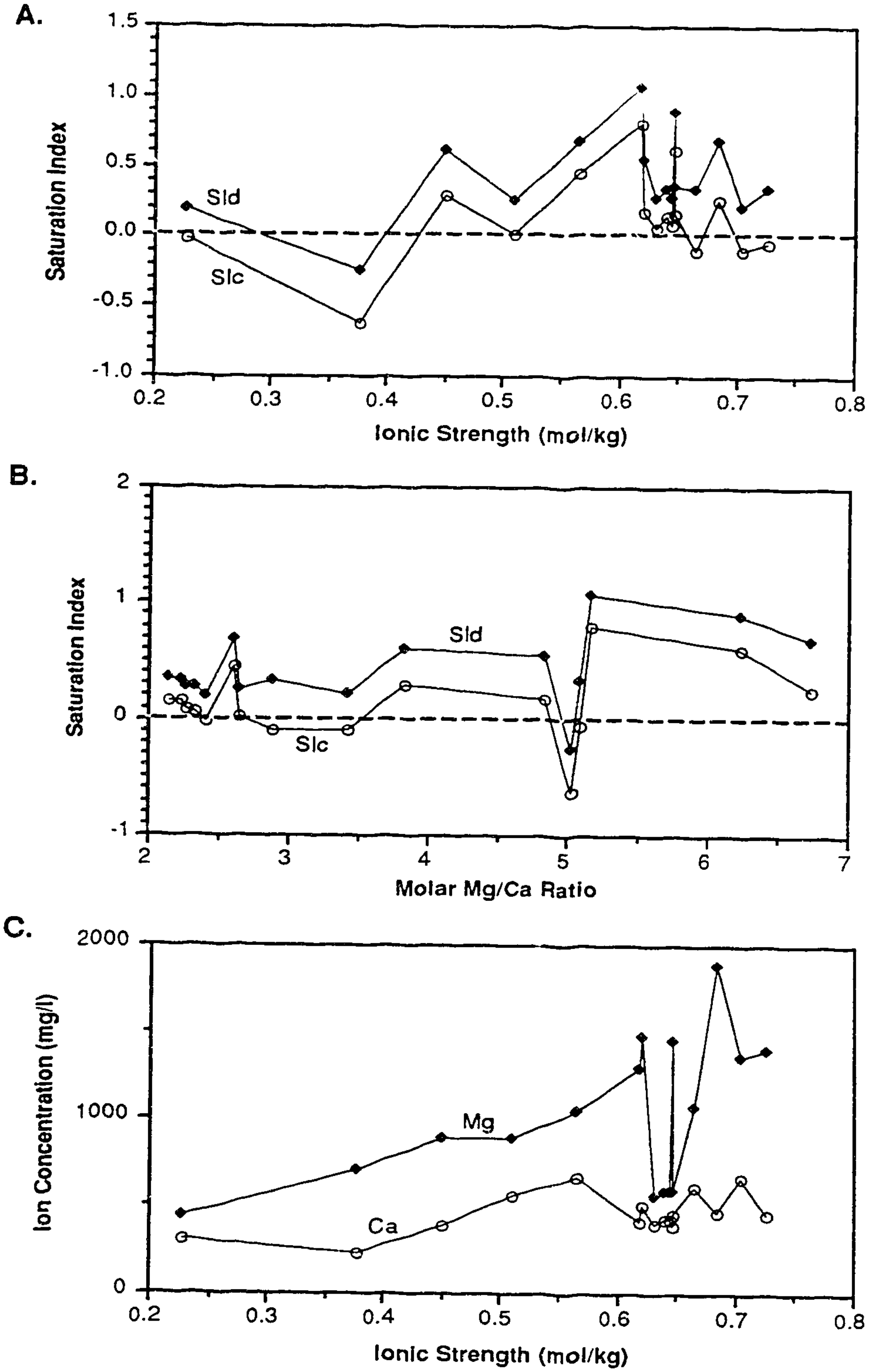


Fig. IV.2 Cross plots of hydrochemical properties of highly brackish to saline ground water. (A) Saturation index versus ionic strength, (B) saturation index versus molar Mg/Ca ratio, and (C) magnesium and calcium ion concentrations versus ionic strength.

as suggested by Badiozamani (1973), Plummer (1975), and Back *et al.* (1986). Furthermore, there is no simple relationship between the ionic strength of the solutions and the Mg^{2+} and Ca^{2+} content (Fig. IV.2C).

The applicability of simple mixing of the fresh water in the dolostone aquifer and the sea water to describe the molar Mg/Ca ratio of the ground water in the highly brackish and saline water zones was examined by a simple mass balance calculation. A molar Mg/Ca ratio of 1.0 is assumed for the unmixed ground water in the dolostone aquifer (dissolution of stoichiometric dolomite) and 5.17 for the sea water (Table IV.8). Thus, the molar Mg/Ca of the mixed fresh water-sea water equals to 5.17*(% sea water)+1.0*(1-% sea water). Percent sea water in the ground water is calculated from the chloride ion concentration because Hem (1970) suggested that chloride ions do not significantly enter into chemical or biochemical processes in the aquatic system. The measured Mg/Ca ratios are generally not in agreement with those calculated from the mass balance equation (Table IV.9). These differences suggest that at least six possible phenomena may be occurring in the dolostone aquifer of the Bluff Formation.

(1) Mixed water formed by volumetric mixing of ground water of varying compositions and sea water is indicated when the measured and calculated Mg/Ca are about equal (CF, GT1, SW2, Table IV.9),

(2) Mixed water having higher measured than calculated Mg/Ca ratio suggests that precipitation of carbonate minerals has occurred (WB1, Table IV.9),

(3) Mixed water having lower measured than calculated Mg/Ca ratio suggests that dissolution of carbonate minerals has occurred (WB2, GT2, Table IV.9),

(4) Ground water of about sea water salinity in which precipitation of calcite and/or dolomite has occurred resulting in a higher measured than calculated Mg/Ca ratio (SW1, Table IV.9),

Table IV.9 Interpretation of the possible make-up of the highly brackish ground water on Grand Cayman.

Sample #	Cl^- (mg/l)	% of sea water	(Mg/Ca) calculated*	(Mg/Ca) measured	(Mg)/(Ca) of gw for mixing	ground water make-up
CF	6625	33.9	2.41	2.40	0.98	1
WB1	11000	56.3	3.35	5.03	4.85	2
GT1	13366	68.4	3.85	3.84	0.96	1
WB2	15300	78.3	4.27	2.64	?	3
GT2	16794	86.0	4.59	2.61	?	3
SW2	18103	92.7	4.87	4.84	0.65	1
SW1	19644	100.5	5.20	6.75	-	4
WB3	20500	105.0	5.43	2.33	-	5
WB4	20500	105.0	5.43	2.24	-	5
WB5	20600	105.5	5.45	5.10	-	6
WB6	20700	106.0	5.48	2.89	-	5
WB7	20800	106.5	5.51	2.27	-	5
WB8	21000	107.5	5.56	2.14	-	5
WB9	21400	109.6	5.48	3.42	-	5

Note: * Assuming molar (Mg/Ca) of pure ground water in dolostone aquifer as 1.0 while sea water as 5.17, (Mg/Ca) of the mixed ground-sea water = 5.17* (% sea water) + 1.0* (1- % sea water).

1. Ground water formed by volumetric mixing of fresh ground water and sea water.
2. Mixed fresh ground water-sea water with carbonate mineral precipitation.
3. Mixed fresh ground water-sea water with carbonate mineral dissolution.
4. Ground water of sea water salinity with calcite and/or dolomite precipitation.
5. Ground water of sea water salinity with calcite and/or dolomite dissolution.
6. Ground water of sea water composition.

(5) Ground water of about sea water salinity in which dissolution of calcite and/or dolomite has occurred resulting in a lower measured than calculated Mg/Ca ratio (WB3, WB4, WB6 to WB9, Table IV.9), and

(6) Ground water of about sea water salinity and chemical composition (WB5, Table IV.9).

It is, therefore, evident that simple mixing rarely occurs in the joint and karst controlled dolostone aquifers of the Cayman Islands. Similar phenomena probably occur in other carbonate environments.

Ground Water – Type II Saline Water Zone

The type II saline ground water is supersaturated with respect to calcite and dolomite. Its salinity is similar to that of the surrounding sea water (Tables III.3, 8). However, the molar Mg/Ca ratios of the saline water are in the range of 4.46 to 4.86 which are lower than the sea water; the bicarbonate content is higher than that in sea water (Tables III.3, 8). These data suggest that the original sea water has been modified by calcite and/or dolomite dissolution in the subsurface environment, a phenomenon similar to that occurring in the Type I saline water zone.

F. CONTROLLING FACTORS OF SPECIATION CALCULATIONS

This section investigates the major factors that would have impact on the validity of the results obtained from equilibrium speciation calculations. It includes the effect of (1) ion complexation, (2) pH, (3) temperature, (4) pe, (5) tidal fluctuation, (6) rain water recharge, and (7) ground water abstraction and recovery.

Ion Complexation

Chemical analyses of dissolved constituents in ground water, such as Ca^{2+}, Mg^{2+}, and HCO_3^-, indicate their total concentrations. However, these constituents may be present in the form of free ions (e.g. Ca^{2+}), uncharged ion pairs (e.g. $CaCO_3^{\circ}$) and charged ion pairs (e.g. $CaHCO_3^{+}$). The uncharged and charged ion pairs are commonly referred to as ion complexes (Freeze and Cherry, 1979). The effect of ion complexation becomes significant in water of high salinity such as sea water (Reardon and Langmuir, 1974; Johnson and Pyktowicz, 1978). The expressions for the mass balance of Ca^{2+}, Mg^{2+}, SO_4^{2-}, and CO_3^{2-} are:

$$Ca_{(total)} = Ca^{2+} + CaCO_3^{\circ} + CaHCO_3^{+} + CaSO_4^{\circ} + Ca(OH)^{+} + CaCl_2^{\circ}$$

$$Mg_{(total)} = Mg^{2+} + MgCO_3^{\circ} + MgHCO_3^{+} + MgSO_4^{\circ} + Mg(OH)^{+}$$

$$CO_{3(total)} = CO_3^{2-} + CaCO_3^{\circ} + MgCO_3^{\circ} + NaCO_3^{-} + Na_2CO_3^{\circ}$$

$$SO_{4(total)} = SO_4^{2-} + CaSO_4^{\circ} + MgSO_4^{\circ} + NaSO_4^{-} + Na_2SO_4^{\circ}$$

Similar equations can be written for each element present in the solution. These mass balance equations indicate or suggest that (1) the concentrations of free ions decrease as a result of ion complexation, (2) the activities of the free ions decrease accordingly, and (3) the saturation indices of the mineral species also decrease depending on the degree of ion complexing.

The importance of ion complexation is well illustrated by comparing the saturation states of the ground water with respect to calcite and dolomite without and with complex ions considered (Table IV.5). Most samples from the Lower Valley fresh ground water indicate supersaturation with respect to calcite (30 out of 31) and dolomite (29 out of 31) with no complex ions considered (SI_c, SI_d, Table IV.5, Fig. IV.3). When ion complexes were taken into account in the speciation calculations, the saturation indices of calcite and dolomite were significantly reduced (SI_{cI}, SI_{dI}, Table IV.5, Fig.IV.3), with only 15 samples indicating supersaturation with respect to dolomite.

The decrease in the molar Mg/Ca ratio with complex ions considered (Tables IV.3-8) suggests that calcium ions are more prone to form complex ions than are magnesium ions. The effect of complex ions is more significant on the saturation index of dolomite than that of calcite (Fig. IV.3). Furthermore, with ion complexation, the percentage of

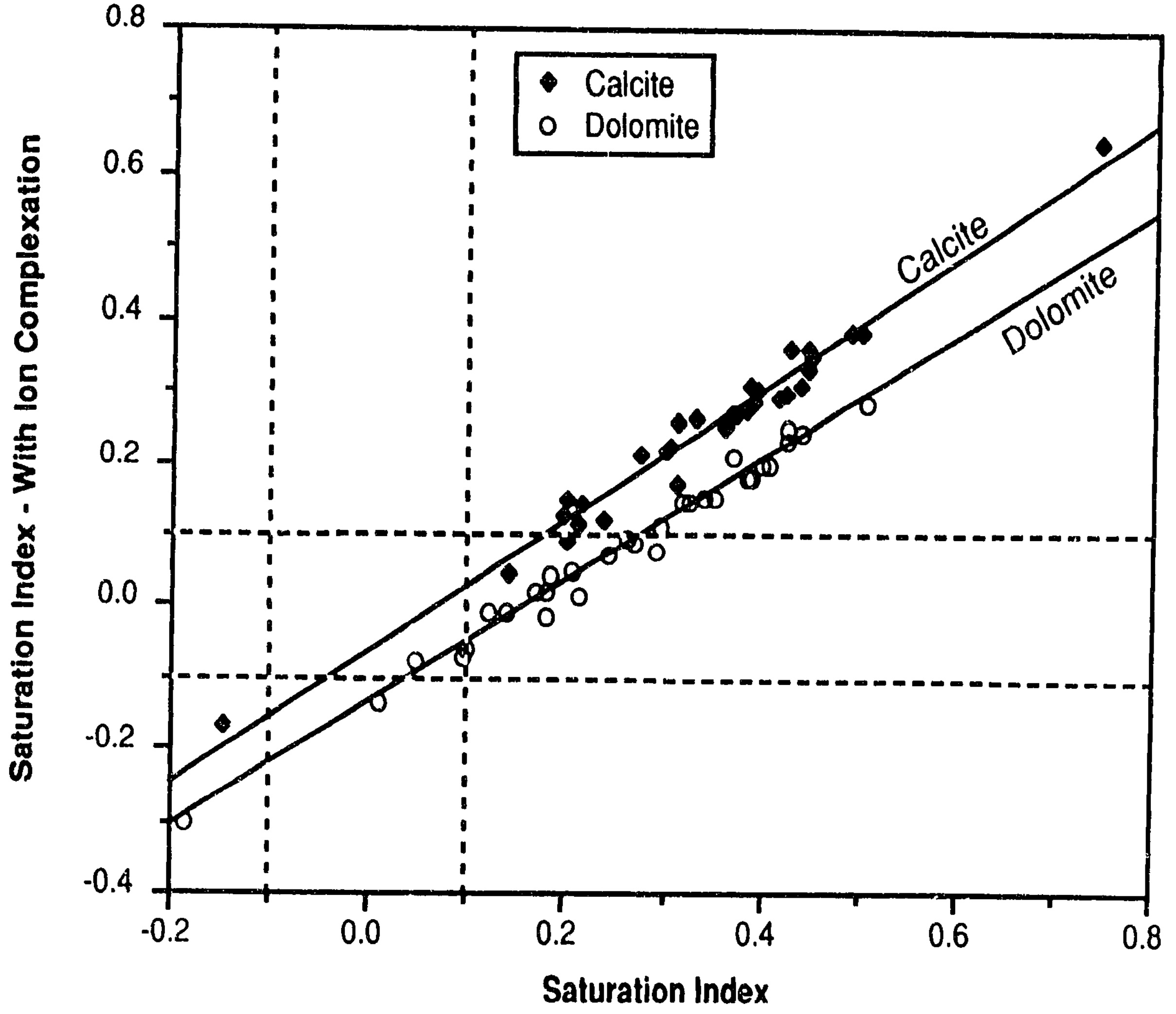


Fig. IV.3 Effect of ion complexation on the saturation states of the Lower Valley ground water with respect to calcite and dolomite. When Saturation index equals to 0.0, the water is saturated with respect to the mineral, ±0.1 are the limits of uncertainty (dashed lines).

reduction on the degree of saturation decreases with increasing saturation states (Fig. IV.3).

pH

The main source of error in water-mineral equilibrium calculations is caused by using pH values that are measured in the laboratory (Back, 1961a; Hem, 1970; Langmuir, 1971a, 1984; Shuster and White, 1971; Freeze and Cherry, 1979). The differences between laboratory and field pH of the ground water of the Cayman Islands are commonly less than 0.20 (Table IV.10) with the exception of the water samples collected from the piezometer pairs of 8-84 and 10-80 at East End (Table IV.10). The general perception is that pH values measured in the laboratory tend to be higher than those measured in the field due to exsolution of CO_2 (Hem, 1970; Freeze and Cherry, 1979). In contrast, the water samples from the piezometer pairs at East End showed a decrease in pH values (Table IV.10).

According to the generalized equations for calcite and dolomite dissolution:

$$CO_{2(aq)} + H_2O = H_2CO_3 = H^+ + HCO_3^-$$

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^-$$

$$CaMg(CO_3)_2 + 2H^+ = Ca^{2+} + Mg^{2+} + 2HCO_3^-$$

the reactions shift to the right in order to have a decrease in pH or an increase in P_{CO_2}. Indeed, P_{CO_2} increases from 0.00017 to 0.00099 atm for piezometer 8-84 and from 0.00019 to 0.00048 atm for piezometer 10-84 (Table IV.11). The increase in P_{CO_2} when the water was exposed to the atmosphere suggests that the waters were in closed conditions in the aquifer which resulted in the depletion of CO_2. In this situation, the saturation states of the ground water with respect to the carbonate minerals shifted from supersaturation in the aquifer system to undersaturation when it was exposed to the atmosphere.

The small differences between the field and laboratory pH of the other water samples (Table IV.10) suggest strong buffering of the carbonate equilibria in the ground waters. However, a small variation in pH could have a significant impact on the saturation

Table IV.10 Measurements of field pH versus laboratory pH on two separate dates. E.C. (electrical conductivity) in µS/cm, Cl^- in mg/l.

Piez. #	Location	Date	E.C.	Cl^-	Field pH	Lab. pH
4-84	Lower Valley	07.04.87	2940	772	7.66	7.70
		22.04.87	3680	1038	7.61	7.69
5-84	Lower valley	07.04.87	1000	208	7.74	7.73
		22.04.87	1055	222	7.69	7.78
9-84	Lower Valley	07.04.88	1970	459	7.48	7.52
		22.04.88	2060	507	7.47	7.60
30(1)-82	Lower Valley	07.04.88	1620	463	9.59	9.67
		22.04.88	1955	507	10.96	10.98
30(2)-82	Lower Valley	07.04.88	2460	724	9.83	9.73
		22.04.88	2360	728	10.81	10.81
4-84	East End	07.04.88	2520	652	7.70	7.66
		22.04.88	2680	676	7.89	7.71
4A-84	East End	07.04.88	1610	377	7.69	7.61
		22.04.88	1712	406	7.66	7.66
6-84	East End	07.04.88	7480	2250	7.44	7.40
		22.04.88	7720	2390	7.45	7.48
6A-84	East End	07.04.88	1460	338	7.46	7.46
		22.04.88	1472	328	7.39	7.44
8-84	East End	07.04.88	4950	1470	8.10	7.36
		22.04.88	5520	1690	8.01	7.66
10-80	East End	07.04.88	823	169	8.42	8.03
		22.04.88	830	169	8.61	8.50

Table IV.11 Effect of field versus laboratory pH on the saturation states with respect to carbonate minerals using ground waters collected from piezometer 8-84EE and 10-80EE as examples.

Chemical Composition: of 8-84EE

Ca^{2+} = 108 mg/l
Mg^{2+} = 63 mg/l
Na^{+} = 790 mg/l
K^{+} = 1.5 mg/l

Cl^{-} = 1470 mg/l
SO_4^{2+} = 100 mg/l
Total Alkalinity = 75.4

I = 0.0495
(Mg/Ca) = 0.96 (no ion complexing)
Field pH = 8.10
Lab. pH = 7.36

pH	**(Mg/Ca)**	**[Mg/Ca]**	**(CO_3^{2-})**	**SIc**	**SIa**	**SId**	**SIm**	**P_{CO_2}**
8.10	0.40	0.41	$0.1237*10^{-4}$	0.3435	0.2117	0.1858	-0.2949	0.00017
7.36	0.76	0.78	$0.2344*10^{-5}$	-0.3830	-0.5149	-0.4014	-0.7425	0.00099

Chemical Composition: of 10-80EE

Ca^{2+} = 12 mg/l
Mg^{2+} = 46 mg/l
Na^{+} = 93 mg/l
K^{+} = 0.3 mg/l

Cl^{-} = 169 mg/l
SO_4^{2+} = 25 mg/l
Total Alkalinity = 155.7

I = 0.0087
(Mg/Ca) = 6.32 (no ion complexing)
Field pH = 8.42
Lab. pH = 8.03

pH	**(Mg/Ca)**	**[Mg/Ca]**	**(CO_3^{2-})**	**SIc**	**SIa**	**SId**	**SIm**	**P_{CO_2}**
8.42	1.35	1.36	$0.4130*10^{-4}$	0.2280	0.0962	0.3304	0.1099	0.00019
8.03	2.51	2.53	$0.1733*10^{-4}$	-0.1494	-0.2812	0.0876	0.0016	0.00048

Note: Round bracket refers to molality or molar ratio, square bracket refers to activity ratio, all calculations with ion complex consideration. Subscripts c, a, d and m refer to calcite, aragonite, dolomite, and magnesite respectively.

states of the ground water regardless of the water salinity (Table IV.12). This is due to the fact that carbonate ion concentration increases logarithmically with increasing pH (Table IV.10) in accordance with the dissociation equation of bicarbonate: $[CO_3^{2-}] = K_2 [HCO_3^-] * 10^{pH}$. It is important to note that the pH values fluctuate on a day-to-day basis (Table IV. 10) as a result of (1) influxes of CO_2 from time to time in relation to both the local and regional flow regime, and/or (2) water-rock interactions. Therefore, the pH should be measured in the field and not be assumed as a constant value at a specific well point or piezometer.

Temperature

The temperature of the ground water on the Cayman Islands is relatively constant all year round. It is about 27-30°C for the shallow zone and about 25-27°C in the deeper saline water zone. In the range of temperature considered in aquatic chemistry, the effect of temperature on equilibrium can be calculated by the van't Hoff equation (Morel, 1983):

$$\ln\left(\frac{K_T}{K_{T_o}}\right) = \frac{-\Delta H^\circ}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)$$

where ΔH° is the change in enthalpy, K_T and K_{T_o} are equilibrium constants at T and T_o °K, $T_o = 298.13$°K, R is the gas constant. Temperature dependence of the equilibrium constant can also be represented by an analytical expression (Parkhurst *et al.*, 1980):

$$\log K = A_1 + A_2T + \frac{A_3}{T} + A_4T^2 + \frac{A_5}{T^2}$$

where A_1, A_2, A_3, A_4, and A_5 are coefficients that are reaction specific (Plummer and Busenberg, 1982; Reardon and Langmuir, 1974; Langmuir, 1971, 1984).

On the Cayman Islands, waters that are susceptible to temperature variation are the surface waters. A daily temperature fluctuation of 5°C or more is common. In this connection, the effect of temperature on the saturation states of the cave pool water (Old Man Bay Cave) and pond water (Colliers Pond) was examined. The effect of temperature

Table IV.12 Sensitivity analyses of pH effect on the saturation states with respect to carbonate minerals using ground water samples collected from PW1 and W5 as examples.

East End Well PW1 (fresh ground water), field pH = 7.5:

pH	I	(Mg/Ca)	[Mg/Ca]	(CO_3^{2-})	SIc	SIa	SId	SIm	P_{CO_2}
6.5	0.0134	0.84	0.85	$0.1130*10^{-5}$	-0.5893	-0.7212	-0.5901	-0.9137	0.0337
6.8	0.0133	0.81	0.82	$0.2252*10^{-5}$	-0.2892	-0.4211	-0.2986	-0.6308	0.0169
7.0	0.0132	0.77	0.78	$0.3562*10^{-5}$	-0.0892	-0.2210	-0.1083	-0.4501	0.0106
7.2	0.0130	0.72	0.71	$0.5629*10^{-5}$	0.1108	-0.0211	0.0772	-0.2792	0.0067
7.5	0.0127	0.61	0.61	$1.1150*10^{-5}$	0.4101	0.2782	0.3417	-0.0497	0.0034
8.0	0.0120	0.38	0.38	$3.4375*10^{-5}$	0.9022	0.7704	0.7267	0.2283	0.0010

Well W5 (saline ground water), field pH = 7.11:

pH	I	(Mg/Ca)	[Mg/Ca]	(CO_3^{2-})	SIc	SIa	SId	SIm	P_{CO_2}
6.50	0.7317	4.91	5.72	$0.1382*10^{-5}$	-0.6630	-0.7997	-0.2628	-0.1874	0.0403
6.80	0.7303	4.82	5.61	$0.2749*10^{-5}$	-0.3641	-0.5007	0.0320	0.1032	0.0201
7.00	0.7287	4.72	5.49	$0.4343*10^{-5}$	-0.1654	-0.3020	0.2260	0.2925	0.0127
7.11	0.7275	4.64	5.40	$0.5582*10^{-5}$	-0.0562	-0.1929	0.3315	0.3944	0.0098
7.20	0.7263	4.57	5.31	$0.6848*10^{-5}$	0.0326	-0.1040	0.4167	0.4760	0.0080
7.50	0.7207	4.20	4.87	$1.3481*10^{-5}$	0.3272	0.1906	0.6929	0.7336	0.0040
8.00	0.7045	3.11	3.61	$4.0289*10^{-5}$	0.8039	0.6672	1.1042	1.0796	0.0012

Note: Round bracket refers to molality or molar ratio, square bracket refers to activity ratio, all calculations with ion complex consideration, SIc, SIa, SId, and SIm refer to saturation indices of calcite, aragonite, dolomite, and magnesite respectively.

on the equilibrium constants (Kc and Kd), and hence, the saturation states (SIc and SId) is significant even with a small temperature range of 25-30°C for the cave pool water and 27-33°C for the pond water (Tables IV.13,14). The calculations show that the temperature dependence increases with decreasing pH. For the cave pool water (Tables IV.13), when temperature increases from 25 to 30°C, SId increases by 16% at pH of 7.8, by 30% at pH of 7.5, and by 164% at pH of 7.2. It is apparent that the pH values play a more important role than temperature in controlling the saturation states of the mineral species in the solution (Tables IV.13, 14). Temperature variation becomes an important parameter in a stable pH environment such as sea water.

pe

pe, a parameter used in describing the equilibrium redox conditions (Freeze and Cherry, 1979), is defined as –log[e], where [e] is the electron activity. pe and the more commonly used term, Eh (redox potential), are related by:

$$pe = \frac{nF}{2.3RT} Eh$$

where n is the number of electrons in the half reactions, F the faraday constant, R the gas constant, and T the temperature in °K. At 27°C, which is the average temperature of the ground water in the Cayman Islands, pe = 16.8 Eh.

Measurements of Eh are difficult for carbonate ground waters due to the presence of electroactive species in the solution (Langmuir, 1971). In this study, dissolved oxygen (DO) was measured and related to Eh (Krauskopf, 1967) by:

$$Eh = Eh^{\circ} - \frac{0.0591}{2} \log \frac{1}{(H^{+})^{2} \sqrt{P_{O_2}}}$$

where Eh° is the standard potential, $(H^{+}) = 10^{pH}$, and P_{O_2} (in atm) = 0.0246 * DO (Langmuir, 1984). For the range of pH and DO values of the ground water on the Cayman Islands, pe values are primarily controlled by the pH (Fig. IV.4).

Table IV.13 Effects of pH and temperature on the saturation states of the Old Man Bay Cave pool water with respect to calcite and dolomite. $(Mg/Ca)_I$ and $[Mg/Ca]_I$ are the molar and activity ratio respectively, (CO_3^{2-}) is the molality of carbonate.

		25°C	**27°C**	**30°C**
	log(Kc)	-8.48	-8.49	-8.50
	log(Kd)	-17.00	-17.04	-17.12
	(Mg/Ca)	1.46	1.46	1.46
pH = 7.2	$(Mg/Ca)_I$	1.25	1.24	1.23
	$[Mg/Ca]_I$	1.28	1.27	1.26
	(CO_3^{2-})	$0.0508*10^{-4}$	$0.0535*10^{-4}$	$0.0572*10^{-4}$
	SIc	-0.0129	0.0173	0.0601
	SId	0.0626	0.1053	0.1655
	P_{CO_2}	0.0129	0.0045	0.0009
pH = 7.5	$(Mg/Ca)_I$	1.09	1.08	1.06
	$[Mg/Ca]_I$	1.13	1.11	1.09
	(CO_3^{2-})	$0.1006*10^{-4}$	$0.1060*10^{-4}$	$0.1130*10^{-4}$
	SIc	0.2860	0.3161	0.3586
	SId	0.3337	0.3749	0.4330
	P_{CO_2}	0.00644	0.00225	0.00047
pH = 7.8 (field)	$(Mg/Ca)_I$	0.89	0.87	0.84
	$[Mg/Ca]_I$	0.91	0.89	0.86
	(CO_3^{2-})	$0.1980*10^{-4}$	$0.2083*10^{-4}$	$0.2222*10^{-4}$
	SIc	0.5829	0.6125	0.6543
	SId	0.5838	0.6229	0.6778
	P_{CO_2}	0.00320	0.00112	0.00023

Table IV.14 Effects of pH and temperature on the saturation states of the Colliers Pond water with respect to calcite and dolomite. $(Mg/Ca)_I$ and $[Mg/Ca]_I$ are the molar and activity ratio respectively, (CO_3^{2-}) is the molality of carbonate.

		27°C	**30°C**	**33°C**
	log(Kc)	-8.49	-8.50	-8.53
	log(Kd)	-17.04	-17.12	-17.19
	(Mg/Ca)	0.82	0.82	0.82
pH = 7.5	**$(Mg/Ca)_I$**	0.66	0.65	0.64
	$[Mg/Ca]_I$	0.79	0.78	0.77
	(CO_3^{2-})	$0.9617*10^{-4}$	$0.9980*10^{-4}$	$1.0449*10^{-4}$
	SIc	0.8086	0.8328	0.8653
	SId	0.7933	0.8282	0.8767
	P_{CO_2}	0.00086	0.00030	0.00006
pH = 8.0	**$(Mg/Ca)_I$**	0.48	0.47	0.46
	$[Mg/Ca]_I$	0.58	0.56	0.54
	(CO_3^{2-})	$0.2770*10^{-4}$	$0.2886*10^{-4}$	$0.2972*10^{-4}$
	SIc	1.2685	1.2983	1.3243
	SId	1.1852	1.2277	1.2657
	P_{CO_2}	0.00025	0.00005	0.00001
pH = 8.5 (field)	**$(Mg/Ca)_I$**	0.26	0.25	0.24
	$[Mg/Ca]_I$	0.31	0.30	0.28
	(CO_3^{2-})	$0.6816*10^{-4}$	$0.6906*10^{-4}$	$0.6913*10^{-4}$
	SIc	1.6598	1.6775	1.6913
	SId	1.4436	1.4694	1.4911
	P_{CO_2}	0.00006	0.00001	0.000002

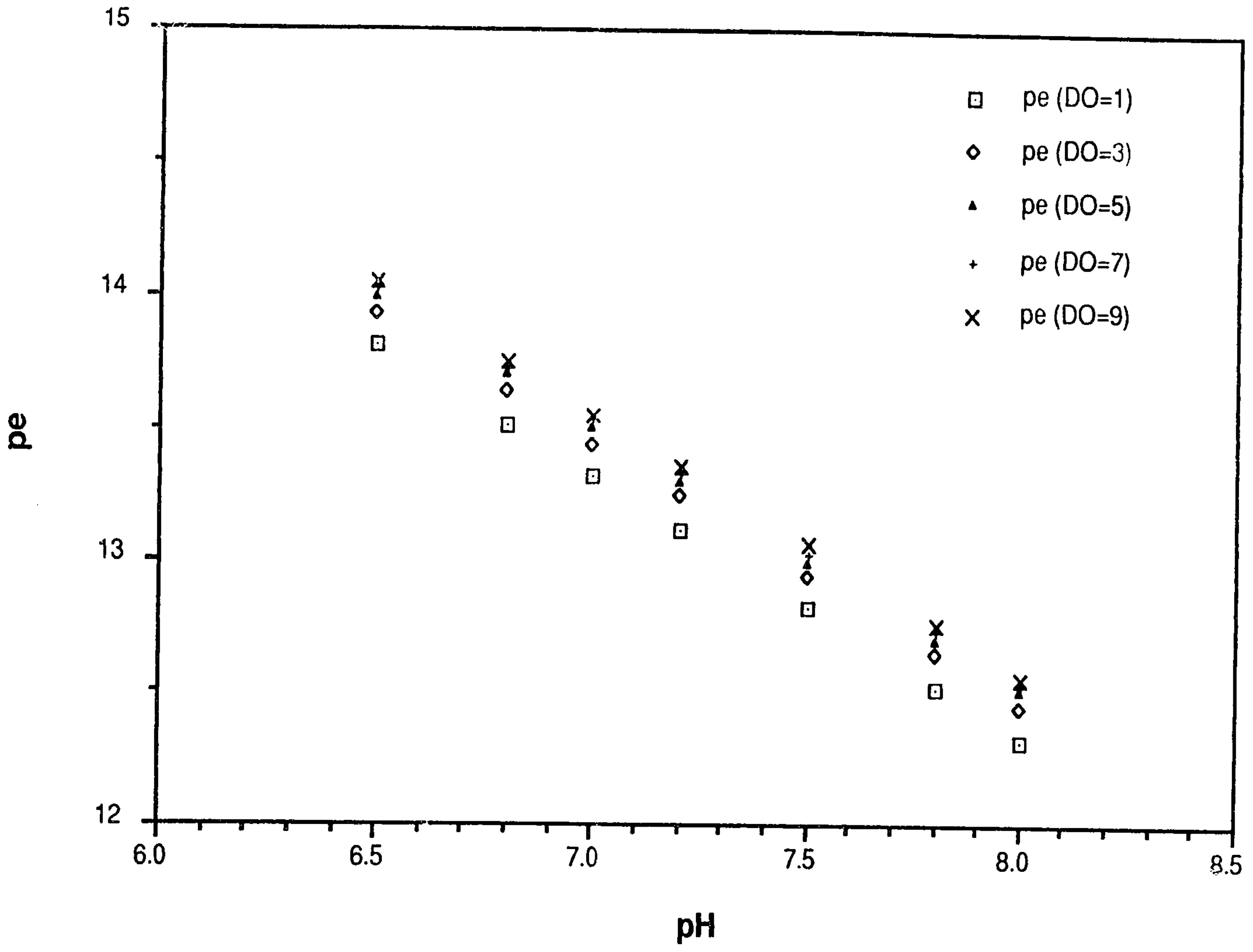


Fig. IV.4 Cross plots of pe versus pH at various dissolved oxygen contents.

In an oxidizing environment, pe variations cause no apparent effect on the saturation states of the ground water with respect to the carbonate minerals within the stability field of water (Table IV.15A) which is pH dependent. In the sensitivity analysis, when pe value exceeds 12.0, the water begins to oxidize (Table IV.15A); that is not the case in the aquifers of the Cayman Islands. Therefore, pe values of 4.0-12.0 were used in the speciation calculations in most cases without causing any errors.

In a reducing environment, pe simulation shows that for waters containing 1-3 mg/l of H_2S (common in the deep saline zone), pe values are -0.5 to 1.0 (Table IV.15B). In this pe range, however, there is no apparent effect on the saturation states (Table IV.15B). Therefore, it appears that pe is not an important parameter in the speciation calculation providing that it is within the ground water stability field.

Tidal Fluctuation

It has been suggested that tidal oscillation around Grand Cayman causes fluctuation in the ground water salinity, particularly in the fractured and cavernous zones, where hydrodynamic dispersion is enhanced due to turbulent flow conditions. The effect of semi-diurnal tidal oscillation on the chemical compositions of the ground water is shown by sampling the water at high tide and low tide (Table IV.16). In general, water salinity (E.C., Na^+, Cl^-) increases at high tide and decreases at low tide; however, the Ca^{2+}, Mg^{2+}, and HCO_3^- content does not appear to follow any particular trend (Table IV.16).

Another example is illustrated by the data collected from a shallow trench well (opened only to 0.8 m below water table) designed to monitor the changes of water chemistry in the uppermost part of the Lower Valley lens. A sample was collected at 6 hours intervals over a two day period (Table IV.17). The Cl^- and HCO_3^- content were fairly constant, but HCO_3^- and Mg^{2+} concentration fluctuated widely with no apparent relation to the water salinity (Table IV.17).

Table IV.15A Sensitivity analyses of pe effect on the saturation states of fresh ground water with respect to calcite and dolomite in an oxidizing condition. Calculations used test results of ground water sample from East End well PW1 (pH = 7.5).

pe	$[H_2O]$	(Mg/Ca)	[Mg/Ca]	(HCO_3^-)	(CO_3^{2-})	SIc	SId	P_{CO_2}	P_{O_2}
4.0	0.9997	0.61	0.62	$0.5166*10^{-2}$	$0.1115*10^{-4}$	0.4101	0.3417	0.00335	$0.353*10^{-36}$
8.0	0.9997	0.61	0.62	$0.5166*10^{-2}$	$0.1115*10^{-4}$	0.4101	0.3417	0.00335	$0.353*10^{-20}$
12.0	0.9997	0.61	0.62	$0.5166*10^{-2}$	$0.1115*10^{-4}$	0.4101	0.3417	0.00335	$0.352*10^{-4}$
14.0	0.9427	0.62	0.63	$0.5165*10^{-2}$	$0.1115*10^{-4}$	0.4098	0.3451	0.00355	$0.313*10^{4}$
16.0	0.3200	0.77	0.78	$0.5154*10^{-2}$	$0.1117*10^{-4}$	0.4060	0.3870	0.01043	$0.361*10^{11}$

Table IV.15B Sensitivity analyses of the pe effect on the saturation states of saline ground water with respect to calcite and dolomite in a reducing condition. Calculations used test results of ground water collected from well W5 (pH = 7.11).

pe	$[H_2O]$	(Mg/Ca)	[Mg/Ca]	(HCO_3^-)	SIc	SIa	SId	P_{CO_2}	H_2S
8.0	0.9783	4.64	5.40	$0.2818*10^{-2}$	-0.0562	-0.1928	0.3315	0.0098	$8.58*10^{-60}$
4.0	0.9783	4.64	5.40	$0.2818*10^{-2}$	-0.0562	-0.1928	0.3315	0.0098	$8.58*10^{-28}$
0.5	0.9783	4.64	5.40	$0.2818*10^{-2}$	-0.0562	-0.1928	0.3315	0.0098	8.58
0.0	0.9783	4.64	5.40	$0.2818*10^{-2}$	-0.0562	-0.1928	0.3315	0.0098	$8.58*10^{4}$
-4.0	phase rule has been violated								

Note: Round bracket refers to molality or molar ratio, square bracket refers to activity or activity ratio, all calculations with ion complex consideration.

Table IV.16 Effect of semi-diurnal tide on the chemical compositions of the Lower Valley ground water. Samples collected on 4th October 1985. L and H refer to samples collected at low and high tide respectively. All ion concentrations are in mg/l.

Well #	Tide	E.C.	Cl^-	HCO_3^-	SO_4^{2-}	Na^+	Ca^{2+}	Mg^{2+}
9	L	1375	267	319	42	145	95	29
	H	1457	296	311	63	135	102	46
12	L	1528	330	320	39	120	147	35
	H	1667	389	308	54	220	97	30
14	L	1792	427	323	60	245	102	33
	H	1846	442	280	48	245	82	44
15	L	1282	253	323	54	140	82	41
	H	1474	301	341	69	175	89	41
18	L	1453	301	366	35	175	96	33
	H	1521	306	353	42	171	96	37
24	L	1702	413	210	42	205	80	35
	H	1998	496	256	54	265	92	37
35	L	1821	442	333	48	250	95	38
	H	1884	452	268	60	185	88	71

Table IV.17 Temporal variation of chemical compositions of ground water. Samples collected from a Lower Valley trench well (about 1 m deep into the saturation zone) at 6 hours intervals. All ion concentrations are in mg/l.

Sample #	pH	Cl^-	HCO_3^-	Ca^{2+}	Mg^{2+}	(Mg/Ca)
TR1	7.6	145	333	120	15	0.21
TR2	7.6	126	326	100	19	0.31
TR2A	7.4	145	330	80	36	0.74
TR2B	7.6	145	322	100	17	0.28
TW1	7.5	121	364	100	36	0.59
TW2	7.7	145	332	88	61	1.14
TW3	7.6	145	327	88	32	0.60
TW4	7.7	217	337	76	46	1.00
TW5	7.5	169	331	84	34	0.67

In both examples (Tables IV.16, 17), the ground water indicates saturation to supersaturation with respect to both calcite and dolomite. The effect of tidal fluctuation is particularly important at the coastal zone or on an oceanic island where ground water is in hydraulic connection with the surrounding ocean (Mather and Buckley, 1973; Vacher, 1978; Custodio, 1987). The fluctuation of water chemistry, and hence, the degree of saturation could have significant influence on the mineralogical compositions of carbonate cements if the kinetic conditions favour mineral precipitation.

Rain Water Recharge

On the Cayman Islands, there are two distinct types of recharge phenomena: (1) slow recharge by infiltration through the unsaturated zone (vadose zone), and (2) rapid recharge through the well-developed joint and karst system. Thus, the slow recharge water consists of rain water and chemical constituents that dissolved in the rain water during the infiltration process. Conversely, the rapid recharge water has essentially the same composition as rain water.

The changes in chemical properties of ground water caused by slow rain water infiltration include (Table IV.18): (1) decrease in ionic strength, (2) increase in HCO_3^- content, (3) decrease in Ca^{2+} and Mg^{2+} concentration, and (4) increase in SIc, SId, and P_{CO_2}. The significant increase in HCO_3^- concentration suggests dissolution of dolostone bedrock in the unsaturated zone, which leads to an increase in the saturation indices of calcite and dolomite. Conversely, the decrease in Ca^{2+} and Mg^{2+} content may be an indication of carbonate precipitation in the saturation zone. The precipitation of carbonate minerals may be induced by an increase in ionic activities and a decrease in ion complexation due to dilution effect as a result of the rain water recharge.

Ground water recharged by rapid infiltration was studied by artificially injecting 7.6 m^3 of rain water directly into the shallow aquifer of the Lower valley lens through piezometer 5-84LV at a injection rate of 0.5 l/s. The mixed ground water-sea water

Table IV.18 Effect of **slow** rain water recharge on the saturation states of ground water with respect to calcite and dolomite. All ion concentrations are in mg/l.

Date	Condition	I	pH	HCO_3^-	Ca^{2+}	Mg^{2+}	SIc	SId	P_{CO_2}
Piezometer 4-84LV									
11.4.86	end of dry season	0.0697	7.70	128	139	84	0.1397	0.0899	0.00060
30.5.86	after rain storm	0.0390	7.85	209	83	69	0.3668	0.3469	0.00073
21.1.87	end of wet season	0.0295	7.70	276	88	56	0.4096	0.3566	0.00140
Piezometer 9-84LV									
2.5.86	end of dry season	0.0200	7.70	255	72	36	0.3371	0.2261	0.00133
30.5.86	after rain storm	0.0161	7.72	287	67	35	0.4021	0.2938	0.00145

Table IV.19 Effect of **rapid** rain water recharge on the saturation states of the ground water with respect to calcite and dolomite. All ion concentrations are in mg/l. The phenomenon of rapid recharge was simulated by injecting 7.6 m^3 of rain water directly into the shallow aquifer through piezometer 5-84LV at a rate of about 0.5 l/s.

Date	Condition	I	pH	HCO_3^-	Ca^{2+}	Mg^{2+}	SIc	SId	P_{CO_2}
19.9.86	gw prior to mixing	0.0110	7.90	226	51	32	0.4021	0.2858	0.00077
28.10.86	rain water	0.0010	7.30	24.2	8	1.5	-1.7925	-2.0768	0.00036
31.10.86	mixed rain-gw	0.0057	7.90	126	36	15	0.0632	-0.1527	0.00044
7.4.87	after reequilibration	0.0116	7.74	238	52	34	0.2728	0.2037	0.00117

showed a significa crease in SIc, SId and P_{CO_2} (Table IV.19) and the ground water became saturated with respect to calcite and undersaturated with respect to dolomite. The mixed zone took about 6 months to disperse and re-equilibriate with the surrounding ground water (Table IV.19). Therefore, rain water recharge can cause two completely different variations in the saturation states of the ground water although both slow and rapid recharge result in a drastic decrease in the ionic strength (salinity) of the ground water.

Ground Water Abstraction and Recovery

The effect of ground water abstraction and recovery on the chemical equilibrium of the ground water with respect to the carbonate minerals was studied by sampling three production wells at the Lower Valley lens at three different times (Table IV.20). Firstly, samples were collected prior to the well field operation, that is when the lens was in its pristine condition. Secondly, samples were collected after four months of abstraction. Finally, samples were collected after the pumps were switched off for about a year to allow for the disturbed zone to recover.

Speciation calculations of the nine samples indicate that (Table IV.20):

(1) ground water from all three wells was originally supersaturated or saturated with respect to calcite and dolomite respectively,

(2) saturation indices of calcite and dolomite increased after four months of pumping, and

(3) after a year of recovery, all saturation indices of calcite and dolomite showed a slight decrease except SId of well 10A.

The increase in ionic strength after pumping was probably caused by upconing of the underlying saline water due to the drawdown of the water table. The phenomenon of upconing is common in small lenses and coastal aquifers due to ground water abstraction (Cant and Weech, 1986; Vacher, 1978; Das Gupta, 1985; Kemblowski, 1985; Custodio,

Table IV.20 Effects of abstraction and recovery on the saturation states of the fresh ground water with respect to calcite and dolomite in the Lower Valley Lens.

Well #		**Pre-pumping**	**Abstraction**	**Recovery**
10A	**pH**	7.38	7.49	7.45
	I	0.0100	0.0218	0.0140
	(Mg/Ca)	0.21	0.24	0.58
	$[CO_3^{2-}]$	$0.5321*10^{-5}$	$0.4577*10^{-5}$	$0.5643*10^{-5}$
	SIc	0.3059	0.3519	0.3418
	SId	-0.0007	0.0762	0.2597
16A	**pH**	7.51	7.60	7.50
	I	0.0114	0.0181	0.0162
	(Mg/Ca)	0.21	0.30	0.51
	$[CO_3^{2-}]$	$0.5381*10^{-5}$	$0.5123*10^{-5}$	$0.4394*10^{-5}$
	SIc	0.2688	0.3438	0.1790
	SId	-0.0376	0.1546	0.0717
26A	**pH**	7.66	7.48	7.55
	I	0.0095	0.0209	0.0161
	(Mg/Ca)	0.10	0.53	0.60
	$[CO_3^{2-}]$	$0.6961*10^{-5}$	$0.7805*10^{-5}$	$0.6194*10^{-5}$
	SIc	0.3604	0.4685	0.3293
	SId	-0.0925	0.3706	0.2552

Note: 'Pre-pumping' refers to samples collected prior to well field operation.
'Abstraction' refers to samples collected after 4 months of pumping.
'Recovery' refers to samples collected after the well pumps were switched off for about 1 year.
(Mg/Ca) is the molar ratio, $[CO_3^{2-}]$ is the activity of carbonate ion.

1987). The saline water provides the additional Ca^{2+} and Mg^{2+} content needed to raise the saturation states of the ground water with respect to calcite and dolomite.

During the recovery period, the ground water quality was improved through rain water recharge as shown by the decrease in the ionic strength of the solutions. Furthermore, the increase in the molar Mg/Ca ratios suggest that water-rock interactions became significant during the recovery period because the increase in Mg^{2+} content cannot be attributed to the underlying saline water. The differences in the degree of improvement between the three wells probably resulted from the differences in the subsurface aquifer conditions and/or the recharge processes.

It is therefore apparent that it is extremely difficult to collect samples that are representative of the original aquifer condition. One would tend to consider that a recovery period of over a year is sufficient to allow the lens to re-equilibriate to its original condition; however, the results show that this assumption is not entirely true. Therefore, it is also important to know the history of the well prior to using the well water for geochemical equilibrium studies.

At this point, it is postulated that the upconing effect on the fresh water lens may have produced results similar to those noted with a rise in sea level. That is, it enhances the mixing of the fresh ground water and the saline water. Conversely, the recovery process may be considered as equivalent to the ground water lens behaviour in response to sea level drop by providing additional area for rain water recharge.

G. SYNOPSIS

Chemical equilibrium considerations of the ground water in the carbonate aquifer system on the Cayman Islands permit the following conclusions.

(1) Chemical equilibrium of water-rock reactions in the shallow carbonate aquifers are difficult to achieve due to the (i) external influences such as rainfall recharge and evapotranspiration, and (ii) active circulation in the well developed joint and karst

system. Kinetic concepts are needed to understand the diagenetic processes that are operative in such a hydrogeological setting.

(2) Saturation states of the ground water with respect to calcite and dolomite are assessed by comparing the ion activity products with the thermodynamic solubility product constants. An uncertainty limit of ±0.1 is used to account for the possible analytical errors and inaccurate thermodynamic data base.

(3) The PHREEQEX program was used to carry out all the speciation calculations. The program gives comparable results with seven other geochemical models that are currently in use for such calculations.

(4) Ground waters on the Cayman Islands are formed from various combinations of mixing between rain water, sea water, ground water from different aquifers, saline ground water and surface water. These complex mixing phenomena have rendered the generalized mixing model between fresh ground water and sea water invalid.

(5) Most of the fresh, brackish and saline ground waters on the Cayman Islands are supersaturated with respect to calcite and dolomite. This means that the waters are capable of precipitating calcite and dolomite.

(6) The fresh water of the Lower Valley lens has a variable degree of saturation due to (i) influx of Ca-enriched ground water from the limestone aquifer of the Ironshore Formation and possible influx of swamp water from the northern and eastern margin of the lens, and (ii) mixing of saline water from the southern margin of the lens.

(7) The highly brackish to Type I saline waters have variable saturation states due to (i) influx of CO_2 from the brackish water swamps or decomposition of organic matter in intruding sea water, and (ii) water-rock interactions.

(8) Simulation study shows that geochemical calculations in a ground water-carbonate aquifer system require the consideration of the (i) complex ions, (ii) field pH

measurement, (iii) temperature effect, (iv) oxidizing or reducing condition, (v) tidal fluctuation, (vi) recharge process, and (vii) human disturbance such as abstraction.

V. ISOTOPE HYDROLOGY

The isotopic composition of a mineral is a function of the isotopic content and the temperature of the fluid from which the mineral precipitated (Hudson, 1977; Savin, 1980; O'Neil, 1987; Longstaffe, 1987). Thus, in the application of stable isotopes to diagenetic studies, it is important to examine the isotopic composition of the water from which the authigenic minerals were formed. The isotopic composition of the formation fluids (ground water) also reflects a variety of processes that may occur during deposition and diagenesis (Anderson and Arthur, 1983; Sheppard, 1986; Longstaffe, 1987; O'Neil, 1987). In this connection, this study determines the composition and origin of the isotopic content (δ^2H and $\delta^{18}O$) of the surface and ground waters on the Cayman Islands.

A. BASIC PRINCIPLES

Stable (non-radioactive) isotopes are atoms which have different mass due to a different numbers of neutrons. For most geochemical applications, it is sufficient to know the relative abundance of an isotope with respect to a standard value. The relative isotope concentration is called the "δ-value" (Fritz and Fontes, 1980b; Anderson and Arthur, 1983) and is given as :

$$\delta_x = \frac{R_x - R_{std}}{R_{std}} * 10^3$$

where R_x is the isotopic ratio of the sample ($^2H/^1H$, $^{18}O/^{16}O$) and R_{std} is the corresponding ratio in a standard.

The δ-value is expressed in parts per thousands (‰, per mil). The SMOW (standard mean ocean water) is a water standard for ^{18}O and ^2H in all hydrologic investigations (Craig, 1961a; Fritz and Fontes, 1980b; Anderson and Arthur, 1983).

Isotopic fractionation results from differences in the isotopic mass, and hence, in the physico-chemical properties of the isotopically substituted molecules or crystals

(Anderson and Arthur, 1983). The fractionation factor (α) between substances A and B (Fritz and Fontes, 1980b; Anderson and Arthur, 1983; O'Neil, 1986) is given as :

$$\alpha_{A\text{-}B} = \frac{R_A}{R_B} = \frac{1000 + \delta_A}{1000 + \delta_B}$$

where α-values can apply to processes involving either kinetic or equilibrium isotope effects. Friedman and O'Neil (1977) noted that for many important equilibrium fractionations over a wide temperature range, $\ln\alpha$ varies with $1/T^2$. Conversely, the Rayleigh distillation concept is applied for kinetic isotope fractionation where reaction products are continuously being removed (e.g. partial condensation, Fritz and Fontes, 1980b; Sheppard, 1986; Welhan, 1987).

The application of stable isotopes to hydrologic studies utilized the conservation behaviour of ^{18}O and ^{2}H in the water. This behaviour means that the stable isotope concentrations in low temperature ground water do not change in the ground, even over tens of thousands of years (Siegenthaler, 1979). Furthermore, in the absence of isotopic fractionation during phase changes, the abundance of heavy isotopes depends only on the source(s) of water involved, whereas in the presence of isotopic separations, the isotope effect can be related to the intensity of the fractionation process (Welhan, 1987).

In order to understand the full spectrum of the diagenetic fluids, it is necessary to investigate not only the ground waters from different lenses and from different hydrochemical zones, but also their precursors such as rain and sea water (Figs. II.2, 3, 4, III.2). This sampling technique permits the identification of the spatial and temporal effect.

B. ISOTOPIC COMPOSITION OF THE WATERS

Naturally occurring waters on the Cayman Islands possess distinct stable isotope compositions (Tables V.1, 2, 3, 4, 5). Rain water (Fig. III.3) has the largest isotopic variation (Table V.1), ranging from -1.56 to -7.34‰ SMOW for $\delta^{18}O$ and -8.4 to -53.8‰ SMOW for $\delta^{2}H$. A similar $\delta^{18}O$ range of +0.2 to -7.4‰ SMOW was recorded for rain

Table V.1 Stable isotope data of surface waters (rain, sea, and pond) on Grand Cayman.

Sample #	**Location (time)**	**E.C.** (μS/cm)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)
Rain Water:				
C1	George Town (April 1987)	83	-2.34	-9.2
R1	Lower Valley (September 1987)	75	-1.56	-8.4
R2	Lower Valley (October 1987)	29	-7.34	-53.8
R2A	Lower Valley (October 1987)	29	-7.33	-53.8
R3	Lower Valley (November 1987)	65	-2.78	-11.1
Average Stable Isotope of Rain Water on Grand Cayman			-4.27	-27.3
Sea Water:				
S1	Gun Bay (April 1987)	50000	+1.19	+6.8
S2	Prospect Point/Beach (April 1987)	51000	+1.88	+9.1
S3	Frank Sound (November 1987)	49800	+1.18	+5.8
	(re-test)		+1.18	+4.2
S4	North Sound (November 1987)	50200	+1.21	+6.6
	(re-test)		+1.21	+5.6
Average Stable Isotope of Sea Water around Grand Cayman			+1.31	+6.4
Water from Sinkholes (Natural Wells):				
N1	East End (April 1987)	1718	-2.73	-14.7
N2	Lower Valley (April 1987)	3400	-2.97	-15.7
N3	Lower Valley (April 1987)	4390	-2.54	-7.6
		(re-test)	-2.50	-7.6
Average Stable Isotope of Water from Sinkholes			-2.69	-11.4

Table V.2 Stable isotope data of ground water in Tibbetts Turn lens on Cayman Brac. All samples collected in July/August 1986 during the ground water exploratory drilling program.

Sample #	Location	E.C. (µS/cm)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)
Perched Water:				
CB1/2	B1 (perched water at 15 m)	912	-5.22	-35.3
		(re-test)	-5.36	-35.3
CB3	B1 (perched water at 20 m)	948	-5.53	-35.0
Average Stable Isotope of Perched Ground Water			-5.37	-35.2
Fresh Water:				
CB7	B3 (at water table)	880	-4.39	-29.8
CB8	B3	940	-4.42	-29.6
		(re-test)	-4.42	-30.5
CB9	B3	1218	-4.43	-31.1
CB11	B5 (at water table)	963	-4.65	-31.3
CB12	B5	1555	-4.83	-30.6
		(re-test)	-4.74	-30.6
Lightly Brackish Water:				
CB6	B2	4300	-4.31	-29.3
CB10	B4	3260	-3.96	-26.3
CB16	K1	6250	-4.08	-27.8
		(re-test)	-3.93	-27.8
CB18	CR	2900	-4.53	-30.9
		(re-test)	-4.53	-30.1
Average Stable Isotope of Cayman Brac Ground Water			-4.40	-29.7

Table V.3 Stable isotope data of ground water in the East End lens on Grand Cayman.

Sample #	**Location**	E.C.(μS/cm)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)
Fresh Water:	(all samples collected in February 1987)			
EE11	New Hut Farm BH11	1121	-3.94	-23.2
EE12	New Hut Farm BH12	1252	-4.24	-29.0
EE12B	New Hut Farm BH12B	950	-4.59	-29.2
EE15	New Hut Farm BH15	1326	-3.99	-25.8
EE16	New Hut Farm BH16	1361	-3.99	-24.9
EE17	New Hut Farm BH17	745	-4.30	-29.5
EE18	New Hut Farm BH18	587	-4.02	-27.3
		(re-test)	-4.02	-27.0
EE19	New Hut Farm BH19	1092	-3.52	-24.9
		(re-test)	-3.52	-22.4
Average Stable Isotope of Ground Water at New Hut Farm			-4.01	-26.3
Fresh Water:	(E1 & E2 refer to samples collected at about 2 weeks apart in April 1987))			
5E1	Piezometer 4A-84EE	1610	-5.26	-35.4
5E2	Piezometer 4A-84EE	1712	-5.33	-35.0
7E1	Piezometer 6A-84EE	1460	-4.82	-29.4
7E2	Piezometer 6A-84EE	1472	-4.85	-29.7
9E1	Piezometer 10-80EE	823	-5.09	-32.4
9E2	Piezometer 10-80EE	860	-4.36	-35.9
Lightly Brackish Water:	(E1 & E2 refer to samples collected at about 2 weeks apart in April 1987)			
4E1	Piezometer 4-84EE	2520	-5.25	-33.7
		(re-test)	-5.21	-33.7
4E2	Piezometer 4-84EE	2680	-5.25	-34.0
6E1	Piezometer 6-84EE	7480	-4.46	-30.0
6E2	Piezometer 6-84EE	7720	-4.40	-29.7
		(re-test)	-4.53	-29.6
8E1	Piezometer 8-84EE	4950	-4.70	-28.2
8E2	Piezometer 8-84EE	5520	-4.45	-30.4
		(re-test)	-4.45	-33.9
Average Stable Isotope of East End Ground Water from Piezometers			-4.83	-32.1

Table V.4 Stable isotope data of ground water in the Lower Valley lens on Grand Cayman.

Sample #	**Location**	**E.C.** (µS/cm)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)
Fresh Water: (L1 & L2 refer to samples collected at about 2 weeks apart in April 1987)				
1L1	Piezometer 30(1)-82LV	1620	-3.89	-25.3
1L2	Piezometer 30(1)-82LV	1955	-3.81	-24.5
5L1	Piezometer 5-84LV	1000	-3.70	-25.6
5L2	Piezometer 5-84LV	1055	-3.88	-25.6
9L1	Piezometer 9-84LV	1970	-4.06	-27.7
9L2	Piezometer 9-84LV	2060	-3.83	-26.1
		(re-test)	-3.83	-27.6
Lightly Brackish Water: (L1 & L2 refer to samples collected at about 2 weeks apart in April 1987)				
2L1	Piezometer 30(2)-82LV	2460	-3.86	-25.8
		(re-test)	-3.86	-26.5
2L2	Piezometer 30(2)-82LV	2360	-3.95	-25.9
4L1	Piezometer 4-84LV	2940	-4.04	-28.0
4L2	Piezometer 4-84LV	3680	-4.14	-28.1
Average Stable Isotope of Lower Valley Ground Water			-3.90	-26.4

Table V.5 Stable isotope data of highly brackish to saline ground waters on Grand Cayman. All samples collected in October 1987 from deep wells on the west side of Grand Cayman.

Sample #	**Location**	**E.C.** (µS/cm)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)
CF	George Town Cricket Field	20600	-1.82	-8.9
GT1	George Town Reservoir	34300	-0.34	-5.2
GT2	George Town Reservoir	44700	+0.19	-6.5
SW1	Treatment Works Site	50900	+1.30	+6.7
SW2	Treatment Works Site	51400	+1.36	+6.3
		(re-test)	+1.36	+5.7

water on Bermuda (Gross, 1964). The isotopically enriched rain water samples have a $\delta^{18}O$ content close to that of the mean annual value in precipitation (-2‰ SMOW) for the Caribbean region given by Yurtsever (1975).

Sea water around Grand Cayman (Fig. III.3) has an average $\delta^{18}O$ and $\delta^{2}H$ value of +1.31‰ and +6.4‰ SMOW respectively (Table V.1). These values are higher than those of the Standard Mean Ocean Water ($\delta^{18}O = \delta^{2}H = 0$‰; Craig, 1961a).

The stable isotopes of the ground water indicate that each ground water lens (Figs. II.2, 3, 4) has its own isotopic characteristics (Tables V.2, 3, 4). The fresh and lightly brackish ground water have similar isotopic contents of about -3.5 to -5.3‰ for $\delta^{18}O$ and -22.0 to -35.0‰ SMOW for $\delta^{2}H$ contents (Tables V.2, 3, 4). The highly brackish to saline ground water (Fig. III.2) have isotopic compositions ranging from -1.82 to +1.36‰ for $\delta^{18}O$ and -8.9 to +5.79‰ SMOW for $\delta^{2}H$ contents (Table V.5). It is also apparent that the isotopic enrichment increases with increasing water salinity (Table V.5).

C. ORIGIN OF THE WATER ISOTOPES

Meteoric water, derived from ocean water through the atmospheric circulation process, includes most continental surface waters and shallow ground waters (Sheppard, 1986). Variations in the isotopic composition of the meteoric water are caused mostly by evaporation and condensation.

Rain Water

Most meteoric waters, which have not undergone extensive evaporation, have their $\delta^{2}H$ and $\delta^{18}O$ relationships (Craig ,1961b; Dansgaard, 1964; Yurtsever, 1975; Gat, 1980) expressed as

$$\delta^{2}H = 8*\delta^{18}O + 10 \quad \text{(in per mil)}$$

which is known as the meteoric water line (MWL). The linear regression of the rain water isotopes on Grand Cayman (Fig. V.1) is:

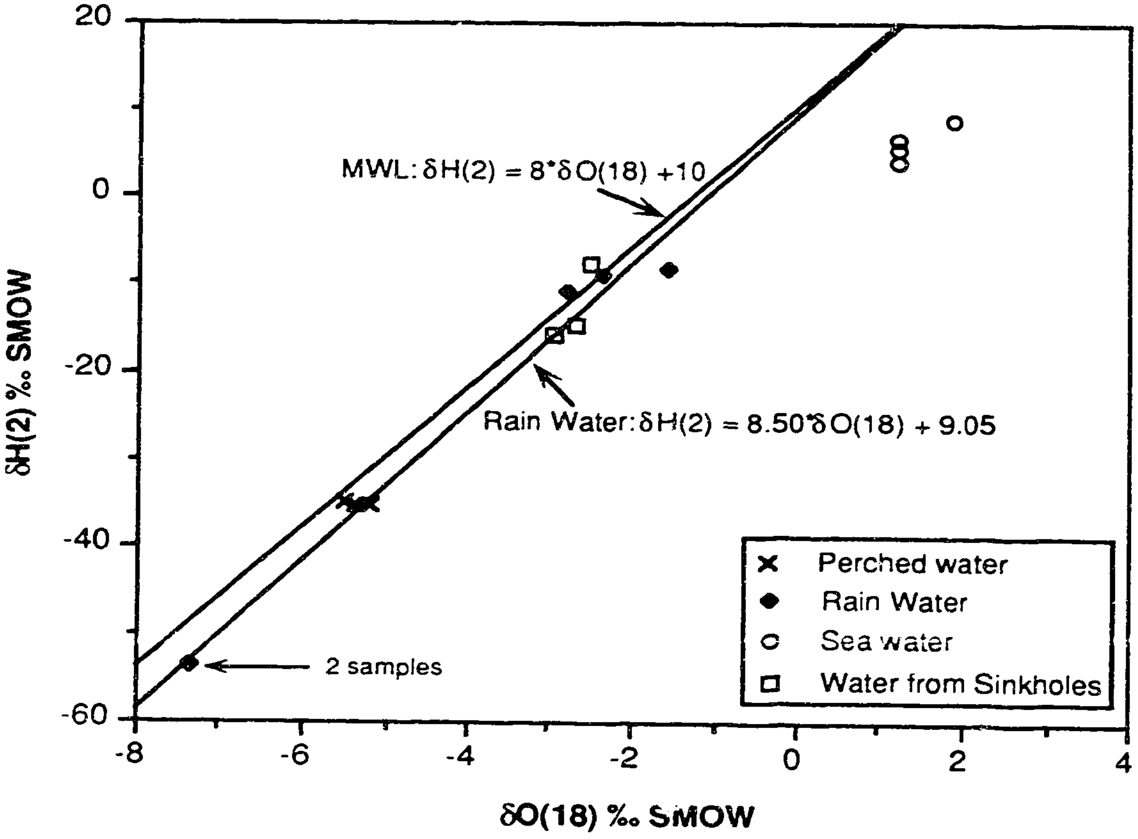


Fig. V.1 Cross plots of δH(2) versus δO(18) of surface waters (rain water, sea water, and water from sinkholes) and perched ground water from Cayman Brac. MWL refers to global meteoric water line.

$$\delta^2H = 8.5*\delta^{18}O + 9.1 \quad \text{(in per mil)}$$

which is similar to the global meteoric water line (Fig. V.1). Rainfall on Grand Cayman (Fig. III.3), however, falls into the isotopically heavy ($\delta^{18}O$ of about -2.0‰) and the isotopically light ($\delta^{18}O$ of about -7.5‰ SMOW) groups (Table V.1, Fig. V.1).

The isotopic variation of precipitation is the result of condensation of atmospheric water vapour at surface air temperature (Dansgaard, 1964; Welhan, 1987). ^2H and ^{18}O are concentrated in the condensed phase because of differences in the vapour pressure of the isotopic species of water. The correlation of δ^2H and $\delta^{18}O$ in atmospheric precipitation suggests that it follows a Rayleigh distillation process at liquid-vapour equilibrium (Dansgaard, 1964; Gat, 1980; Sheppard, 1986). The classical Rayleigh process assumes equilibrium evaporation at the ocean surface followed by continuous condensation from atmospheric water resulting in rainfall that is continuously depleted in ^2H and ^{18}O.

Yurtsever (1975) showed that isotopic variations can be described by the temperature variations. Thus, precipitation during winter months is depleted in the heavy isotopic species relative to the summer rains. On Grand Cayman, air temperature alone cannot account for the differences in the rain water isotopes because annual temperature variation between summer and winter is small, generally about 5°C, and most of the rainfall occurs during the wet season when temperature fluctuation is minimal.

According to the Rayleigh process, by further condensation the vapour preferentially loses the heavy isotopic components; consequently, the newly formed condensate becomes more depleted in heavy isotopes. Dansgaard (1964) suggested the amount effect (i.e. the rainfall quantity) as the reason for high isotope content occurring in sparse rain. Gat (1980) also found that the first shower of many storms is enriched in the heavy isotopic species compared to later rains at the same site. This effect is attributed to the partial evaporation of rain drops in the undersaturated surface air under non-equilibrium conditions. Conversely, at high relative humidity, isotopic exchange between the rain drops and the atmospheric vapour is the dominating factor (Friedman *et al.*, 1962;

Dansgaard, 1964). The amount effect is probably responsible for the high isotope contents of sample R1 (Table V.1), which was collected from the first rain in September 1987 after about a month of dry weather. Similarly, samples C1 and R3 (Table V.1) were collected from rainfalls that were of low intensity. Efforts were made to ensure that the rain water samples were transferred from the rain gauges to sealed bottles in order to protect the waters from evaporation. However, rainfall of low intensity requires a relatively long time to collect sufficient quantity so the samples might have been affected by evaporation to a small extent (e.g. samples C1 and R3).

In areas where precipitation exceeds evaporation, Hubner *et al.* (1979), Fontes (1980), and Welhan (1987) suggested that high rainfall intensity bias the isotope composition of precipitation to more negative values. This phenomenon may account for the low isotopic values of samples R2 and R2A (Fig. III.2, Table V.1); they were obtained during a tropical storm in early October, 1987 that brought in about 170 mm of rainfall over a three-days period. During the passage of the storm, the air temperature dropped to an average of 25°C (annual average is about 30°C). The low isotopic content of the rain water samples indicates that the air mass of the tropical storm may have had a different geographic origin. A similar situation was recorded by Bortolami *et al.* ([illegible]) in Val Corsaglia of northern Italy, where isotopic variations of the precipitation were due to air masses originating in the Mediterranean Sea and the Atlantic Ocean as a consequence of different wind patterns.

The fresh ground waters (< 2300 µS/cm) on Grand Cayman and Cayman Brac have $\delta^{18}O$ values ranging from -3.50 to -5.50‰ SMOW (Tables V.2, 3, 4). These values suggest that ground water recharge on the Cayman Islands occurs during heavy rainfall, when stable isotopes of the condensate are low. This is in agreement with the data obtained from the water table hydrograph and water salinity monitoring (Figs. II.8, 9). The $\delta^{18}O$ content of rain water samples C1, R1 and R3 (Table V.1) are higher than that of the fresh ground water (Tables V.2, 3, 4). If rain water of similar isotopic contents is responsible for the ground water recharge, it requires (1) a significant isotopic exchange between the ground water and the host rocks, (2) mixing of infiltrated rain water and isotopically depleted ground water, or (3) that the shallow fresh ground waters be paleo-waters.

Isotopic exchange between carbonate minerals and water in low temperature environments is very slow (Savin, 1980; Anderson and Arthur, 1983; O'Neil, 1987; Welhan, 1987). On the Cayman Islands, at an average annual ground water temperature of about 27°C, isotopic exchange between the ground water and the host rock is probably insignificant. If isotopic exchange has occurred, an increase in the $\delta^{18}O$ content in the ground water is expected because of the high ^{18}O content of the dolostone host rocks (Table 10 of Pleydell, 1987); the $\delta^{2}H$ values should remain unchanged because ^{2}H content in carbonate minerals is negligible. However, the stable isotopic content of the fresh ground water (Tables V.2, 3, 4) does not show any preferential shift in $\delta^{18}O$ relative to $\delta^{2}H$.

The low $\delta^{18}O$ content of the fresh ground water cannot be the result of mixing because the underlying brackish to saline ground water (Table V.2, 3, 4, 5) and surface water (Table V.1) have higher $\delta^{18}O$ values. Furthermore, the shallow ground water in the unconfined aquifer of the Cayman Islands is in active circulation and in hydraulic connection with the surrounding ocean. Therefore, the ground water was probably derived from recent rainfall recharge and not from paleo-rainfalls occurring when climatic conditions might have been cooler than the present time.

Sea Water

Present day ocean waters are relatively uniform in isotopic compositions with $\delta^{2}H$ and $\delta^{18}O$ values equal to +5 to -7‰ and +0.5 to 1.0‰ SMOW respectively (Sheppard, 1986). The mean values are closed to the defined SMOW standard of $\delta^{2}H = \delta^{18}O = 0‰$ (Craig, 1961a). Sea water is the largest reservoir of low temperature water on earth; thus, isotopic variations in the ocean water are small (Anderson and Arthur, 1983).

Welhan (1987) and Longstaffe (1987) noted that isotopic variations in sea water are mostly dependent on local conditions of evaporation, precipitation, freezing, and dilution with fresh water. The isotopic composition of the sea water around Grand Cayman (Figs. III.3, V.1, Table V.1) suggests that evaporation is the dominant factor. This is particularly apparent for the relatively isotopically enriched sample S2 ($\delta^{18}O$ = +1.88‰, $\delta^{2}H$ = +9.1‰ SMOW) which was collected near Prospect Beach (Fig. III.3). The positive correlation between the enrichment of the stable isotopes and salinity (E.C.) suggests that in the shallow water areas, evaporation exceeds precipitation. Craig and Gordon (1965) also recognized a similar pattern between $\delta^{18}O$ and the salinity of the equatorial surface waters. The rest of the samples (S1, S3, S4) collected from sounds around Grand Cayman (Fig. III.3) have a narrow isotopic range (Table V.1, Fig. V.1).

Current views on the isotopic compositions of ancient water remains a controversial topic (Anderson and Arthur, 1983; Sheppard, 1986; Muehlenbachs, 1986; Longstaffe, 1987). Savin and Yeh (1981) concluded that the variation in the $\delta^{18}O$ value of sea water due to glacial-interglacial effect was in the order of 0.8 to 1.3‰; however, the isotopic composition of the low latitude planktonic foraminifera shows little change (Anderson and Arthur, 1983).

The $\delta^{18}O$ value of marine carbonates, cherts and phosphorites has apparently decreased with time (Degens and Epstein, 1962; Keith and Weber, 1964; Perry, 1967; Perry and Tan, 1972; Knauth and Epstein, 1976; Knauth and Lowe, 1978; Veizer *et al.*, 1982; Shemesh *et al.*, 1983). This phenomenon has been interpreted as (1) progressive isotopic exchange with isotopically light ground water over time (Degens and Epstein, 1962; Keith and Weber, 1964), (2) progressive increase in $\delta^{18}O$ of the ocean from the Archean (about -8 to -12‰) to the present at constant temperature (Perry, 1967; Perry and Tan, 1972; Veizer *et al.*, 1982), and (3) progressive decrease in the temperature of the ocean (±20 to 30°C) whereas $\delta^{18}O$ of sea water remains constant (Knauth and Epstein, 1976; Knauth and Lowe, 1978). The first hypothesis is generally not considered to be a viable explanation (Longstaffe, 1987). Conversely, the last hypothesis has been supported by oxygen isotope studies of coexisting chert-phosphate pairs (Karhu and Epstein, 1986) and of fluid inclusions in halite (Knauth and Beeunas, 1986).

Despite the continual investigation in the secular variation of the $\delta^{18}O$ with time the controversy is not yet resolved (Muehlenbachs, 1986). In any event, it is important to note that the ancient ocean water might have been more enriched in $\delta^{18}O$ or might have a higher temperature than the present time. As a result, the interpretation of the diagenetic history of the sediments utilizing stable isotopes is not uneqivocal.

Water from Sinkholes (Natural Wells)

The salinity of the surface water lies in the range of the fresh to lightly brackish ground water but is substantially higher than that of the rain water (Tables V.1, 2, 3, 4). The isotopic compositions of the water samples collected from sinkholes (Figs. II.3, 4) indicate that (Table V.1, Fig. V.1):

(1) the stable isotopes ($\delta^{18}O$ and $\delta^{2}H$) of the surface water (Table V.1, Fig. V.1) are higher than those of the ground water (Tables V.2, 3, 4) even though the water in the sinkholes is essentially ground water outcropping at land surfaces, and

(2) the surface water has similar isotopic compositions to the isotopically enriched rain water (samples C1, R1, R3, Table V.1) and falls close to the rain water line (Fig. V.1).

These characteristics suggest that the isotopic composition of water from sinkholes is derived from ground water isotopes which are subsequently modified by evaporation and precipitation. This surface-ground water relationship is similar to that described by Fontes (1980) and Gonfiantini (1986) for the connection between lake and ground water. The surface water is of significance to the ground water isotopes because reverse flow of water from the sinkholes to the ground water lenses may occur during periods of high rainfall.

Although individual water-filled sinkholes are only of local importance, large ponds and mangrove swamps are of regional significance to the ground water isotopes.

Ground Water - Perched Water Zone

The stable isotopic concentrations of the perched ground waters collected from Cayman Brac show that (1) the data points cluster closely about the global meteoric water line and rain water line of Grand Cayman (Fig. V.1), (2) the stable isotopes are heavier than the isotopically depleted rain water (Fig. V.1), and (3) the perched ground waters are the most isotopically depleted among the ground waters of different hydrochemical zones (Tables V.2, 3, 4, 5).

Carbonate mineral precipitation in the perched water zone may occur because the perched ground water is supersaturated with respect to calcite and dolomite (Table IV.4). The perched water, which is not connected to the water table aquifer, is not influenced by the sea water mixing effect. Therefore, the factors controlling the isotopic composition of the perched water are (1) evaporation of the rain water prior to leaving the land surface and during infiltration through the unsaturated zone, (2) direct evaporation of water from the perched water lens, and (3) precipitation of carbonate minerals.

The evaporation effect is supported by the increase in salinity relative to rain water (Tables V.1, 2). Gat and Tzur (1967) also documented an enrichment of up to 0.5‰ of $\delta^{18}O$ by evaporation during rain water infiltration in the upper part of the soil zone in Israel. The fact that the $\delta^{2}H$ and $\delta^{18}O$ concentrations of the perched water lie close to the meteoric line and are the lowest among the ground waters suggest that evaporation is of minor effect.

The effect of mineral precipitation on the stable isotopes of the perched water is probably insignificant because the well developed joint and karst system of the Bluff Formation has a high water/rock ratio. This is because the effect of mineral precipitation on the isotopic composition of the pore water is measurable unless the water/rock ratio is very low or the ground water circulation is restricted (Savin, 1980; Sverjensky, 1981; Brand and Veizer, 1981; O'Neil, 1987).

Ground Water - Fresh Water Zone

The isotopic signatures of the fresh ground water on Grand Cayman and Cayman Brac (Figs. II.2, 3, 4, Tables V.2, 3, 4) show that:

(1) there is no correlation between $\delta^{18}O$ and the water salinity (Fig. V.2A),

(2) each fresh water lens has its own stable isotope identity (Fig. V.3A),

(3) waters from different portions of the East End lens have different isotopic compositions (Table V.3, Fig. V.3A).

(4) the data points fall along a $\Delta\delta^{2}H/\Delta\delta^{18}O$ slope of 5.91 (Fig. V.3A),

(5) temporal variation of $\delta^{18}O$ is less than ±0.2‰ except in sample 9E1 and 9E2 (Tables V.3, 4), and

(6) the water at the water table (CB7, CB11, Table V.2) is more enriched in ^{18}O than the water immediately below (CB8, CB12, Table V.2).

The lack of positive correlation between $\delta^{18}O$ and salinity together with the isotopic distinction between the fresh water lenses suggest that in addition to evaporation, the $\delta^{2}H$ and $\delta^{18}O$ values of the shallow ground water are controlled by factors such as

(1) different recharge patterns - rapid recharge versus slow infiltration through the unsaturated zone,

(2) recharge of isotopically enriched low intensity rainfall,

(3) irregular rainfall distribution, intensity and amount over the islands,

(4) influx of surface water from sinkholes and mangrove swamps,

(5) different thickness of the unsaturated zone - shallow water table is susceptible to direct evaporation effect, and

(6) variable degree of mixing with the underlying isotopically enriched brackish to saline water.

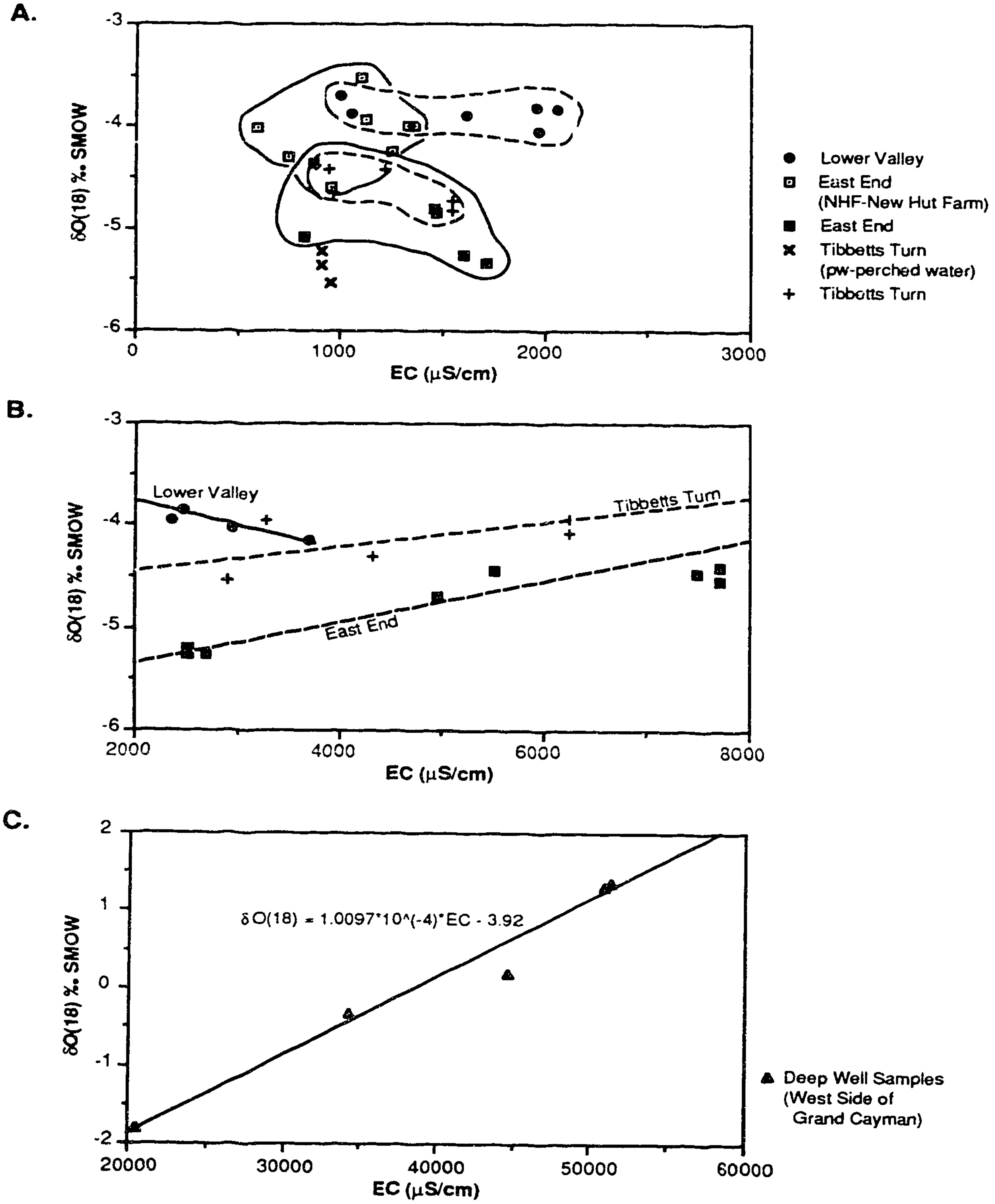


Fig. V.2 Cross plots of δO(18) versus EC (electrical conductivity) of the (A) fresh, (B) lightly brackish, and (C) highly brackish to saline ground waters on the Cayman Islands.

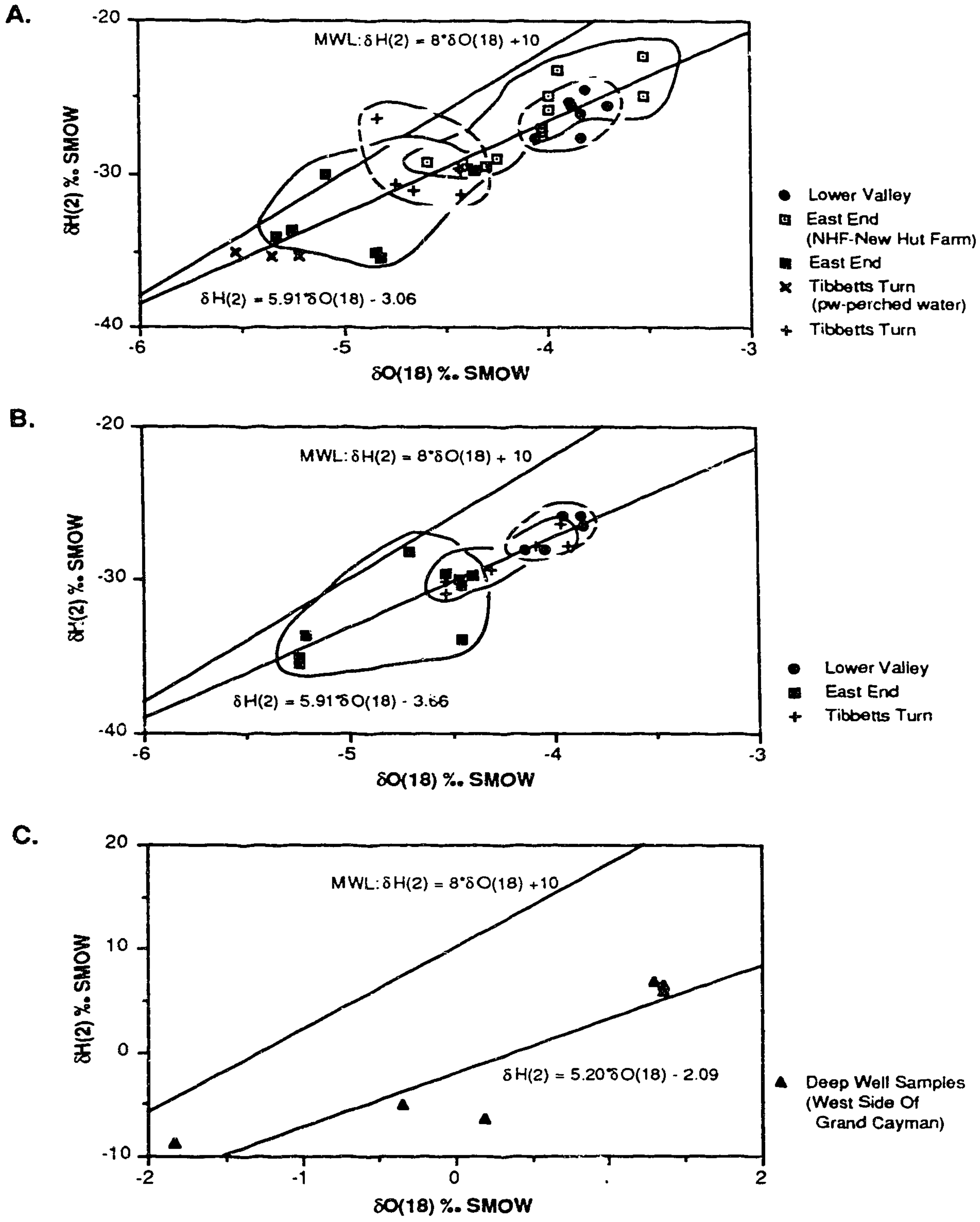


Fig. V.3 Cross plots of δH(2) versus δO(18) of the (A) fresh, (B) lightly brackish, and (C) highly brackish to saline ground waters on the Cayman Islands. MWL refers to meteoric water line.

Evapotranspiration, which does not cause isotopic fractionation, has no effect on the isotopic compositions of the ground water (Gat, 1980; Salomons and Mook, 1986).

In the East End lens, the isotopic variation between the waters from the New Hut Farm (NHF) wells and the piezometers (Table V.3) may have resulted from different degrees of mixing with the surrounding and underlying brackish to saline water. The ground water at New Hut Farm, which is located near the lens boundary, is probably more liable to mixing with the isotopically enriched brackish to saline water than the ground water sampled by the piezometers situated near the centre of the East End lens (Fig. II.4). This mixing phenomenon is a complex interplay between the depth and location of the sampling wells, the aquifer permeability, and the ground water flow regime in the well-developed joint and karst system of the Bluff Formation. Fontes (1980) suggested that in fractured rocks, independent ground water systems might develop in the aquifer system. Furthermore, Issar and Gat (1982) noted that in the fractured areas, there is little effect of evaporation in relation to precipitation due to direct and rapid infiltration of rain water through the open fractures.

When water evaporates from surface water under natural conditions, it becomes enriched in δ^2H and $\delta^{18}O$. The departure of the ground water line ($\Delta\delta^2H/\Delta\delta^{18}O = 5.91$, Fig. V.3A) from the meteoric water line ($\Delta\delta^2H/\Delta\delta^{18}O = 8.0$) indicates that the ground water has undergone evaporation. The evaporation process might have occurred before the rain fell on the land surface, during infiltration through the unsaturated zone, and/or direct evaporation from the shallow water table. Craig *et al.* (1963) and Dansgaard (1964) suggested that this deviation is due to kinetic isotope effects during evaporation into the unsaturated air. Fontes (1980) noted that the slope of the evaporation line ($\Delta\delta^2H/\Delta\delta^{18}O$) lies in the range of 2-5. The low slope reflects low relative humidity and high daily temperature (Welhan, 1987). The intercept of the ground water line ($\delta^2H = 5.91*\delta^{18}O - 3.06$) and the global meteoric line ($\delta^2H = 8*\delta^{18}O + 10$) gives the average $\delta^{18}O$ of the rain water recharge as -6.25‰ SMOW. This low $\delta^{18}O$ value suggests that recharge occurred during heavy rain storms when the rainfall is isotopically depleted.

The large variation in isotopic compositions between samples 9E1 and 9E2 (Table V.3), taken from piezometer 10-80EE about 2 weeks apart, is an enigma. Whether it is caused by periodic influx of isotopically enriched and depleted of surface or ground water is difficult to assess. It is also possible that one of the water samples might have been contaminated during the sampling procedure.

An interesting feature shown by the Tibbetts Turn lens on Cayman Brac (Fig. II.2), is the $\delta^{18}O$ enrichment of the waters collected at the water table relative to those sampled immediately below the water table (e.g. CB7 and CB8, CB11 and CB12, Table V.2). This increase cannot result from mixing with the underlying brackish water because it is difficult to envisage a condition in which mixing preferentially affects the water table zone and not the underlying fresh water zone. Furthermore, at a depth of more than 20 m below the land surface, direct evaporation from the water table is probably ineffective. Therefore, it is suggested that the isotopic enrichment is probably due to differential exsolution of the isotopically light carbon dioxide (i.e. $C^{16}O_2$) from the water table zone to the unsaturated zone. This argument is supported by the inverse relationship of δ^2H between the water at the water table and water immediately below the water table (Table V.2).

Ground Water - Lightly Brackish Zone

The lightly brackish ground water (<15% sea water salinity) has a similar isotopic composition to that of the overlying fresh ground water (Tables V.2, 3, 4). In fact, a few of the brackish water samples are more depleted in ^2H and ^{18}O than those of the fresh water (sample 4E1 and 4E2, Table V.3; sample 4L1 and 4L2, Table V.4).

Like the fresh water zones, the lightly brackish ground waters from different lenses have distinct isotopic identity (Fig. V.3B). This spatial variation is also shown in the relationship between $\delta^{18}O$ content and the ground water salinity (Fig. V.2B). Waters from the East End lens of Grand Cayman and Tibbetts Turn lens of Cayman Brac indicate an increase in $\delta^{18}O$ with increasing water salinity, whereas waters from the Lower Valley lens of Grand Cayman show a decrease in $\delta^{18}O$ with increasing water salinity (Fig. V.2B).

A plot of $\delta^{2}H$ versus $\delta^{18}O$ gives an equation of $\delta^{2}H = 5.91*\delta^{18}O - 3.66$, which is similar to that of the fresh water ($\delta^{2}H = 5.91*\delta^{18}O - 3.06$). The improvement in the correlation coefficient of $\delta^{2}H$ and $\delta^{18}O$ of the lightly brackish ground water relative to that of the fresh water suggests a reduction of surface influence such as direct evaporation, direct rain water recharge, and influx of surface water. However, the overlap of the two ground water lines (Figs. V.3A, 3B) suggests that evaporation is the dominant factor, whereas mixing with the underlying saline water is of minor importance.

The intercept of the ground water line and the global meteoric water line gives an average $\delta^{18}O$ value of -6.45‰ SMOW for the recharge water. This suggests that recharge occurs during rainfall of high intensity when rain water is isotopically more depleted than that of the sparse rainfall of low intensity.

Ground Water - Highly Brackish to Saline Water Zone

The highly brackish to saline ground waters collected from the western part of Grand Cayman are characterized by a linear correlation between $\delta^{18}O$ content and salinity (Fig. V.2C) which is probably caused by mixing between the fresh and saline end members of the ground water, and/or salinization of the ground water through continual evaporation.

The chemical composition of the ground water (Table III.7) suggests that the brackish ground water originated from mixing between the fresh and saline water, whereas the saline ground water was derived from sea water which was subsequently modified by water-rock interactions. The isotopic composition of the saline water (SW1, SW2, Table V.5) is similar to the average stable isotopic content of sea water (Table V.1). This suggests that the linear relationship of salinity versus $\delta^{18}O$ is indicative of mixing between the isotopically depleted fresh ground water and the isotopically enriched saline ground water. A similar conclusion was drawn by Rozkowski and Przewlocki (1974) in their studies of the mixing of meteoric waters with deep, saline fluids in the Upper Silesian Basin of Poland. Welhan (1987) also noted that mixing in the ground water flow systems results in a positive correlation between the $\delta^{18}O$ and salinity of the two end members (fresh and saline water).

Gonfiantini *et al.* (1974) argued that salinization of the ground water in the Hodna region of Algeria resulted in salt enrichment and a corresponding increase in $\delta^{18}O$. They suggested that this relationship was due to direct evaporation of water from the shallow water table. On the Cayman Islands, there is no geochemical and hydrogeological evidence to indicate that such a process occurs in the deep ground water zone. Even in the shallow zone where direct evaporation from the water table occurs the water is not affected by excessive evaporation.

Mixing is the dominant factor in controlling the isotopic composition of the ground water in the highly brackish to saline hydrochemical zones. The intercept between the ground water line ($\delta^2H = 5.20*\delta^{18}O - 2.09$, Fig. V.3C) and the global meteoric water line, therefore, does not give the average $\delta^{18}O$ content of the recharge water. Instead, the intercept ($\delta^{18}O = -4.32‰$ SMOW) represents the isotopic content of the fresh water end member in the mixing process, whereas the other end member is the saline water with an average $\delta^{18}O$ value of +1.34‰ SMOW.

D. SYNOPSIS

Detailed studies of the stable isotopes of the surface and ground water indicate that:

(1) the isotopic variation of the rain water on Grand Cayman results from the (i) degree of evaporation, (ii) amount and intensity of the rainfall, and (iii) origin of the air mass;

(2) the sea water around Grand Cayman is isotopically enriched relative to the standard mean ocean water (SMOW) due to evaporation effect;

(3) the isotopic signatures of the waters from sinkholes are obtained through evaporation of the outcropping ground water and periodic influx of rain water;

(4) ground water recharge occurs during rainfall of high intensity which is isotopically depleted relative to sparse rainfall of low intensity;

(5) the isotopic compositions of the perched ground water are essentially rain water modified by evaporation during infiltration through the unsaturated zone;

(6) the isotopic compositions of the fresh and lightly brackish ground water are controlled by evaporation and cluster about a $\Delta\delta^{2}H/\Delta\delta^{18}O$ slope of 5.91;

(7) mixing between fresh and saline ground water is the dominant factor in controlling the isotopic compositions of the highly brackish ground water; and

(8) similar to that of the water chemistry, the ground water isotopes show spatial and temporal variation.

VI. DIAGENETIC FABRICS OF THE BLUFF FORMATION

Diagenesis of the Bluff Formation has been the subject of a few studies (Jones *et al.*, 1984, 1989; Pleydell, 1987). The important role of algae, fungi, lichen, and plant roots in the diagenetic alteration of the carbonate rocks on the Cayman Islands has also been investigated by Folk *et al.* (1973), Jones (1987, 1988), Jones and Kahle (1985, 1986), Jones and Pemberton (1987a, 1987b), Jones and Ng (1988b), and Squair (1988). These diagenetic studies, however, were restricted to rock samples collected from scattered coastal outcrops and quarries. Consequently, they do not permit the concomitant investigation of the fluids which may be responsible for the diagenetic signatures in the rocks. By using rock cores and cuttings collected from specific sites and depths, this study describes the petrography of the diagenetic fabrics, and examines the diagenetic fabrics of the rocks of the Bluff Formation from different hydrochemical zones of the present day. The diagenetic pattern, occurring in rocks from different hydrochemical zones, and including both the matrix dolomites and the carbonate cements, is the focus of this study.

A. METHOD OF STUDY

Rock samples used for petrographic studies included cores and cuttings. Rock cores (50 mm in diameter) were obtained from the fresh water and lightly brackish water hydrochemical zones during the ground water exploration of the Lower Valley lens in 1982 and East End lens in 1984. The Lower Valley rock cores of 1.5-3.0 m in length are from 15 wells (Fig. VI.1; Appendix 1A), and the East End samples are from a continuous core (12 m beginning at the water table) from one well (Fig. II.4; Appendix 1B). These cores provide the spatial and depth control in the study of the diagenetic pattern of the rocks in the fresh water and lightly brackish water hydrochemical zones, and allow a comparison of the diagenetic pattern of the rocks from the Lower Valley and East End areas. The second point is of particular importance because there is a distinct difference between the water properties of the fresh ground water in the Lower Valley and that in the East End lens

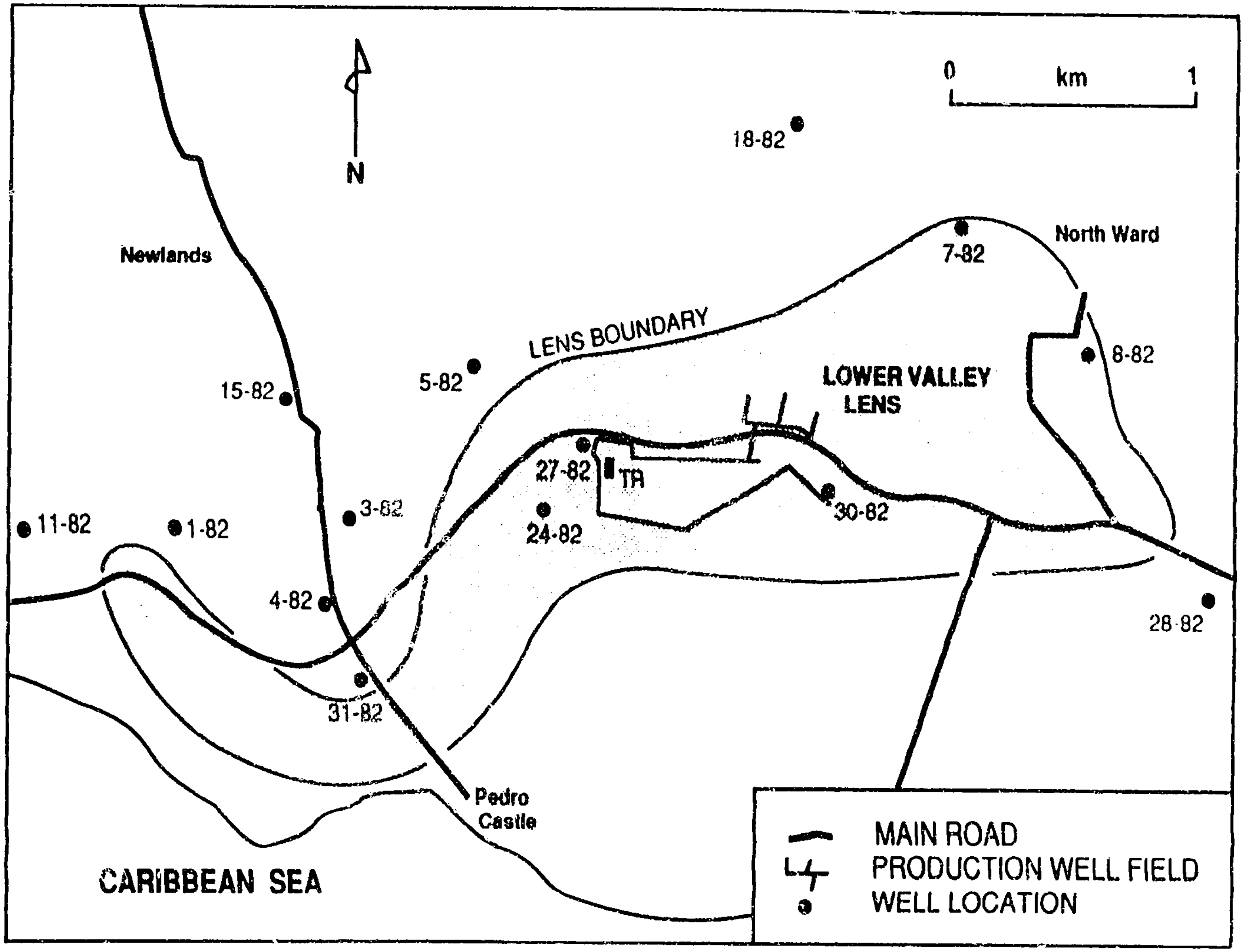


Fig. VI.1 Sketch map of Lower Valley area showing the well locations where rock cores were collected. Well 19-82 (not shown in map) is about 0.85 km northeast of well 18-82.

(Tables III. 3, 4, 5; IV.5, 6). Rock samples were also collected from outcrops around Lower Valley wellfield and from trench well T8 (Fig. VI.1).

Most rock samples from the highly brackish to saline water hydrochemical zones were well cuttings (average 10 mm in length) from the western part of Grand Cayman (Fig. III.2, Appendix 1C). A few samples cored during the Lower Valley exploration program were from the highly brackish water zone (>15% sea water salinity).

Samples of rock cuttings that came to the surface during drilling of water wells on Cayman Brac in 1986 (Fig. VI.2; Appendix 1D) were collected at each ten foot (3 m) interval in depth. All these cuttings were from the thick unsaturated zone (20-40 m). Although the wells also penetrated the saturated zone, the cuttings were not included in this study because it is difficult to ensure that these samples were indeed from the saturated zone. Where open fracture or caves were encountered, drilling commonly lost circulation and samples were not recovered from those sections.

B. POROSITY STYLE

Dolostones of the Bluff Formation have variable porosity owing to the diversity of pore types. Primary intergranular porosity is found in the skeletal grainstone which is composed of fragments of red algae and foraminifera and in the rubble facies on Cayman Brac. Rare secondary intercrystalline and intracrystalline porosity are commonly associated with the poikilotopic calcite-dolomite fabric. Leaching of aragonitic skeletal materials such as corals, molluscs and gastropods created most of the secondary moldic porosity, locally greater than 25% (Fig.II.13, Table II.1). Significant vuggy and cave porosity have been generated by jointing and karstification (Fig.II.12).

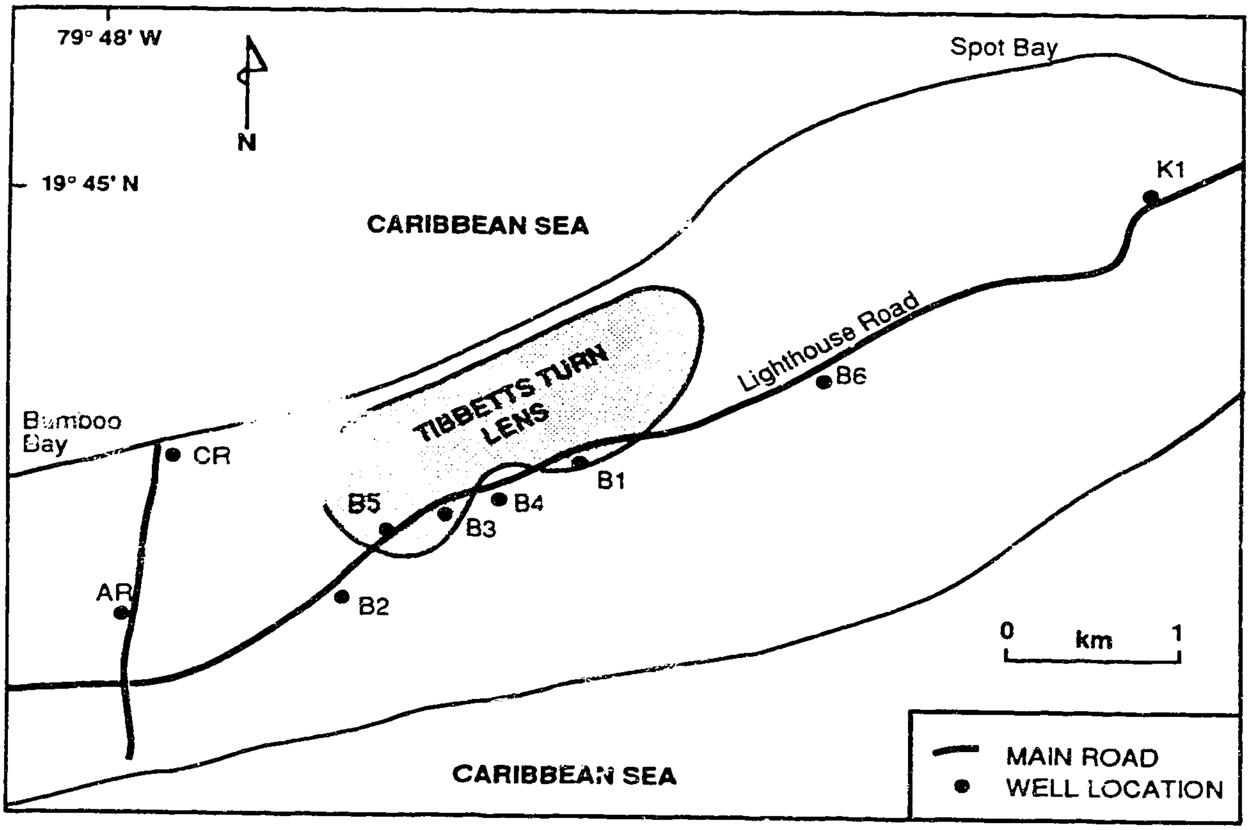


Fig. VI.2 Sketch map of eastern part of Cayman Brac showing the well locations where rock cuttings were collected. Cuttings from well AR, CR and K2 were also examined but were not included in Fig. VI.8. Well K2 is about 3 km west of well AR by the Lighthouse Road.

C. PETROGRAPHY OF THE DIAGENETIC FABRICS

The Bluff Formation is formed of hard, white to cream, finely crystalline to microcrystalline dolostone. The original limestone of the Bluff Formation was pervasively dolomitized with the precursor texture commonly preserved.

Matrix Dolomite

The matrix dolomite is a mosaic of equant crystals that forms a xenotopic to hypidiotopic crystal fabric. The subhedral to anhedral dolomite crystals are microcrystalline to finely crystalline, with crystals 5 to 10 µm long. Dark minute inclusions, probably of precursor carbonate origin, give the dolomite crystals a cloudy appearance (Plate VI.1A).

In places, coarser, euhedral dolomite [illegible] 40 µm long are scattered throughout the microcrystalline dolomite [illegible] (Plate VI.1A). These euhedral crystals are commonly clear with fewer inclusions than the very fine dolomite crystals (Plate VI.1A) or they are zoned with cloudy centres and clear rims (Plate VI.1B).

Intercrystalline porosity is rare in the dolostone of the Bluff Formation due to pervasive dolomitization. However, some rock cuttings recovered from well drilling on Cayman Brac have high intercrystalline porosity (Plate VI.1C). In such cases, partial dissolution of the matrix dolomite is common (Plate VI.1D). This porous dolostone is comparable to rocks which Rose (1972) and Chafetz and Butler (1980) termed pulverulite. Zogovic (1966) also described crushed dolomite from the Dinaric Karst of Yugoslavia and suggested that the high intercrystalline porosity is probably caused by dissolution of calcite cement. Ng (1985) and Jones *et al.* (1989) also documented the presence of porous dolostone along major joints that transect the Bluff Formation on Grand Cayman. Therefore, the porous dolostone identified in the cuttings were probably derived from weathered zones developed around the joints in the unsaturated zone. The intercrystalline pores in some of the cuttings are filled with sparry calcite (Plate VI.1E).

PLATE VI.1

Photomicrographs of matrix dolomite. All depths are measured from land surface.

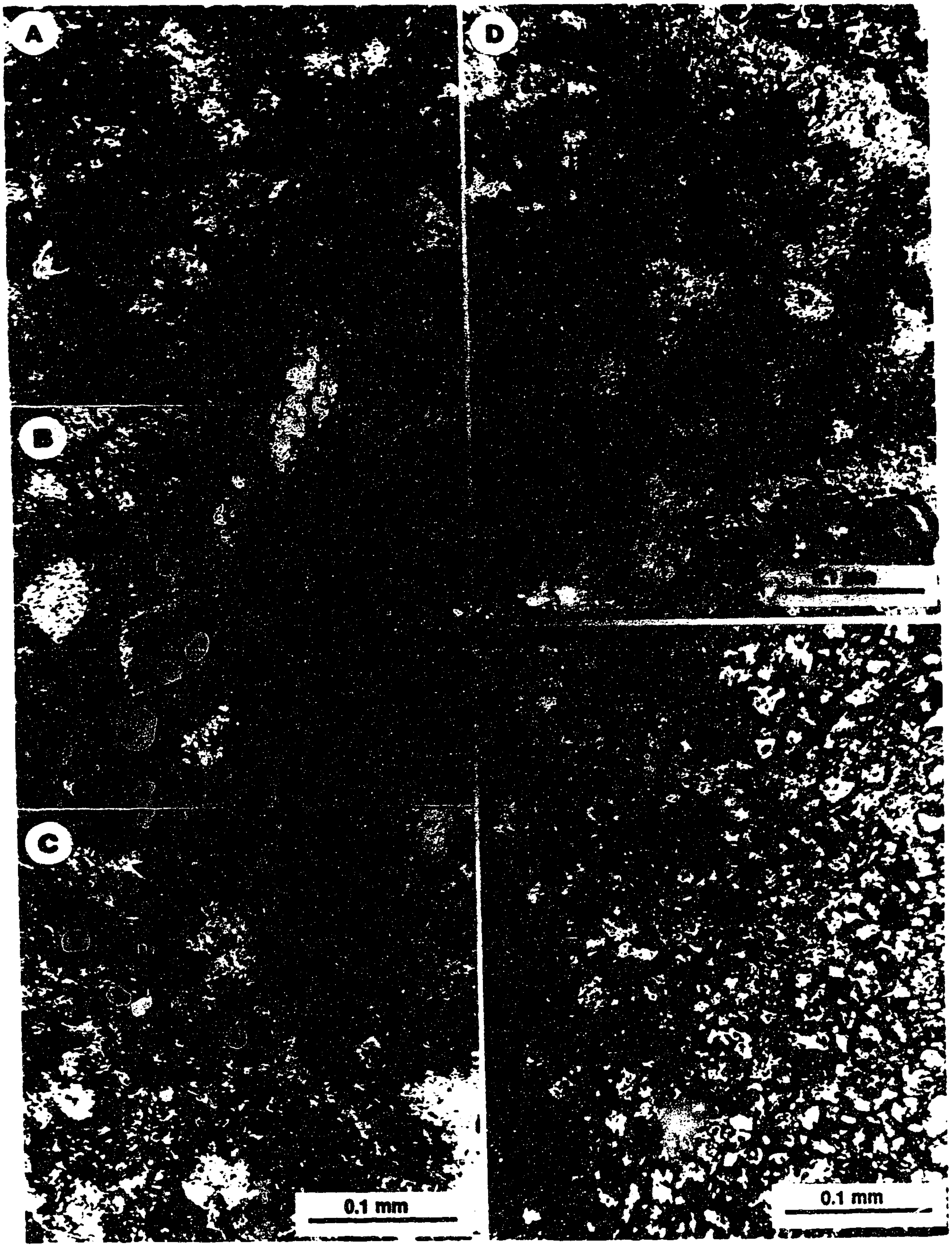
(A) Clear, euhedral dolomite crystals (d) scattered in the microcrystalline cloudy dolomite groundmass (m). Rock cutting from West Bay Road well WB#2 in the saline water zone at a depth of about 27 m .

(B) Clear, euhedral, zoned dolomite crystals (z) with cloudy centres and clear rims scattered in the microcrystalline cloudy dolomite groundmass (m). Rock cutting from Cayman Brac well K1 in the unsaturated zone at a depth of about 30 m.

(C) Intercrystalline (sucrosic) porosity (s) in the finely crystalline dolomite matrix (m). Rock cutting from Cayman Brac well B3 in the unsaturated zone at a depth of about 18 m.

(D) Intercrystalline porosity (s) and intracrystalline porosity (p) which was formed by partial dissolution of the zoned matrix dolomite crystals (m). Rock cutting from Cayman Brac well B4 in the unsaturated zone at a depth of about 15 m.

(E) Intercrystalline pores of microcrystalline dolomite (d) filled by sparry calcite (c). Rock cutting from Cayman Brac well B4 in the unsaturated zone at a depth of about 6 m.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Dolomite Cement

Euhedral, clear dolomite typically developed as the first phase of cement lining the cavities. The dolomite crystals commonly rooted on the matrix dolomite and only rarely occluded the cavities (Plates VI.2A, 3B). A rare form of dolomite spar, up to 150 μm long, rooted on sparry calcite cement, was documented by Pleydell (1987) but was not seen in this study.

Following Jones *et al.* (1984), the dolomite cements are divided into types I and II. Type I, formed of clear dolomite crystals up to 50 μm long (Plates VI.2A, 2B), is analogous to the limpid dolomite described by Folk and Land (1975). Type II dolomite cements are zoned (Plate VI.2C) and crystals are up to 100 μm long. Although the two cement types may be present in adjacent cavities, they do not occur in the same cavity. Two generations of dolomite cement are present; one occurred prior to internal sedimentation (Plate VI.6F) and the other occurred after internal sedimentation (Plate VI.6E).

Partial dissolution of the dolomite cements is common. It commonly involves preferential dissolution of individual zones, cores, or the entire crystals (Plate VI.2D, 2E, 2F).

Sparry Calcite Cement

Precipitation of sparry calcite cements commonly followed the dolomite cements (Plate VI.3A) and commonly occluded the cavities (Plates VI.3B, 3C). This dolomite-calcite couplet, previously documented by Jones *et al.* (1984) in the dolostone of the Bluff Formation, also occurs in dolomitic limestone on Jamaica (Land, 1973a), the Bahamas (Kaldi and Gilman, 1982) and the Yucatan Peninsula (Ward and Halley, 1985). In the fresh water zone of the Lower Valley lens, where dolomite cement is commonly absent, sparry calcite cement is rooted on the matrix dolomite (Plate VI.3D).

PLATE VI.2

Photomicrographs and scanning electron photomicrographs of dolomite cement. All depths are measured from land surface.

(A) Photomicrograph of clear, euhedral dolomite cement crystals (d) lining cavity formed by selective leaching of aragonitic coral structure. Rock cutting from West Bay Road well #2 in the saline water zone at a depth of about 33 m.

(B) Scanning electron photomicrograph of coarse, euhedral dolomite cements (d) lining cavity. Note the xenotopic crystalline fabric of the matrix dolomite (m). Rock cutting from George Town well CF in the highly brackish water zone at a depth of about 19 m.

(C) Photomicrograph of clear, euhedral, zoned dolomite (z) cement lining cavity. Rock core from Lower Valley well 11-82 in the highly brackish water zone at a depth of about 3 m.

(D) Photomicrograph of preferential dissolution (p) of certain zones, cores of dolomite cement crystals. Rock cutting from George Town well CF in the highly brackish water zone at a depth of about 21 m.

(E) and (F) Scanning electron photomicrographs of leached dolomite rhombs. Rock sample from weathered dolostone outcrop, Lower Valley.

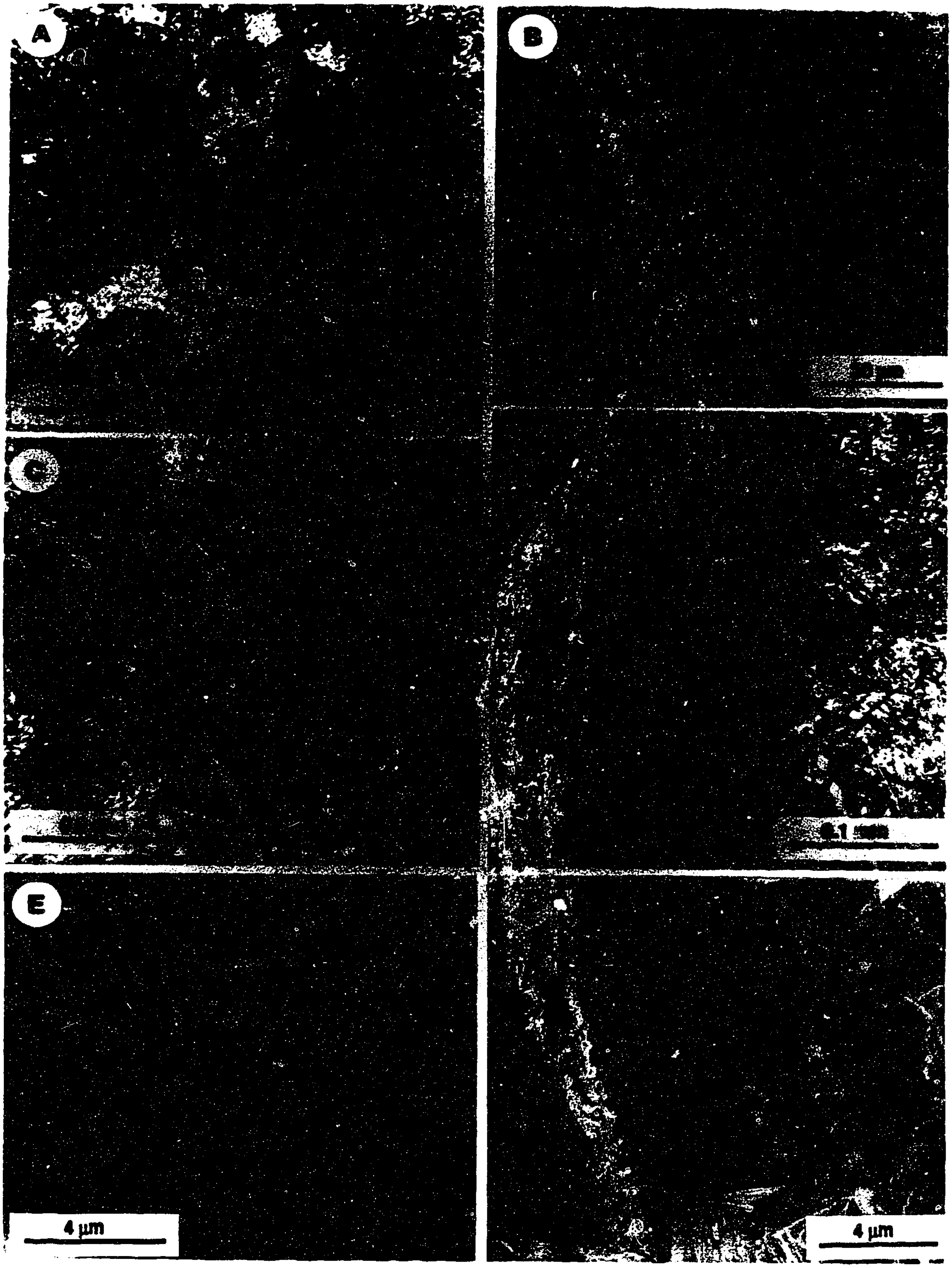

A
B
C
E
0.1 mm
4 µm
4 µm

PLATE VI.3

Photomicrographs of calcite cement. All depths are measured from land surface.

(A) Thin rind of calcite cement (c) lining cavity wall after dolomite cement (d). Sample from East End core #6.22 in the fresh water zone at a depth of about 12 m.

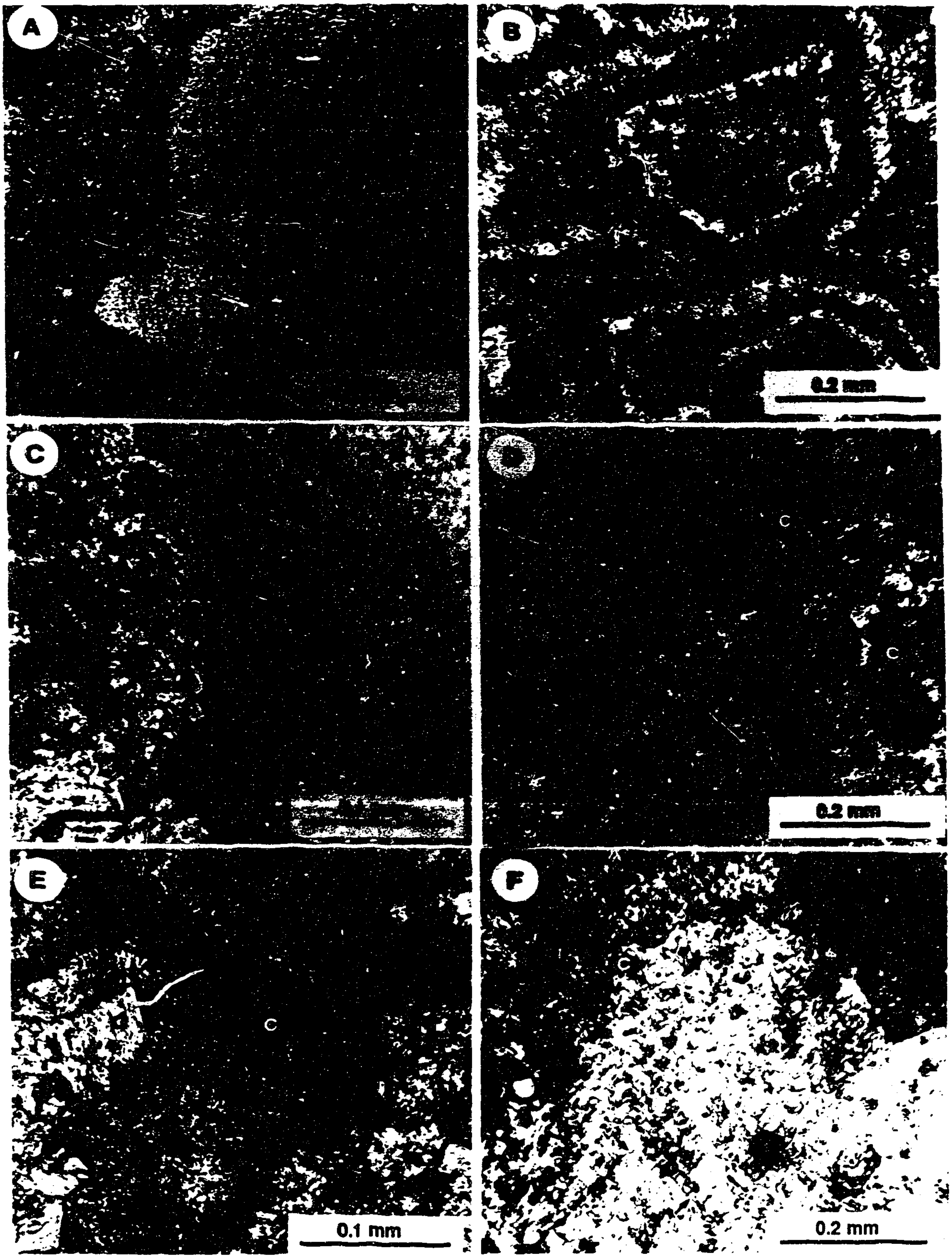
(B) Dolomite cement (d) lining cavities of coral structure followed by sparry calcite (c) which completely filled the cavities. Sample from East End core #3.6 in the fresh water zone at a depth about 8 m.

(C) Zoned dolomite cements (z) lining cavity followed by sparry calcite cement (c). Rock cutting from Cayman Brac well B2 in the undersaturated zone at a depth of about 21 m.

(D) Large cavities lined with calcite cement (c), whereas small cavities completely filled by sparry calcite (c). Note the absence of dolomite cement. Rock core from Lower Valley well 24-82 in the fresh water zone at a depth of about 6 m.

(E) Dolomite cement (d) followed by zoned sparry calcite (c). The zonation was highlighted by thin, dark organic or clay rich zones (arrows). Sample from East End core #1.22 in the fresh water zone at a depth of about 5 m.

(F) Partial dissolution of sparry calcite (c). Note the preferential dissolution along the cleavage planes (arrows). Rock cutting from West Bay Road well #2 in the highly brackish water zone at a depth of about 24 m.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D
c
c
E
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0.1 mm
F
c
0.2 mm

Some calcite spar cements are zoned with individual zones separated by a thin (1 µm), dark coloured band of clay or organic materials (Plate VI.3E). Rarely, partial dissolution of the sparry calcite also occurs, with preferential dissolution along the cleavage planes (Plate VI.3F).

Alternating Zones of Dolomite and Calcite

Cements composed of alternating zones of dolomite and calcite occur in two forms. The first type consists of alternating zones of about 10 µm thick that are laterally continuous from crystal to crystal (Plates VI.4A, 4B). The calcite band appears to follow the outlines of the preceding dolomite crystals and is subsequently encased by a further zone of dolomite (Plates VI.4A, 4B).

The second type of alternate zoning of dolomite and calcite occurs in a single crystal (Plates VI.4C, 4D). The zoned cements are probably equivalent to the zoned dolomite-calcite cements described by Jones *et al.* (1984). Commonly, the core of the zoned crystals is clear dolomite. In most cases, these zoned crystals were encased by poikilotopic calcite (Plate VI.4D).

Poikilotopic Calcite-Dolomite

Poikilotopic calcite that encases dolomite cement and matrix dolomite produced fabrics comparable to those considered indicative of dedolomite by Shearman *et al.* (1961), Evamy (1967) and Katz (1971). The poikilotopic calcite-dolomite fabrics in the Bluff Formation include (1) hollow zones in dolomite rhombs (Plate VI.5A), (2) calcite zones and cores in dolomite rhombs (Plates VI.5A, 5B, 5C, 5D), and (3) rounded and corroded outlines of dolomite crystals (Plates VI.5B, 5C). Where matrices have two distinct crystal sizes, poikilotopic calcite preferentially replaced the smaller dolomite crystals (Plates VI.5A, 5E).

PLATE VI.4

Photomicrographs of alternating dolomite and calcite cement. All depths are measured from land surface.

(A) and (B) Alternating zones of dolomite (d) and calcite (c) that are laterally continuous from crystal to crystal. Note indistinct intercrystalline boundaries. Rock cutting from West Bay Road well #1 in the highly brackish water zone at a depth of about 12.5 m.

(C) Alternating zones of dolomite (d) and calcite (c) in individual crystals. Rock cutting from Cayman Brac well K1 in the unsaturated zone at a depth of about 9 m.

(D) Alternating zones of dolomite (d) and calcite (c) in individual crystals which were subsequently encased by poikilotopic calcite (pc). Sample from East End core #1.22 in the fresh water zone at a depth of about 5 m.


A
B
C
D
0.1 mm
0.1 mm

PLATE VI.5

Photomicrographs of poikilotopic calcite-dolomite fabrics. All depths are measured from land surface.

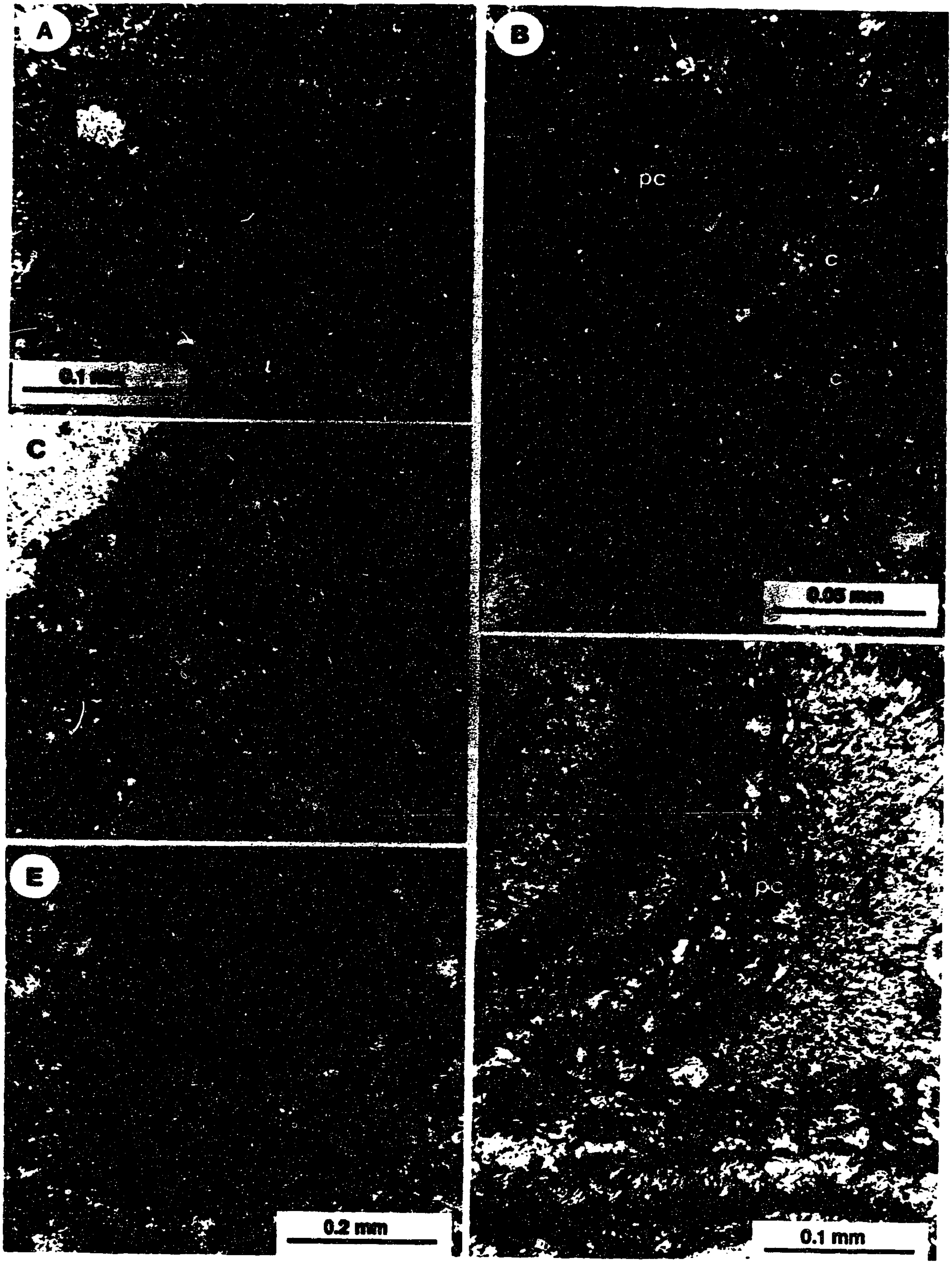
(A) Clear, euhedral dolomite rhombs (d) with hollow cores (h). Rock sample from weathered dolostone outcrop, Lower Valley.

(B) Matrix dolomite crystals (d) with calcite cores and calcite zones (c). Note corroded outline of dolomite (arrows) encased by poikilotopic calcite (pc). Rock sample from Lower Valley trench well at the water table zone at a depth of about 1.5 m.

(C) Dolomite spar (d) replaced and encased by poikilotopic calcite (pc). Rock cutting from Cayman Brac well B2 in the unsaturated zone at a depth of about 9 m.

(D) Dolomite cement zone (arrows) replaced by poikilotopic calcite (pc). Note remnants of dolomite zones (d). Rock cutting from West Bay Road well #1 in the highly brackish water zone at a depth of about 24 m.

(E) Poikilotopic calcite (pc) preferentially replaced smaller sized matrix dolomites (m), leaving coarser euhedral dolomite unreplaced (d). Rock core from Lower Valley well 5-82 in the highly brackish water zone at a depth of about 3 m.


A
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B
pc
c
c
0.05 mm
C
E
0.2 mm
pc
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Internal Sediments

Caymanite is a microcrystalline dolomite characterized by (1) white, orange/red and black colour bands (Fig. 11 of Lockhart, 1986), (2) tightly interlocking anhedral dolomite crystals (Plates VI.6C-6F), (3) angular grains or fragments of dolostone (Plates VI.6C, 6D), (4) geopetal texture (Plates VI. 6E, 6F), and (5) cross bedding, and (6) cut and fill channels (Fig. 12 of Lockhart, 1986). Rare examples a [illegible] contain foraminifera and gastropods.

The laminae of the caymanite, when viewed under the petrographic microscope, show slight differences in the amount of darker-coloured matrix (<0.02 mm) and lighter-coloured angular grains and rock fragments. The grains and fragments are dolostone from 0.02 to 0.50 mm long in thin sections (Plate VI.6C) and up to 50 mm long in field samples. Some angular rock fragments were probably the end result of removal of irregular projections from the underlying bedrock (Plate VI.6D).

Another form of internal sediment is dolomitized skeletal grainstone, which commonly deposited on top of the caymanite. In places, the white coloured grainstone is poorly lithified with high original porosity. The skeletal component is predominantly foraminifera which appear to be leached. Fragments of red algae are also common.

The relationship between the caymanite and other cavity fills include (1) caymanite sedimentation prior to dolomite cementation (Plate VI.6E), (2) dolomite cementation prior to caymanite deposition (Plate VI.6F), (3) sparry calcite precipitation after caymanite sedimentation (Plate VI.6F), (4) flowstone precipitation and terra rossa influx after caymanite sedimentation, and (5) caymanite sedimentation prior to influx of skeletal grainstone.

Terra Rossa

Terra rossa present in the Bluff Formation is formed of organic-rich glaebules embedded in microcrystalline carbonate and clay matrix (Plate VI.6A). The glaebules are

PLATE VI.6

Photomicrographs of cavity fills (terra rossa, caymanite and flowstone). All depths are measured from land surface.

(A) Two phases of terra rossa fill. One phase is characterized by dark, organic rich glaebules (g) embedded in the microcrystalline calcium carbonate matrix, whereas the other phase is characterized by light coloured glaebules. Rock cutting from Cayman Brac well B2 in the unsaturated zone at a depth of about 3 m.

(B) Dolomite cement (d) followed by terra rossa breccia (b). Note the angular dolostone fragments (f) in the terra rossa. Rock cutting from Cayman Brac well B5 in the unsaturated zone at a depth of about 27 m.

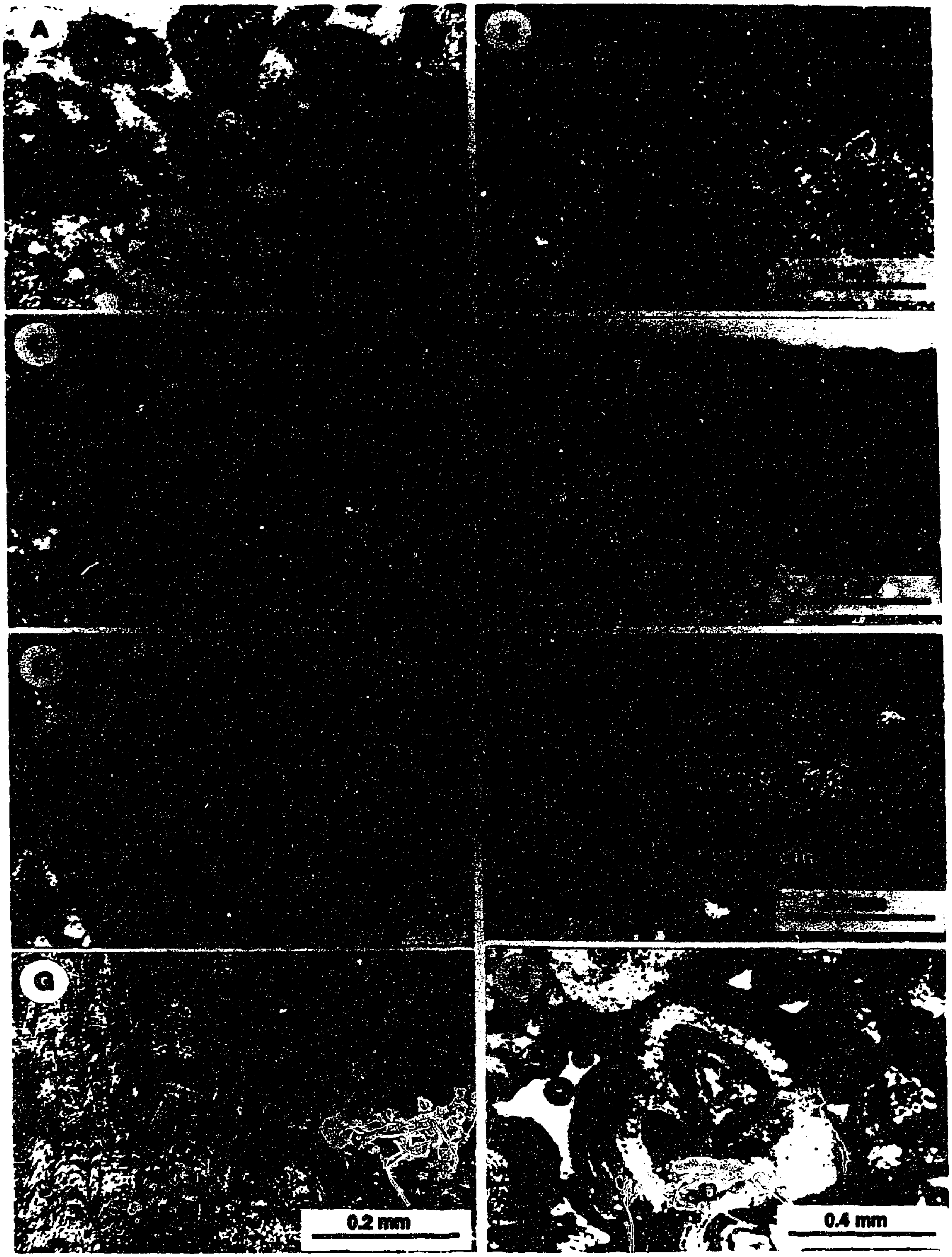
(C) Caymanite sample showing bands resulting from differences in matrix dolomite crystal sizes and content of angular dolostone fragments (f). Sample from East End core #1.15 in the fresh water zone at a depth of about 4 m.

(D) Cavity partially filled by caymanite (cm). Note the angular dolostone fragments (f) apparently ripped from the cavity wall. Sample from East End core #7.22 in the fresh water zone at a depth of about 13 m.

(E) Caymanite (cm) in cavity of coral structure showing geopetal texture, which was followed by euhedral dolomite cement (d). Sample from East End core #5.2 in the fresh water zone at a depth of about 10 m.

(F) Dolomite cementation (d) prior to caymanite sedimentation (cm) with the rest of the cavity subsequently filled by sparry calcite (c). Sample from East End core #3.2 in the fresh water zone at a depth of about 7 m.

(G) and (H) Longitudinal and cross section view of a flowstone sample showing the laminated, columnar calcite crystals (G) and trigonal crystal morphology (H). Note dark inclusion rich growth bands (arrows). Rock cutting from Cayman Brac well B6 in the unsaturated zone at a depth of about 3 m.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G
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0.4 mm

made up predominantly of clay minerals with minor calcium carbonate. Terra rossa breccia (Plate VI.6B), which has dolostone fragments embedded in the soil, is common in some cavities and open joints. Commonly, the less well consolidated terra rossa is red in colour whereas the well consolidated terra rossa is brown in colour. However, it is important to note that there are many different colour shades in the consolidated terra rossa. Some cavities were filled by two phases of terra rossa that differ in colour and the amount and size of the glaebules (Plate VI.6A). In places, dolomite cementation preceded the emplacement of terra rossa in the cavity (Plate VI.6B).

Flowstone

Brown, banded flowstone, formed of columnar calcite (Plates VI.6G, 6H), commonly filled cavities, joints and caverns in the Bluff Formation (Lockhart, 1986; Smith, 1987; Jones and Smith, 1988). Locally, flowstone is intercalated with terra rossa.

D. DISTRIBUTION OF THE CARBONATE CEMENTS IN THE PRESENT DAY HYDROCHEMICAL ZONES

A systematic analysis of the carbonate cementation pattern and distribution in each hydrochemical zone should provide insight into the relationship between the cement fabrics and pore fluids. Of particular importance is the late-phase carbonate cements and the present-day ground waters. This relationship is investigated for each of the present day hydrochemical zones in terms of the paragenetic sequence of the cements present in the rocks, and the type and abundance of the last phase of cement.

Fresh Water Zone

There are distinct differences in the diagenetic fabrics of the Bluff Formation between the Lower Valley and East End lens of Grand Cayman. Carbonate cement fabrics

recognized in **individual** cavities of the rocks sampled from the Lower Valley fresh water zone include:

(1) poikilotopic calcite-dolomite near the water table zone, and

(2) sparry calcite cement (voids rarely lined by dolomite cement).

Carbonate cement fabrics recognized in **individual** cavities of the rocks sampled from the East End fresh water zone include:

(1) dolomite cement followed by sparry calcite,

(2) dolomite cement lining voids (not followed by sparry calcite),

(3) alternating zones of dolomite and calcite,

(4) sparry calcite cement only, and

(5) zoned sparry calcite cement.

In the Lower Valley aquifer, the paragenetic sequence of the cements is simple (Fig.VI.3A). The cavities were rarely lined by dolomite cement. Instead, more than 80% of the cavities were lined or filled by calcite as the only cement phase. The poikilotopic calcite-dolomite, which occurs near the water table zone of the Lower Valley lens (Plate VI.5B), is probably related to near surface influences such as rain water infiltration, and evaporation. In the East End aquifer, the cement types indicates the following carbonate cementation sequence (Fig.VI.3B): (1) clear, euhedral dolomite, (2) zoned dolomite, (3) alternating bands of dolomite and calcite, and (4) clear or zoned sparry calcite.

Petrographic studies indicate that the calcite cement is the most common last phase cement in cavities in the fresh water zone of both the Lower Valley and East End lens (Fig.VI.4). Thus, it may be suggested that calcite cement formed in close association with the fresh ground water.

Lightly Brackish Water Zone (<15% sea water salinity)

Like the rocks in the fresh water zone, there are differences in the diagenetic features between those in the Lower Valley and East End lens. Carbonate cement fabrics

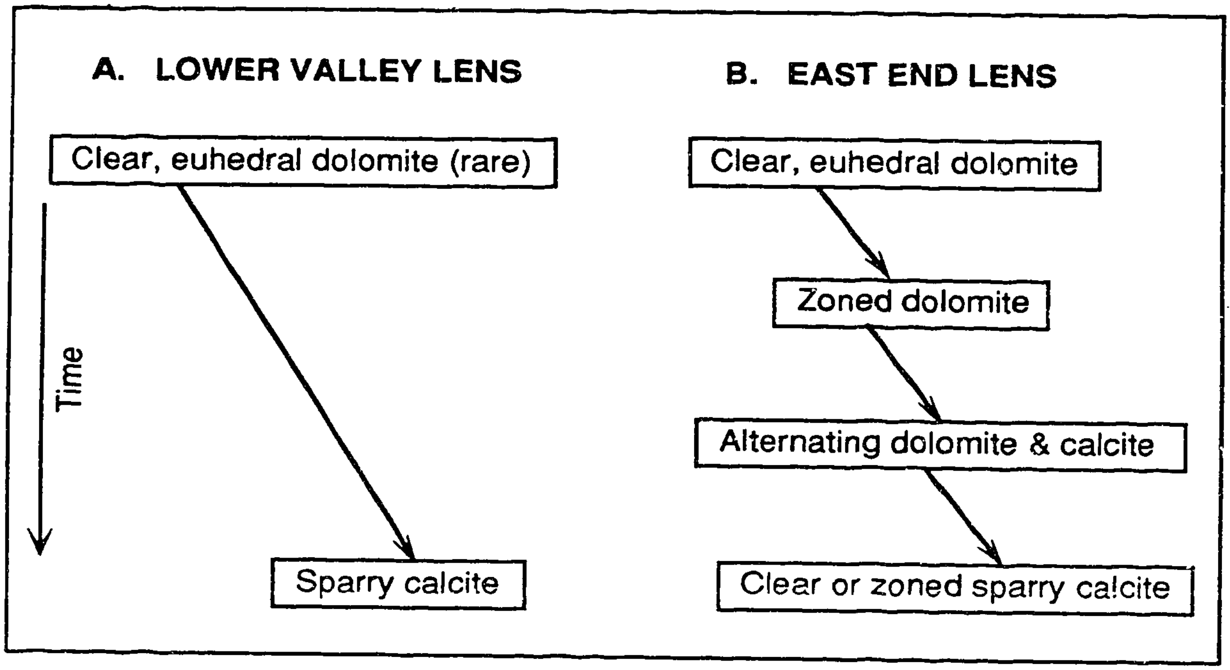


Fig. VI.3 Paragenetic sequence of carbonate cements in the fresh water zone of the (A) Lower Valley and (B) East End aquifers.

LOWER VALLEY	WATER TABLE	EAST END
Poikilotopic calcite-dolomite	Water Table Zone (<1 m)	Sparry calcite
Sparry calcite	Fresh Water Zone Lower Valley lens <10 m East End lens <25 m	
>60% of the cavities have calcite <40% of the cavities have dolomite	Lightly Brackish Water Zone (salinity <15% sea water) Variable Thickness	Dolomite

Fig. VI.4 Types of last carbonate cement phase in the fresh water and lightly brackish water zones of the Lower Valley and East End aquifers.

recognized in **individual** cavities of rocks sampled from the Lower Valley lightly brackish water zone include:

(1) dolomite cement followed by sparry calcite,

(2) dolomite cement with hollow zones or cores, and

(3) sparry calcite cement only.

Carbonate cement fabrics recognized in **individual** cavities of the rocks sampled from the East End lightly brackish water zone:

(1) dolomite cement,

(2) zoned and hollow dolomite, and

(3) open cavities.

In the Lower Valley aquifer, the paragenetic sequence of carbonate cements (Fig.VI.5A) is (1) clear, euhedral dolomite, (2) zoned dolomite (selective leaching of certain zones), and (3) sparry calcite. Approximately 60% of the cavities in the lightly brackish water zone of the Lower Valley lens have calcite as the last phase of cement (Fig.VI.

In the East End lens, calcite cement is not seen in the rocks from the lightly brackish water zone (Fig.VI.5B). All the voids were lined by clear, euhedral dolomite cement or zoned dolomite. Thus, dolomite cement becomes the most common last cement phase in the brackish water zone of the East End lens (Fig.VI.4).

It appears that the brackish water has a much higher potential to precipitate dolomite than the fresh water, particularly in the East End lens. The presence of calcite cement in the rocks of the Lower valley lens but not in those of the East End lens suggests that salinity is probably not the only consideration in carbonate cementation. It appears that the concentrations of the chemical constituents such as Mg^{2+}, Ca^{2+} and HCO_3^- or CO_3^{2-}, and Mg^{2+}/Ca^{2+} ratio (Tables III.3, IV.7) are probably the controlling factors.

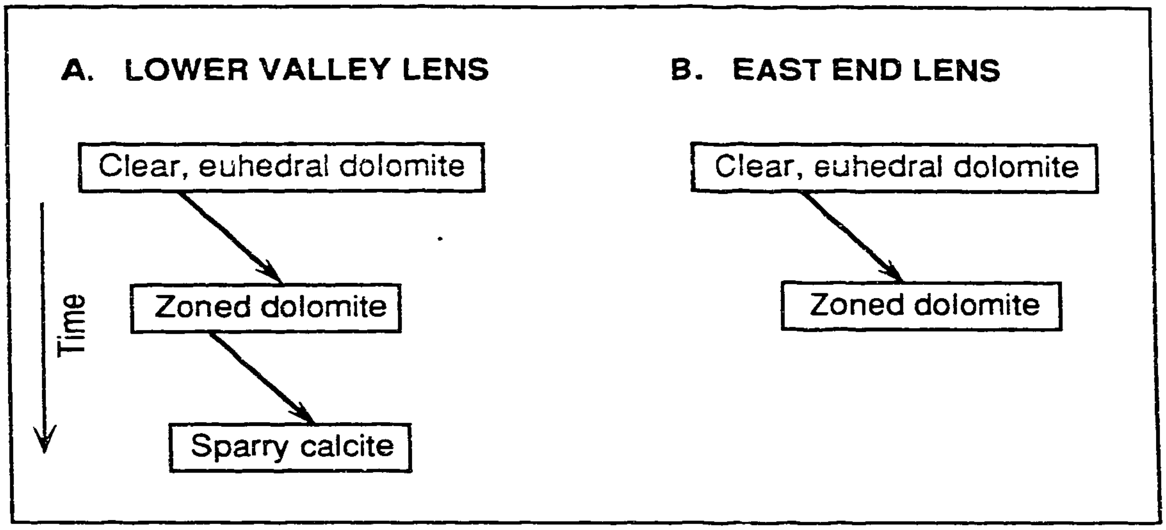


Fig. VI.5 Paragenetic sequence of carbonate cements in the lightly brackish water zone of the (A) Lower Valley and (B) East End aquifers.

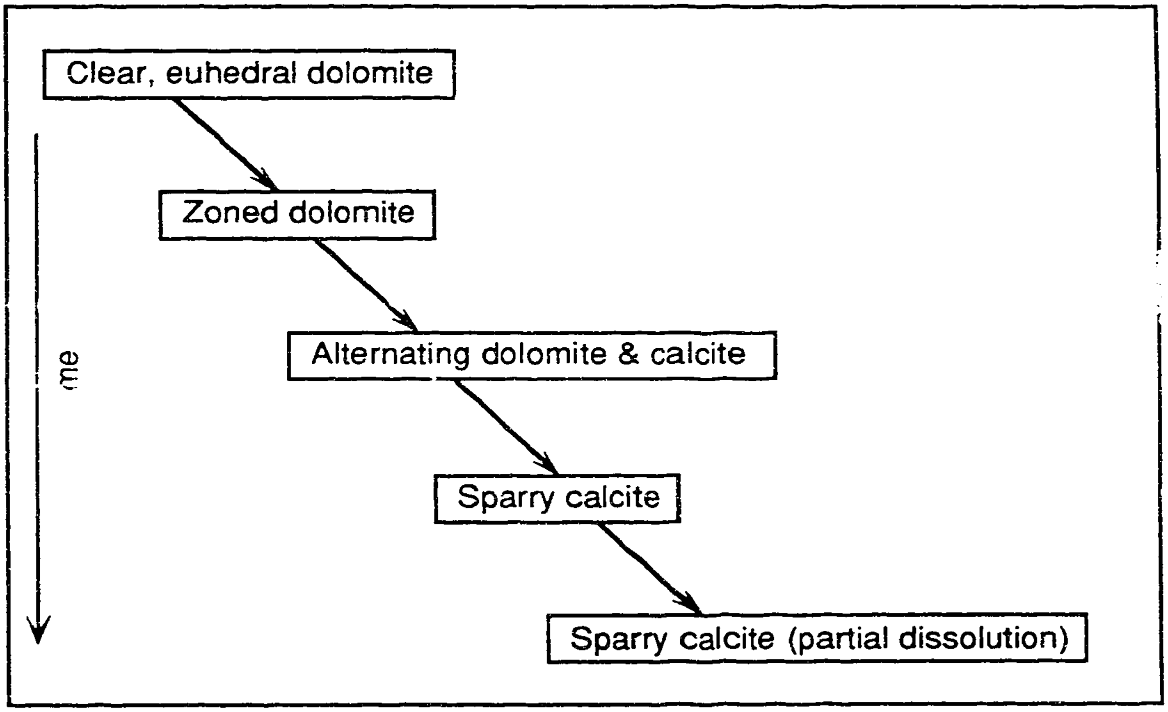


Fig. VI.6 Paragenetic sequence of carbonate cements in the highly brackish water zone.

Highly Brackish Water Zone

Carbonate cement fabrics present in **individual** cavities of the rocks sampled from the highly brackish water zone include:

(1) dolomite cement followed by sparry calcite,

(2) dolomite cement lining voids,

(3) zoned dolomite cement showing selective dissolution of certain zones,

(4) alternating zones of dolomite and calcite cement, and

(5) calcite spar showing partial dissolution.

The paragenetic sequence (Fig.VI.6) comprises (1) clear, euhedral dolomite, (2) zoned dolomite, (3) alternating zones of dolomite and calcite, (4) sparry calcite, and (5) partially dissolved sparry calcite. Most cavities have dolomite as the only cement phase (Fig.VI.7); only 10-20% of the cavities contain some sparry calcite. Therefore, it appears that dolomite is the most common carbonate cement associated with the present-day highly brackish ground water.

Saline Water Zone

Rocks from the saline water zone typically lack calcite cement; however, some 20-30% of the cavities are lined by dolomite cement (Fig.VI.7). Sparry calcite cement is rare. Conversely, about 40-50% of the cavities have no carbonate cements. Rocks in the saline water zone are presently bathed in water that is similar to the sea water in terms of water salinity.

The petrographic data suggest, therefore, that saline water is less favourable for calcite precipitation than fresh water and is also less favourable for dolomite cementation than the brackish water. This phenomenon may be partly related to the presence of inhibitors in the saline water and partly due to the slow ground water flow rate in this zone.

LAST CEMENT PHASE	HYDROCHEMICAL ZONE
Dolomite	Highly Brackish Water (salinity >15% and <100% sea water)
20-30% of the cavities have dolomite 40-50% of the cavities remain open Minor % of the cavities have calcite	Saline Water (salinity ≥100% sea water)

Fig. VI.7 Types of last carbonate cement phase in the highly brackish and saline water zones of the dolostone aquifer. Rock samples from deep wells drilled on the west side of Grand Cayman.

E. AN EXAMPLE OF COMPLEX DIAGENETIC PATTERNS

Rock cuttings, which were collected from the unsaturated (vadose) zone at ten foot intervals from 10 water wells on Cayman Brac (Fig. VI.2, Appendix 1D), provided an excellent opportunity to examining the distribution of diagenetic fabrics over a wide area. Detailed petrographic studies of the rock cuttings indicate a complex distribution of diagenetic fabrics (Fig. VI.8) present in **individual** cavities, which include:

(A) dolomite cement followed by sparry calcite,
(B) dolomite cement lining voids with no calcite cement ,
(C) zoned dolomite cement, dissolution of zones in places,
(D) zoned dolomite cement followed by sparry calcite,
(E) alternating zones of dolomite and calcite,
(F) sparry calcite cement only,
(G) poikilotopic calcite-dolomite,
(H) flowstone,
(I) terra rossa, and
(J) internal sediments (caymanite and skeletal grainstone).

The complicated diagenetic patterns (Fig. VI.8) are a reflection of the complexity of the diagenetic environments. The sediments/rocks were under increasing meteoric influence as Cayman Brac gradually emerged from the sea. The rocks, therefore, record a complete diagenetic history from saline water to brackish water to fresh water to vadose zone. If this is so, the rocks should have been affected by similar pore fluids at the same stratigraphic horizons, and hence, should have similar diagenetic fabrics at those stratigraphic levels. However, the distribution of the diagenetic fabrics (Fig. VI.8) does not seem to display any pattern with respect to a particular aquifer system. This variability in diagenetic signatures probably resulted from the subenvironments created in the joint and karst controlled system of the Bluff Formation, and hence, zones of different fluid chemistry. This feature is important because it demonstrates that samples from the same

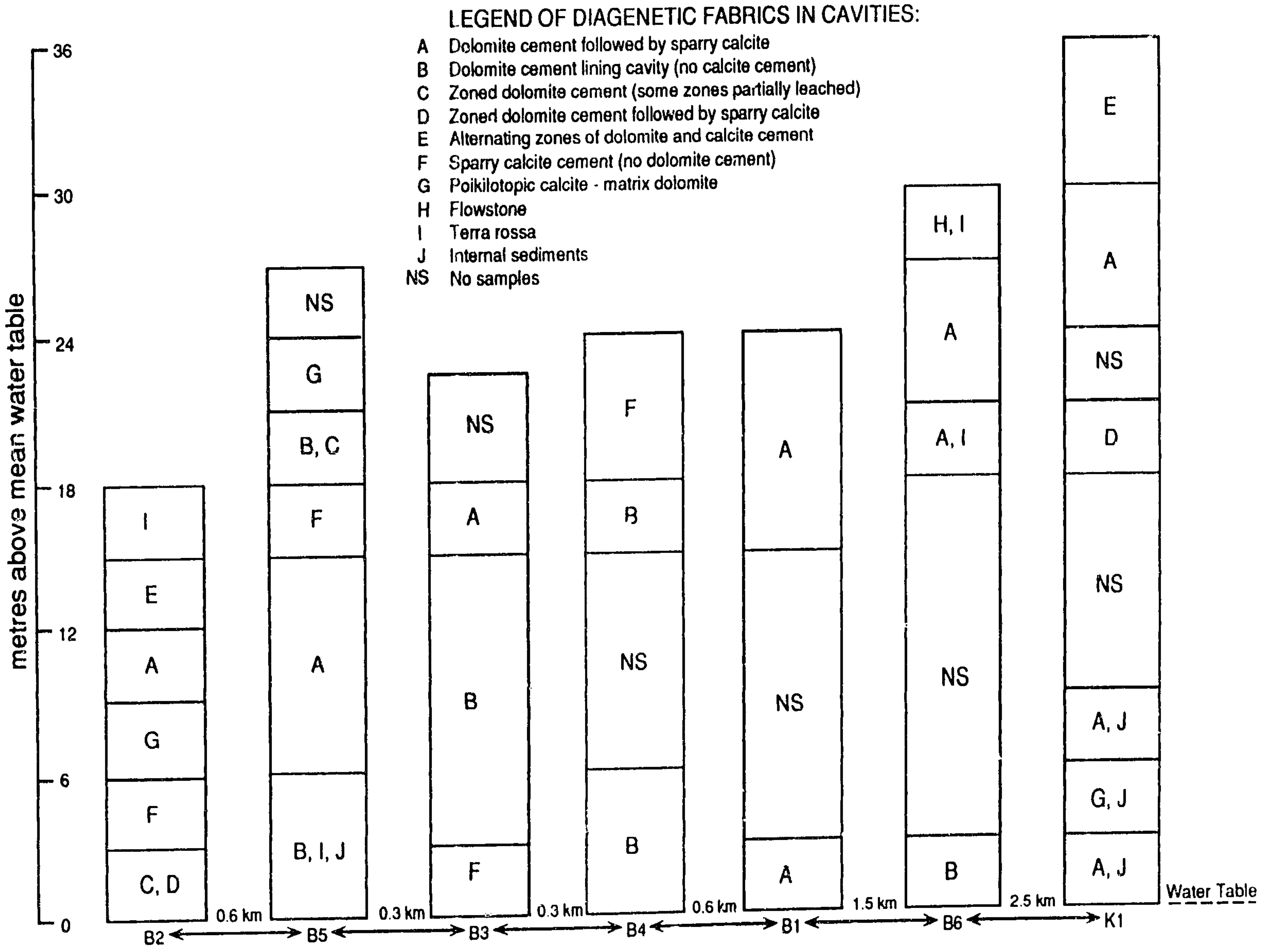


Fig. VI.8 Distribution of the most dominant diagenetic fabrics in the vadose zone of the Bluff Formation on Cayman Brac (refer to Fig. VI.2 for well location).

stratigraphic level of close proximity may have different diagenetic processes due to the heterogeneity of the ground-water flow regime.

It is also important to note that the carbonate cement fabrics in the rocks presently in vadose zones of Cayman Brac (Fig. VI.8) are similar to those in association with the present day hydrochemical regimes of Grand Cayman (Figs. VI.3-7). This suggests that the rocks from the unsaturated zone of Cayman Brac underwent at least one complete cycle of diagenetic environments ranging from marine to meteoric to vadose settings.

F. SYNOPSIS

Detailed petrographic studies of the rocks of the Bluff Formation indicate that:

(1) the Bluff Formation is formed of finely crystalline to microcrystalline dolostone; calcite only occurs as cavity filling and intercrystalline cement or as poikilotopic calcite-dolomite couplet;

(2) the matrix dolomites are characterized by (i) scattered euhedral dolomites up to 40 μm long in microcrystalline dolomite groundmass (5-10 μm), (ii) intercrystalline porosity in leached matrix dolomite, and (iii) poikilotopic calcite encasing corroded matrix dolomites in weathered zones and in the vicinity of the water table in Lower Valley;

(3) paragenetic sequence of carbonate cements commonly is (i) clear and zoned dolomite, (ii) alternating zones of dolomite and calcite as laterally continuous bands from crystal to crystal or within a single crystal, (iii) coarse, unzoned and zoned sparry calcite, (iv) partial dissolution of sparry calcite and zoned dolomite cements, and (v) poikilotopic calcite encasing and infilling leached dolomite cements;

(4) cavity fills other than carbonate cements include terra rossa, flowstone, and internal sediments;

(5) the most important difference in the cement fabrics of the rocks from the two fresh water lenses on Grand Cayman is the rare occurrence of dolomite cement in the

Lower Valley lens although dolomite cement is common in the East End lens; this distinction is probably related to differences in chemical compositions of the two types of ground water which have similar salinity;

(6) the quantity of calcite as last-cement phase decreases from the fresh water to brackish water to saline water zones, and conversely, the abundance of dolomite as last-cement phase increases from the fresh water to brackish water zone;

(7) the rocks in the saline water zone are characterized by minor amounts of dolomite cement and unfilled cavities;

(8) sparry calcite cement is commonly associated with fresh to lightly brackish ground water; dolomite cement is more commonly affiliated with brackish ground water; and

(9) the complex distribution of the diagenetic fabrics of the rocks from the unsaturated zone of Cayman Brac is due to the heterogeneity of the joint and karst controlled aquifer, and hence, is responsible to the variability of fluid chemistry in the subenvironments.

VII. ISOTOPE GEOLOGY

Diagenetic carbonate minerals formed in equilibrium with pore fluids acquire isotopic compositions characteristic of those fluids and the temperature of the diagenetic environment (Hudson, 1977; Savin, 1980; Brand and Veizer, 1981; Anderson and Arthur, 1983; Veizer, 1983; O'Neil, 1986, 1987; Longstaffe, 1987). Thus, where isotopic equilibrium between the carbonate minerals and the diagenetic fluids has been achieved, the isotopic compositions of the diagenetic minerals should provide information about the paleo-environmental conditions. In this context, this study examines the equilibrium fractionation effect of the oxygen isotope between the carbonate minerals and diagenetic fluids, and assesses the salinity of the fluids from which the minerals were precipitated.

A. BASIC PRINCIPLES

Precipitation of carbonate minerals under natural conditions of equilibrium is known to occur (Anderson and Arthur, 1983; Veizer, 1983; O'Neil, 1987). However, carbonate minerals also form under kinetic isotope effects (non-equilibrium) such as biological activity (Keith and Weber, 1965; Weber, 1968; Shackleton *et al.*, 1973) and rapid precipitation or loss of volatiles (Gonfiantini *et al.*, 1968; Hendy, 1971; Turi, 1986; Schwarcz, 1986). Furthermore, the isotopic composition of the diagenetic minerals can be altered by later diagenesis, particularly recrystallization (Land, 1980, 1983b; Longstaffe, 1987; O'Neil, 1987).

The degree of exchange of the oxygen isotope during a reaction is controlled by the oxygen fractionation factor between the carbonate minerals and the diagenetic fluids (Savin, 1980; Brand and Veizer, 1981; Anderson and Arthur, 1983; Land, 1983b; O'Neil, 1986). Oxygen isotopic fractionation between calcite and water has been thoroughly investigated (Anderson and Arthur, 1983; Veizer, 1983). Conversely, the fractionation between dolomite and water is less well established because of the variable stoichiometric

compositions of the dolomite and the inability of dolomite to synthesize under conditions of sedimentary environments (Land, 1980, 1983b, 1985; Hardie, 1987).

Significant isotopic exchange occurs through chemical or mineralogical reactions such as mineral dissolution and precipitation, and recrystallization (Savin, 1980; O'Neil, 1987). Conversely, in low temperature environments, isotopic exchange between the carbonate minerals and water is negligible (Savin, 1980; Anderson and Arthur, 1983; O'Neil, 1987; Welhan, 1987).

B. OXYGEN ISOTOPES OF THE BLUFF FORMATION

The oxygen isotopic data of the rocks and cavity fills of the Bluff Formation used in this study are those determined by Pleydell (1987), Smith (1987), and Jones *et al.* (1989). All isotopic values, which were originally presented in the per mil (‰) notation relative to PDB standard, are converted to the SMOW standard for the temperature dependence equilibrium fractionation calculation. PDB is an oxygen standard for carbonates, derived from the rostrum of *Belemnitella americana* from the Pee Dee Formation of South Carolina, U.S.A. (Craig, 1957; Anderson and Arthur, 1983). The relationship between PDB calcite and SMOW calcite (Anderson and Arthur, 1983) is defined as:

$$\delta^{18}O_{(\text{calcite vs. SMOW})} = 1.03086 * \delta^{18}O_{(\text{calcite vs. PDB})} + 30.86$$

Matrix Dolomite of the Bluff Formation

In order to ensure that the oxygen isotopic compositions are representative of the matrix dolomites, values selected for this study are those that were obtained from dolostone samples of greater than 98% dolomite according to XRD analysis (Pleydell, 1987). The dolomites of the Bluff Formation have a narrow $\delta^{18}O$ range of +2.0 to +3.0‰ PDB and an average value of +2.5‰ (Table VII.1).

Table VII.1 Stable oxygen isotope data of matrix dolomite of the Bluff Formation. Data adapted from Pleydell (1987).

Sample #	**Location**	$\delta^{18}O$ **‰ SMOW**	$\delta^{18}O$ **‰ PDB**
801a	High Rock Quarry	+33.2	+2.3
801b	High Rock Quarry	+33.0	+2.1
1209a	High Rock Quarry	+33.7	+2.8
1195	High Rock Quarry	+33.0	+2.1
842	High Rock Quarry	+33.8	+2.9
1242b	Pedro Castle Quarry	+33.5	+2.6
1243b	Pedro Castle Quarry	+33.7	+2.8
1240	Pedro Castle Quarry	+33.2	+2.2
1247	Pedro Castle Quarry	+33.5	+2.5
1230	Blow Hole	+33.1	+2.2
1185	Queen's Road	+33.6	+2.7
1184b	Queen's Road	+32.9	+2.0
1184a	Queen's Road	+32.3	+2.5
1063	Paul Bodden Quarry	+33.6	+2.6
1171	Cayman Kai	+33.9	+2.8
1297c	Cayman Brac	+33.7	+2.8
1297d	Cayman Brac	+33.7	+2.8
Average Stable Oxygen Isotope of Bluff Dolostone		+33.4	+2.5

Note: Sample numbers refer to catalogue numbers of the Cayman Islands rock collection.

Cavity Fills in the Bluff Formation

Cavity fills in the Bluff Formation analysed for the $\delta^{18}O$ content are internal sediments (dolomite) and carbonate mineral precipitates (calcite and dolomite spar, flowstone, and poikilotopic calcite-dolomite).

Dolomite (Caymanite)

The $\delta^{18}O$ contents of the caymanite samples analysed by Pleydell (1987) are similar to those of the dolostone host rocks with an average value of +2.3‰ PDB (Table VII.2). These values are also in agreement with the unpublished data of Collar (1985, per. comm.).

Calcite and Dolomite Spar

Calcite spar cements, their composition confirmed by XRD analysis (Pleydell, 1987), have $\delta^{18}O$ values ranging from -3.9 to -5.6‰ PDB (Table VII.2). One sample of dolomite spar rooted on calcite spar, coarse enough to be isolated for analysis (Pleydell, 1987), has an oxygen isotopic composition of -3.6‰ PDB (Table VII.2). The calcite and dolomite spar cements analysed came from different cavities.

Flowstone

Smith (1987) carried out a detailed examination of stable isotopes of the flowstones collected from different localities of Grand Cayman and Cayman Brac. In an individual flowstone sample, a slight variation in the isotopic content is recorded in each successive calcite layer (Smith, 1987). $\delta^{18}O$ concentrations of the flowstone lie in the -3.0 to -6.5‰ PDB range (Table VII.3). The exceptionally high values of speleothem 1252 (Table VII.3) are due to the presence of a small amount of dolomite (Smith, 1987).

Table VII.2 Stable oxygen isotope data of caymanite, calcite spar and dolomite spar of the Bluff Formation. Data adapted from Pleydell (1987).

Sample #	Location	$\delta^{18}O$ ‰ SMOW	$\delta^{18}O$ ‰ PDB
Dolomite (Caymanite):			
1209d	High Rock Quarry	+33.4	+2.5
1184	Queen's Road	+32.9	+2.0
Average Stable Oxygen Isotopes of Caymanite		+33.2	+2.3
Calcite Spar:			
1223a	East End Quarry	+25.6	-5.1
843	East End Quarry	+25.1	-5.6
1212	High Rock Quarry	+26.8	-3.9
Average Stable Oxygen Isotope of Calcite Spar		+25.8	-4.9
Dolomite Spar:			
1062A	Paul Bodden Quarry	+27.2	-3.6

Note: Sample numbers refer to catalogue numbers of the Cayman Islands rock collection.

Table VII.3 Stable oxygen isotope data of flowstones of the Bluff Formation. Data adapted from Smith (1987).

	$\delta^{18}O$ ‰ **SMOW**	$\delta^{18}O$ ‰ **PDB**
Average Stable Oxygen Isotope of Speleothem 1219 (5 calcite layers: max = -5.2‰, min = -5.9‰ PDB)	+25.2	-5.5
Average Stable Oxygen Isotope of Speleothem 726 (6 calcite layers: max = -4.6‰, min = -6.4‰ PDB)	+25.3	-5.4
Average Stable Oxygen Isotope of Speleothem 727 (4 calcite layers: max = -2.3‰, min = -5.0‰ PDB)	+27.1	-3.7
Average Stable Oxygen Isotope of Speleothem 728 (9 calcite layers: max = -3.2‰, min = -5.7‰ PDB)	+25.6	-5.1
Average Stable Oxygen Isotope of Speleothem 730 (4 calcite layers: max = -5.4‰, min = -6.6‰ PDB)	+24.6	-6.1
Average Stable Oxygen Isotope of Speleothem 1250 (8 calcite layers: max = -3.9‰, min = -6.3‰ PDB)	+25.3	-5.4
Average Stable Oxygen Isotope of Speleothem 1252 (6 calcite layers: max = -1.3‰, min = -6.5‰ PDB)	+26.9	-3.9

Note: Speleothem numbers refer to catalogue numbers of the Cayman Islands rock collection.

Poikilotopic Calcite-Dolomite

The $\delta^{18}O$ content of the poikilotopic calcite ranges from -1.0 to -3.7‰ PDB, whereas the $\delta^{18}O$ composition of the associated dolomite cement varies from +1.4 to +2.6‰ PDB (Table VII.4). The limpid dolomite is more depleted in ^{18}O than the matrix dolomite, but is more enriched in ^{18}O than the coarse dolomite spar. (Tables VII.1, 2, 3). Conversely, the poikilotopic calcite is more enriched in ^{18}O than the calcite spar cement and the calcitic flowstone (Tables VII.2, 3, 4).

C. EQUILIBRIUM ISOTOPIC FRACTIONATION OF OXYGEN

The equilibrium isotopic fractionation of oxygen between minerals and water is commonly determined by (1) theoretical calculations, (2) isotopic exchange experiments, and (3) systematic regularities in naturally occurring phases which formed under well-defined geological conditions. Isotopic equilibrium in experimental systems is generally limited to high temperatures where isotopic exchange rates are sufficiently rapid to be monitored in the laboratory. Commonly, the fractionation factors were obtained by extrapolation of partial exchange data (Anderson and Arthur, 1983; O'Neil, 1986; Kyser, 1987). Consequently, fractionation factors determined from various methods are slightly different, particularly when applied to the low temperature range (Savin, 1980; Anderson and Arthur, 1983; Land, 1983b; Kyser, 1987).

The oxygen fractionation factors typically vary with temperature over large temperature ranges according to the relationship (Anderson and Arthur, 1983; Veizer, 1983; O'Neil, 1986; Kyser, 1987):

$$10^3 \ln\alpha = \frac{A}{T^2} + B$$

where α is the fractionation factor, T is in °K, A and B vary between different minerals and methods of determination. The fractionation factor (Fritz and Fontes, 1980b; Anderson and

Table VII.4 Stable oxygen isotope data of poikilotopic calcite and dolomite of the Bluff Formation. Data adapted from Pleydell (1987) and Jones *et al.* (1989).

Sample #	**Location**	**$\delta^{18}O$ ‰ SMOW**	**$\delta^{18}O$ ‰ PDB**
Dolomite Cement (Limpid Dolomite):			
52	High Rock Quarry	+32.3	+1.4
92	High Rock Quarry	+33.6	+2.6
1201b	High Rock Quarry	+33.1	+2.2
1201a	High Rock Quarry	+33.3	+2.4
Average Stable Oxygen Isotope of Dolomite		+33.1	+2.2
Poikilotopic Calcite:			
52	High Rock Quarry	+29.8	-1.1
92	High Rock Quarry	+27.9	-2.9
1201b	High Rock Quarry	+27.0	-3.7
1201a	High Rock Quarry	+29.8	-1.0
283	High Rock Quarry	+27.8	-2.9
1062a	Paul Bodden Quarry	+29.6	-1.2
Average Stable Oxygen Isotope of Calcite		+28.7	-2.1

Note: Sample numbers refer to catalogue numbers of the Cayman Islands rock collection.

Arthur, 1983) between a mineral and the associated water (α_{m-w}) is related to the isotopic composition of the mineral ($\delta^{18}O_m$) and the associated aqueous phase ($\delta^{18}O_w$) by:

$$\alpha_{m-w} = \frac{1000 + \delta^{18}O_m}{1000 + \delta^{18}O_w}$$

O'Neil (1986) argued that the sign and magnitude of α are controlled by (1) temperature, (2) chemical composition (e.g. magnesian calcite versus pure calcite), (3) crystal structure (e.g. aragonite versus calcite), and (4) pressure, although temperature is the dominant factor.

Fractionation between Calcite and Water

The most widely used relationship on the temperature dependence of oxygen isotopic fractionation between calcite and the water phase is that of Craig (1965):

$$t°C = 16.9 - 4.2(\delta_c - \delta_w) + 0.13(\delta_c - \delta_w)^2$$

where δ_c is the $\delta^{18}O$ of CO_2 liberated by reaction with 100‰ phosphoric acid at 25°C and δ_w is that of CO_2 in equilibrium at 25°C with which the calcite was precipitated. δ_c and δ_w are relative to PDB standard. This relationship was based on analysis of $CaCO_3$ (both calcite and aragonite) precipitated by molluscs grown in controlled laboratory experiment or from well-defined natural environments.

Friedman and O'Neil (1977) determined the oxygen isotopic fractionation between inorganically precipitated calcite and water over the temperature range of 0-500°C. Their relationship is:

$$10^3 \ln\alpha_{(calcite\text{-}water)} = \frac{2.78*10^6}{T^2} - 2.89$$

where T is in °K.

The two sets of experimental relationships are in excellent agreement because direct precipitation of calcite under low temperature sedimentary environment permits accurate establishment of the isotopic fractionation between calcite and water. Using a $\delta^{18}O$ value

of -2.8‰ PDB (28.0‰ SMOW) for calcite as an example, the two temperature equations (Craig, 1965; Friedman and O'Neil, 1977) give comparable results (Fig. VII.1). Therefore, in low temperature setting, the $\delta^{18}O$ values of the waters obtained by equilibrium fractionation calculation should be reliable providing the minerals were precipitated under equilibrium condition. Furthermore, the experimental results agree with the fractionation factors calculated by Bottinga (1968) using theoretical considerations.

Fractionation between Dolomite and Water

The relationship between the isotopic fractionation of dolomite and water, and temperature has been determined by a number of investigators using different experimental techniques:

(1) O'Neil and Epstein (1966) obtained the relationship

$$10^3 \ln\alpha_{(\text{dolomite-water})} = \frac{3.34*10^6}{T^2} - 3.34$$

by mineral-CO_2 exchange experiments combined with calcite-water fractionation at 350-400°C,

(2) Northrup and Clayton (1966) obtained the relationship

$$10^3 \ln\alpha_{(\text{dolomite-water})} = \frac{3.2*10^6}{T^2} - 1.50$$

using partial exchange experiments at 300-510°C,

(3) Sheppard and Schwarcz (1970) obtained the relationship

$$10^3 \ln\alpha_{(\text{dolomite-water})} = \frac{3.23*10^6}{T^2} - 3.29$$

by combining empirical fractionations between dolomite and calcite with calcite-water relationship at 100-650°C,

(4) Fritz and Smith (1970) obtained the relationship

$$10^3 \ln\alpha_{(\text{dolomite-water})} = \frac{2.78*10^6}{T^2} + 0.11$$

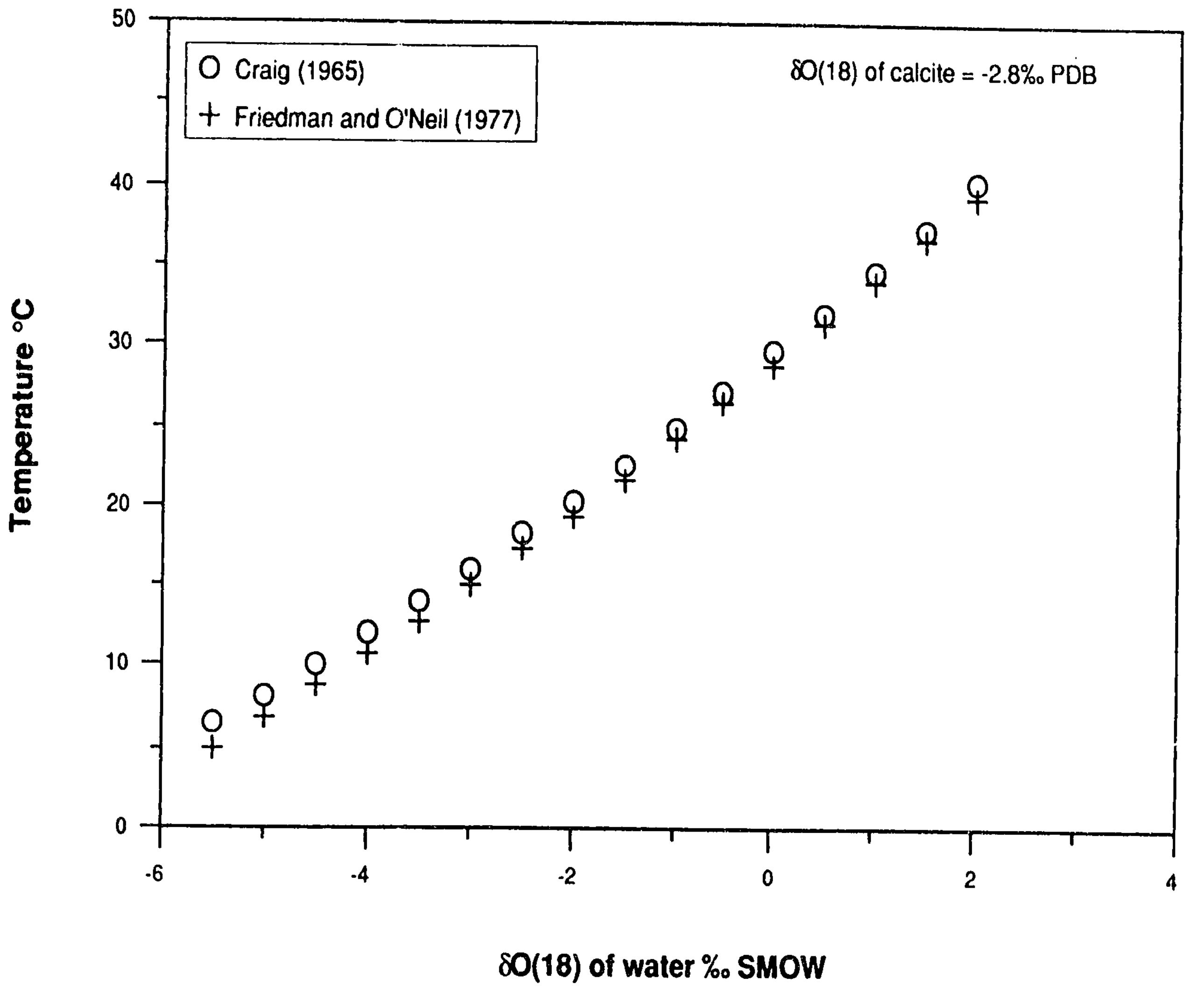


Fig. VII.1 Equilibrium fractionation of oxygen (18) between calcite and water using temperature equations given by Craig (1965) and Friedman and O'Neil (1977).

by carrying out direct precipitation of proto-dolomite (40-45 mole % $MgCO_3$) at 25-78°C, and

(5) Matthews and Katz (1977) obtained the relationship

$$10^3 \ln\alpha_{(\text{dolomite-water})} = \frac{3.06*10^6}{T^2} - 3.24$$

by dolomitization of $CaCO_3$ in apparent isotopic equilibrium with the solution at 252-295°C.

The first four equations were corrected by Land (1983b) to be consistent with Friedman and O'Neil (1977). Using a $\delta^{18}O$ value of +33.4‰ SMOW (+2.5‰ PDB) for dolomite, the equations give significantly different results in the temperature of interest (Fig. VII.2). At 25°C, the $\delta^{18}O$ values of the diagenetic fluids lie between -1.6 to +1.3‰ SMOW (Fig. VII.2). Land (1983b) also noted that at a given $\delta^{18}O$ of dolomite, the range of uncertainty in temperature is 15°C, whereas at a given temperature, the range of uncertainty in $\delta^{18}O$ of water is about 4‰.

The equilibrium fractionation between dolomite and calcite ($\Delta^{18}O$) can be obtained by the difference between $\delta^{18}O_{\text{dolomite}}$ and $\delta^{18}O_{\text{calcite}}$ for cogenetic dolomite and calcite. Dolomite formed in isotopic equilibrium with calcite in sedimentary environment is enriched in $\delta^{18}O$ by 4 to 7‰ relative to calcite (O'Neil and Epstein, 1966; Northrup and Clayton, 1966). Conversely, the fractionation relationships of Fritz and Smith (1970) and Matthews and Katz (1977) gave $\Delta^{18}O_{(\text{dolomite-calcite})}$ values in the range of 2 to 4‰. Land (1980, 1983b) also suggested that the equilibrium ^{18}O-fractionation value is probably 3 ± 1‰ at 25°C. In studies of coastal sabkhas of Abu Dhabi, McKenzie (1981) suggested that the naturally occurring dolomite and calcite mixtures have fractionation value of +3.2‰. Hardie (1987), however, suspected that the dolomite studied by McKenzie (1981) might not be formed by replacement.

It is apparent that caution be exercised in accepting the results obtained from these fractionation relationships. This study, therefore, takes into account the results obtained

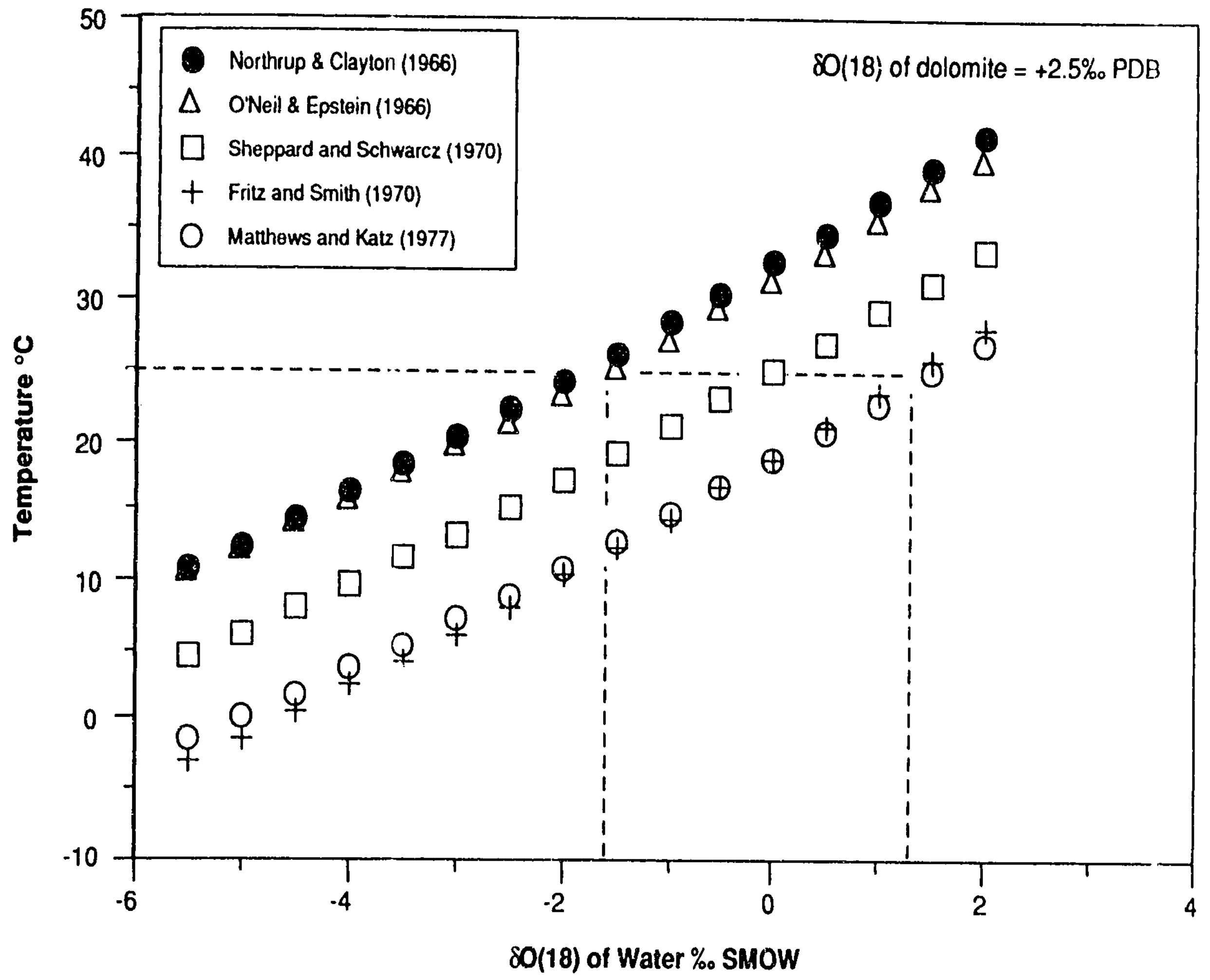


Fig. VII.2 Equilibrium fractionation of oxygen (18) between dolomite and water using five different temperature equations. At 25°C, δO(18) of water differs by about 3‰ depending on the fractionation equations.

from all five equations. Although this conservative approach results in a wide range of $\delta^{18}O$ values in the interpretation of the diagenetic fluids, it avoids the bias resulting from the poor understanding of the fractionation relationship between dolomite and calcite.

D. EQUILIBRIUM FRACTIONATION CALCULATION

Equilibrium fractionation equations of oxygen isotopes allow the evaluation of the relationships of the carbonate minerals, ground water (diagenetic fluid), and the temperature of the aqueous environment in which the minerals formed. The results thus obtained are based on the assumption that the minerals and diagenetic fluids have achieved isotopic equilibrium. Another important assumption is that the diagenetic minerals (dolomite and calcite) have retained the original isotopic signatures since their formation. Unfortunately, there is no assurance that this is the actual situation.

Chemical reactions such as recrystallization, dissolution, and reprecipitation that involve breaking and reforming chemical bonds in the minerals would complicate the interpretation of the results obtained from the equilibrium-fractionation calculation. Furthermore, analytical cross contamination during the separation of calcite and dolomite is possible, particularly when dolomite and calcite are intimately associated with one another as in the case of zoned calcite and dolomite cements.

On the basis of the present day atmospheric and ground water conditions, a temperature range of 22 to 33°C was chosen as the temperatures of the diagenetic fluids for the calculations. Furthermore, because the Cayman Islands are located in low latitudes, it is probable that the ambient temperature in the Tertiary period was similar to that of the present time. The water salinity was determined by the established relationships between the $\delta^{18}O$ content and electrical conductivity (E.C.) of the ground water (Figs. V.2A, 2B, 2C).

Matrix Dolomite of the Bluff Formation

The temperature dependence equilibrium ^{18}O fractionation calculation of dolomite and water is complicated by a variety of temperature equations that were obtained from high temperature experiments (O'Neil and Epstein, 1966; Northrup and Clayton, 1966; Sheppard and Schwarcz, 1970; Matthews and Katz, 1977) or by precipitation of proto-dolomite (Fritz and Smith, 1970). In the temperature range of 22-33°C, the $\delta^{18}O$ values of the fluids are equivalent to waters of 25 to >95% sea water salinity, depending on the equations used (Table VII.5).

The oxygen isotopic composition of the matrix dolomite determined by Pleydell (1987) is the average isotope value of the dolomite crystals in each analysed sample. Therefore, the calculated $\delta^{18}O$ content of the water based on such a bulk $\delta^{18}O$ value of the dolomite may not provide the actual isotopic properties of the dolomitizing fluid(s) if dolomitization occurred in more than a single phase. Land (1983b) suggested that few dolomitized rocks result from a single, short lived event, although it is difficult to recognize single event versus multiple-event dolomitization. Land (1980), however, suggested that inhomogeneities on a single crystal scale are indicative of diagenetic stages.

Caymanite

In the temperature range of 22-33°C, the calculations indicate that the diagenetic fluids that were in association with the caymanite had $\delta^{18}O$ contents ranging from -2.5 to >+1.0‰ SMOW (Table VII.5). These oxygen isotopic compositions correspond to an aqueous phase of 25 to >95% sea water salinity (Table VII.5). This implies that the fluids responsible for the dolomitization of the host rock and the caymanite sediments were of similar salinity, assuming there was no masking of isotopic composition by later phase diagenetic fluids.

Table VII.5 $\delta^{18}O$ and salinity of ground water in equilibrium with different dolomite phases. Temperature range used for the ^{18}O fractionation calculation between dolomite and water is 22 to 33°C.

EQUATION	N & C	O & E	S & S	F & S	M & K
Matrix Dolomite (Average $\delta^{18}O$ +33.4‰ SMOW):					
$\delta^{18}O$ of water (‰ SMOW)	-2.5 to 0.0	-2.5 to +0.5	-0.5 to +2.0	+1.0 to >+1.0	+1.0 to >+1.0
water salinity (% sea water)	25 to 80	25 to 90	65 to 100	>95	>95
Caymanite (Average $\delta^{18}O$ +33.2‰ SMOW):					
$\delta^{18}O$ of water (‰ SMOW)	-2.5 to 0.0	-2.5 to +0.5	-0.5 to +2.0	+1.0 to >+1.0	+1.0 to >+1.0
water salinity (% sea water)	25 to 80	25 to 90	65 to 100	>95	>95
Limpid Dolomite (Average $\delta^{18}O$ +33.1‰ SMOW):					
$\delta^{18}O$ of water (‰ SMOW)	-2.5 to 0.0	-2.5 to +0.5	-0.5 to +2.0	+0.5 to >+0.5	+1.0 to >+1.0
water salinity (% sea water)	25 to 80	25 to 90	65 to 100	>90	>95
Coarse Dolomite Spar (Average $\delta^{18}O$ +27.2‰ SMOW):					
$\delta^{18}O$ of water (‰ SMOW)	<-5.5	<-5.5 to -5.5	-4.0 to <-4.0	-5.0 to -3.0	-5.0 to -2.5
water salinity	perched/fresh	perched/fresh	fresh	fresh to lightly brackish	fresh to 25% sea water

Note: N&C: Northrup and Clayton, 1966; O&E: O'Neil and Epstein, 1966; S&S: Sheppard and Schwarcz, 1970; F&S: Fritz and Smith, 1970; M&K: Matthews and Katz, 1977.

Calcite Spar

Using the average $\delta^{18}O$ content of the calcite spar (Table VII.2), the temperature calculation shows that the diagenetic fluids had $\delta^{18}O$ values of -3.5 to -1.5‰ SMOW (Table VII.6). These isotopic compositions suggest that the diagenetic fluids that were responsible for the precipitation of the calcite spar were fresh to brackish water up to 45% sea water salinity (Table VII.6).

Dolomite Spar

The coarse dolomite spar was formed in equilibrium with diagenetic fluids having $\delta^{18}O$ compositions of <-5.5 to -2.5‰ SMOW (Table VII.5). At the low $\delta^{18}O$ range (<-5.5‰ SMOW), the associated fluid is perched to fresh water, and at the high $\delta^{18}O$ value (-2.5‰ SMOW), the associated pore fluid is brackish water of 25% sea water salinity.

Flowstone

The oxygen isotopic fractionation calculation between flowstone and water indicates that the flowstones probably precipitated in waters having $\delta^{18}O$ compositions of -5.0 to 0.0‰ SMOW (Table VII.6). These $\delta^{18}O$ values suggest that the diagenetic fluids were fresh to brackish water up to 80% sea water salinity (Table VII.5). The actual precipitating fluids were probably fresh to brackish water up to 45% sea water salinity since the high $\delta^{18}O$ values of the flowstones are due to the presence of detrital dolomite in the flowstone (Smith, 1987).

Disequilibrium precipitation of flowstone, however, has also been known to occur (Hendy, 1971; Schwarcz, 1986). If so, the results obtained from equilibrium calculations become meaningless.

Table VII.6 $\delta^{18}O$ and salinity of ground water in equilibrium with calcite. Temperature range used for the ^{18}O fractionation calculation between calcite and water is 22 to 33°C.

EQUATION	**Craig (1965)**	**Friedman & O'Neil (1977)**
Poikilotopic Calcite (Average $\delta^{18}O$ +28.7‰ SMOW):		
$\delta^{18}O$ of water (‰ SMOW)	-0.5 to +1.5	-0.5 to +1.5
water salinity (% sea water)	65 to >100	65 to >100
Calcite Spar (Average $\delta^{18}O$ +25.8‰ SMOW):		
$\delta^{18}O$ of water (‰ SMOW)	-3.5 to -1.5	-3.5 to -1.5
water salinity	fresh water to 45% sea water	fresh water to 45% sea water
Speleothem 726 (Average $\delta^{18}O$ +25.3‰ SMOW):		
$\delta^{18}O$ of water (‰ SMOW)	-4.0 to -2.0	-4.0 to -1.5
water salinity	fresh water to 35% sea water	fresh water to 45% sea water
Speleothem 727 (Average $\delta^{18}O$ +27.1‰ SMOW):		
$\delta^{18}O$ of water (‰ SMOW)	-2.5 to 0.0	-2.0 to 0.0
water salinity (% sea water)	25 to 80	35 to 80
Speleothem 728 (Average $\delta^{18}O$ +25.6‰ SMOW):		
$\delta^{18}O$ of water (‰ SMOW)	-3.5 to -1.5	-3.5 to -1.5
water salinity	fresh water to 45% sea water	fresh water to 45% sea water
Speleothem 730 (Average $\delta^{18}O$ +24.6‰ SMOW):		
$\delta^{18}O$ of water (‰ SMOW)	-5.0 to -2.5	-4.5 to -2.5
water salinity	fresh water to 25% sea water	fresh water to 25% sea water
Speleothem 1219 (Average $\delta^{18}O$ +25.2‰ SMOW):		
$\delta^{18}O$ of water (‰ SMOW)	-4.0 to -2.0	-4.0 to -2.0
water salinity	fresh water to 35% sea water	fresh water to 35% sea water
Speleothem 1250 (Average $\delta^{18}O$ +25.3‰ SMOW):		
$\delta^{18}O$ of water (‰ SMOW)	-4.0 to -2.0	-5.0 to -2.5
water salinity	fresh water to 35% sea water	fresh water to 25% sea water
Speleothem 1252 (Average $\delta^{18}O$ +26.9‰ SMOW):		
$\delta^{18}O$ of water (‰ SMOW)	-2.5 to -0.5	-2.5 to 0.0
water salinity (% sea water)	25 to 65	25 to 80

Poikilotopic Calcite-Dolomite

The diagenetic fluids in equilibrium with the dolomite cement (limpid dolomite) had $\delta^{18}O$ content ranging from -2.5 to >+1.0‰ SMOW (Table VII.5) and the fluids in equilibrium with the poikilotopic calcite had $\delta^{18}O$ composition varying from -0.5 to +1.5‰ SMOW (Table VII.6). Therefore, the diagenetic fluids for the precipitation of the dolomite cement were brackish water of 25 to >90% sea water salinity (Table VII.5), whereas the fluids for the precipitation of the poikilotopic calcite were brackish water of 65 to >100% sea water salinity (Table VII.6). These values suggest that a slight change in the water composition would shift the dolomite formation to calcite or vice versa.

E. SYNOPSIS

Lohmann (1982, 1983) and Meyers and Lohmann (1985) suggest that carbonate minerals precipitated in a progressively more distal phreatic setting commonly display a negative $\delta^{18}O$ trend. The decreasing $\delta^{18}O$ content from dolomite cement to calcite spar probably represents increasing meteoric influence. Detailed studies of the stable isotope geochemistry of the carbonates of the Bluff Formation permit the following conclusions.

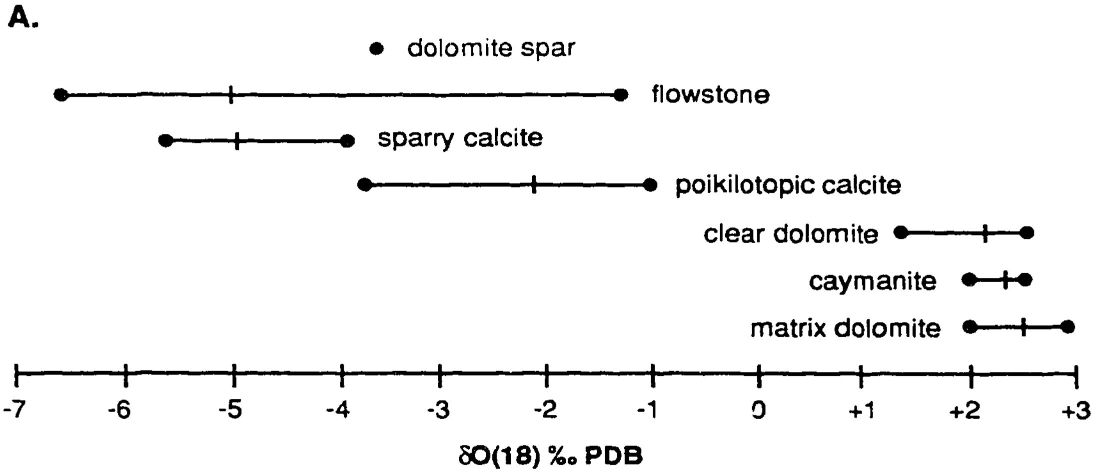
(1) For dolomite, the order of decreasing $\delta^{18}O$ content is matrix dolomite, caymanite, dolomite cement (limpid dolomite), and coarse dolomite spar (Fig.VII.3A).

(2) For calcite, the order of decreasing $\delta^{18}O$ content poikilotopic calcite, sparry calcite, and flowstone (Fig.VII.3A).

(3) The equilibrium oxygen fractionation relationship between calcite and water is well established, whereas the fractionation relationship between dolomite and water at low temperature is equivocal.

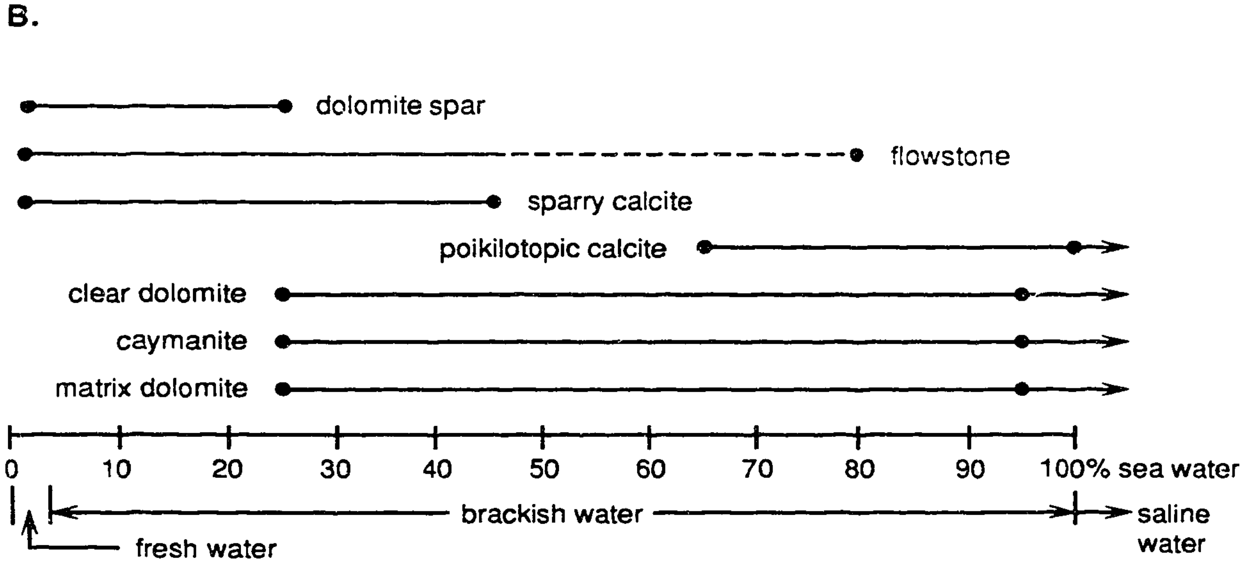
(4) The poikilotopic calcite and dolomite cement having $\Delta^{18}O_{(dolomite\text{-}calcite)}$ values of 2.4 to 6.3‰ PDB are probably not cogenetic phases.

(5) Results of the equilibrium oxygen fractionation between the carbonate minerals and the waters at 22-33°C using different fractionation equations (Fig.VII.3B) conclude



●—● indicates the range of δO(18) values for each mineral phase.
–+– indicates the average δO(18) value.

Fig. VII.3A Summary diagram showing the range of δO(18) values for the various carbonate minerals present in the Bluff Formation.



●—● indicates the range of water salinity in which the mineral phase may precipitate. Interpretation based on average δO(18) values.
—➤ indicates the salinity range may extend to higher values.
--- indicates the high salinity values (>45%) rarely occur.

Fig. VII.3B Summary diagram showing the range of water salinity in which the various carbonate minerals may precipitate.

that (i) matrix dolomite and caymanite formed in water of 25 to >95% sea water salinity, (ii) calcite spar and flowstone precipitated in fresh to brackish water up to 45% sea water salinity, (iii) poikilotopic calcite precipitated in water of 65 to >100% sea water salinity, (iv) dolomite cement (in association with poikilotopic calcite) formed in water of 25 to >90% sea water salinity, and (v) coarse dolomite spar precipitated in perched, fresh to brackish water up to 25% sea water salinity.

VIII. DIAGENETIC MODELS

The major controlling factors on the diagenetic realms are past tectonic activity that caused uplift and down faulting of the islands and sea level fluctuations. Periods of relatively high sea level stand were characterized by coral reef development and carbonate deposition. Conversely, periods of relative sea level low stand were characterized by carbonate diagenesis, karst development, and increased erosion. This apparently simple concept with reference to relative sea level changes is complicated by the fact that at times the islands might be partially submerged. Submarine diagenetic textures are rare in the Bluff Formation. Pleydell (1987), however, documented the occurrence of minor amounts of submarine textures such as micrite and isopachous cements. Numerous cycles of carbonate deposition and diagenesis have made the interpretation of the diagenetic signatures present in the rocks of the Bluff Formation a challenge.

A. STRATIGRAPHIC SETTING

In Pedro Castle Quarry on Grand Cayman, Jones and Hunter (1989) documented a distinct disconformity which they used to divide the Bluff Formation into the lower Cayman Member and the upper Pedro Castle Member. On the basis of paleontological data and by comparison with sea level curves constructed by Vail *et al.* (1977), Hallam (1984), and Haq *et al.* (1989), it is apparent that the disconformity separates Oligocene and Miocene strata (Jones and Hunter, 1989).

Correlation of the coral fauna in the Cayman Member with the Caribbean wide Antiguan coral fauna (Vaughan, 1919; Thomas, 1942; Cooke *et al.*, 1943; Woodring, 1957) suggests that the Cayman Member is early late Oligocene in age (Jones and Hunter, 1989). The assignment of an age for the Pedro Castle Member is less confident because of the lack of biostratigraphic markers (Jones and Hunter, 1989). Nevertheless, Jones and Hunter (1989) suggest that the Pedro Castle Member may be middle Miocene in age. The Ironshore Formation that unconformably overlies the Bluff Formation is of late Pleistocene

age (approximately 125,000 years old), based on conventional U-series dating of four coral samples from the upper part of the formation (Woodroffe *et al.*, 1983).

As far as carbonate diagenesis is concerned, it is apparent that the major regressions in late Oligocene to early Miocene and in late Miocene to early Pliocene times would have had considerable impact on the diagenetic alteration of the carbonate sediments of the Bluff Formation. Furthermore, the sea level fluctuations during the Pliocene and Pleistocene epoch would have led to additional diagenetic modifications of the rocks.

B. SEQUENCE OF DIAGENETIC EVENTS

Integration of available stratigraphic, sedimentological and diagenetic information in the Bluff Formation does not permit a definitive interpretation on the sequence and timing of the diagenetic events. Two models can be invoked to satisfy the available data. On the basis of petrographic and geochemical data, Pleydell (1987), Jones (1989a), and Pleydell *et al.* (in preparation) proposed that pervasive dolomitization of the Bluff Formation was a single event involving sea water as the diagenetic fluid. This model is herein called 'Paragenetic Model I' (Fig. VIII.1). This study, however, suggests an alternative interpretation of the geochemical data. Based on the re-evaluation of the geochemical information, mineralogical, petrographic, and circumstantial evidence, this study proposes that dolomitization of the Bluff Formation was achieved through two separate events by mixed meteoric-marine water. The latter model is herein termed 'Paragenetic Model II' (Fig. VIII.1).

Paragenetic Model I

The following sequence of major depositional and diagenetic events (Fig. VIII.1) is summarized from Pleydell (1987), Jones (1989a), Jones and Hunter (1989), Pleydell *et al.* (1989), and from personal discussion with Jones (1989).

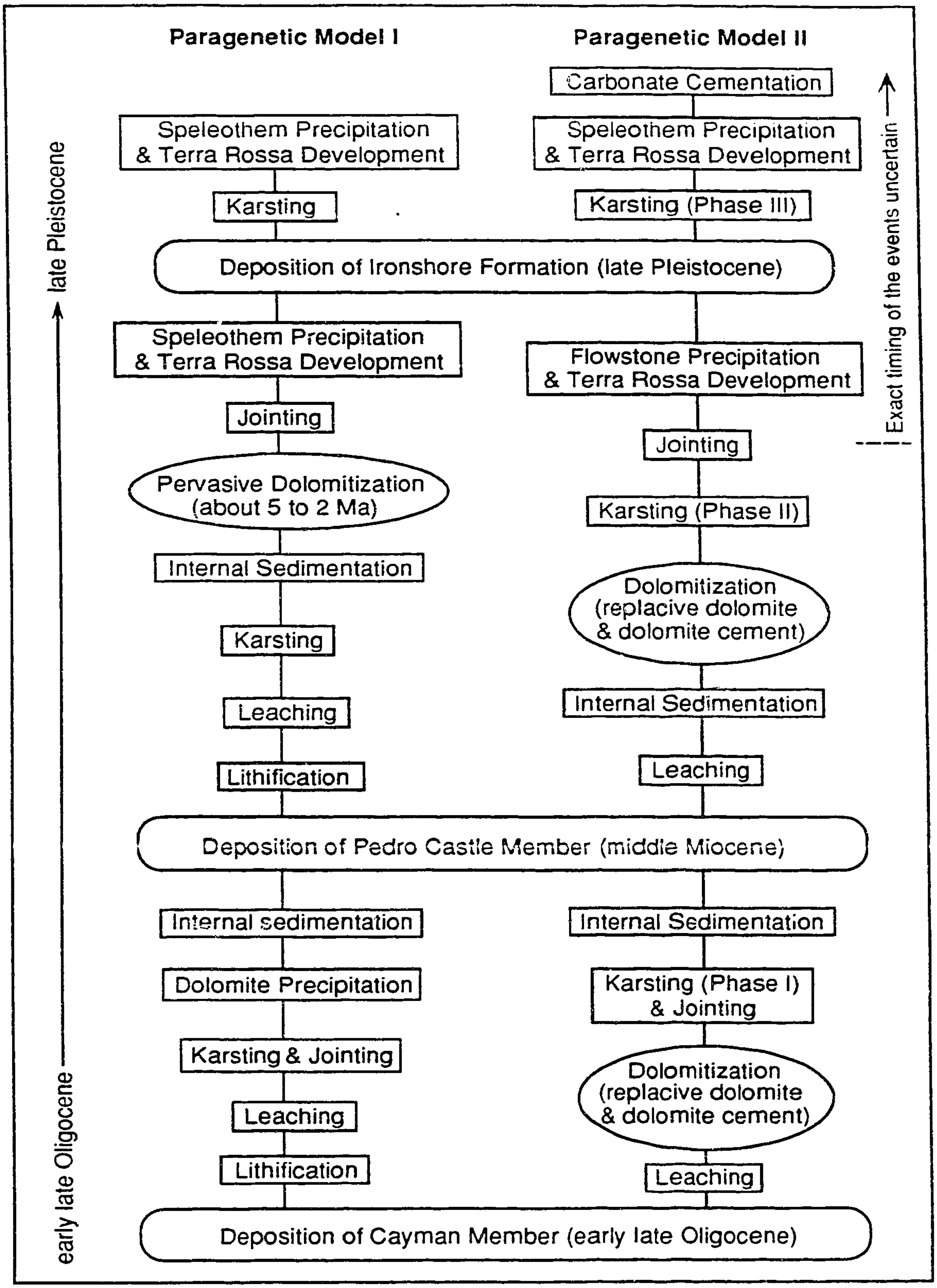


Fig. VIII.1 Sequence of events associated with Paragenetic Model I and II.

(1) Deposition of carbonate sediments of the Cayman Member until early late Oligocene (approximately 30 Ma).

(2) Major regression in late Oligocene with resultant subaerial exposure.

(3) Lithification of carbonate sediments.

(4) Leaching of aragonitic skeletal components, which may have been contemporaneous with lithification of carbonate sediments.

(5) Karst development, and jointing of lithified carbonates.

(6) Precipitation of cavity lining clear dolomite.

(7) Internal sedimentation of fine grained carbonate (caymanite) and skeletal sands during the early Miocene transgression.

(8) Decoration of seafloor (disconformable surface) with a diverse fauna of boring sponges, worms, and bivalves.

(9) Deposition of carbonate sediments of the Pedro Castle Member during middle Miocene (approximately 16 Ma).

(10) Major regression in late Miocene.

(11) Lithification of carbonate sediments.

(11) Leaching of aragonitic skeletal components.

(12) Karst development on the Cayman and Pedro Castle members.

(13) Internal sedimentation of fine grained carbonate and skeletal sands.

(14) Pervasive dolomitization of the Cayman and Pedro Castle members and cavity fills in late Pliocene (approximately 5 to 2 Ma).

(15) Development of joints and fissures.

(16) Precipitation of flowstone and development of terra rossa.

(17) Deposition of carbonate sediments of the Ironshore Formation during late Pleistocene (approximately 125,000 a).

(18) Karst development on dolostones of the Bluff Formation and speleothem precipitation in some caves.

Paragenetic Model II

This study suggests the following sequence of major depositional and diagenetic events (Fig. VIII.1). The depositional history of the Bluff Formation is that of Jones (1989a) and Jones and Hunter (1989).

(1) Deposition of carbonate sediments of the Cayman Member during late Oligocene time (approximately 30 Ma).

(2) Major regression in late Oligocene time with resultant island emergence and meteoric influence.

(3) Leaching of aragonitic skeletal components.

(4) Replacive dolomitization of metastable carbonates and precipitation of dolomite in intergranular space and fossil molds, probably occurring during or shortly after aragonite dissolution.

(5) Jointing and Phase I karst development.

(6) Internal sedimentation of fine grained carbonate (caymanite) and skeletal sands, probably during the early Miocene transgression.

(7) Decoration of the seafloor (disconformable surface) with a diverse fauna of boring sponges, worms, and bivalves.

(8) Deposition of carbonate sediments of the Pedro Castle Member during middle Miocene (approximately 16 Ma).

(9) Major regression in late Miocene with resultant island emergence and meteoric influence.

(10) Leaching of aragonitic skeletal components.

(11) Influx of a small amount of fine grained carbonate and skeletal sands into the fossil molds of the Pedro Castle Member and possibly into the cavities and caves of the Cayman Member.

(12) Replacive dolomitization of metastable carbonate sediments of the Pedro Castle Member and internal sediments in both members, and recrystallization (increase in cation-ordering and stoichiometry) of previously formed dolomites.

(13) Phase II karst development.

(14) Precipitation of flowstone and development of terra rossa.

(15) Extensive joint development.

(16) Deposition of carbonate sediments of the Ironshore Formation during late Pleistocene (approximately 125,000 a).

(17) Phase III karst development (joint controlled) and speleothem precipitation in some caves.

(18) Precipitation of dolomite and calcite cement in cavities that were not occluded by internal sediments and/or speleothemic calcite.

The above sequence is not meant to imply that each diagenetic process was a discrete, separate event. Instead, processes such as dolomitization and recrystallization were probably ongoing events that lasted until the sediments were completely dolomitized and recrystallized to the stable forms.

IX. DIAGENETIC INTERPRETATION OF THE BLUFF FORMATION I: MATRIX DOLOMITIZATION

Dolomitization or replacement of calcium carbonate by dolomite has continued to receive great interest because dolostones form important reservoirs for hydrocarbon (e.g. Thomas and Glaister, 1960; Yan and Zhai, 1980; Watson, 1982) and are host rocks for base-metal deposits (e.g. Kyle, 1983; Force *et al.*, 1986; Buelter and Guillemette, 1988). Recent reviews show that no concensus exists regarding the diagenetic environments and fluid compositions that are responsible for massive dolomitization of thick limestone sequences (Morrow, 1982a, 1982b; Land, 1980, 1983a, 1985; Machel and Mountjoy, 1986, 1987; Hardie, 1987). In addition to the inability to produce dolomitization in the laboratory under low temperature setting, the problem is compounded by the complexity of the cation disordering and cation nonstoichiometry of dolomite.

In light of the present day hydrogeological and hydrochemical information and petrographic and geochemical data, this study attempts to examine the conditions that led to the pervasive dolomitization of the Bluff Formation in terms of the chemical equilibria, chemical kinetics, timing, fluid, and mechanism of dolomitization.

A. CHEMICAL EQUILIBRIA OF DOLOMITIZATION

The replacement of calcium carbonate by dolomite is commonly expressed by

$$2CaCO_3 + Mg^{2+} = CaMg(CO_3)_2 + Ca^{2+} \cdots\cdots\cdots\cdots (1)$$

which represents a mole for mole replacement reaction. This process has been used to account for the formation and redistribution of porosity in dolostone reservoir rocks (Murray, 1960). If the CO_3^{2-} ion is brought to the site of dolomitization from an outside source, porosity destruction occurs according to the following reaction (Murray, 1960; Lippman, 1973):

$$CaCO_3 + Mg^{2+} + CO_3^{2-} = CaMg(CO_3)_2 \cdots\cdots\cdots\cdots (2)$$

This process of overdolomitization involves a volume gain of 75% to 88% (aragonite or calcite replacement). Such a replacement process is inconsistent with the petrographic fabrics of the Bluff Formation which have a fairly high effective porosity.

A volume for volume replacement (Friedman and Sanders, 1967) rather than a mole for mole replacement probably occurred during the dolomitization of the Bluff Formation as exemplified by the retention of the original skeletal structure such as red algae and foraminifera. Morrow (1982a) proposed that for a volume for volume reaction, the net dolomitization is

$$(2\text{-}x)CaCO_3 + Mg^{2+} + xCO_3{}^{2-} = CaMg(CO_3)_2 + (1\text{-}x)Ca^{2+} \text{ ....} (3)$$

where the coefficient x is 0.11 and 0.25 for aragonite and calcite respectively.

At three phase equilibrium (at a particular temperature and pressure), calcite and dolomite are in equilibrium with the solution according to the following reactions:

$$CaCO_3 = Ca^{2+} + CO_3{}^{2-} \text{ ....} (4)$$

$$CaMg(CO_3)_2 = Ca^{2+} + Mg^{2+} + CO_3{}^{2-} \text{ ....} (5)$$

Stoessell (1987) showed that the equilibrium constant for the dolomitization reaction (Kcd) of equation (3) is

$$Kcd = \frac{Kc^{2-x}}{Kd} = \frac{[Ca^{2+}]}{[Mg^{2+}]}\left(\frac{1}{Kc^{x}}\right) \text{ ....} (6)$$

where Kc and Kd are the solubility constants for calcite and dolomite respectively according to equations (4) and (5) and $[Ca^{2+}]$ and $[Mg^{2+}]$ are the activities of calcium and magnesium ions in solution. The relationship shown in equation (6) suggests that the activity of $CO_3{}^{2-}$ is not a factor according to concepts of chemical equilibrium.

On the basis of ground water data in the Floridan aquifer, Hanshaw *et al.* (1971) showed that a Mg/Ca activity ratio close to 1 is indicative of a three phase equilibrium system between calcite, dolomite and the solution. Using the thermodynamic properties of carbonate minerals tabulated by Carpenter (1980), Hardie (1987) demonstrated the importance of cation order-disorder in the evaluation of the Mg/Ca activity ratio. For fully

ordered dolomite, the activity ratio of Mg/Ca is the lowest at 0.10, whereas for disordered dolomite, the ratio is 3.31 (Hardie, 1987). A ratio of 1.0 is only applicable for partly ordered dolomite. The Mg/Ca activity ratio required for dolomitization, therefore, must be used with extreme caution because it depends strongly on the cation-disordering and nonstoichiometry of the dolomite mineral. If calcite is not present as a discrete phase, there is no constraint on the Mg/Ca ratio which may have any value greater than that necessary for three phase equilibrium. Most brackish and saline ground waters on the Cayman Islands are supersaturated with respect to dolomite and have a Mg/Ca activity ratio greater than 1.0 (Tables IV.7, 8). Therefore, from a thermodynamic standpoint, the brackish to saline ground waters are capable of dolomitizing any limestone sequences.

The matrix dolomite of the Bluff Formation ranges in composition from stoichiometric dolomite with 50 mole % $CaCO_3$ to calcian dolomite with 55 mole % $CaCO_3$ (Pleydell, 1987). Fuchtbauer and Goldschmidt (1965), Lumsden and Chimahusky (1980), Sass and Katz (1982), and Sperber *et al.* (1984) suggest that stoichiometric dolomites are commonly associated with micritic lithologies that are indicative of evaporitic depositional environments. Morrow (1982b) also noted that solutions in evaporative settings have high Mg/Ca ratios and commonly form stoichiometric dolomites. Conversely, at Mg/Ca ratios between 2.5 to 5.1, and at salinity less than sea water, precipitation of calcium rich dolomites is common (Morrow, 1982b). Thus, the nonstoichiometric composition of the matrix dolomite of the Bluff Formation argues against a hypersaline dolomitization setting. This contention is further supported by the lack of evaporites in the rocks of the Bluff Formation.

Sperber *et al.* (1984) suggest that complete replacement of calcium carbonate by dolomite requires a continuous influx of magnesium ions. In such open systems, the generalized reaction is

$$CaCO_3 + (0.45\text{-}0.50)Mg^{2+} = Ca_{0.55\text{-}0.50}Mg_{0.45\text{-}0.50}(CO_3)_2 + (0.45\text{-}0.50)Ca^{2+}$$

Therefore, the stoichiometry of the matrix dolomite in the Bluff Formation suggests that the pervasive dolomitization probably occurred in an open system with a sufficient supply of Mg^{2+}.

B. CHEMICAL KINETICS OF DOLOMITIZATION

Some insights concerning the kinetic factors on dolomitization of calcium carbonate have been obtained from experimental works done under hydrothermal conditions (Katz and Matthews, 1977; Matthews and Katz, 1977; Gaines, 1980; Baker and Kastner, 1981; Bullen and Sibley, 1984; Morrow and Ricketts, 1988; Sibley *et al.*, 1988). High temperature experimental conditions were used because dolomite synthesized under earth-surface conditions form only metastable phases.

Dolomitization is a multi-step process involving dissolution of calcium carbonate (aragonite and calcite) and precipitation of dolomite from the solution (Katz and Matthews, 1977; Matthews and Katz, 1977; Gaines, 1980; Baker and Kastner, 1981; Bullen and Sibley, 1984; Sibley *et al.*, 1988). The replacement process proceeds through an intermediate phase(s) of magnesian calcite or calcium rich dolomite which, in turn, converts to dolomite (Katz and Matthews, 1977; Baker and Kastner, 1981; Bullen and Sibley, 1984; Morrow and Ricketts, 1988; Sibley *et al.*, 1988). Katz and Matthews (1977) also concluded that on a submicroscopic scale, the intermediate phases are formed in reaction zones surrounding the replacing grains or crystals, which are not in equilibrium with the bulk solution. On the basis of partitioning models of Sr^{2+} and Mg^{2+} and oxygen isotope data, the reaction zones in the transformation of aragonite to low-magnesian calcite were calculated to occupy <4% of the total solution volume (Katz and Matthews, 1977; Matthews and Katz, 1977).

Gaines (1980) suggested that nucleation of the dolomite phase is the major factor in reaction kinetics. In addition to the normal nucleation and growth stages that are well established for crystal growth, Sibley *et al.* (1988) noted an induction stage. The induction

stage refers to nucleation and growth of dolomite to a detectable limit (Sibley *et al.*, 1988). It is a critical part of the calcite-to-dolomite transformation because it is the slowest step in the overall replacement (Sibley *et al.*, 1988). Rate of dolomite replacement is, therefore, related to the kinetic effects on the length of the induction period.

In low temperature diagenetic environments, physico-chemical parameters that kinetically affect the rate of dolomitization include (1) hydration of Mg^{2+}, (2) molar Mg/Ca ratio, (3) salinity, (4) sulfate reduction, (5) concentration of HCO_3^-, and (6) organic materials.

In aqueous solutions, Mg^{2+} is strongly bound by water with a much higher hydration energy than Ca^{2+} (Lippman, 1973; Lahann, 1978; Hanshaw and Back, 1979). The hydrated Mg^{2+} must be dehydrated (removal of the water molecules from the hydrated ions) before it can be incorporated into the crystal lattice of dolomite. Gaines (1980) demonstrated that Li^{2+} acts as a catalyst for dehydrating Mg^{2+}, and hence, accelerates the dolomitization process. Fe^{2+} probably enhances dolomitization in a similar manner (Gaines, 1980).

The induction stage of dolomitization increases with decreasing molar Mg/Ca ratio (Sibley *et al.*, 1988); therefore, the rate of dolomitization increases with increasing Mg/Ca ratio of the solution. Sibley *et al.* (1988) further demonstrated that a higher Mg/Ca ratio increases the stoichiometry of the dolomite and that the intermediate product is more calcium rich at low Mg/Ca ratio. Baker and Kastner (1981) noted that the molar Mg/Ca ratios for the calcite-dolomite phase boundary lie between 0.57 and 1.06. Gaines (1980) showed that an increase in the transformation rate of dolomite with increasing Mg/Ca ratio occurs only within the dolomite stability field and, because at high ratios, the replacement proceeds to form magnesite.

The reaction rate increases significantly with increasing salinity (Gaines, 1980) due to a reduction in the induction stage (Sibley *et al.*, 1988). Folk and Land (1975) postulated that micritic dolomite, which is commonly calcium rich, forms in hypersaline condition

with a high Mg/Ca ratio. At reduced salinities, with low Mg/Ca ratios close to 1.0, the rate of dolomitization decreases, and the resulting dolomite tends to be limpid, euhedral and more stoichiometric (Folk and Land, 1975). However, Gunatilaka *et al.* (1987) documented the occurrence of calcium poor dolomites in a sabkha environment, where calcium rich dolomites are known to occur in such a setting (Gunatilaka *et al.*, 1984; McKenzie, 1981; Patterson and Kinsman, 1982). Thus, it appears that the effect of salinity on the stoichiometry of dolomite may not be directly correlatable and is probably more complicated than currently perceived.

Under experimental conditions, Baker and Kastner (1981) noted that the presence of even minor amount of SO_4^{2-} in the solution significantly inhibits the rate and degree of calcite-to-dolomite transformation. This inhibition occurs even if the SO_4^{2-} concentration is less than 5% of the sea water content (i.e. about 140 mg/l for the Caribbean sea water). The influence of SO_4^{2-} on dolomitization of calcium carbonate is due to poisoning of surface sites via surface adsorption or to surface precipitation (Baker and Kastner, 1981; Kastner, 1988). Land (1983a) suggested that SO_4^{2-} in solution may reduce the activity of Mg^{2+} by forming a $MgSO_4^{\circ}$ ion pair. However, Morrow and Ricketts (1988) showed that the presence of SO_4^{2-} in solution may inhibit dolomitization by retarding the rate of calcite dissolution, rather than by inhibiting the direct precipitation of dolomite from solution. Therefore, it appears that SO_4^{2-} content is the main kinetic factor in controlling dolomitization instead of the Mg/Ca ratio as suggested by Folk and Land (1975).

Although, according to thermodynamic concepts (equation 6), the dolomitization process is independent of CO_3^{2-} concentration, Morrow (1982a) argued that an increase in the CO_3^{2-} concentration of the solution may promote dolomitization by providing sufficient energy to push aside the hydration shield of Mg^{2+}. This proposition appears to be in agreement with the experimental results of Morrow and Ricketts (1988) and Sibley *et al.* (1988) which showed that higher CO_3^{2-} or HCO_3^{-} concentrations shorten the induction stage and expedite dolomitization.

Extensive dolomitization is known to occur in organic rich hemipelagic sediments (Baker and Burns, 1985; Burns *et al.*, 1988) and hypersaline sediments (Gunatilaka *et al.*, 1984). Baker and Kastner (1981), Kastner (1983, 1984, 1988), Gunatilaka *et al.* (1984), and Burns *et al.* (1988) concurred that dolomitization in these settings was promoted by an increase in the HCO_3^- content in the pore waters because of sulfate reduction. This process is particularly attractive because it raises the concentration of the dolomitization promoter (HCO_3^-) by reducing the content of the inhibitor (SO_4^{2-}). However, there are numerous examples of dolomites forming in marine conditions that have undergone little or no sulfate reduction (Saller, 1984; Aharon *et al.*, 1987; Mazzullo *et al.*, 1987; Carballo *et al.*, 1987; Mitchell *et al.*, 1987). Gunatilaka *et al.* (1984) and Kastner (1984) suggested that meteoric-sea water mixing may be an effective process in reducing the SO_4^{2-} content in solutions. Therefore, it may be suggested that the schizohaline environment is a favourable setting for dolomitization because of SO_4^{2-} dilution, rather than a result of Mg/Ca ratio decrease as suggested by Folk and Land (1975).

Gaines (1980) showed that organic materials and animal proteins associated with biogenic calcium carbonates inhibit dolomitization. He suggested that this negative kinetic effect can be effectively removed in fresh water diagenetic environments through oxidation.

On the basis of the kinetic aspects of dolomitization, it appears that mixed meteoric-sea water remains a viable medium for dolomitizing any carbonate sequences. However, pervasive dolomitization is probably site specific and only occurs when all the factors for dolomitization such as mineralogical, geological, climatic, and time conditions are favourable.

C. TIMING OF DOLOMITIZATION EVENT(S)

The clear cut evidence that serves to constrain the timing of dolomitization of the Bluff Formation is the absence of dolomite in the Pleistocene Ironshore Formation (Jones *et al.*, 1984). This indicates that the Bluff Formation was dolomitized prior to deposition

of the Ironshore Formation at about 125,000 years ago. Two important points remain to be considered. First, did the pervasive dolomitization occur in a single phase as suggested in Paragenetic Model I or did it occur in two stages as proposed in Paragenetic Model II (Fig. VIII.1). Second, is there any other evidence that can be used to better constrain the timing of the dolomitization event(s).

Aragonite Dissolution

Preferential dissolution of original skeletal aragonite in the molluscs, gastropods and corals was common in the Bluff Formation. Conversely, skeletal components formed of high-magnesian calcite, such as red algae and most foraminifera, have been dolomitized and their textures preserved (Fig. 16a of Lockhart, 1986; Plates 9A, 9F of Pleydell, 1987). Similar dissolution of aragonitic bioclasts has been documented in the Pleistocene Belmont Formation of Bermuda (Land, 1967), the Pleistocene Hope Gate Formation of Jamaica (Land, 1973a), the Pliocene Seroe Domi Formation of Bonaire (Sibley, 1980, 1982), the Pleistocene limestones of Yucatan Peninsula (Ward and Halley, 1985), the Miocene dolostones of Gulf of Suez, Egypt (Coniglio *et al.*, 1988), and the Pliocene Blessing Formation of St. Croix, U.S. Virgin Islands (Gill *et al.*, 1989).

Kinetics

The commonly perceived sequence of carbonate dissolution, in order of decreasing solubility, is magnesian calcite, aragonite and calcite (Chave *et al.*, 1962; Pytkowicz, 1969). This is only observed in solution at or near aragonite saturation state (Walter, 1985). The dissolution rate constants are commonly an inverse function of the grain size (Keir, 1980; Dreiss, 1984; Walter and Morse, 1984). More importantly, experimental studies by Walter (1985) and Walter and Morse (1985) showed that differences in grain microstructures can override thermodynamic constraints and lead to selective dissolution of more stable mineral phase. Furthermore, Walter (1985) concluded that the microstructural

control on dissolution rate is related to the saturation state of the solution. If the solution is undersaturated with respect to all the carbonate mineral phases, the reactive surface area of the grain microstructure controls the relative rate of dissolution (Walter, 1985). In this connection, the preferential dissolution of the aragonitic bioclasts in the Bluff Formation is probably related to their complex microstructures which have large reactive surface areas. For example, branching corals such as *Stylophora* were completely dissolved, whereas some massive corals such as *Montastrea* were partly preserved.

Timing

The selective dissolution phenomenon is due to the fact that aragonite is not thermodynamically stable under earth-surface conditions (Bathurst, 1975; Berner, 1981; Morse, 1983). Thus, aragonitic sediments that are stable when bathed in sea water will dissolve or be transformed to low-magnesian calcite when exposed to fresh water. Subaerial exposure of metastable carbonate sediments of the Bluff Formation undoubtedly occurred during the relative sea level drops in late Oligocene and late Miocene times. Therefore, most of the fossil molds in the Bluff Formation may have been formed in relation to sea level falls.

Studies of Pleistocene limestones led Land (1970), Steinen and Matthews (1973), Pingitore (1976), Longman (1980), and James and Choquette (1984) to conclude that dissolution of biogenic aragonite is much more effective in the fresh water phreatic environment than in the vadose setting. Thus, the extensive dissolution of the aragonitic skeletal components of the Bluff Formation may have occurred in the phreatic diagenetic realm. The preservation of the fossil molds also indicates that aragonite dissolution probably occurred after the sediments had undergone some degree of lithification.

Land (1973a) suggested that aragonite dissolution and dolomitization of the Pleistocene Hope Gate Formation of Jamaica occurred almost contemporaneously because aragonitic fossil molds have void-lining dolomite cement but no calcite cement. A similar

conclusion was drawn by Sibley (1982) in the study of the Pliocene Seroe Domi Formation of Bonaire. The common absence of aragonite in the dolomitized portions of the Pleistocene limestones also led Ward and Halley (1985) to suggest that dolomitization occurred during or shortly after aragonite dissolution. Sibley and Gregg (1987) also suggested that because allochem molds are much more common in dolostones than limestones, the molds probably formed during or after dolomitization. Experimental dolomitization of calcareous skeletal components also suggested that dolomitization and aragonite dissolution are near contemporaneity (Bullen and Sibley, 1984).

Aragonite dissolution and dolomitization appear to be closely related in some dolomitized limestone sequences (Land, 1973a; Sibley, 1982; Ward and Halley, 1985; Coniglio *et al.*, 1988). In other dolomitic limestone sequences, the relationship between aragonite dissolution and dolomite replacement is not clear. Examples cited in the Pleistocene coral terraces on Barbados (Humphrey, 1988), the Pliocene Blessing Formation on St. Croix, U.S. Virgin Islands (Gill *et al.*, 1989), and the Eocene to Miocene Gambier Limestone on South Australia (James and Bone, 1989) do not suggest any particular relationship between aragonite dissolution and dolomite replacement in the sequences.

In the case of the Bluff Formation, the rocks are completely dolomitized; therefore, it is difficult to establish the timing of aragonite dissolution with respect to dolomitization using petrographic analysis. However, it is important to note that in all the partially or completely dolomitized Tertiary and Pleistocene limestone sequences, aragonite dissolution is common (Land, 1973a; Sibley, 1982; Jones *et al.*, 1984; Ward and Halley, 1985; Coniglio *et al.*, 1988; Humphrey, 1988; Gill *et al.*, 1989; James and Bone, 1989). Perhaps aragonite dissolution and dolomitization is a kinetic relationship because aragonite dissolution provides additional CO_3^{2-}/HCO_3^- ions for the volume to volume dolomite replacement of the calcium carbonate skeletal materials. Morrow (1982a), Machel and Mountjoy (1986), and Morrow and Ricketts (1988) also suggested that an increase in

CO_3^{2-} favours dolomitization. Because preferential dissolution of most of the aragonite fossils in the Bluff Formation would provide an additional source of CO_3^{2-}, it is suggested that their dissolution probably occurred contemporaneous with dolomite replacement (i.e. Paragenetic Model II). Furthermore, early lithification can also be achieved by dolomite precipitation in the intergranular space during dolomitization.

Mineralogical Considerations

Petrographic studies generally indicate that dolomite has selectively replaced former lime mud (Murray and Lucia, 1967; Cander *et al.*, 1988). This is because substrates with a high surface-to-volume ratio, such as micrite, provide abundant active sites for nucleation (Sibley and Gregg, 1987; Sibley *et al.*, 1988). It has also been noted that aragonite and high magnesian calcite are more susceptible to dolomitization than low magnesian calcite because metastable carbonates have higher standard free energy (Fairbridge, 1957; Sibley, 1980, 1982; Sibley and Gregg, 1987). These observations are consistent with the experimental results obtained by Gaines (1974), Bullen and Sibley (1984), and Sibley *et al.* (1988).

Sibley *et al.* (1988) showed that the mineralogical selectivity of dolomite replacement of calcium carbonate is due to the shorter induction stage for aragonite than for calcite. This shorter induction stage results in the higher dolomitization rate of aragonite than of calcite. Dolomitization of aragonite was also found to proceed at higher SO_4^{2-} concentrations than that of calcite (Baker and Kastner, 1981).

Bullen and Sibley (1984) noted that there is no difference in the dolomitization rate of cryptocrystalline aragonite, high magnesian calcite and low magnesian calcite. They concluded that crystal size rather than mineralogy is the determining factor in the abundance of nucleation sites, and hence, the rate of dolomite formation. Furthermore, the preservation of replacement fabrics is also a function of the crystal size of the original skeletal components. Cryptocrystalline skeletal components such as coralline algae,

echinoids, and foraminifera generally have their microstructures preserved during dolomitization (Bullen and Sibley, 1984). Conversely, microcrystalline fossils such as corals and molluscs commonly lose their microstructures during dolomitization (Bullen and Sibley, 1984).

The matrix dolomite of the Bluff Formation was formed by replacement of precursor calcium carbonate as shown by the dolomitized bioclasts. Mimic replacement (i.e. microstructure preserved) of the high magnesian calcitic skeletal components (e.g. red algae, foraminifera) but not the aragonitic skeletal components (e.g. corals, molluscs) suggests that the allochems had not been transformed to low magnesian calcite prior to dolomitization. This conclusion is consistent with Bullen and Sibley's (1984) experimental results. Although conversion of high magnesian calcite to low magnesian calcite may not lead to destruction of original fossil fabrics (Friedman, 1964; Land, 1967; James and Choquette, 1984), dolomitization of diagenetic low magnesian calcite is kinetically not favourable (Gaines, 1974; Sibley, 1980, 1982; Bullen and Sibley, 1984). In this connection, it is suggested that dolomitization of the Bluff Formation probably occurred prior to the stabilization of the metastable carbonates (i.e. Paragenetic Model II) in a manner similar to that suggested by Land (1973a) for the Pleistocene Hope Gate Formation of Jamaica, Sibley (1982) for the Pliocene Seroe Domi Formation of Bonaire, and Coniglio *et al.* (1988) for the Miocene carbonates of Gulf of Suez, Egypt.

Geochemical Considerations

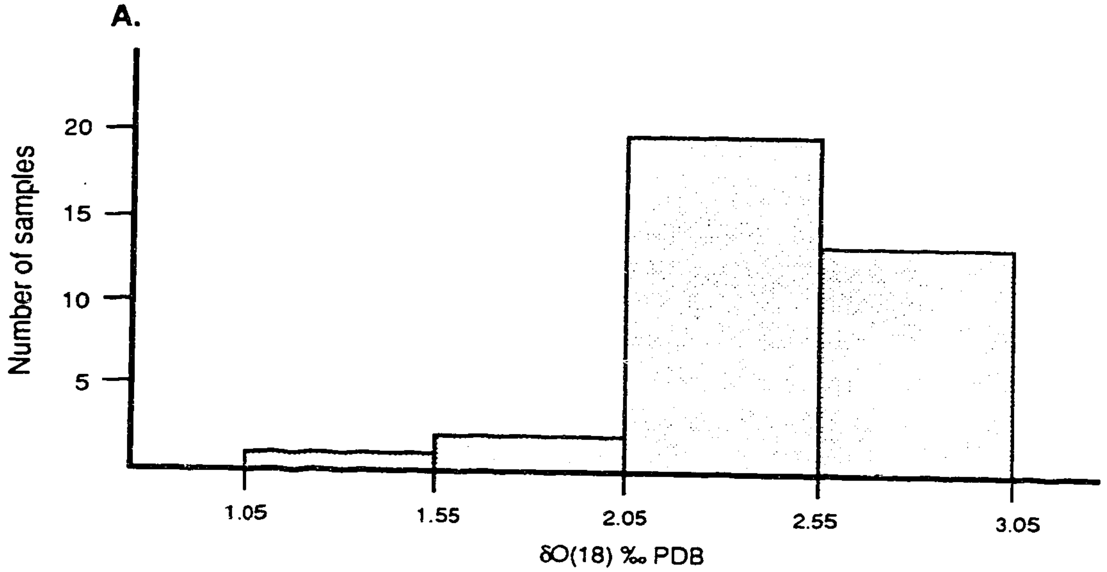
The Cayman and Pedro Castle members of the Bluff Formation have similar $\delta^{18}O$ contents and $^{87}Sr/^{86}Sr$ ratios (Pleydell, 1987; Jones, 1989a; Pleydell *et al.*, in preparation). This geochemical information led Jones (1989a) and Pleydell *et al.* (in preparation) to suggest that dolomitization of the Bluff Formation (Paragenetic Model I) was a single event at about 5 to 2 million years ago. Therefore, in order for Model II (Fig. VIII.1) to be viable alternative, it must take into account the geochemical data.

Stable Oxygen Isotopes

The stable oxygen isotopic composition of a mineral is controlled by the isotopic composition of the fluid from which the mineral precipitates and the temperature of precipitation (Land, 1980, 1983a; Anderson and Arthur , 1983; Lohmann, 1983). The $\delta^{18}O$ composition of the diagenetic mineral can, therefore, provide useful information on the diagenetic environment.

More than 90% of the $\delta^{18}O$ values of the matrix dolomite of the Oligocene Cayman Member fall between 2.05 and 3.05‰ PDB (Fig. IX.1A), although the values range from 1.4 to 3.0‰ PDB. The low values probably resulted from calcite contamination during the separation procedure. The $\delta^{18}O$ contents of the matrix dolomite of the Miocene Pedro Castle Member are slightly higher, ranging from 2.4 to 3.4 ‰ PDB; however, most of the values are between 2.55 to 3.05 ‰ PDB (Fig. IX.1B). The similar stable oxygen isotopic contents of dolomites from the Cayman Member and the Pedro Castle Member (Fig. IX.1) may have resulted from other diagenetic phenomena rather than the single dolomitization event as suggested by Jones (1989a) and Pleydell *et al.* (in preparation). Similar data could be achieved (1) if the various dolomitization events occurred under similar diagenetic conditions, or (2) if the isotopic signatures of previously formed dolomites were overprinted by later phase diagenetic fluids.

On the basis of the geological history of the Bluff Formation (Jones and Hunter, 1989), it is likely that the two members were subjected to similar diagenetic fluids (i.e. meteoric and sea water) during island emergence in late Oligocene and late Miocene times. However, the isotopic content of the Bluff Formation was probably reset by later phase diagenetic fluids in a manner suggested by Coniglio *et al.* (1988) and Moore *et al.* (1988). It has been noted by numerous workers that stable oxygen isotopic values can be reset by recrystallization as a result of late stage diagenesis (Land, 1980, 1983a, 1985; Machel and Mountjoy, 1986; Hardie, 1987; Longstaffe, 1987). Recrystallization of earlier formed dolomites by later diagenetic fluids was suggested by McKenzie (1981), Coniglio *et al.*



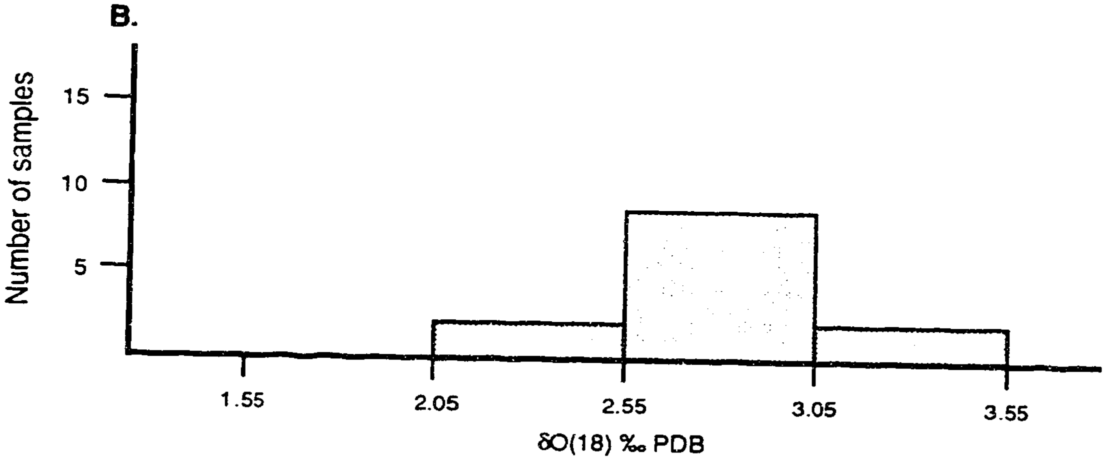


Fig. IX.1 Histograms showing distribution of δO(18) values of (A) Cayman Member dolostone and (B) Pedro Castle dolostone. Isotope data courtesy of Dr. B. Jones.

(1988), and Moore *et al.* (1988) to explain the stable isotopic composition of the dolostones from Holocene, Miocene and Jurassic ages, respectively. Thus, it appears that the stable oxygen isotopic signature of the diagenetic mineral is not a reliable means of differentiating the various stages of dolomitization without other supporting evidence.

Strontium Isotopes

The premise for using Sr isotopic ratio ($^{87}Sr/^{86}Sr$) for age dating is based on the following criteria:

(1) The Sr isotopic composition in sea water is uniform at any given time (Brass, 1976) because the oceanic residence time of Sr (~10^6 years) is much longer than the oceanic mixing time (~10^3 years).

(2) The Sr contained in marine carbonate, sulfate, and phosphate samples records the $^{87}Sr/^{86}Sr$ values of the sea water from which they were formed.

(3) the Sr isotopic ratio changes slowly over millions of years in a predictable trend (Burke *et al.*, 1982; Koepnick *et al.*, 1985; DePaolo and Ingram, 1985; DePaolo, 1986; Hess *et al.*, 1986; Richter and DePaolo, 1987; Rundberg and Smalley, 1989).

Studies by Saller (1984) on the Eocene strata of Enewetak Atoll and Swart *et al.* (1987) on the Pliocene and Miocene strata of the Bahamas suggest that the Sr isotopic composition may provide the age of dolomitization. This is possible because the isolated geologic location of the Enewetak Atoll and the Bahamas means that the sequence is removed from any source of dolomitizing fluids other than sea water and meteoric water. The contribution of Sr from fresh water is generally negligible relative to that of the sea water (8 ppb vs. 8 ppm; Faure *et al.*, 1967). Therefore, the Sr isotopic content of the dolomite is essentially a measurement of the Sr isotopic composition of the sea water at the time of dolomitization. Thus, the age of the dolomitization event can be obtained from the $^{87}Sr/^{86}Sr$ trend versus time data of Burke *et al.* (1982), Koepnick *et al.* (1985), DePaolo

and Ingram (1985), DePaolo (1986), Hess *et al.* (1986), Richter and DePaolo (1987), and Rundberg and Smalley (1989).

Following the approach of Saller (1984) and Swart *et al.* (1987), Jones (1989a) and Pleydell *et al.* (in preparation) showed that the Sr isotopic data fall in a narrow range (Table IX.1), with an average value of 0.7090. Using the $^{87}Sr/^{86}Sr$ sea water versus time curve of Koepnick *et al.* (1985), the average value suggests that dolomitization of the Bluff Formation was a single event that took place about 5 to 2 Ma (Jones, 1989a; Pleydell *et al.*, in preparation).

The $^{87}Sr/^{86}Sr$ sea water data are relatively well defined for the Cenozoic; nevertheless, Sr isotope versus time curves derived from different sampling sites show variation (cf. Keopnick *et al.*, 1985; DePaolo and Ingram, 1985; DePaolo, 1986; Hess *et al.*, 1986). The variation is probably caused by sample alteration (recrystallization) and uncertainty in biostratigraphic dating (Hess *et al.*, 1986; Richter and DePaolo, 1987; Rundberg and Smalley, 1989; Wardlaw, 1989). According to Koepnick *et al's*. (1985, Figs. 3 and 4) Sr-isotopic sea water curve, the present day sea water is the most radiogenic and has a $^{87}Sr/^{86}Sr$ ratio slightly less than 0.70910. This means that any $^{87}Sr/^{86}Sr$ ratios in excess of 0.70910 are meaningless values; however, a close examination of the Sr isotopic data of the Bluff Formation shows that almost half of the data are above this critical value (Table IX.1). Using the latest Sr isotope versus age trends determined by DePaolo (1986), Hess *et al.* (1986), Richter and DePaolo (1987), and Rundberg and Smalley (1989), the Sr isotopic ratios give a rather different interpretation (Table IX.1). The age of dolomitization of the Bluff Formation may be as early as 9 million years ago (Table IX.1). Although the Pedro Castle Member is presently assigned an age of approximately 16 million years, the actual age of the member is open to debate due to the lack of biostratigraphic markers in dating the sequence (Jones and Hunter, 1989; Jones, 1989a). The Pedro Castle Member may be as young as 9 million years old (I. Hunter, 1989, per. comm.). Furthermore, it is not possible to determine how much of the Pedro Castle strata

Table IX.1 $^{87}Sr/^{86}Sr$ ratios and interpretation of the age of dolomitization for dolostones from the Bluff Formation on Grand Cayman. Sr isotopic data courtesy of Dr. B. Jones.

Sample #	Age	$^{87}Sr/^{86}Sr$	Age[1] Ma	Age[2] Ma
1264	Oligocene	0.709125	NA	2.0±0.5
2002	Oligocene	0.709124	NA	2.0±0.5
2023	Oligocene	0.709062	<1.5	4.0±1.5
		0.709042*	1.5±1.0	4.0±1.5
2036	Oligocene	0.709134	NA	2.0±0.5
2037	Oligocene	0.709106	NA	2.5±0.5
		0.709045*	1.5±1.0	4.0±1.5
3077	Oligocene	0.709070	<1.0	4.0±1.5
3126	Oligocene	0.709000	3.0±2.0	6.0±3.0
3152	Oligocene	0.709000	3.0±2.0	6.0±3.0
2013	Miocene	0.709009	3.0±2.0	6.0±3.0
2018	Miocene	0.708999	3.0±2.0	6.0±3.0
2019	Miocene	0.709115	NA	2.0±0.5
2024	Miocene	0.709060	0.5±1.0	4.0±1.5
2033	Miocene	0.709080	<0.5	3.5±1.5
		0.708983*	3.5±2.0	6.0±3.0
2035	Cavity fill (skeletal grainstone)	0.709331	NA	NA
3167	Cavity fill (caymanite)	0.709140	NA	1.5±0.5

Note: (1) Sample # refers to the catalogue no. of the Cayman Islands rock collection.
(2) All samples were analyzed at the University of Alberta, Sr isotopic data marked by an asterisk* refer to results determined by the University of Saskatchewan on the same samples.
(3) Age[1] refers to age of dolomitization determined from Sr isotopic sea water curve of Koepnick *et al.* (1985).
(4) Age[2] refers to age of dolomitization determined from Sr isotopic sea water curves of DePaolo (1986), Hess *et al.* (1986), Richter and DePaolo (1987), and Rundberg and Smalley (1989).
(5) NA means that no age can be assigned to the Sr isotopic value because it exceeds the Sr isotopic ratio of the present day sea water.

was lost by erosion, and hence, to determine the age of the missing strata. Based on the older dolomitization age and the uncertainty in the age assignment of the Miocene Pedro Castle Member, it would appear that sediments of the Pedro Castle Member may have been dolomitized early in the diagenetic history, probably in relation to the late Miocene sea level fall at about 10 Ma (Vail *et al.*, 1977; Haq *et al.*, 1987). If this age interpretation is correct, it would suggest that the dolomitization of the Pedro Castle Member occurred prior to the stabilization of the metastable calcium carbonate minerals. Thus, the dolomite fabric of the Miocene Pedro Castle Member resulted from an early dolomitization event. If so, the petrographic fabric of the Oligocene Cayman Member, which is similar to the Miocene Pedro Castle Member, might also have resulted from early dolomitization of metastable carbonate sediments during late Oligocene times.

Another source of uncertainty is shown by the Sr isotopic values obtained from the same samples by two separate laboratories (Table IX.1). The results are generally similar, but there are measurable differences, particularly for sample #2033 (Table IX.1). The $^{87}Sr/^{86}Sr$ ratio determined by the University of Alberta gives an age of 3.5±1.5 Ma whereas the ratio determined by the University of Saskatchewan gives an age of 6.0±3.0 Ma (Table IX.1). This indicates that results obtained from different laboratories may vary.

It is also important to note that the skeletal grainstone and the caymanite samples from the Cayman Member have the highest radiogenic Sr isotopic ratios (Table IX.1), and hence, the youngest dolomitization age. This indicates that the latest dolomitization fluid had penetrated deep into the Oligocene Cayman Member. This young Sr isotopic age is consistent with the Paragenetic Model II which suggests that the caymanite and skeletal sands in the Cayman Member were dolomitized at a later time than the host rock. However, the Sr isotopic value for the skeletal grainstone is questionable because it exceeds the highest point of the $^{87}Sr/^{86}Sr$ curves determined by DePaolo (1986), Hess *et al.* (1986), Richter and DePaolo (1987), and Rundberg and Smalley (1989).

Machel and Mountjoy (1986) noted that Sr isotopic ratios can be reset by recrystallization. Land (1985) also suggested that the radiogenic Sr ratios may indicate fluid that stabilizes a previously formed dolomite. Studies of the Upper Jurassic Smackover dolomites by Moore *et al.* (1988) also suggested that Sr isotopic ratios of the dolomite may have been reset by later-phase recrystallization. Therefore, overprinting of the Sr isotopic ratios of the previously formed dolomites of the Cayman Member may explain the generally uniform Sr isotopic composition of the Bluff Formation. The spread in the dolomitizing age data (2.0±0.5 to 6.0±3.0 Ma; Table IX.1) may indicate the continual equilibration of the previously formed dolomites until late Pliocene and early Pleistocene times. The Sr ratios also suggest that dolomitization is a slow and gradual process.

Recrystallization

The term recrystallization is commonly used to describe any change in the fabric of a mineral (Bathurst 1975). In the context of this study, recrystallization of the matrix dolomite of the Bluff Formation refers to transformation of poorly ordered and/or nonstoichiometric dolomite to ordered and stoichiometric dolomite. Sibley and Gregg (1987) preferred the term neomorphism to recrystallization because such transformation can be considered a change in mineralogy. Changes of the $\delta^{18}O$ contents and $^{87}Sr/^{86}Sr$ ratios probably accompany recrystallization.

Experimental studies by Glover and Sippel (1967) showed that cation-disordered rhombohedral carbonates of dolomitic composition, precipitated at room temperature, slowly transformed to aragonite when left in contact with their supernatant solutions or with pure water. Similarly, Gaines (1974), Katz and Matthews (1977), Baker and Kastner (1981), Bullen and Sibley (1984), and Sibley *et al.* (1988) showed that the initial products of experimental dolomitization was metastable, poorly ordered, calcium rich dolomite which converted to well ordered dolomite with sufficient time.

Land (1980), Sperber *et al.* (1984), and Hardie (1987) noted that any poorly ordered Ca-rich phase formed at or near earth surface will have a large thermodynamic drive to undergo spontaneous ordering as time progresses because of the large order-disorder energies in dolomites. Lumsden and Chimahusky (1980) and Sperber *et al.* (1984) also suggested that dolomite stoichiometry may be strongly time dependent as the rocks are exposed to the ever changing pore fluids after their initial precipitation. The stoichiometry of the dolomites of the Bluff Formation, therefore, may reflect the result of diagenetic stabilization.

Petrographic Considerations

Paragenetic Model I (Fig. VIII.1; Pleydell, 1987; Jones, 1989a; Pleydell *et al.*, in preparation) suggests that dolomitization of the Bluff Formation occurred about 5 to 2 million years ago. If so, the metastable carbonate sediments (aragonite and high magnesian calcite) would have been subjected to extensive meteoric influence in late Oligocene and late Miocene times as a result of relative sea level falls prior to dolomitization. During these periods of subaerial exposure, most of the metastable carbonates would have transformed to low magnesian calcite in a manner similar to that documented for the Pleistocene limestones of Bermuda (Land, 1970), Barbados (Steinen and Matthews, 1973; James, 1974; Pingitore, 1976), and Florida (Martin *et al.*, 1986; Schmoker and Hester 1986). These studies concluded that significant diagenetic modification takes place in the fresh water phreatic zone where the matrix was cemented by microspar and metastable carbonates were inverted to low magnesian calcite or partially dissolved. Because the time for the inversion of aragonite to calcite is in the order of thousands to hundred of thousands of years (Harrison, 1975; Halley and Harris, 1979), it is reasonable to suggest that most carbonate sediments were inverted to low magnesian calcite prior to the Model I dolomitization about 5 to 2 Ma.

Studies of marine shorelines and coral terraces on Barbados (Mesolella *et al.*, 1969; Bender *et al.*, 1973; Steinen *et al.*, 1973), Bahamas (Neumann and Moore, 1975), Bermuda (Harmon *et al.*, 1978), New Guinea (Bloom *et al.*, 1974), and Hawaii (Ku *et al.*, 1974) established that eustatic sea level has changed at least six times during the past 125,000 years. These frequent sea level changes probably resulted in the formation of unstable hydrogeological systems that were not conducive to mineral stabilization of the carbonate sediments. If so, the sediments of the Ironshore Formation were exposed to the marine phreatic and vadose diagenetic zones at different times after their deposition. Furthermore, marine phreatic and vadose diagenetic realms are not active diagenetic environments for mineral stabilization and cementation relative to the fresh water phreatic zone (Land, 1970; Steinen and Matthews, 1973; Longman, 1980; James and Choquette, 1984). This is probably the main reason the Ironshore Formation still contains a high content of aragonite. The Bluff Formation, however, was subaerially exposed over long periods of time (in the order of 10^6 years) as a result of the major regression in late Oligocene to early Miocene and late Miocene to early Pliocene times. These periods of island emergence would have resulted in extensive meteoric influence, particularly in the central part of the islands where marine influence is less severe. Therefore, the lack of diagenetic modification of the Ironshore Formation cannot be used as a direct reference for the study of the diagenesis of the Bluff Formation.

Pleydell (1987) and Jones (1989a) suggested that the petrographic homogeneity of the Bluff Formation is indicative of single stage dolomitization (i.e. Paragenetic Model I). According to Jones and Hunter (1989), Cayman Member was subaerially exposed for about 15 million years prior to deposition of the Pedro Castle Member whereas the Pedro Castle Member was exposed for less than 10 million years prior to dolomitization. Furthermore, the Cayman Member probably experienced an additional phase of subaerial exposure and meteoric diagenesis when the Pedro Castle Member was emerged above sea level. If dolomitization was a single event, the carbonate precursors of the two members

would have to be altered to the same fabric, particularly the crystal size, prior to the pervasive dolomitization in order to form petrographically identical dolostones for the two members. The mineral stabilization and cementation during meteoric diagenesis would certainly make it difficult to preserve the microfabrics of the skeletal components as well as they are preserved.

The finely crystalline to microcrystalline fabrics of the Bluff Formation (Plates VI.1A, 1B) also argue against inversion of metastable carbonates prior to dolomitization because mineral stabilization commonly results in an increase in crystal size (Steinen and Matthews, 1973; Steinen, 1978, 1982; Longman, 1980). Folk (1973) and Morrow (1982b) argued that finely crystalline dolomites are indicative of early replacement. Modern dolomites reported from Jamaica (Mitchell *et al.*, 1987) and Florida (Carballo *et al.*, 1987) have dolomite crystal size similar to that of the Caymanian matrix dolomite. Therefore, based on the petrographic fabrics of the Bluff Formation, it is suggested the dolomites of the Bluff Formation probably formed by early replacement of metastable carbonates as suggested by Paragenetic Model II.

Other Circumstantial Considerations

The following features are circumstantial evidence that assist in supporting the argument for Paragenetic Model II.

Cavity Lining Dolomite Cements

Cavity lining dolomite cement is common in the Oligocene Cayman Member, but it is absent in the Pedro Castle Member (Jones and Hunter, 1989). In the Cayman Member the dolomite cements lining aragonitic fossil molds were subsequently overlain by internal sediments (Plate VI.6F). The internal sediments were probably deposited during the early stages of the marine transgression in early Miocene times prior to deposition of the Pedro Castle Member (Fig. VIII.1; Jones and Hunter, 1989).

In support of Paragenetic Model I, Jones (1989, pers. comm.) suggested that the dolomite crystals were formed in the cavities prior to host rock dolomitization (Fig. VIII.1) and were not affected by later pervasive dolomitization because of their stable form. Void-lining and filling dolomite cement is common in dolostone formations (Beales, 1971). Dolomite cements rooted on limestone are not common, but are reported from the late Pleistocene Falmouth Formation of Jamaica (Land, 1973b) and from the Pleistocene Yucatecan limestones of Yucatan Peninsula (Ward and Halley, 1985). In both sequences, replacive dolomite is present in the matrix, and other forms of meteoric cement such as calcite spar and/or zoned dolomite and calcite are commonly associated with the dolomite cement. There is, however, no petrographic evidence to indicate that precipitation of other types of meteoric cement accompanyed the precipitation of the dolomite cement in the Cayman Member.

Land (1973a, 1973b) suggested that replacive dolomite and dolomite cement were formed at or near contemporaneity in the middle Pleistocene Hope Gate Formation and the late Pleistocene Falmouth Formation of Jamaica. Similarly, Holocene dolomitization of supratidal sediments from Sugarloaf Key, Florida also showed dolomite replacement and contemporaneous dolomite precipitation (Carballo *et al.*, 1987). Experimental dolomitization of calcareous components by Bullen and Sibley (1984) also showed that dolomite cementation accompanies dolomitization of the substrates in some cases. In this connection, it is suggested that the void lining dolomite cements that predated the influx of internal sediments were probably formed at or near contemporaneity with early dolomite replacement of the Cayman Member.

Cave Development

Cave development probably began in late Oligocene times when the Cayman Member was subaerially exposed due to a sea level drop. This early karst development

(Phase I in Fig. VIII.1) is indicated by the filling of caymanite and skeletal sands prior to deposition of the Pedro Castle Member.

Most caves in the Cayman Member were not completely filled by internal sediments, suggesting that the Cayman Member was lithified prior to karst development or it would have been subject to cave collapse. From studies of the Eocene to Miocene Gambier Limestone of southern Australia, James and Bone (1989) presented an example where karst is developed in the soft to friable sediments without significant cementation. In the Gambier Limestone, the original sediments were entirely calcite or Mg-calcite (James and Bone, 1989). Conversely, the original sediments of the Bluff Formation were predominantly aragonite. For aragonitic sediments, leaching or inversion of skeletal aragonite and cementation are common when the sediments are exposed to meteoric diagenetic realm (Longman, 1980; James and Choquette, 1984).

According to Paragenetic Model I (Fig. VIII.1, Jones, 1989a; Pleydell *et al.*, in preparation), lithification of the carbonate sediments was probably accomplished by calcite cementation in the meteoric vadose and phreatic realms. Conversely, in Model II (Fig. VIII.1), it suggests that lithification was achieved by dolomite precipitation in intergranular space at about the same time as early dolomite replacement. There is, however, no petrographic evidence indicating pre-existing meteoric calcite cement. Furthermore, the originally high lime mud (micrite) content of the carbonate sediments of the Cayman Member would have facilitated extensive diagenesis of the sediments when exposed to meteoric phreatic realm. Steinen (197[illegible], 1982) and Lasemi and Sandberg (1984) noted that diagenesis of lime mud in fresh w[illegible]ironments involves rapid stabilization of aragonite and high magnesian calcite to low magnesian calcite and considerable precipitation of microspar in intergranular voids. This diagenetic modification would have resulted in significant loss of primary matrix porosity and in permeability of the carbonate sediments of the Cayman Member, characteristics required for the movement of the dolomitizing fluid and for delivering Mg^{2+} to the site of reaction. In order to form a homogeneous dolostone,

high intergranular porosity and permeability is particularly important. Late dolomitization after extensive meteoric diagenesis and cave development suggests that dolomitizing fluid would flow preferentially along open joints and cave passages. If so, dolomitization fronts would probably develop in the vicinity of the main avenues of fluid flow. Dolomite dikes found in the Precambrian Wyman Formation of northeastern Inyo Mountains of California were postulated by Zenger (1976) to have been formed from dolomitization along fractures. The absence of any recognizable dolomitization fronts in the vicinity of caves suggests that dolomitization of the Cayman Member probably occurred prior to transformation of metastable carbonates and cave development.

Synopsis

The one time dolomitization event (Model I) suggested by Jones (1989a) and Pleydell *et al.* (in preparation) is a simple model that satisfies the geochemical and petrographic data. However, the geochemical data (oxygen and strontium isotopes) do not permit a definitive interpretation on the timing of the dolomitization event(s). On the basis of the cumulative information on aragonite dissolution, mineralogy, petrography, isotope geochemistry and on circumstantial evidence, it is suggested that the Bluff Formation was probably dolomitized in two separate times (Model II). The earlier phase dolomitized the Cayman Member and the later phase dolomitized the Pedro Castle Member and the internal sediments (caymanite and skeletal sands). The second dolomitization event also affected the Cayman Member by resetting the geochemical signatures of previously formed dolomites, probably through increased cation ordering and stoichiometry.

D. HYDROGEOLOGICAL SYSTEM

A fluid-transport mechanism is a basic requirement for dolomitization of calcium carbonate (Hanshaw *et al.*, 1971; Morrow, 1982b; Land, 1983a, 1985; Simms, 1984; Machel and Mountjoy, 1986; Hardie, 1987). For extensive dolomitization to occur, the

diagenetic fluid must have an adequate supply of Mg^{2+} and probably CO_3^{2-}, and the diagenetic environment must have an active hydrogeological system for delivering the Mg^{2+} and CO_3^{2-} to the reaction sites and for carrying away the Ca^{2+}. Land (1985) also suggested that dynamic systems may promote dolomitization by substrate preparation or removal of crystal poisons. This dynamic system is necessary regardless of fluid type. Calcite dissolution-reprecipitation occurs in thin reaction zones surrounding the dissolving grains (Katz and Matthews, 1977); therefore, ion diffusion probably plays an important role on a submicroscopic scale. However, advection (fluid flow) is the dominant mass-transfer process, and it is controlled by the hydrogeological conditions of the aquifer.

Sources of Mg^{2+} and CO_3^{2-}

Goodell and Garman (1969), and Hanshaw *et al.* (1971) suggested that dissolution of high magnesian calcite and a subsequent downward percolation of the Mg-enriched fluid (solution-cannibalism) can be important dolomitization processes provided that the sediments have a high proportion of magnesian calcite. In the Bluff Formation of the Cayman Islands, high magnesian calcite such red algae, foraminifera and echinoids probably formed less than 10% of the original carbonate sediments. This low proportion suggests that the high magnesian calcite could be only a minor source of Mg^{2+} for dolomitizing the calcium carbonates. The major available source of Mg^{2+} apparently is sea water or its derivatives. An external source of CO_3^{2-} is also needed for volume for volume dolomitization with retention of microstructures (Sibley, 1980, 1982; Morrow, 1982a: Sibley *et al.*, 1988). Most of the CO_3^{2-} was probably obtained from dissolution of aragonitic skeletal components and from sea water.

Static versus Dynamic System

The following calculation adapted from Hanshaw *et al.* (1971) illustrates the importance of fluid dynamics in the dolomitization of calcium carbonate. For a calcite grain

of 1 ml in volume with 40 % porosity, the number of Ca^{2+} positions is related to the grain porosity by

$$Ca^{2+} = \frac{\rho \, N_A \, (1 - \phi)}{M_c} = 9.7 * 10^{21}$$

where ρ = density of calcite = 2.7 g/cc

N_A = Avogadro's No. = $6.022 * 10^{23}$/mole

ϕ = grain porosity = 0.40

M_c = molecular weight of calcite = 100.09 g

Thus, replacement of one half of the Ca^{2+} by Mg^{2+} requires $4.85 * 10^{21}$ Mg^{2+} ions. Using sea water as the dolomitizing fluid, the number of Mg^{2+} ions in the pore fluid is

$$Mg^{2+} = \frac{C_m \, N_A \, \phi}{M_m * 10^6} = 1.29 * 10^{19}$$

where C_m = concentration of Mg^{2+} in sea water = 1300 mg/l

M_m = atomic weight of Mg = 24.31 g

The results show that Mg^{2+} ions available in the pores are much lower than that required to replace half of the Ca^{2+} in the calcite grain. This pore fluid obviously cannot result in complete dolomitization if the solution is static. More importantly, the calculation shows that the efficiency of replacement is a function of the rock porosity and Mg^{2+} concentration in the solution. Land (1983a, 1985) also demonstrated that, dependant on the water salinity and rock porosity, several tens (for hypersaline water) to several thousands (for brackish water) of volumes of water are needed to dolomitize a unit volume of limestone. Therefore, pervasive dolomitization can only be accomplished by active, long lasting fluid flow that facilitates continual replenishment and supply of Mg^{2+} to the dolomitization sites and removal of excess Ca^{2+}.

Dolomitization Fluids

Currently, five types of waters have been suggested as dolomitizing fluids in various diagenetic environments. They are (1) hypersaline fluid (Adams and Rhodes, 1960; Deffeyes *et al.*, 1965; Illing *et al.*, 1965; Hsu and Siegenthaler, 1969; Zenger, 1972; Morrow, 1978; McKenzie *et al.*, 1980; Patterson and Kinsman, 1982), (2) subsurface formational fluid related to burial (Jodry, 1969; Mattes and Mountjoy, 1980; Zenger, 1983; Machel, 1984; Gregg, 1985), (3) alkaline continental water (von der Borch, 1976; von der Borch and Lock, 1979; Muir *et al.*, 1980; Botz and von der Borch, 1984), (4) sea water (Fanning *et al.*, 1981; Saller, 1984; Simms, 1984; Compton and Siever, 1986; Aharon *et al.*, 1987; Carballo *et al.*, 1987; Coniglio *et al.*, 1988), and (5) mixed meteoric-marine water (Hanshaw et al., 1971; Badiozamani, 1973; Land, 1973; Randazzo and Hickey, 1977; Choquette and Steinen, 1980; Magaritz *et al.*, 1980; Randazzo and Bloom, 1985; Ward and Halley, 1985; Force *et al.*, 1986; Coniglio *et al.*, 1988; Humphrey, 1988; Searl, 1988).

Hypersaline Fluid

Jones and Ng (1988a) documented the occurrence of minor amounts of anhydrite cement in some cavities of a coastal breccia body formed in the Ironshore Formation. Similar conditions might have developed in the coastal areas of the Bluff Formation during periods of land emergence. Although evidence of significant hypersaline diagenetic fluid is absent, saline water (water having salinity slightly greater than sea water) resulting from the evaporation of surface water is common (cf. beach water, pond water and sea water in Table III.2). Salinity measurements of the main water body of North Sound by Rigby and Roberts (1976) also recorded greater than normal marine salinity (total dissolved solids of up to 42,000 ppm versus 38,000 for sea water salinity) depending on the season. Synsedimentary evaporitic environment is ruled out because of the entirely open marine

fauna. Furthermore, the absence of evidence of former evaporites argues against hypersaline diagenetic conditions.

Deep Formational Fluid (Burial)

Diagenetic fluids related to burial can be precluded in the dolomitization of the Bluff Formation because there is no stratigraphic or petrographic evidence to suggest that the formation has been subjected to deep burial.

Alkaline Continental Fluid

The lack of a large hinterland in the Cayman Islands precludes an influx of alkaline water from a continent as possible diagenetic fluid; it is not analogous to the present day Coorong area of South Australia.

Sea Water

Using the ^{18}O fractionation-temperature equation of Land (1983b), which is essentially the same as Matthews and Katz (1977), Pleydell (1987) attempted to deduce the type of dolomitization fluid based on the $\delta^{18}O$ values of the dolostone of the Bluff Formation. She concluded that dolomitization of the Bluff Formation occurred in normal marine water. At low temperature setting, however, there is much disagreement among the oxygen isotopic fractionation equations (Fig. VII.2) of Northrup and Clayton (1966), O'Neil and Epstein (1966), Sheppard and Schwarcz (1970), Fritz and Smith (1970), and Matthews and Katz (1977). Compounding the problem is the variety in forms of cation-disordered and nonstoichiometric dolomites present in the near surface setting as well as the later phase recrystallization that can reset the isotopic content. Indeed, using the same oxygen isotopic data of Pleydell (1987), the five fractionation relationships indicate dolomitizing fluid varying from 25% to 100% sea water salinity over a temperature range of 22-33°C (Table VII.5).

Although sea water has been indicated as a dolomitizing fluid in numerous carbonate sequences, it commonly requires some form of kinetic booster, such as elevated temperature (e.g. Fanning *et al.*, 1981; Saller, 1984; Aharon *et al.*, 1987), elevated salinity (e.g. Sass and Katz, 1982; Bein and Land, 1983), or sulfate reduction (e.g. Baker and Kastner, 1981; Burns *et al.*, 1988). Similarly, the Pleistocene Ironshore Formation (about 125,000 years old), which is bathed in present day sea water, shows no indication of dolomitization. Therefore, it appears that normal sea water alone is not an effective agent.

Mixed Fresh-Sea Water (Brackish Water)

It has been suggested that dolomitization of the Cayman and Pedro Castle members of the Bluff Formation occurred early in the diagenetic history in relation to the major regressions during late Oligocene and late Miocene times. Island emergence during the major regressions may have provided a land area for the recharge of meteoric water. The selective dissolution of aragonitic skeletal components in association with the contemporaneous dolomitization evidently indicates that there was a certain degree of meteoric influx. The stable oxygen isotopic data of the matrix dolomite (Table VII.1) also indicate that the dolomitizing fluids were probably brackish (25% sea water salinity) to saline water (Table VII.5, Fig. VII.3B). Unfortunately, poor understanding of the isotopic oxygen fractionation between dolomite and the precipitating fluid does not permit further refinement of the salinity range of the diagenetic fluids.

Several lines of evidence appear to suggest that the brackish ground water (Tables III.3, 7, IV.7, 8), particularly the highly brackish type (>15% sea water salinity), are kinetically favourable for dolomitization of the Bluff Formation.

(1) The water has higher salinity than the fresh water even though the latter may also be supersaturated with respect to dolomite.

(2) Molar Mg/Ca ratio of the water is greater than 1.0 and lies within the stability field of dolomite.

(3) The water has higher HCO_3^- content than the sea water, apparently through dissolution of skeletal components in the shallow zones.

(4) The water has lower SO_4^{2-} than the sea water as a result of mixing with fresh water.

(5) The shallow diagenetic environment favours removal of organic materials by oxidation.

Sulfate reduction occurs locally only in the shallow ground water on the Cayman Islands. Only one out of eleven piezometers (Table III.1) indicated SO_4^{2-} reduction with corresponding increase in HCO_3^- content (Fig. III.8). It is important to note that the water that showed sulfate reduction is from the brackish water zone. This also suggests that the brackish water zone is favourable for dolomitization because of reduction of SO_4^{2-} ions and with a corresponding increase in the HCO_3^- content.

The mixed meteoric-marine model, however, has been critically reviewed by Machel and Mountjoy (1986) and Hardie (1987) who concluded that it is not an effective mechanism for dolomitizing a thick limestone sequence. Specifically, Machel and Mountjoy (1986) and Hardie (1987) cited the lack of dolomite formation in present day mixing zone setting such as Bermuda, Barbados, Bahamas, Florida, and Yucatan Peninsula. Instead of causing dolomitization, modern mixing zone waters appear to cause subsurface karstification (Machel and Mountjoy, 1986; Hardie, 1987).

The following points attempt to highlight some of the conditions that have been overlooked in rejecting the mixed water dolomitization model:

(1) Brackish water (commonly known as mixed water) encompasses water of >4% to <100% sea water salinity (Table III.9); therefore, it has a very variable chemical composition (Tables III.3, 6, 7, IV.7, 8). Any discussion of mixed water without defining this complete spectrum of water chemistry and water-rock interaction is futile and can only add to the confusion. Furthermore, mixing can occur at an early stage of land emergence without significant water lens development. The mixing zone is a dynamic regime that has a variable thickness (Figs. II.12, 19) and

chemical properties depending on the types of flow mechanism involved. James and Choquette (1984) also illustrated that the thickness of the mixing zone on Bermuda may exceed the thickness of the fresh water zone, particularly in a karst environment.

Pigott and Land (1986) noted that meteoric influence extends from land to the offshore reef tract at Discovery Bay in Jamaica and provides a mixing zone diagenetic environment in a supposedly marine environment. If this is so, many marine limestones may have been influenced by meteoric water depending on the ground water flow system. Involvement of meteoric waters in deep formation fluids has also been noted by Hitchon and Friedman (1969).

(2) Subsurface karst present in the modern mixing zone does not necessarily mean it is forming at present. Machel and Mountjoy (1987) noted that the mixing zones in most Caribbean islands and the adjacent landmasses have shifted six times during the past 120,000 years due to eustatic sea level changes. Therefore, many subsurface karsts may well be paleokarsts. Major regressions in Late Oligocene, Late Miocene and Pliocene times (Vail *et al.*, 1977; Haq *et al.*, 1987) may also have caused karst development in the Tertiary carbonate sequences.

(3) Hydrogeological conditions should encompass the whole spectrum of surface and subsurface hydrology. On Bermuda, undersaturation of ground water with respect to carbonate minerals is largely due to the influx of CO_2 from surface peat marshes (Plummer *et al.*, 1976). On Barbados, the high topographic relief, the large catchment area, and the presence of an impermeable rock formation beneath the limestone aquifer results in the extremely high efficiency of rain water recharge (Dr. S. Foster, 1988, pers. comm.). This high volume of rain water, laden with CO_2, would greatly influenced the saturation states of the ground water. The Floridan aquifer is in a confined condition (Kohout, 1967); therefore, hydrogeological behaviour of such an aquifer is not comparable to that of unconfined aquifers that

are common on most small limestone islands. The aquifers of the Yucatan Peninsula are fed by a large continental recharge area (Sanford and Konikow, 1989) absent in small islands or atolls. Although all of the examples cited are from carbonate aquifers, they all exhibit different ground water chemistry due to differences in ground water flow systems.

(4) The presence of dolomite in three late Pleistocene raised reef terraces in southeastern Barbados was first documented by Humphrey (1988) after many years of research on the island, indicating that the lack of documentation of dolomite forming in mixing zones may be due to lack of exposures for such studies. On the basis of petrographic, stable isotope, and trace element data, Humphrey (1988) concluded that the dolomites, ranging from trace amounts to 100% in places, were formed in a mixed meteoric-sea water environment. Using a forward modelling technique, Humphrey and Quinn (1989) suggested that mixed water is capable of dolomitizing a thick limestone sequence. Furthermore, pervasive dolomitization is probably site-specific and occurs only in environments where all the conditions are favourable.

(5) The frequent eustatic sea level changes during the Pleistocene times probably produced unstable hydrogeological systems that were not conducive to dolomitization. More importantly, these sea level changes would have caused mineral stabilization and cementation; both would make the sediments/rocks more resistant to dolomitization.

Mechanism of Fluid Flow

At present, the aquifers of the Bluff Formation are characterized by heterogeneous ground water flow because of dolomitization and karstification. During the initial stage of ground water lens development resulting from island emergence, ground water flow through the poorly lithified sediments was probably predominantly intergranular. Furthermore, the fresh water lens was probably poorly developed and at an incipient stage

of formation (Fig. IX.2). However, regardless of the differences in flow characteristics between the pre-dolomitized sediments and the present day dolostone aquifers, the flow regimes of the two hydrogeological systems are probably similar (cf. Figs. II.19, IX.2).

In order for the hydrogeological system to be effective in dolomitizing the sediments/rocks, it is important that the flow regime be operative over a long period of time. Flow mechanisms (Fig. IX.2) that were responsible for delivering the Mg^{2+} and CO_3^{2-} for dolomitization of the Bluff Formation probably included (1) downward gravitational flow, (2) downward reflux, (3) upward convection, (4) tidal pumping, and (5) diffusion.

Downward gravitational flow of rain water recharge (Fig. IX.2) is a function of the hydraulic head, which is, in turn, dependent on the rainfall quantity and intensity, land area, topographic relief, and permeability of the sediments/rocks (Figs. II.6, 8, 9, 10). Rain water recharge is important in providing the additional CO_3^{2-} through dissolution of calcium carbonate in the vadose and/or phreatic zone, particularly the selective dissolution of aragonitic skeletal components. Dilution of sea water by rain water reduces the thermodynamic drive for dolomitization; however, it significantly reduces the kinetic constraints that inhibit dolomitization through SO_4^{2-} dilution, CO_3^{2-} increase, and organic oxidation. Furthermore, the lower sea levels in the past also increased the topographic relief of the islands, and hence, the hydraulic head for the ground water flow.

Downward reflux of saline water concentrated by evaporation occurs in shallow water ponds and in shallow carbonate bank/shelf (Fig. IX.2). Reflux of hypersaline brines due to density difference (Adams and Rhodes, 1960) and elevation head differential (Hsu and Siegenthaler, 1969; McKenzie, 1980) have been described for sabkha and hypersaline lagoon settings. Sass and Katz (1982) and Bein and Land (1983) documented downward reflux of sea water to slightly hypersaline fluids on shallow carbonate platforms and broad shelves respectively. Simms (1984) suggested that reflux may occur with sea water of only slightly elevated salinity on modern carbonate platforms. In the case of the Cayman

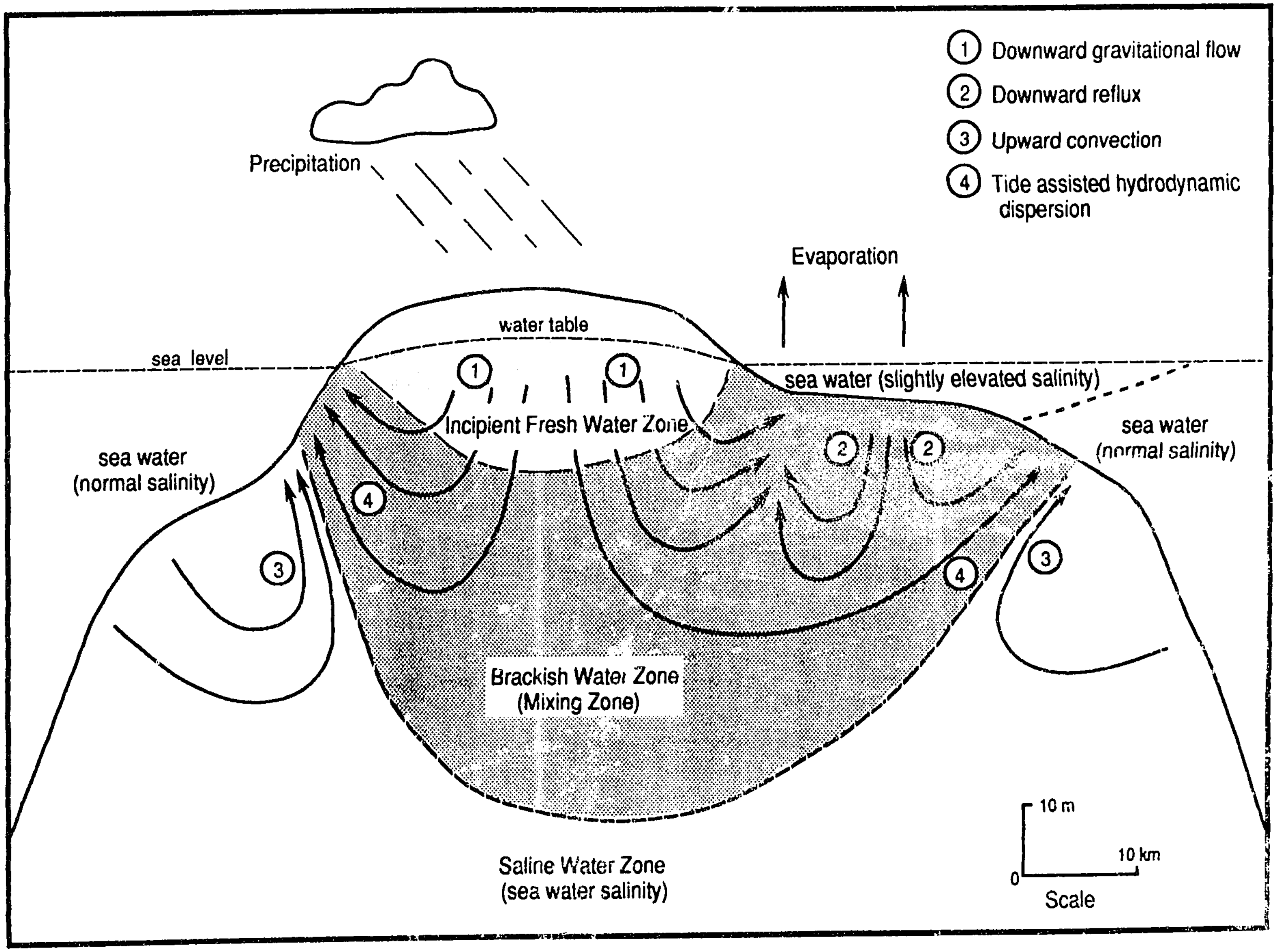


Fig. IX.2 Schematic diagram showing ground water flow regime in an emerging landmass.

Islands, the rain water recharge would have reduced the density of the pore waters and should facilitate this downward flow of sea water and/or saline water.

Upward convection of thermally circulated sea water was originally documented by Kohout (1967) and Kohout *et al.* (1977) in the Floridan aquifer. This thermal convection model, a means of conveying geothermally heated sea water for dolomitization of calcium carbonate, has been proposed for the west coast of Florida (Fanning *et al.*, 1981), Enewetak Atoll (Saller, 1984) and the atoll of Niue Island (Aharon *et al.*, 1987). In these studies, the upward convectional flow of sea water was confirmed by geochemical data. Simms (1984) suggested that convective flow should be present in all steep marginal platforms where there is a strong horizontal pore water density gradient between warm water in platform interiors and surrounding sea water. On the Cayman Islands, it is difficult to determine whether or not there was a heat source at times of dolomitization. The proximity of the Cayman Islands to the mid-oceanic rise, however, suggests the possibility of some forms of heat flow in the past. Fluid density gradient resulting from thermal effect, however, may be caused by the salinity reduction of pore fluids in the aquifers due to rain water recharge on the landward side (Fig. IX.2).

Tidal pumping of Florida Bay sea water has been suggested as the mechanism for the dolomitization of small scale supratidal crusts on Sugarloaf Key of Florida (Carballo *et al.*, 1987). The effect of tidal fluctuation on the ground water system of the Cayman Islands (Figs. II.17, 18) is well exemplified by the thick transition zone (brackish water) developed between the fresh water and the underlying saline water (Figs. II.12, 19). The transition zone of brackish water is formed as a result of tide-generated hydrodynamic dispersion (Fig. IX.2; Cooper, 1964; Kohout, 1964). The ground water table fluctuates in response to semi-diurnal and seasonal tides. The inflow of sea water into the aquifer is a function of the tidal amplitude, and time lag between the sea water and ground water tide (Table II.2). The latter is inversely related to the permeability of the aquifer.

Diffusion of Mg^{2+} from sea water through the sediments is a very slow and ineffective pumping mechanism (Land, 1985; Hardie, 1987). Using a Mg mass balance calculation, Compton and Siever (1986) concluded that Mg^{2+} diffusion from overlying sea water can account for the early diagenetic dolomite (0.5-20% by volume) formed in the uppermost 100 m of the Monterey Formation, Santa Maria basin area of California. Although diffusion alone is probably not able to cause pervasive dolomitization, it is a viable mechanism of supplying Mg^{2+} to the accumulating sediments. These early dolomites may act as seed crystals for pervasive dolomitization at a later stage.

Synopsis

Mixed fresh-marine water, which has fewer kinetic barriers, remains a viable medium for dolomitization. The fresh water recharge also creates density gradients in the flow system to facilitate ground water movement through the sediments/rocks. The diagenetic fluids that caused the pervasive dolomitization of the Bluff Formation were probably sea water that was modified to a certain extent by rain water during an early stage of land emergence in late Oligocene (for the Cayman Member) and late Miocene (for the Pedro castle Member) times. Stable oxygen isotopic results suggest that the degree of meteoric influence ranges from 0 to 75% fresh water by volume depending on the fractionation equations used and temperatures of the diagenetic fluids (Fig. VII.3). The flow mechanism (Fig. IX.2) was similar to that at present, but the fresh water lenses were probably irregularly distributed. It is also important to note that higher land relief in the past, due to lower sea levels, would have facilitated fluid movement through the sediments/rocks by increasing the hydraulic gradient.

Meteorological records on Grand Cayman for the last twenty years have shown appreciable changes in rainfall, temperature, and the amount of sunshine (Figs. II.7, 11). The paleoclimatological regimes might play a role in reducing some of the kinetic constraints so as to promote dolomitization. Kastner (1984, 1988) and Land (1985) also

suggested that the SO_4^{2-} content and the Mg/Ca ratio of sea water might have changed throughout geological time. All of these would have a significant impact on the nature of the mixed water environment.

X. DIAGENETIC INTERPRETATION OF THE BLUFF FORMATION II: KARSTIFICATION

The Bluff Formation has undergone numerous stages of karstification as a result of sea level fluctuations since late Oligocene times (Jones and Smith, 1988). This study (1) identifies the stages of karst development, (2) highlights the chemical equilibria, kinetic concepts and biological effects on carbonate dissolution, and (3) examines the mechanism for karstification.

A. STAGES OF KARSTIFICATION

Jones and Hunter (1989) suggested that the Oligocene Cayman Member of the Bluff Formation was exposed and subjected to karst development during late Oligocene and early Miocene times. Similarly, following regression in late Miocene times, the Miocene Pedro Castle Member and the underlying Oligocene Cayman Member were also subjected to karsting (Jones, 1989a). Frequent fluctuations of sea level in the Caribbean region during late Pleistocene times (Mesolella *et al.*, 1969; Bender *et al.*, 1973; Steinen *et al.*, 1973; Neumann and Moore, 1975; Harmon *et al.*, 1978) means that karst formation has been an ongoing process.

Precise dating of the different stages of karstification is difficult because each stage of karst development further modified the inherited karst features. Stringfield *et al.* (1979) noted that in areas where paleokarst is not too deeply buried, it may be incorporated into present circulation systems such as the artesian aquifer of Tertiary age in southeastern Georgia and Florida. Thus, the present day hydrogeological regime is the end product of numerous past and the present karst processes. It is also difficult to assess the depth of karstification in response to each base (sea) level change because of the overlapping karst effect. Furthermore, changes in the surface and ground water drainage began as soon as the carbonate rocks were elevated above sea level and circulation was established (Stringfield and LeGrand, 1971; Longman, 1980).

Jones and Smith (1988) suggested that some cave formations post-dated dolomitization of the Bluff Formation because the caves cut through dolomitized cavity fills and unaltered speleothemic calcite. The exposures of Miocene Pedro Castle Member give no indication of karst development (Fig. X.1); however, this may simply be due to limited number of outcrops. The different periods of karst development (Fig. VIII.1) on the Bluff Formation can be termed Phase I' (late Oligocene to early Miocene), 'Phase II' (late Miocene to early Pliocene), and 'Phase III' (late Pliocene to late Pleistocene).

Speleothemic precipitation and internal sedimentation may partly or completely fill many caverns and fissures on the Cayman Islands (Lockhart, 1986; Smith, 1987; Jones and Smith, 1988). On the basis of the type and amount of cave fills, the cave systems in the Oligocene Cayman Member of the Bluff Formation can be divided into four categories (Figs. X.1, 2):

(1) Caves filled with completely dolomitized caymanite (colour banded) and/or skeletal grainstone, which may or may not be overlain by undolomitized flowstone and/or terra rossa (Figs. X.1, 2). Examples of Type 1 cave systems include caves exposed in Pedro Castle Quarry on Grand Cayman and caves cut by Faith Caves opposite Faith Hospital on Cayman Brac (Figs. X.2, 3).

(2) Caves filled with undolomitized flowstone and terra rossa but no caymanite (Figs. X.1, 2). Examples of Type 2 cave systems include caves exposed in Pedro Castle Quarry, caves cut by Pirates Caves near Bodden Town on Grand Cayman and caves cut by Great Caves near Pollard Bay on Cayman Brac (Figs. X.2, 3).

(3) Caves partially filled with assorted speleothems such as flowstones, stalactites, stalagmites, terraced rimstones, and cave pisoliths (Fig. X.2). Examples of Type 3 cave system include Old Man Bay Caves near Old Man Bay Village on Grand Cayman, Great Caves near Pollard Bay, Hurricane Caves near Spot Bay and Salt Water Point Caves on Cayman Brac (Fig. X.3).

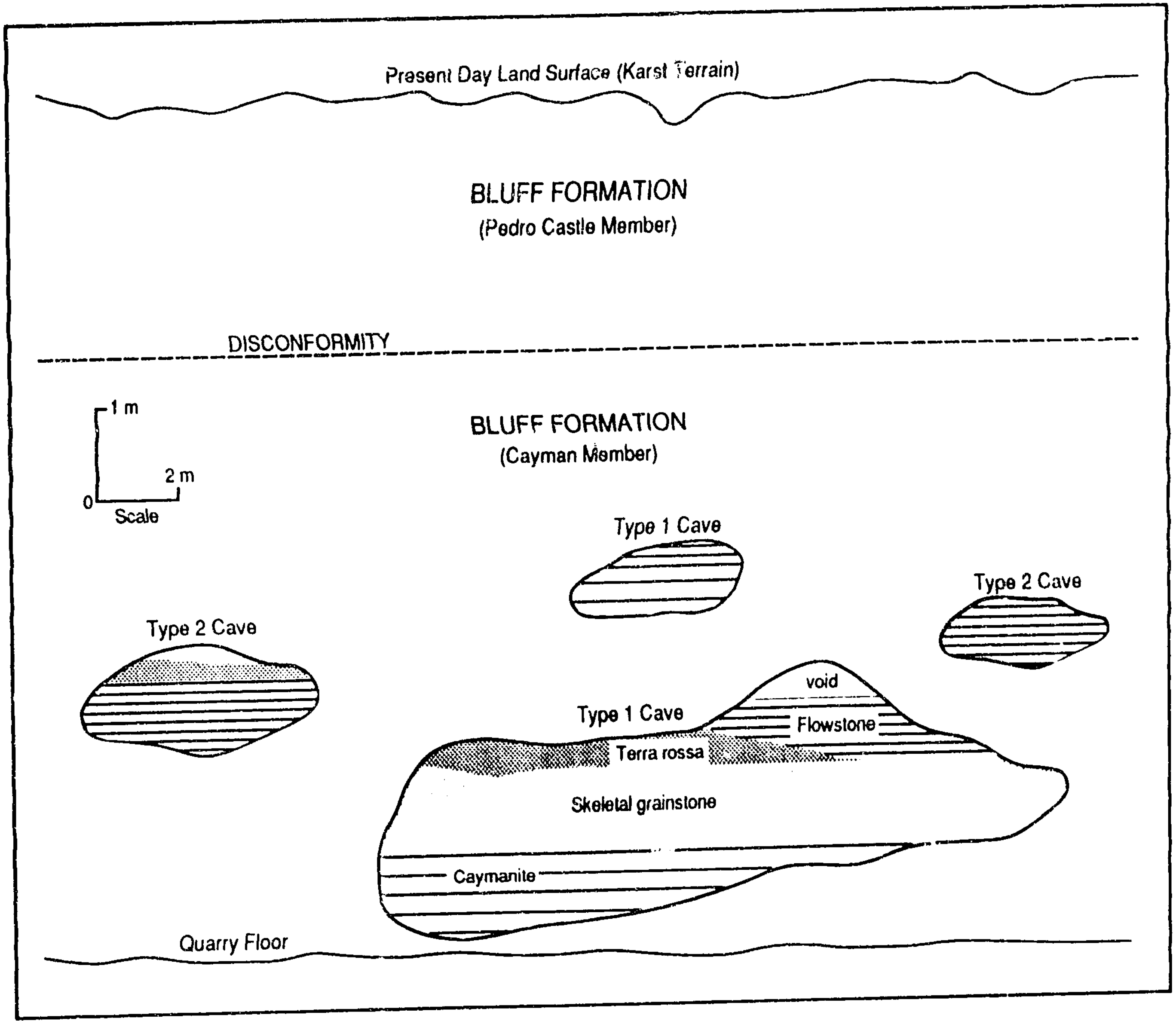


Fig. X.1 Schematic diagram of quarry wall exposure at Pedro Castle Quarry on Grand Cayman showing cavity fills in Type 1 and 2 cave systems.

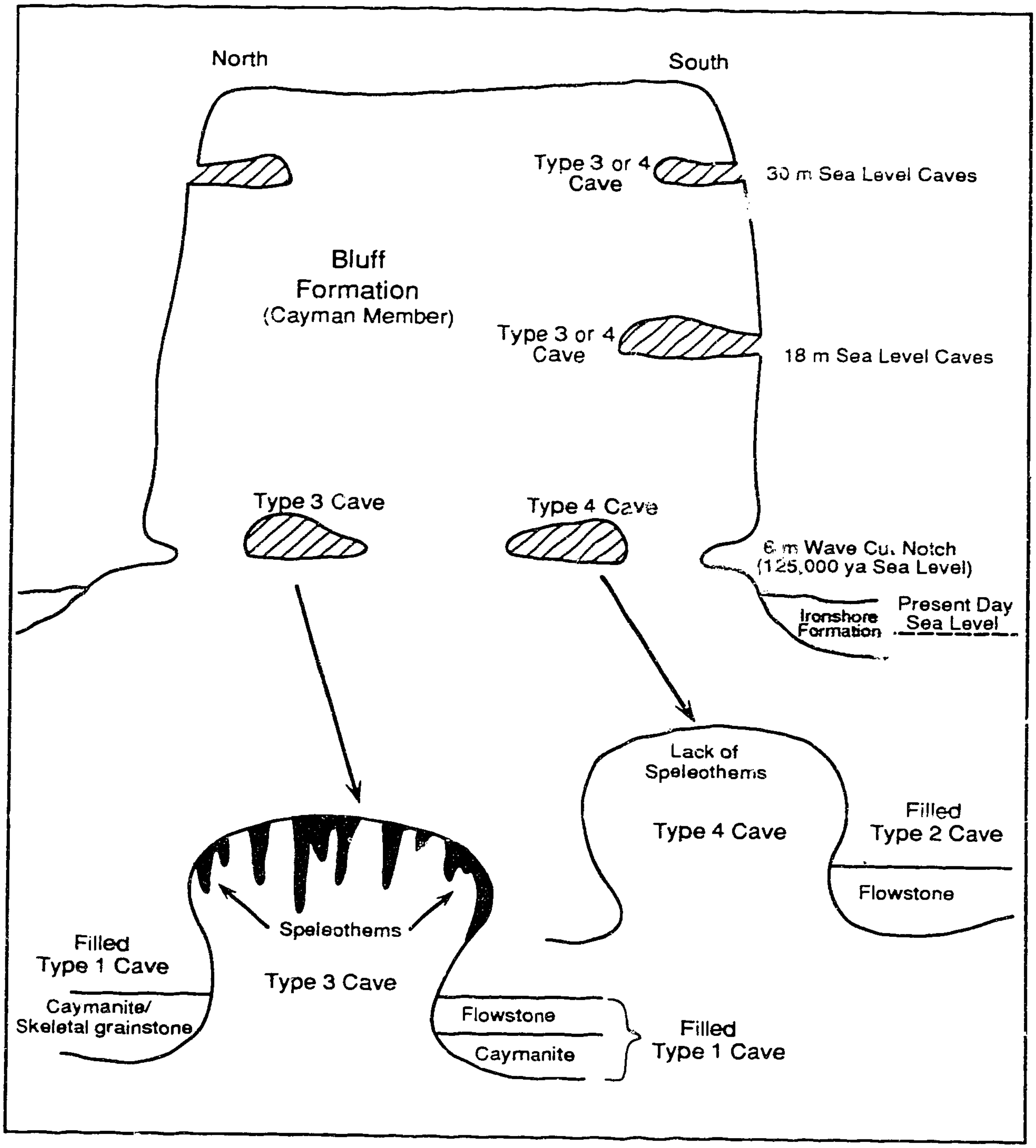


Fig. X.2 Schematic north-south cross-section of Cayman Brac showing the different levels of sea level caves and the four types of cave systems. Diagram not in scale.

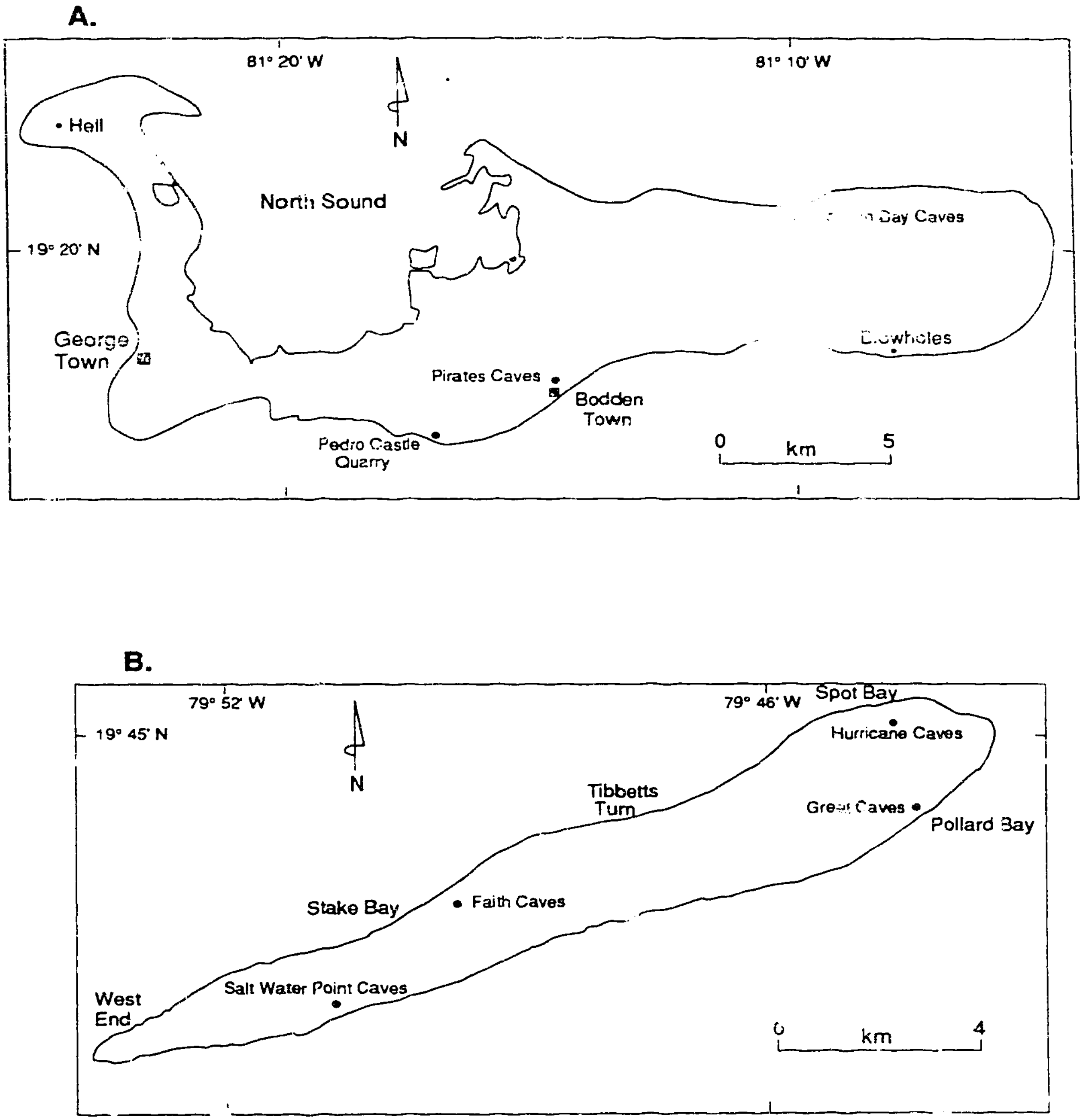


Fig. X.3 Sketch map of (A) Grand Cayman and (B) Cayman Brac showing localities of caves cited in text.

(4) Open caves with no speleothems but commonly floored with terra rossa (Fig. X.2). Examples of Type 4 cave system include Pirates Caves on Grand Cayman and Faith Caves on Cayman Brac (Fig. X.3).

The first two types (Type 1 and 2) of cave are generally less than 20*5 m^2 in vertical section (observed in quarry wall of Pedro Castle Quarry) and do not appear to form extensive cave networks. Conversely, the last two types (Type 3 and 4) commonly measure up to 5*5 m^2 in cross section and form extensive networks of cave passages (in the order of km) and chambers.

Type 1 caves probably formed during late Oligocene to early Miocene times when the Cayman Member was subaerially exposed due to sea level drop. The timing of their formation is inferred from the presence of caymanite fill because Jones and Hunter (1989) noted that caymanite probably entered the cave system prior to the deposition of the middle Miocene Pedro Castle Member (Jones and Hunter, 1989). Thus, the Type 1 caves are related to the 'Phase I' karst development (Fig. VIII.1).

Dating of Type 2 caves is problematic. The absence of dolomitized caymanite suggests that the Type 2 caves might have formed in late Miocene to early Pliocene times when the strata was again exposed in response to sea level drop. If so, the Type 2 cave system might be related to the 'Phase II' karst development (Fig. VIII.1). However, the absence of caymanite may be the result of blockage of solution channels that prevented the influx of internal sediments.

Type 3 and 4 cave systems are clearly younger than Type 1 and 2 caves because they cut through the latter two systems (Fig. X.2; e.g. Old Man Bay Caves and Pirates Caves on Grand Cayman, and Faith Caves and Great Caves on Cayman Brac). They also cut through the undolomitized flowstones in Type 1 and 2 caves suggesting that Type 3 and 4 cave formation were post-dolomitization. The youngest dolomitization age given by the Sr isotopic data (Table IX.1) is 2.0±0.5 Ma, which implies that the caves probably formed

in Pleistocene times. Type 3 and 4 cave systems appear to be genetically related because the two types of cave can be traced along the same horizon on Cayman Brac. Some caves developed at the wave-cut notch about 6 m above present day sea level (Jones and Ng, 1988a, Jones and Smith, 1988). Jones and Smith (1988) also suggested that the wave cut notch probably developed when the carbonate sediments of the Ironshore Formation were deposited about 125,000 years ago (Woodroffe *et al.*, 1983). Thus, it can be postulated that the Type 3 and 4 caves that are associated with the 6 m wave-cut notch probably formed in the late Pleistocene. On Cayman Brac, two other levels of caves, formed at about 18 m (e.g. Great Caves) and 30 m (e.g. Hurricane Caves) above present day sea level, probably belong to the Type 3 and/or 4 categories (Fig. X.2). They are either open or partially filled with speleothems. The horizontal orientation of the cave passages probably indicates former sea level high stands or earlier tectonic uplift of the island. It appears that the latter proposition is more reasonable because eustatic sea levels in the last 125,000 years (Mesolella *et al.*, 1969; Bender *et al.*, 1973; Steinen *et al.*, 1973; Bloom *et al.*, 1974; Ku *et al.*, 1974; Neumann and Moore, 1975; Harmon *et al.*, 1978) were lower than the sea level high stand 125,000 years ago. Thus, it appears that most of the sea level caves are correlated to the 'Phase III' karst development (Fig. VIII.1).

Other evidence of cave development is present in the Oligocene Cayman Member. On Cayman Brac, a cavern 2 m in height, encountered by well B5 (Fig. VI.2) at about 20 m above present sea level, may be correlatable with the sea level cave at about 18 m. Similarly, the perched water lens in well B1 (Fig. VI.2), at about 3.5-10 m above present sea level, may be related to the wave-cut notch at 6 m. Deep well drilling (> 20 m) on the western part of Grand Cayman (Fig. III.2) commonly encountered large caves at about 25-40 m below present sea level, which may correspond with the submerged wave-cut notch at about 21 m below present sea level. Therefore, most of the Type 3 and 4 cave development is probably related to the various levels of sea level high in late Pleistocene.

However, the relationship between sea level elevation and the Type 1 and 2 cave systems is difficult to define.

Cave development in association with the sea or base levels has been noted in many areas. Different levels of cave development effected by changes in Pleistocene sea level were recorded in the Ingleborough district of England (Sweeting. 1950), in Peloponnesus, Greece (Burdon, 1967), on the southern coast of Australia (Jenning, 1963) and on the south coast of Tallahassee, Florida (Stringfield, 1966). Similarly, distinct levels of horizontal cave passages resulting from changes in base level were documented in the southwest Edwards Plateau of Texas (Kastning, 1983) and in Dejiang, Guizhou Province of China (Song *et al.*, 1983).

In addition to the effect of past sea level high stands, the extensive networks of Type 3 and 4 cave systems are probably related to solution features preferentially developed along joints and fractures in a manner suggested by Ford and Ewers (1978) and Ford (1988). If so, a phase of intense joint development probably occurred prior to Type 3 and 4 cave formation but after Type 1 and 2. The lack of extensive networks in Type 1 and 2 caves, however, may be indicative of a different climatic regime or of a much lower sea level in late Oligocene times which exposed the rocks predominantly to the vadose zone.

Jointing is a multi-phase phenomenon (Fig. VIII.1). Joints of different attitudes contained diverse fills. The best example is illustrated by the joint sets exposed near Blowholes on Grand Cayman (Figs. II.14, X.3A). The north northwest - south southeast oriented vertical joints commonly remain open whereas the east northeast - west southwest oriented vertical joints commonly filled with flowstones and terra rossa/terra rossa breccia. Conversely, the gently dipping (about 30° to the north-west), northeast -southwest oriented joints commonly filled with caymanite, terra rossa and/or rarely flowstones. Jones (1989, per. comm.) also noted that the east northeast - west southwest oriented joints exposed on Queen's Road (north coast) on Grand Cayman also contained dolomitized breccia. There appears to be a relation between joint and karst development (Table X.1) in that (1) the

Table X.1 Relationship between joint and karst development based on type of fills.

PHASE	JOINT TYPE & FILL	CAVE TYPE & FILL	RELATIVE TIMING
Phase III Late Pliocene to Late Pleistocene	NNE-SSW/Vertical — Open	Type 4 — Open Type 3 — Assorted Speleothems	Post - Dolomitization
Phase II Late Miocene to Early Pliocene	ENE-WSW/Vertical — Flowstone Terra Rossa	Type 2 — Flowstone Terra Rossa	
Phase I Late Oligocene to Early Miocene	NE-SW/30°NW — Caymanite Flowstone (rare) Terra Rossa	Type 1 — Caymanite Skeletal Grainstone Flowstone Terra Rossa	Pre - Dolomitization

Type 1 cave fills are similar to those in the northeast-southwest trending joints, (2) the Type 2 cave fills are similar to those in the east northeast - west southwest trending joints, and (3) both the Type 4 caves and the north northwest - south southeast trending joints remain open. Thus, the similarity in joint and cavity fills may be an indication of related timing of the phases (Phase I, II, and III) of joint development with that of the karst formation (Fig. VIII.1, Table X.1). This genetic relationship supports the argument that jointing/fracturing is one of the pre-requisite parameters for cave formation, providing avenues for fluid flow, and hence, carbonate dissolution. It is also important to note that filling of joints is an active process that is ongoing at the present time. Some open joints at Hell on Grand Cayman (Fig. X.3A) are presently being filled by swamp sediments.

B. CHEMICAL EQUILIBRIA OF CARBONATE DISSOLUTION

Using chemical equilibrium concepts, speciation calculations of ground waters in the aquifers of the Bluff Formation indicate that the waters in all hydrochemical zones are capable of dissolving or precipitating carbonates, depending on their chemical properties. Some fresh water samples from the Lower Valley lens are undersaturated with respect to both calcite and dolomite (Table IV.5). The low Mg/Ca ratio of the Lower Valley fresh ground water suggests that influx of calcium enriched ground water from the limestone aquifer of the Ironshore Formation and subsequent mixing with the ground water in the Bluff Formation may be the cause of the undersaturation. Furthermore, it has also been demonstrated by artificial injection that rapid rain water recharge through open fractures can cause significant undersaturation at the water table zone (Table IV.19). The shallow water zone is also most likely to receive CO_2 from the respiration of plant roots and organic decay. The corrosiveness of the ground water acts according to the simplified reactions:

$$CO_2 + H_2O = H^+ + HCO_3^-$$

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^-$$

$$CaMg(CO_3)_2 + 2H^+ = Ca^{2+} + Mg^{2+} + 2HCO_3^-$$

In the brackish water (mixed water) zone, undersaturation with respect to carbonate minerals (Table IV.8) probably results from periodic influx of CO_2-ladened water from the surrounding mangrove swamps or from decomposition of organic materials in the aquifers.

C. CHEMICAL KINETICS OF CARBONATE DISSOLUTION

In the ground water systems of the Cayman Islands, the temporal and spatial variation of the ground water chemistry (Tables IV.10, 16, 17, Figs.II.10, III.1, III.5-10) suggests that most of the hydrochemical reactions in the aquifers have not reached thermodynamic equilibrium. Berner (1978) suggested that under earth surface conditions, mineral dissolution is governed by surface chemical reactions. Wigley and Plummer (1976) also demonstrated that the rate of calcite dissolution in natural environments depends on the hydrodynamics of the mineral-water system and the reaction kinetics at the mineral surface.

Weyl (1958) concluded that the rate of limestone dissolution is controlled by diffusion of Ca^{2+} from the surface. Weyl's (1958) results showed that water entering the rocks quickly becomes saturated with respect to calcite, with a saturation length (penetration distance before water reaches calcite saturation state) in the order of a few centimetres. The first comprehensive treatment of solution kinetics of $CaCO_3$ in the H_2O-CO_2 system was the theoretical model of Plummer *et al.* (1978, 1979) where the rate of calcite dissolution (Rc) is given as:

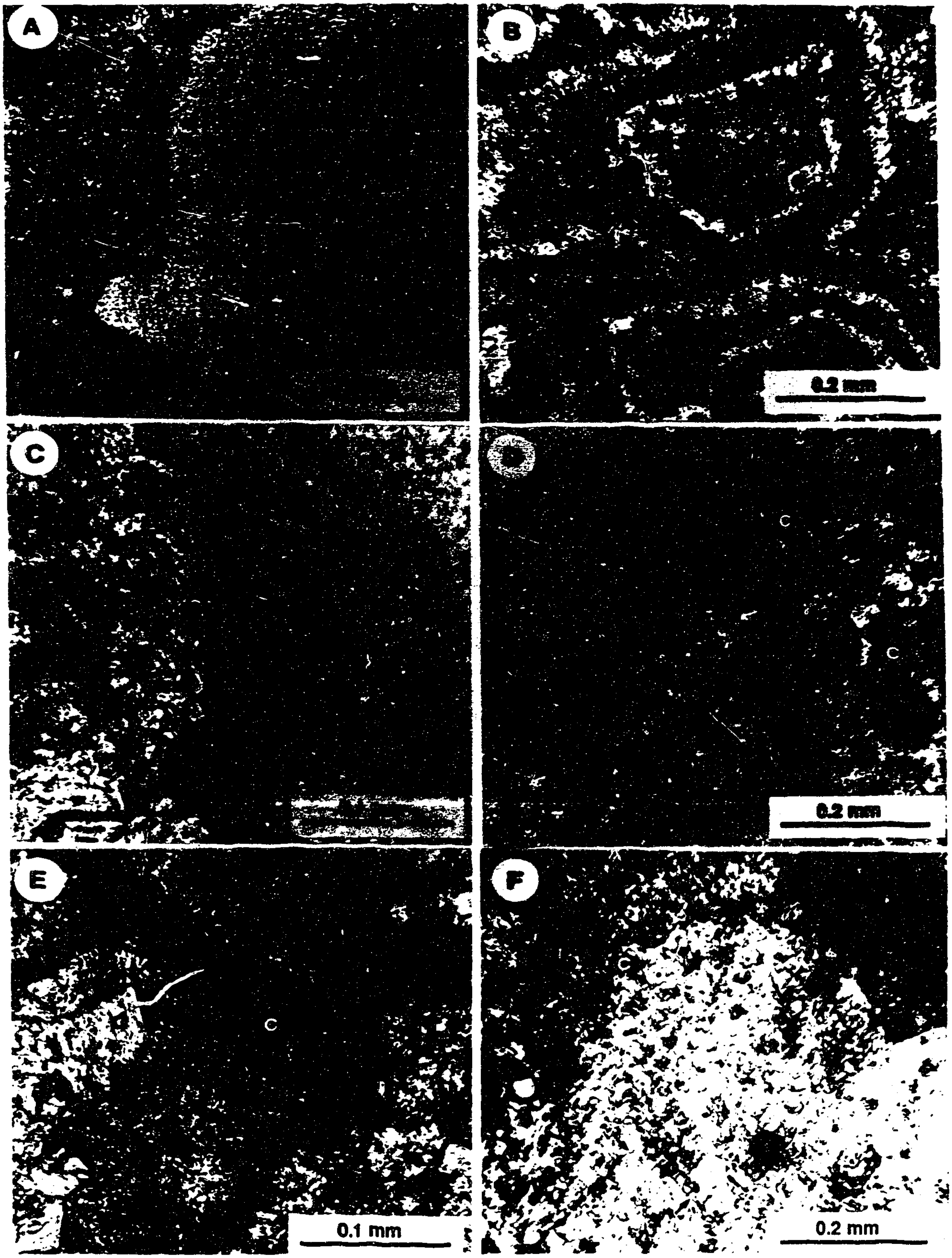
$$Rc = k_1[H^+] + k_2[H_2CO_3] + k_3[H_2O] - k_4[Ca^{2+}][HCO_3^-] \quad ....(1)$$

where k_1, k_2 and k_3 are the forward rate constants which are temperature dependent, k_4 is the backward rate constant depending on both temperature and P_{CO_2}. Three mechanistic reactions for k_1 through k_3 are:

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^-$$

$$CaCO_3 + H_2CO_3 = Ca^{2+} + 2HCO_3^-$$

$$CaCO_3 + H_2O = Ca^{2+} + HCO_3^- + OH^-$$


A
B
0.2 mm
C
D
C
C
0.2 mm
E
C
0.1 mm
F
C
0.2 mm

Some calcite spar cements are zoned with individual zones separated by a thin (1 µm), dark coloured band of clay or organic materials (Plate VI.3E). Rarely, partial dissolution of the sparry calcite also occurs, with preferential dissolution along the cleavage planes (Plate VI.3F).

Alternating Zones of Dolomite and Calcite

Cements composed of alternating zones of dolomite and calcite occur in two forms. The first type consists of alternating zones of about 10 µm thick that are laterally continuous from crystal to crystal (Plates VI.4A, 4B). The calcite band appears to follow the outlines of the preceding dolomite crystals and is subsequently encased by a further zone of dolomite (Plates VI.4A, 4B).

The second type of alternate zoning of dolomite and calcite occurs in a single crystal (Plates VI.4C, 4D). The zoned cements are probably equivalent to the zoned dolomite-calcite cements described by Jones *et al.* (1984). Commonly, the core of the zoned crystals is clear dolomite. In most cases, these zoned crystals were encased by poikilotopic calcite (Plate VI.4D).

Poikilotopic Calcite-Dolomite

Poikilotopic calcite that encases dolomite cement and matrix dolomite produced fabrics comparable to those considered indicative of dedolomite by Shearman *et al.* (1961), Evamy (1967) and Katz (1971). The poikilotopic calcite-dolomite fabrics in the Bluff Formation include (1) hollow zones in dolomite rhombs (Plate VI.5A), (2) calcite zones and cores in dolomite rhombs (Plates VI.5A, 5B, 5C, 5D), and (3) rounded and corroded outlines of dolomite crystals (Plates VI.5B, 5C). Where matrices have two distinct crystal sizes, poikilotopic calcite preferentially replaced the smaller dolomite crystals (Plates VI.5A, 5E).

PLATE VI.4

Photomicrographs of alternating dolomite and calcite cement. All depths are measured from land surface.

(A) and (B) Alternating zones of dolomite (d) and calcite (c) that are laterally continuous from crystal to crystal. Note indistinct intercrystalline boundaries. Rock cutting from West Bay Road well #1 in the highly brackish water zone at a depth of about 12.5 m.

(C) Alternating zones of dolomite (d) and calcite (c) in individual crystals. Rock cutting from Cayman Brac well K1 in the unsaturated zone at a depth of about 9 m.

(D) Alternating zones of dolomite (d) and calcite (c) in individual crystals which were subsequently encased by poikilotopic calcite (pc). Sample from East End core #1.22 in the fresh water zone at a depth of about 5 m.


A
B
0.1 mm
0.1 mm

PLATE VI.5

Photomicrographs of poikilotopic calcite-dolomite fabrics. All depths are measured from land surface.

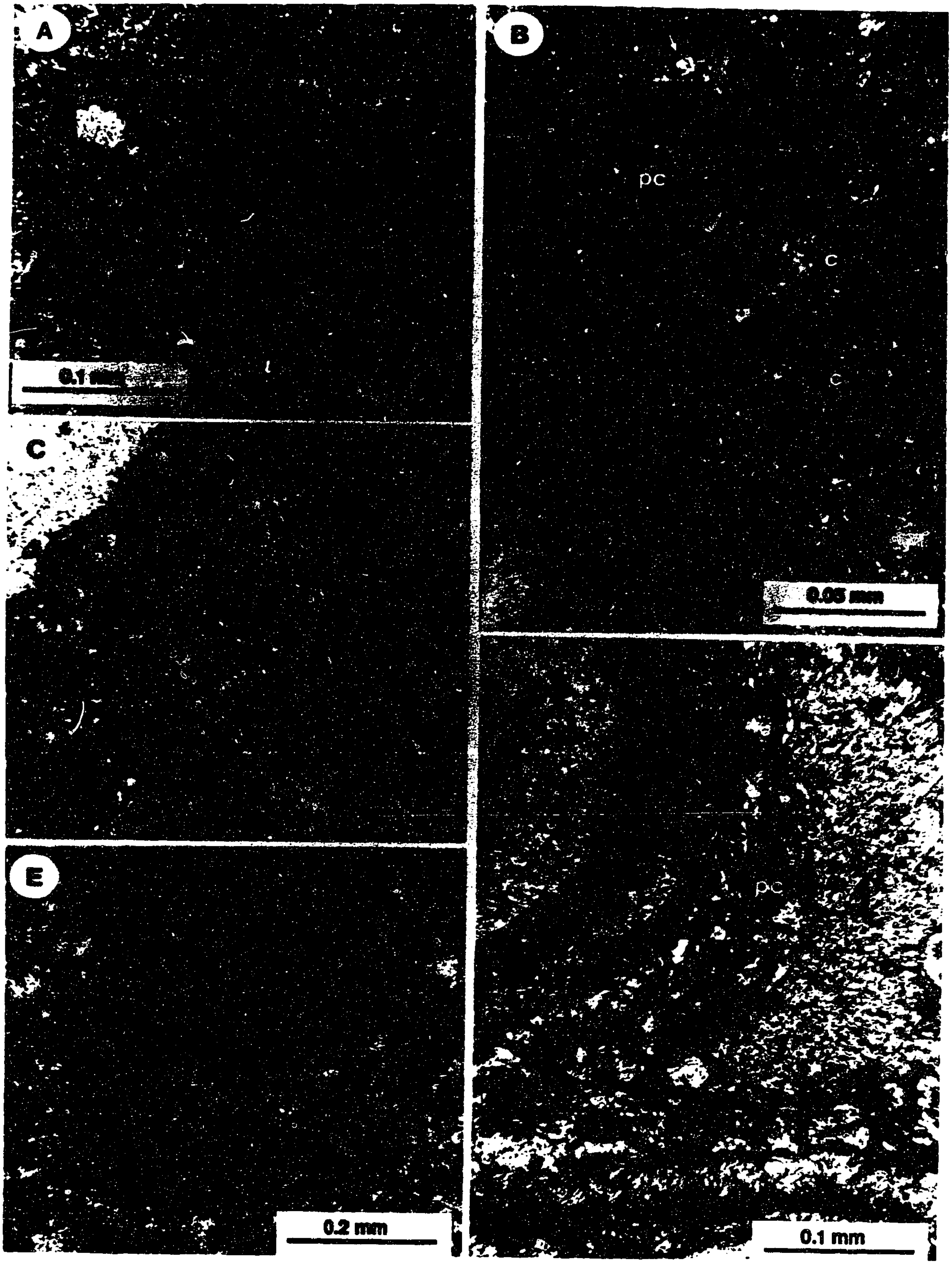
(A) Clear, euhedral dolomite rhombs (d) with hollow cores (h). Rock sample from weathered dolostone outcrop, Lower Valley.

(B) Matrix dolomite crystals (d) with calcite cores and calcite zones (c). Note corroded outline of dolomite (arrows) encased by poikilotopic calcite (pc). Rock sample from Lower Valley trench well at the water table zone at a depth of about 1.5 m.

(C) Dolomite spar (d) replaced and encased by poikilotopic calcite (pc). Rock cutting from Cayman Brac well B2 in the unsaturated zone at a depth of about 9 m.

(D) Dolomite cement zone (arrows) replaced by poikilotopic calcite (pc). Note remnants of dolomite zones (d). Rock cutting from West Bay Road well #1 in the highly brackish water zone at a depth of about 24 m.

(E) Poikilotopic calcite (pc) preferentially replaced smaller sized matrix dolomites (m), leaving coarser euhedral dolomite unreplaced (d). Rock core from Lower Valley well 5-82 in the highly brackish water zone at a depth of about 3 m.


A
0.1 mm
B
pc
c
c
0.05 mm
C
E
0.2 mm
pc
0.1 mm

Internal Sediments

Caymanite is a microcrystalline dolomite characterized by (1) white, orange/red and black colour bands (Fig. 11 of Lockhart, 1986), (2) tightly interlocking anhedral dolomite crystals (Plates VI.6C-6F), (3) angular grains or fragments of dolostone (Plates VI.6C, 6D), (4) geopetal texture (Plates VI. 6E, 6F), and (5) cross bedding, and (6) cut and fill channels (Fig. 12 of Lockhart, 1986). Rare examples a[illegible] contain foraminifera and gastropods.

The laminae of the caymanite, when viewed under the petrographic microscope, show slight differences in the amount of darker-coloured matrix (<0.02 mm) and lighter-coloured angular grains and rock fragments. The grains and fragments are dolostone from 0.02 to 0.50 mm long in thin sections (Plate VI.6C) and up to 50 mm long in field samples. Some angular rock fragments were probably the end result of removal of irregular projections from the underlying bedrock (Plate VI.6D).

Another form of internal sediment is dolomitized skeletal grainstone, which commonly deposited on top of the caymanite. In places, the white coloured grainstone is poorly lithified with high original porosity. The skeletal component is predominantly foraminifera which appear to be leached. Fragments of red algae are also common.

The relationship between the caymanite and other cavity fills include (1) caymanite sedimentation prior to dolomite cementation (Plate VI.6E), (2) dolomite cementation prior to caymanite deposition (Plate VI.6F), (3) sparry calcite precipitation after caymanite sedimentation (Plate VI.6F), (4) flowstone precipitation and terra rossa influx after caymanite sedimentation, and (5) caymanite sedimentation prior to influx of skeletal grainstone.

Terra Rossa

Terra rossa present in the Bluff Formation is formed of organic-rich glaebules embedded in microcrystalline carbonate and clay matrix (Plate VI.6A). The glaebules are

PLATE VI.6

Photomicrographs of cavity fills (terra rossa, caymanite and flowstone). All depths are measured from land surface.

(A) Two phases of terra rossa fill. One phase is characterized by dark, organic rich glaebules (g) embedded in the microcrystalline calcium carbonate matrix, whereas the other phase is characterized by light coloured glaebules. Rock cutting from Cayman Brac well B2 in the unsaturated zone at a depth of about 3 m.

(B) Dolomite cement (d) followed by terra rossa breccia (b). Note the angular dolostone fragments (f) in the terra rossa. Rock cutting from Cayman Brac well B5 in the unsaturated zone at a depth of about 27 m.

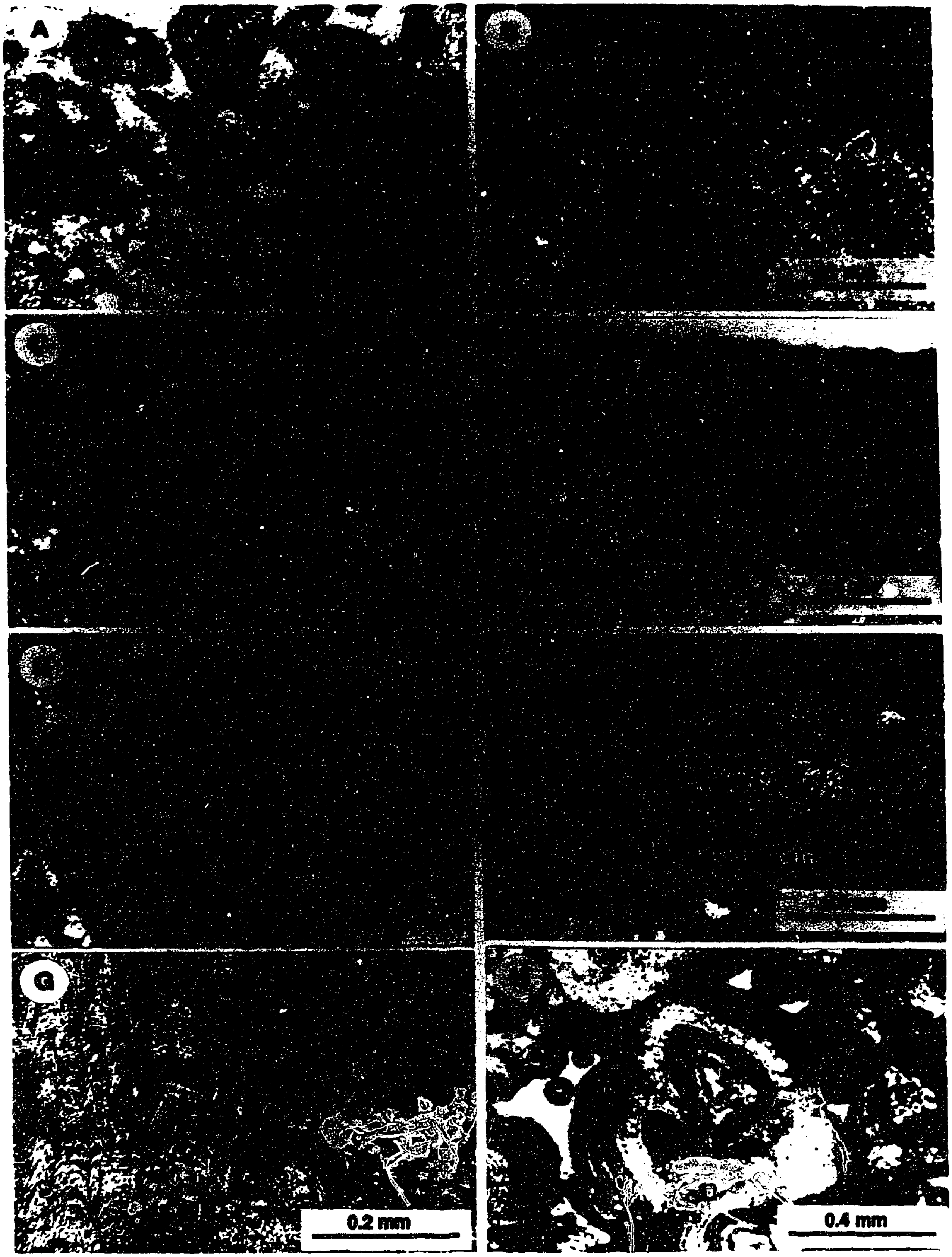
(C) Caymanite sample showing bands resulting from differences in matrix dolomite crystal sizes and content of angular dolostone fragments (f). Sample from East End core #1.15 in the fresh water zone at a depth of about 4 m.

(D) Cavity partially filled by caymanite (cm). Note the angular dolostone fragments (f) apparently ripped from the cavity wall. Sample from East End core #7.22 in the fresh water zone at a depth of about 13 m.

(E) Caymanite (cm) in cavity of coral structure showing geopetal texture, which was followed by euhedral dolomite cement (d). Sample from East End core #5.2 in the fresh water zone at a depth of about 10 m.

(F) Dolomite cementation (d) prior to caymanite sedimentation (cm) with the rest of the cavity subsequently filled by sparry calcite (c). Sample from East End core #3.2 in the fresh water zone at a depth of about 7 m.

(G) and (H) Longitudinal and cross section view of a flowstone sample showing the laminated, columnar calcite crystals (G) and trigonal crystal morphology (H). Note dark inclusion rich growth bands (arrows). Rock cutting from Cayman Brac well B6 in the unsaturated zone at a depth of about 3 m.


A
G
0.2 mm
0.4 mm

made up predominantly of clay minerals with minor calcium carbonate. Terra rossa breccia (Plate VI.6B), which has dolostone fragments embedded in the soil, is common in some cavities and open joints. Commonly, the less well consolidated terra rossa is red in colour whereas the well consolidated terra rossa is brown in colour. However, it is important to note that there are many different colour shades in the consolidated terra rossa. Some cavities were filled by two phases of terra rossa that differ in colour and the amount and size of the glaebules (Plate VI.6A). In places, dolomite cementation preceded the emplacement of terra rossa in the cavity (Plate VI.6B).

Flowstone

Brown, banded flowstone, formed of columnar calcite (Plates VI.6G, 6H), commonly filled cavities, joints and caverns in the Bluff Formation (Lockhart, 1986; Smith, 1987; Jones and Smith, 1988). Locally, flowstone is intercalated with terra rossa.

D. DISTRIBUTION OF THE CARBONATE CEMENTS IN THE PRESENT DAY HYDROCHEMICAL ZONES

A systematic analysis of the carbonate cementation pattern and distribution in each hydrochemical zone should provide insight into the relationship between the cement fabrics and pore fluids. Of particular importance is the late-phase carbonate cements and the present-day ground waters. This relationship is investigated for each of the present day hydrochemical zones in terms of the paragenetic sequence of the cements present in the rocks, and the type and abundance of the last phase of cement.

Fresh Water Zone

There are distinct differences in the diagenetic fabrics of the Bluff Formation between the Lower Valley and East End lens of Grand Cayman. Carbonate cement fabrics

recognized in **individual** cavities of the rocks sampled from the Lower Valley fresh water zone include:

(1) poikilotopic calcite-dolomite near the water table zone, and

(2) sparry calcite cement (voids rarely lined by dolomite cement).

Carbonate cement fabrics recognized in **individual** cavities of the rocks sampled from the East End fresh water zone include:

(1) dolomite cement followed by sparry calcite,

(2) dolomite cement lining voids (not followed by sparry calcite),

(3) alternating zones of dolomite and calcite,

(4) sparry calcite cement only, and

(5) zoned sparry calcite cement.

In the Lower Valley aquifer, the paragenetic sequence of the cements is simple (Fig.VI.3A). The cavities were rarely lined by dolomite cement. Instead, more than 80% of the cavities were lined or filled by calcite as the only cement phase. The poikilotopic calcite-dolomite, which occurs near the water table zone of the Lower Valley lens (Plate VI.5B), is probably related to near surface influences such as rain water infiltration, and evaporation. In the East End aquifer, the cement types indicates the following carbonate cementation sequence (Fig.VI.3B): (1) clear, euhedral dolomite, (2) zoned dolomite, (3) alternating bands of dolomite and calcite, and (4) clear or zoned sparry calcite.

Petrographic studies indicate that the calcite cement is the most common last phase cement in cavities in the fresh water zone of both the Lower Valley and East End lens (Fig.VI.4). Thus, it may be suggested that calcite cement formed in close association with the fresh ground water.

Lightly Brackish Water Zone (<15% sea water salinity)

Like the rocks in the fresh water zone, there are differences in the diagenetic features between those in the Lower Valley and East End lens. Carbonate cement fabrics

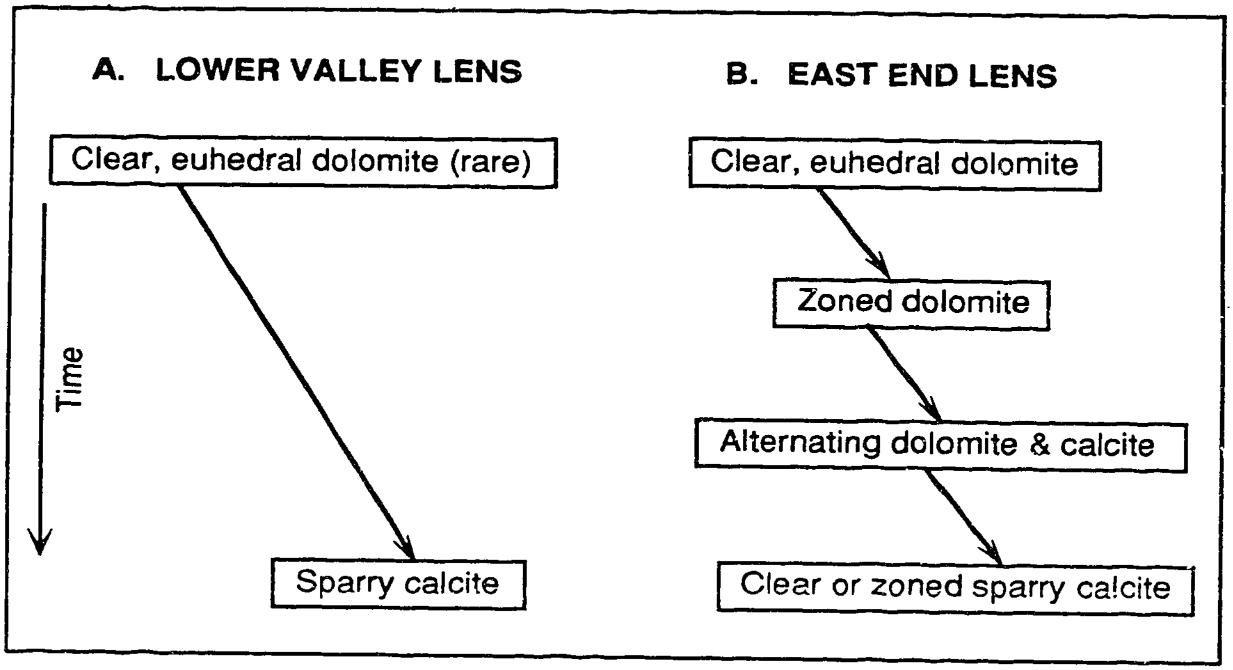


Fig. VI.3 Paragenetic sequence of carbonate cements in the fresh water zone of the (A) Lower Valley and (B) East End aquifers.

LOWER VALLEY	WATER TABLE	EAST END
Poikilotopic calcite-dolomite	Water Table Zone (<1 m)	Sparry calcite
Sparry calcite	Fresh Water Zone Lower Valley lens <10 m East End lens <25 m	
>60% of the cavities have calcite <40% of the cavities have dolomite	Lightly Brackish Water Zone (salinity <15% sea water) Variable Thickness	Dolomite

Fig. VI.4 Types of last carbonate cement phase in the fresh water and lightly brackish water zones of the Lower Valley and East End aquifers.

recognized in **individual** cavities of rocks sampled from the Lower Valley lightly brackish water zone include:

(1) dolomite cement followed by sparry calcite,
(2) dolomite cement with hollow zones or cores, and
(3) sparry calcite cement only.

Carbonate cement fabrics recognized in **individual** cavities of the rocks sampled from the East End lightly brackish water zone:

(1) dolomite cement,
(2) zoned and hollow dolomite, and
(3) open cavities.

In the Lower Valley aquifer, the paragenetic sequence of carbonate cements (Fig.VI.5A) is (1) clear, euhedral dolomite, (2) zoned dolomite (selective leaching of certain zones), and (3) sparry calcite. Approximately 60% of the cavities in the lightly brackish water zone of the Lower Valley lens have calcite as the last phase of cement (Fig.VI.

In the East End lens, calcite cement is not seen in the rocks from the lightly brackish water zone (Fig.VI.5B). All the voids were lined by clear, euhedral dolomite cement or zoned dolomite. Thus, dolomite cement becomes the most common last cement phase in the brackish water zone of the East End lens (Fig.VI.4).

It appears that the brackish water has a much higher potential to precipitate dolomite than the fresh water, particularly in the East End lens. The presence of calcite cement in the rocks of the Lower valley lens but not in those of the East End lens suggests that salinity is probably not the only consideration in carbonate cementation. It appears that the concentrations of the chemical constituents such as Mg^{2+}, Ca^{2+} and HCO_3^- or CO_3^{2-}, and Mg^{2+}/Ca^{2+} ratio (Tables III.3, IV.7) are probably the controlling factors.

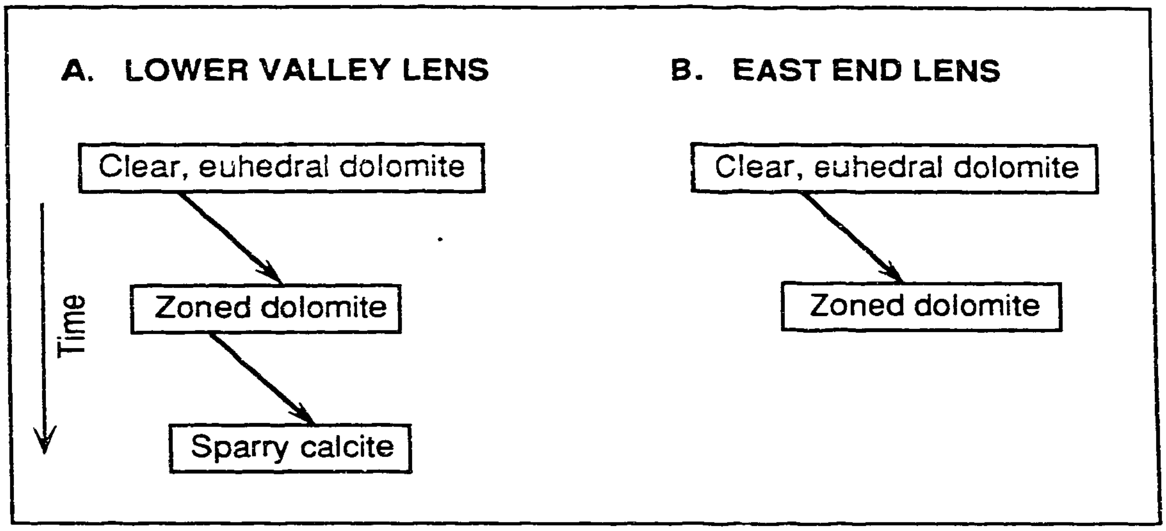


Fig. VI.5 Paragenetic sequence of carbonate cements in the lightly brackish water zone of the (A) Lower Valley and (B) East End aquifers.

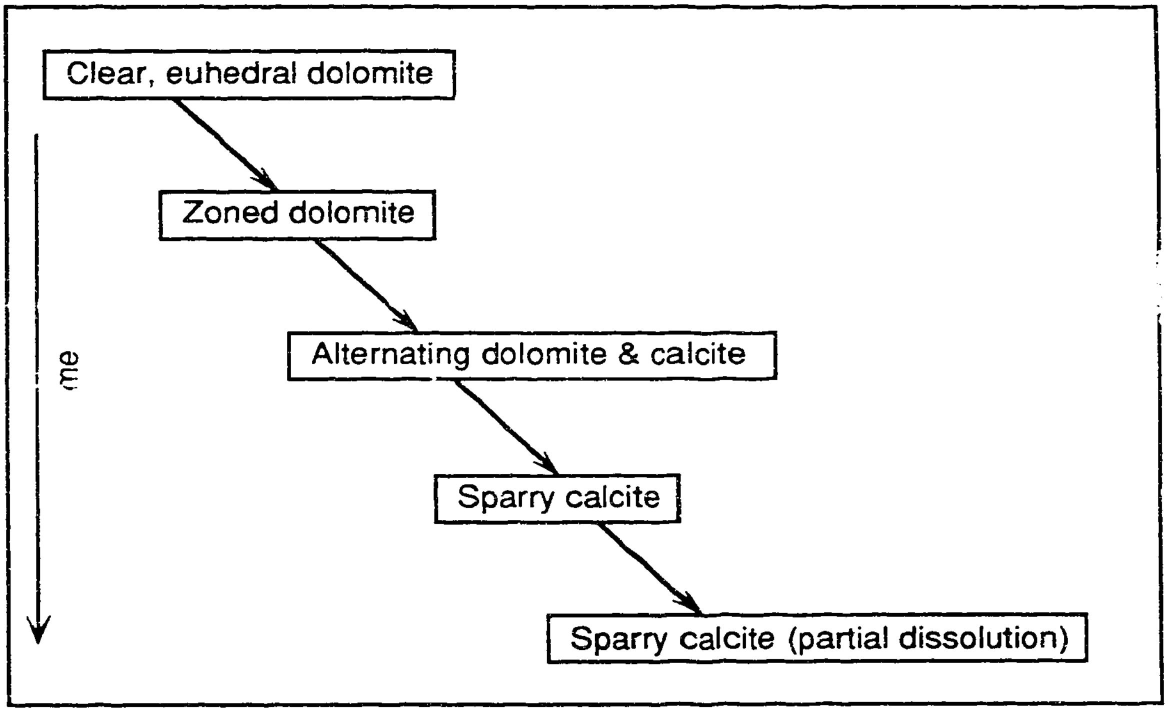


Fig. VI.6 Paragenetic sequence of carbonate cements in the highly brackish water zone.

Highly Brackish Water Zone

Carbonate cement fabrics present in **individual** cavities of the rocks sampled from the highly brackish water zone include:

(1) dolomite cement followed by sparry calcite,

(2) dolomite cement lining voids,

(3) zoned dolomite cement showing selective dissolution of certain zones,

(4) alternating zones of dolomite and calcite cement, and

(5) calcite spar showing partial dissolution.

The paragenetic sequence (Fig.VI.6) comprises (1) clear, euhedral dolomite, (2) zoned dolomite, (3) alternating zones of dolomite and calcite, (4) sparry calcite, and (5) partially dissolved sparry calcite. Most cavities have dolomite as the only cement phase (Fig.VI.7); only 10-20% of the cavities contain some sparry calcite. Therefore, it appears that dolomite is the most common carbonate cement associated with the present-day highly brackish ground water.

Saline Water Zone

Rocks from the saline water zone typically lack calcite cement; however, some 20-30% of the cavities are lined by dolomite cement (Fig.VI.7). Sparry calcite cement is rare. Conversely, about 40-50% of the cavities have no carbonate cements. Rocks in the saline water zone are presently bathed in water that is similar to the sea water in terms of water salinity.

The petrographic data suggest, therefore, that saline water is less favourable for calcite precipitation than fresh water and is also less favourable for dolomite cementation than the brackish water. This phenomenon may be partly related to the presence of inhibitors in the saline water and partly due to the slow ground water flow rate in this zone.

LAST CEMENT PHASE	HYDROCHEMICAL ZONE
Dolomite	Highly Brackish Water (salinity >15% and <100% sea water)
20-30% of the cavities have dolomite 40-50% of the cavities remain open Minor % of the cavities have calcite	Saline Water (salinity ≥100% sea water)

Fig. VI.7 Types of last carbonate cement phase in the highly brackish and saline water zones of the dolostone aquifer. Rock samples from deep wells drilled on the west side of Grand Cayman.

E. AN EXAMPLE OF COMPLEX DIAGENETIC PATTERNS

Rock cuttings, which were collected from the unsaturated (vadose) zone at ten foot intervals from 10 water wells on Cayman Brac (Fig. VI.2, Appendix 1D), provided an excellent opportunity to examining the distribution of diagenetic fabrics over a wide area. Detailed petrographic studies of the rock cuttings indicate a complex distribution of diagenetic fabrics (Fig. VI.8) present in **individual** cavities, which include:

(A) dolomite cement followed by sparry calcite,
(B) dolomite cement lining voids with no calcite cement ,
(C) zoned dolomite cement, dissolution of zones in places,
(D) zoned dolomite cement followed by sparry calcite,
(E) alternating zones of dolomite and calcite,
(F) sparry calcite cement only,
(G) poikilotopic calcite-dolomite,
(H) flowstone,
(I) terra rossa, and
(J) internal sediments (caymanite and skeletal grainstone).

The complicated diagenetic patterns (Fig. VI.8) are a reflection of the complexity of the diagenetic environments. The sediments/rocks were under increasing meteoric influence as Cayman Brac gradually emerged from the sea. The rocks, therefore, record a complete diagenetic history from saline water to brackish water to fresh water to vadose zone. If this is so, the rocks should have been affected by similar pore fluids at the same stratigraphic horizons, and hence, should have similar diagenetic fabrics at those stratigraphic levels. However, the distribution of the diagenetic fabrics (Fig. VI.8) does not seem to display any pattern with respect to a particular aquifer system. This variability in diagenetic signatures probably resulted from the subenvironments created in the joint and karst controlled system of the Bluff Formation, and hence, zones of different fluid chemistry. This feature is important because it demonstrates that samples from the same

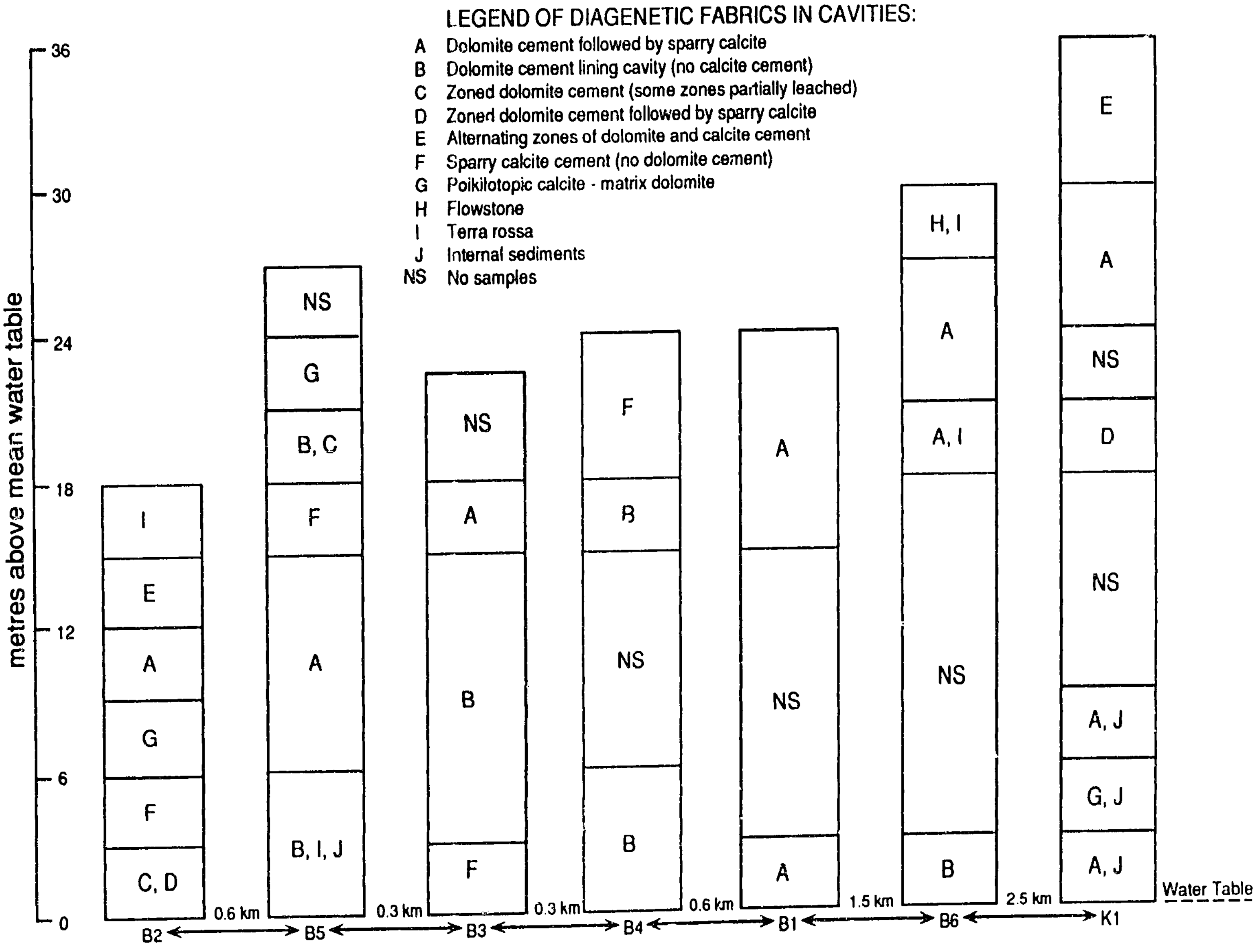


Fig. VI.8 Distribution of the most dominant diagenetic fabrics in the vadose zone of the Bluff Formation on Cayman Brac (refer to Fig. VI.2 for well location).

stratigraphic level of close proximity may have different diagenetic processes due to the heterogeneity of the ground-water flow regime.

It is also important to note that the carbonate cement fabrics in the rocks presently in vadose zones of Cayman Brac (Fig. VI.8) are similar to those in association with the present day hydrochemical regimes of Grand Cayman (Figs. VI.3-7). This suggests that the rocks from the unsaturated zone of Cayman Brac underwent at least one complete cycle of diagenetic environments ranging from marine to meteoric to vadose settings.

F. SYNOPSIS

Detailed petrographic studies of the rocks of the Bluff Formation indicate that:

(1) the Bluff Formation is formed of finely crystalline to microcrystalline dolostone; calcite only occurs as cavity filling and intercrystalline cement or as poikilotopic calcite-dolomite couplet;

(2) the matrix dolomites are characterized by (i) scattered euhedral dolomites up to 40 μm long in microcrystalline dolomite groundmass (5-10 μm), (ii) intercrystalline porosity in leached matrix dolomite, and (iii) poikilotopic calcite encasing corroded matrix dolomites in weathered zones and in the vicinity of the water table in Lower Valley;

(3) paragenetic sequence of carbonate cements commonly is (i) clear and zoned dolomite, (ii) alternating zones of dolomite and calcite as laterally continuous bands from crystal to crystal or within a single crystal, (iii) coarse, unzoned and zoned sparry calcite, (iv) partial dissolution of sparry calcite and zoned dolomite cements, and (v) poikilotopic calcite encasing and infilling leached dolomite cements;

(4) cavity fills other than carbonate cements include terra rossa, flowstone, and internal sediments;

(5) the most important difference in the cement fabrics of the rocks from the two fresh water lenses on Grand Cayman is the rare occurrence of dolomite cement in the

Lower Valley lens although dolomite cement is common in the East End lens; this distinction is probably related to differences in chemical compositions of the two types of ground water which have similar salinity;

(6) the quantity of calcite as last-cement phase decreases from the fresh water to brackish water to saline water zones, and conversely, the abundance of dolomite as last-cement phase increases from the fresh water to brackish water zone;

(7) the rocks in the saline water zone are characterized by minor amounts of dolomite cement and unfilled cavities;

(8) sparry calcite cement is commonly associated with fresh to lightly brackish ground water; dolomite cement is more commonly affiliated with brackish ground water; and

(9) the complex distribution of the diagenetic fabrics of the rocks from the unsaturated zone of Cayman Brac is due to the heterogeneity of the joint and karst controlled aquifer, and hence, is responsible to the variability of fluid chemistry in the subenvironments.

VII. ISOTOPE GEOLOGY

Diagenetic carbonate minerals formed in equilibrium with pore fluids acquire isotopic compositions characteristic of those fluids and the temperature of the diagenetic environment (Hudson, 1977; Savin, 1980; Brand and Veizer, 1981; Anderson and Arthur, 1983; Veizer, 1983; O'Neil, 1986, 1987; Longstaffe, 1987). Thus, where isotopic equilibrium between the carbonate minerals and the diagenetic fluids has been achieved, the isotopic compositions of the diagenetic minerals should provide information about the paleo-environmental conditions. In this context, this study examines the equilibrium fractionation effect of the oxygen isotope between the carbonate minerals and diagenetic fluids, and assesses the salinity of the fluids from which the minerals were precipitated.

A. BASIC PRINCIPLES

Precipitation of carbonate minerals under natural conditions of equilibrium is known to occur (Anderson and Arthur, 1983; Veizer, 1983; O'Neil, 1987). However, carbonate minerals also form under kinetic isotope effects (non-equilibrium) such as biological activity (Keith and Weber, 1965; Weber, 1968; Shackleton *et al.*, 1973) and rapid precipitation or loss of volatiles (Gonfiantini *et al.*, 1968; Hendy, 1971; Turi, 1986; Schwarcz, 1986). Furthermore, the isotopic composition of the diagenetic minerals can be altered by later diagenesis, particularly recrystallization (Land, 1980, 1983b; Longstaffe, 1987; O'Neil, 1987).

The degree of exchange of the oxygen isotope during a reaction is controlled by the oxygen fractionation factor between the carbonate minerals and the diagenetic fluids (Savin, 1980; Brand and Veizer, 1981; Anderson and Arthur, 1983; Land, 1983b; O'Neil, 1986). Oxygen isotopic fractionation between calcite and water has been thoroughly investigated (Anderson and Arthur, 1983; Veizer, 1983). Conversely, the fractionation between dolomite and water is less well established because of the variable stoichiometric

compositions of the dolomite and the inability of dolomite to synthesize under conditions of sedimentary environments (Land, 1980, 1983b, 1985; Hardie, 1987).

Significant isotopic exchange occurs through chemical or mineralogical reactions such as mineral dissolution and precipitation, and recrystallization (Savin, 1980; O'Neil, 1987). Conversely, in low temperature environments, isotopic exchange between the carbonate minerals and water is negligible (Savin, 1980; Anderson and Arthur, 1983; O'Neil, 1987; Welhan, 1987).

B. OXYGEN ISOTOPES OF THE BLUFF FORMATION

The oxygen isotopic data of the rocks and cavity fills of the Bluff Formation used in this study are those determined by Pleydell (1987), Smith (1987), and Jones *et al.* (1989). All isotopic values, which were originally presented in the per mil (‰) notation relative to PDB standard, are converted to the SMOW standard for the temperature dependence equilibrium fractionation calculation. PDB is an oxygen standard for carbonates, derived from the rostrum of *Belemnitella americana* from the Pee Dee Formation of South Carolina, U.S.A. (Craig, 1957; Anderson and Arthur, 1983). The relationship between PDB calcite and SMOW calcite (Anderson and Arthur, 1983) is defined as:

$$\delta^{18}O_{(\text{calcite vs. SMOW})} = 1.03086 * \delta^{18}O_{(\text{calcite vs. PDB})} + 30.86$$

Matrix Dolomite of the Bluff Formation

In order to ensure that the oxygen isotopic compositions are representative of the matrix dolomites, values selected for this study are those that were obtained from dolostone samples of greater than 98% dolomite according to XRD analysis (Pleydell, 1987). The dolomites of the Bluff Formation have a narrow $\delta^{18}O$ range of +2.0 to +3.0‰ PDB and an average value of +2.5‰ (Table VII.1).

Table VII.1 Stable oxygen isotope data of matrix dolomite of the Bluff Formation. Data adapted from Pleydell (1987).

Sample #	**Location**	**$\delta^{18}O$ ‰ SMOW**	**$\delta^{18}O$ ‰ PDB**
801a	High Rock Quarry	+33.2	+2.3
801b	High Rock Quarry	+33.0	+2.1
1209a	High Rock Quarry	+33.7	+2.8
1195	High Rock Quarry	+33.0	+2.1
842	High Rock Quarry	+33.8	+2.9
1242b	Pedro Castle Quarry	+33.5	+2.6
1243b	Pedro Castle Quarry	+33.7	+2.8
1240	Pedro Castle Quarry	+33.2	+2.2
1247	Pedro Castle Quarry	+33.5	+2.5
1230	Blow Hole	+33.1	+2.2
1185	Queen's Road	+33.6	+2.7
1184b	Queen's Road	+32.9	+2.0
1184a	Queen's Road	+32.3	+2.5
1063	Paul Bodden Quarry	+33.6	+2.6
1171	Cayman Kai	+33.9	+2.8
1297c	Cayman Brac	+33.7	+2.8
1297d	Cayman Brac	+33.7	+2.8
Average Stable Oxygen Isotope of Bluff Dolostone		+33.4	+2.5

Note: Sample numbers refer to catalogue numbers of the Cayman Islands rock collection.

Cavity Fills in the Bluff Formation

Cavity fills in the Bluff Formation analysed for the $\delta^{18}O$ content are internal sediments (dolomite) and carbonate mineral precipitates (calcite and dolomite spar, flowstone, and poikilotopic calcite-dolomite).

Dolomite (Caymanite)

The $\delta^{18}O$ contents of the caymanite samples analysed by Pleydell (1987) are similar to those of the dolostone host rocks with an average value of +2.3‰ PDB (Table VII.2). These values are also in agreement with the unpublished data of Collar (1985, per. comm.).

Calcite and Dolomite Spar

Calcite spar cements, their composition confirmed by XRD analysis (Pleydell, 1987), have $\delta^{18}O$ values ranging from -3.9 to -5.6‰ PDB (Table VII.2). One sample of dolomite spar rooted on calcite spar, coarse enough to be isolated for analysis (Pleydell, 1987), has an oxygen isotopic composition of -3.6‰ PDB (Table VII.2). The calcite and dolomite spar cements analysed came from different cavities.

Flowstone

Smith (1987) carried out a detailed examination of stable isotopes of the flowstones collected from different localities of Grand Cayman and Cayman Brac. In an individual flowstone sample, a slight variation in the isotopic content is recorded in each successive calcite layer (Smith, 1987). $\delta^{18}O$ concentrations of the flowstone lie in the -3.0 to -6.5‰ PDB range (Table VII.3). The exceptionally high values of speleothem 1252 (Table VII.3) are due to the presence of a small amount of dolomite (Smith, 1987).

Table VII.2 Stable oxygen isotope data of caymanite, calcite spar and dolomite spar of the Bluff Formation. Data adapted from Pleydell (1987).

Sample #	**Location**	**$\delta^{18}O$ ‰ SMOW**	**$\delta^{18}O$ ‰ PDB**
Dolomite (Caymanite):			
1209d	High Rock Quarry	+33.4	+2.5
1184	Queen's Road	+32.9	+2.0
Average Stable Oxygen Isotopes of Caymanite		+33.2	+2.3
Calcite Spar:			
1223a	East End Quarry	+25.6	-5.1
843	East End Quarry	+25.1	-5.6
1212	High Rock Quarry	+26.8	-3.9
Average Stable Oxygen Isotope of Calcite Spar		+25.8	-4.9
Dolomite Spar:			
1062A	Paul Bodden Quarry	+27.2	-3.6

Note: Sample numbers refer to catalogue numbers of the Cayman Islands rock collection.

Table VII.3 Stable oxygen isotope data of flowstones of the Bluff Formation. Data adapted from Smith (1987).

	$\delta^{18}O$ ‰ **SMOW**	$\delta^{18}O$ ‰ **PDB**
Average Stable Oxygen Isotope of Speleothem 1219 (5 calcite layers: max = -5.2‰, min = -5.9‰ PDB)	+25.2	-5.5
Average Stable Oxygen Isotope of Speleothem 726 (6 calcite layers: max = -4.6‰, min = -6.4‰ PDB)	+25.3	-5.4
Average Stable Oxygen Isotope of Speleothem 727 (4 calcite layers: max = -2.3‰, min = -5.0‰ PDB)	+27.1	-3.7
Average Stable Oxygen Isotope of Speleothem 728 (9 calcite layers: max = -3.2‰, min = -5.7‰ PDB)	+25.6	-5.1
Average Stable Oxygen Isotope of Speleothem 730 (4 calcite layers: max = -5.4‰, min = -6.6‰ PDB)	+24.6	-6.1
Average Stable Oxygen Isotope of Speleothem 1250 (8 calcite layers: max = -3.9‰, min = -6.3‰ PDB)	+25.3	-5.4
Average Stable Oxygen Isotope of Speleothem 1252 (6 calcite layers: max = -1.3‰, min = -6.5‰ PDB)	+26.9	-3.9

Note: Speleothem numbers refer to catalogue numbers of the Cayman Islands rock collection.

Poikilotopic Calcite-Dolomite

The $\delta^{18}O$ content of the poikilotopic calcite ranges from -1.0 to -3.7‰ PDB, whereas the $\delta^{18}O$ composition of the associated dolomite cement varies from +1.4 to +2.6‰ PDB (Table VII.4). The limpid dolomite is more depleted in ^{18}O than the matrix dolomite, but is more enriched in ^{18}O than the coarse dolomite spar. (Tables VII.1, 2, 3). Conversely, the poikilotopic calcite is more enriched in ^{18}O than the calcite spar cement and the calcitic flowstone (Tables VII.2, 3, 4).

C. EQUILIBRIUM ISOTOPIC FRACTIONATION OF OXYGEN

The equilibrium isotopic fractionation of oxygen between minerals and water is commonly determined by (1) theoretical calculations, (2) isotopic exchange experiments, and (3) systematic regularities in naturally occurring phases which formed under well-defined geological conditions. Isotopic equilibrium in experimental systems is generally limited to high temperatures where isotopic exchange rates are sufficiently rapid to be monitored in the laboratory. Commonly, the fractionation factors were obtained by extrapolation of partial exchange data (Anderson and Arthur, 1983; O'Neil, 1986; Kyser, 1987). Consequently, fractionation factors determined from various methods are slightly different, particularly when applied to the low temperature range (Savin, 1980; Anderson and Arthur, 1983; Land, 1983b; Kyser, 1987).

The oxygen fractionation factors typically vary with temperature over large temperature ranges according to the relationship (Anderson and Arthur, 1983; Veizer, 1983; O'Neil, 1986; Kyser, 1987):

$$10^3 \ln\alpha = \frac{A}{T^2} + B$$

where α is the fractionation factor, T is in °K, A and B vary between different minerals and methods of determination. The fractionation factor (Fritz and Fontes, 1980b; Anderson and

Table VII.4 Stable oxygen isotope data of poikilotopic calcite and dolomite of the Bluff Formation. Data adapted from Pleydell (1987) and Jones *et al.* (1989).

Sample #	**Location**	**$\delta^{18}O$ ‰ SMOW**	**$\delta^{18}O$ ‰ PDB**
Dolomite Cement (Limpid Dolomite):			
52	High Rock Quarry	+32.3	+1.4
92	High Rock Quarry	+33.6	+2.6
1201b	High Rock Quarry	+33.1	+2.2
1201a	High Rock Quarry	+33.3	+2.4
Average Stable Oxygen Isotope of Dolomite		+33.1	+2.2
Poikilotopic Calcite:			
52	High Rock Quarry	+29.8	-1.1
92	High Rock Quarry	+27.9	-2.9
1201b	High Rock Quarry	+27.0	-3.7
1201a	High Rock Quarry	+29.8	-1.0
283	High Rock Quarry	+27.8	-2.9
1062a	Paul Bodden Quarry	+29.6	-1.2
Average Stable Oxygen Isotope of Calcite		+28.7	-2.1

Note: Sample numbers refer to catalogue numbers of the Cayman Islands rock collection.

Arthur, 1983) between a mineral and the associated water (α_{m-w}) is related to the isotopic composition of the mineral ($\delta^{18}O_m$) and the associated aqueous phase ($\delta^{18}O_w$) by:

$$\alpha_{m-w} = \frac{1000 + \delta^{18}O_m}{1000 + \delta^{18}O_w}$$

O'Neil (1986) argued that the sign and magnitude of α are controlled by (1) temperature, (2) chemical composition (e.g. magnesian calcite versus pure calcite), (3) crystal structure (e.g. aragonite versus calcite), and (4) pressure, although temperature is the dominant factor.

Fractionation between Calcite and Water

The most widely used relationship on the temperature dependence of oxygen isotopic fractionation between calcite and the water phase is that of Craig (1965):

$$t°C = 16.9 - 4.2(\delta_c - \delta_w) + 0.13(\delta_c - \delta_w)^2$$

where δ_c is the $\delta^{18}O$ of CO_2 liberated by reaction with 100‰ phosphoric acid at 25°C and δ_w is that of CO_2 in equilibrium at 25°C with which the calcite was precipitated. δ_c and δ_w are relative to PDB standard. This relationship was based on analysis of $CaCO_3$ (both calcite and aragonite) precipitated by molluscs grown in controlled laboratory experiment or from well-defined natural environments.

Friedman and O'Neil (1977) determined the oxygen isotopic fractionation between inorganically precipitated calcite and water over the temperature range of 0-500°C. Their relationship is:

$$10^3 \ln\alpha_{(calcite\text{-}water)} = \frac{2.78 * 10^6}{T^2} - 2.89$$

where T is in °K.

The two sets of experimental relationships are in excellent agreement because direct precipitation of calcite under low temperature sedimentary environment permits accurate establishment of the isotopic fractionation between calcite and water. Using a $\delta^{18}O$ value

of -2.8‰ PDB (28.0‰ SMOW) for calcite as an example, the two temperature equations (Craig, 1965; Friedman and O'Neil, 1977) give comparable results (Fig. VII.1). Therefore, in low temperature setting, the $\delta^{18}O$ values of the waters obtained by equilibrium fractionation calculation should be reliable providing the minerals were precipitated under equilibrium condition. Furthermore, the experimental results agree with the fractionation factors calculated by Bottinga (1968) using theoretical considerations.

Fractionation between Dolomite and Water

The relationship between the isotopic fractionation of dolomite and water, and temperature has been determined by a number of investigators using different experimental techniques:

(1) O'Neil and Epstein (1966) obtained the relationship

$$10^3 \ln\alpha_{(\text{dolomite-water})} = \frac{3.34*10^6}{T^2} - 3.34$$

by mineral-CO_2 exchange experiments combined with calcite-water fractionation at 350-400°C,

(2) Northrup and Clayton (1966) obtained the relationship

$$10^3 \ln\alpha_{(\text{dolomite-water})} = \frac{3.2*10^6}{T^2} - 1.50$$

using partial exchange experiments at 300-510°C,

(3) Sheppard and Schwarcz (1970) obtained the relationship

$$10^3 \ln\alpha_{(\text{dolomite-water})} = \frac{3.23*10^6}{T^2} - 3.29$$

by combining empirical fractionations between dolomite and calcite with calcite-water relationship at 100-650°C,

(4) Fritz and Smith (1970) obtained the relationship

$$10^3 \ln\alpha_{(\text{dolomite-water})} = \frac{2.78*10^6}{T^2} + 0.11$$

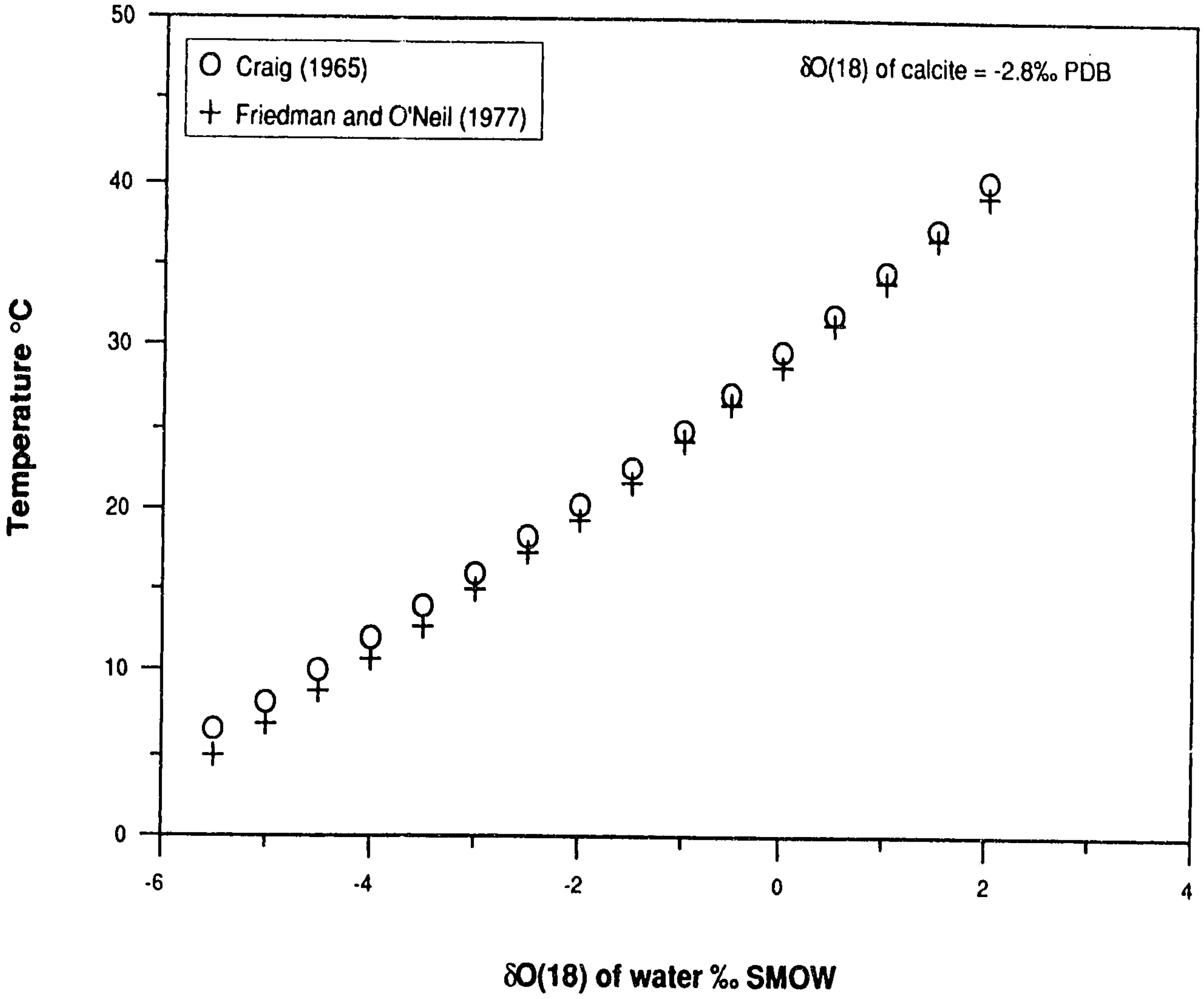


Fig. VII.1 Equilibrium fractionation of oxygen (18) between calcite and water using temperature equations given by Craig (1965) and Friedman and O'Neil (1977).

by carrying out direct precipitation of proto-dolomite (40-45 mole % $MgCO_3$) at 25-78°C, and

(5) Matthews and Katz (1977) obtained the relationship

$$10^3\ln\alpha_{(\text{dolomite-water})} = \frac{3.06*10^6}{T^2} - 3.24$$

by dolomitization of $CaCO_3$ in apparent isotopic equilibrium with the solution at 252-295°C.

The first four equations were corrected by Land (1983b) to be consistent with Friedman and O'Neil (1977). Using a $\delta^{18}O$ value of +33.4‰ SMOW (+2.5‰ PDB) for dolomite, the equations give significantly different results in the temperature of interest (Fig. VII.2). At 25°C, the $\delta^{18}O$ values of the diagenetic fluids lie between -1.6 to +1.3‰ SMOW (Fig. VII.2). Land (1983b) also noted that at a given $\delta^{18}O$ of dolomite, the range of uncertainty in temperature is 15°C, whereas at a given temperature, the range of uncertainty in $\delta^{18}O$ of water is about 4‰.

The equilibrium fractionation between dolomite and calcite ($\Delta^{18}O$) can be obtained by the difference between $\delta^{18}O_{dolomite}$ and $\delta^{18}O_{calcite}$ for cogenetic dolomite and calcite. Dolomite formed in isotopic equilibrium with calcite in sedimentary environment is enriched in $\delta^{18}O$ by 4 to 7‰ relative to calcite (O'Neil and Epstein, 1966; Northrup and Clayton, 1966). Conversely, the fractionation relationships of Fritz and Smith (1970) and Matthews and Katz (1977) gave $\Delta^{18}O_{(dolomite\text{-}calcite)}$ values in the range of 2 to 4‰. Land (1980, 1983b) also suggested that the equilibrium ^{18}O-fractionation value is probably 3 ± 1‰ at 25°C. In studies of coastal sabkhas of Abu Dhabi, McKenzie (1981) suggested that the naturally occurring dolomite and calcite mixtures have fractionation value of +3.2‰. Hardie (1987), however, suspected that the dolomite studied by McKenzie (1981) might not be formed by replacement.

It is apparent that caution be exercised in accepting the results obtained from these fractionation relationships. This study, therefore, takes into account the results obtained

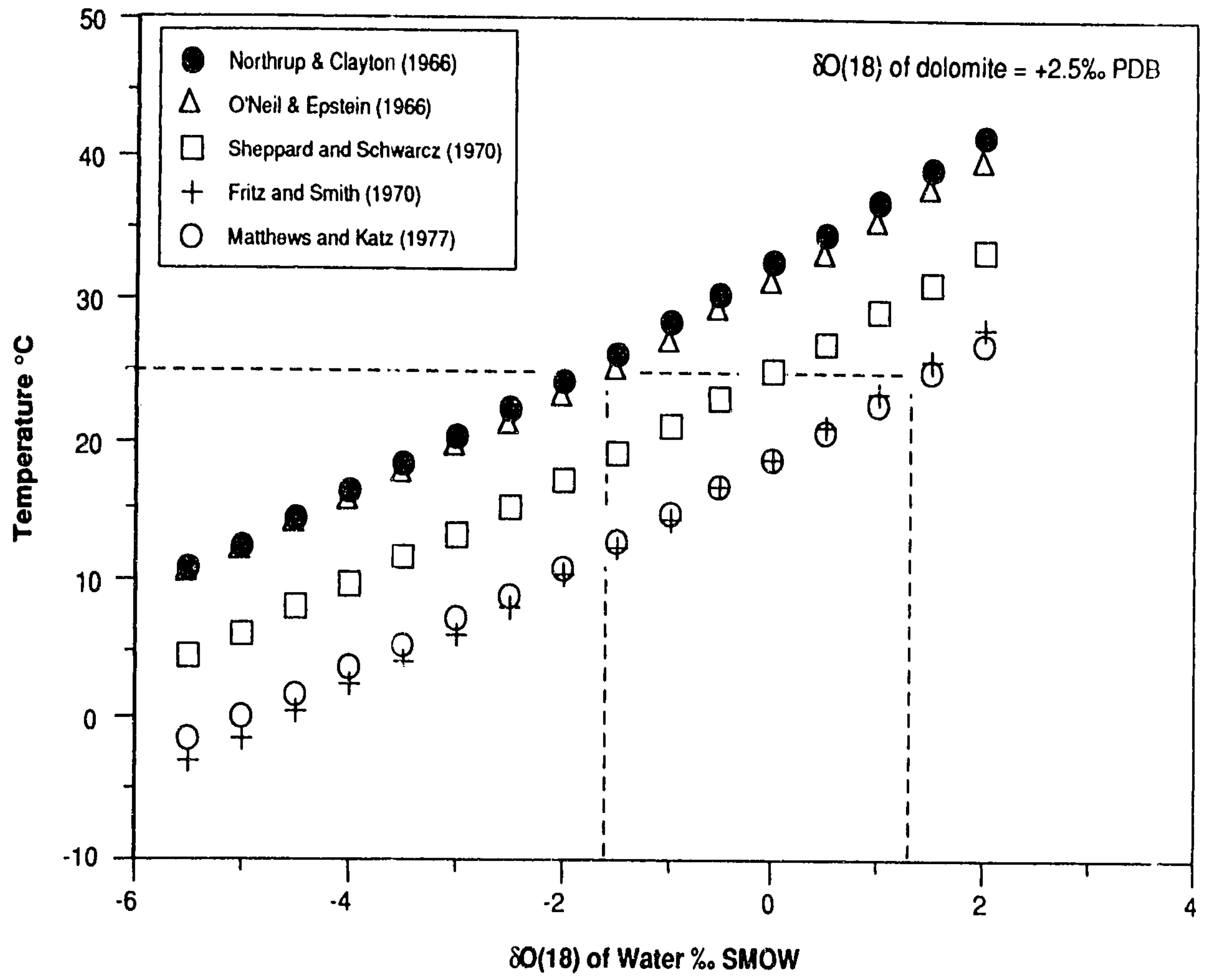


Fig. VII.2 Equilibrium fractionation of oxygen (18) between dolomite and water using five different temperature equations. At 25°C, δO(18) of water differs by about 3‰ depending on the fractionation equations.

from all five equations. Although this conservative approach results in a wide range of $\delta^{18}O$ values in the interpretation of the diagenetic fluids, it avoids the bias resulting from the poor understanding of the fractionation relationship between dolomite and calcite.

D. EQUILIBRIUM FRACTIONATION CALCULATION

Equilibrium fractionation equations of oxygen isotopes allow the evaluation of the relationships of the carbonate minerals, ground water (diagenetic fluid), and the temperature of the aqueous environment in which the minerals formed. The results thus obtained are based on the assumption that the minerals and diagenetic fluids have achieved isotopic equilibrium. Another important assumption is that the diagenetic minerals (dolomite and calcite) have retained the original isotopic signatures since their formation. Unfortunately, there is no assurance that this is the actual situation.

Chemical reactions such as recrystallization, dissolution, and reprecipitation that involve breaking and reforming chemical bonds in the minerals would complicate the interpretation of the results obtained from the equilibrium-fractionation calculation. Furthermore, analytical cross contamination during the separation of calcite and dolomite is possible, particularly when dolomite and calcite are intimately associated with one another as in the case of zoned calcite and dolomite cements.

On the basis of the present day atmospheric and ground water conditions, a temperature range of 22 to 33°C was chosen as the temperatures of the diagenetic fluids for the calculations. Furthermore, because the Cayman Islands are located in low latitudes, it is probable that the ambient temperature in the Tertiary period was similar to that of the present time. The water salinity was determined by the established relationships between the $\delta^{18}O$ content and electrical conductivity (E.C.) of the ground water (Figs. V.2A, 2B, 2C).

Matrix Dolomite of the Bluff Formation

The temperature dependence equilibrium ^{18}O fractionation calculation of dolomite and water is complicated by a variety of temperature equations that were obtained from high temperature experiments (O'Neil and Epstein, 1966; Northrup and Clayton, 1966; Sheppard and Schwarcz, 1970; Matthews and Katz, 1977) or by precipitation of proto-dolomite (Fritz and Smith, 1970). In the temperature range of 22-33°C, the $\delta^{18}O$ values of the fluids are equivalent to waters of 25 to >95% sea water salinity, depending on the equations used (Table VII.5).

The oxygen isotopic composition of the matrix dolomite determined by Pleydell (1987) is the average isotope value of the dolomite crystals in each analysed sample. Therefore, the calculated $\delta^{18}O$ content of the water based on such a bulk $\delta^{18}O$ value of the dolomite may not provide the actual isotopic properties of the dolomitizing fluid(s) if dolomitization occurred in more than a single phase. Land (1983b) suggested that few dolomitized rocks result from a single, short lived event, although it is difficult to recognize single event versus multiple-event dolomitization. Land (1980), however, suggested that inhomogeneities on a single crystal scale are indicative of diagenetic stages.

Caymanite

In the temperature range of 22-33°C, the calculations indicate that the diagenetic fluids that were in association with the caymanite had $\delta^{18}O$ contents ranging from -2.5 to >+1.0‰ SMOW (Table VII.5). These oxygen isotopic compositions correspond to an aqueous phase of 25 to >95% sea water salinity (Table VII.5). This implies that the fluids responsible for the dolomitization of the host rock and the caymanite sediments were of similar salinity, assuming there was no masking of isotopic composition by later phase diagenetic fluids.

Table VII.5 $\delta^{18}O$ and salinity of ground water in equilibrium with different dolomite phases. Temperature range used for the ^{18}O fractionation calculation between dolomite and water is 22 to 33°C.

EQUATION	**N & C**	**O & E**	**S & S**	**F & S**	**M & K**
Matrix Dolomite (Average $\delta^{18}O$ +33.4‰ SMOW):					
$\delta^{18}O$ of water (‰ SMOW)	-2.5 to 0.0	-2.5 to +0.5	-0.5 to +2.0	+1.0 to >+1.0	+1.0 to >+1.0
water salinity (% sea water)	25 to 80	25 to 90	65 to 100	>95	>95
Caymanite (Average $\delta^{18}O$ +33.2‰ SMOW):					
$\delta^{18}O$ of water (‰ SMOW)	-2.5 to 0.0	-2.5 to +0.5	-0.5 to +2.0	+1.0 to >+1.0	+1.0 to >+1.0
water salinity (% sea water)	25 to 80	25 to 90	65 to 100	>95	>95
Limpid Dolomite (Average $\delta^{18}O$ +33.1‰ SMOW):					
$\delta^{18}O$ of water (‰ SMOW)	-2.5 to 0.0	-2.5 to +0.5	-0.5 to +2.0	+0.5 to >+0.5	+1.0 to >+1.0
water salinity (% sea water)	25 to 80	25 to 90	65 to 100	>90	>95
Coarse Dolomite Spar (Average $\delta^{18}O$ +27.2‰ SMOW):					
$\delta^{18}O$ of water (‰ SMOW)	<-5.5	<-5.5 to -5.5	-4.0 to <-4.0	-5.0 to -3.0	-5.0 to -2.5
water salinity	perched/fresh	perched/fresh	fresh	fresh to lightly brackish	fresh to 25% sea water

Note: N&C: Northrup and Clayton, 1966; O&E: O'Neil and Epstein, 1966; S&S: Sheppard and Schwarcz, 1970; F&S: Fritz and Smith, 1970; M&K: Matthews and Katz, 1977.

Calcite Spar

Using the average $\delta^{18}O$ content of the calcite spar (Table VII.2), the temperature calculation shows that the diagenetic fluids had $\delta^{18}O$ values of -3.5 to -1.5‰ SMOW (Table VII.6). These isotopic compositions suggest that the diagenetic fluids that were responsible for the precipitation of the calcite spar were fresh to brackish water up to 45% sea water salinity (Table VII.6).

Dolomite Spar

The coarse dolomite spar was formed in equilibrium with diagenetic fluids having $\delta^{18}O$ compositions of <-5.5 to -2.5‰ SMOW (Table VII.5). At the low $\delta^{18}O$ range (<-5.5‰ SMOW), the associated fluid is perched to fresh water, and at the high $\delta^{18}O$ value (-2.5‰ SMOW), the associated pore fluid is brackish water of 25% sea water salinity.

Flowstone

The oxygen isotopic fractionation calculation between flowstone and water indicates that the flowstones probably precipitated in waters having $\delta^{18}O$ compositions of -5.0 to 0.0‰ SMOW (Table VII.6). These $\delta^{18}O$ values suggest that the diagenetic fluids were fresh to brackish water up to 80% sea water salinity (Table VII.5). The actual precipitating fluids were probably fresh to brackish water up to 45% sea water salinity since the high $\delta^{18}O$ values of the flowstones are due to the presence of detrital dolomite in the flowstone (Smith, 1987).

Disequilibrium precipitation of flowstone, however, has also been known to occur (Hendy, 1971; Schwarcz, 1986). If so, the results obtained from equilibrium calculations become meaningless.

Table VII.6 $\delta^{18}O$ and salinity of ground water in equilibrium with calcite. Temperature range used for the ^{18}O fractionation calculation between calcite and water is 22 to 33°C.

EQUATION	Craig (1965)	Friedman & O'Neil (1977)
Poikilotopic Calcite (Average $\delta^{18}O$ +28.7‰ SMOW):		
$\delta^{18}O$ of water (‰ SMOW)	-0.5 to +1.5	-0.5 to +1.5
water salinity (% sea water)	65 to >100	65 to >100
Calcite Spar (Average $\delta^{18}O$ +25.8‰ SMOW):		
$\delta^{18}O$ of water (‰ SMOW)	-3.5 to -1.5	-3.5 to -1.5
water salinity	fresh water to 45% sea water	fresh water to 45% sea water
Speleothem 726 (Average $\delta^{18}O$ +25.3‰ SMOW):		
$\delta^{18}O$ of water (‰ SMOW)	-4.0 to -2.0	-4.0 to -1.5
water salinity	fresh water to 35% sea water	fresh water to 45% sea water
Speleothem 727 (Average $\delta^{18}O$ +27.1‰ SMOW):		
$\delta^{18}O$ of water (‰ SMOW)	-2.5 to 0.0	-2.0 to 0.0
water salinity (% sea water)	25 to 80	35 to 80
Speleothem 728 (Average $\delta^{18}O$ +25.6‰ SMOW):		
$\delta^{18}O$ of water (‰ SMOW)	-3.5 to -1.5	-3.5 to -1.5
water salinity	fresh water to 45% sea water	fresh water to 45% sea water
Speleothem 730 (Average $\delta^{18}O$ +24.6‰ SMOW):		
$\delta^{18}O$ of water (‰ SMOW)	-5.0 to -2.5	-4.5 to -2.5
water salinity	fresh water to 25% sea water	fresh water to 25% sea water
Speleothem 1219 (Average $\delta^{18}O$ +25.2‰ SMOW):		
$\delta^{18}O$ of water (‰ SMOW)	-4.0 to -2.0	-4.0 to -2.0
water salinity	fresh water to 35% sea water	fresh water to 35% sea water
Speleothem 1250 (Average $\delta^{18}O$ +25.3‰ SMOW):		
$\delta^{18}O$ of water (‰ SMOW)	-4.0 to -2.0	-5.0 to -2.5
water salinity	fresh water to 35% sea water	fresh water to 25% sea water
Speleothem 1252 (Average $\delta^{18}O$ +26.9‰ SMOW):		
$\delta^{18}O$ of water (‰ SMOW)	-2.5 to -0.5	-2.5 to 0.0
water salinity (% sea water)	25 to 65	25 to 80

Poikilotopic Calcite-Dolomite

The diagenetic fluids in equilibrium with the dolomite cement (limpid dolomite) had $\delta^{18}O$ content ranging from -2.5 to >+1.0‰ SMOW (Table VII.5) and the fluids in equilibrium with the poikilotopic calcite had $\delta^{18}O$ composition varying from -0.5 to +1.5‰ SMOW (Table VII.6). Therefore, the diagenetic fluids for the precipitation of the dolomite cement were brackish water of 25 to >90% sea water salinity (Table VII.5), whereas the fluids for the precipitation of the poikilotopic calcite were brackish water of 65 to >100% sea water salinity (Table VII.6). These values suggest that a slight change in the water composition would shift the dolomite formation to calcite or vice versa.

E. SYNOPSIS

Lohmann (1982, 1983) and Meyers and Lohmann (1985) suggest that carbonate minerals precipitated in a progressively more distal phreatic setting commonly display a negative $\delta^{18}O$ trend. The decreasing $\delta^{18}O$ content from dolomite cement to calcite spar probably represents increasing meteoric influence. Detailed studies of the stable isotope geochemistry of the carbonates of the Bluff Formation permit the following conclusions.

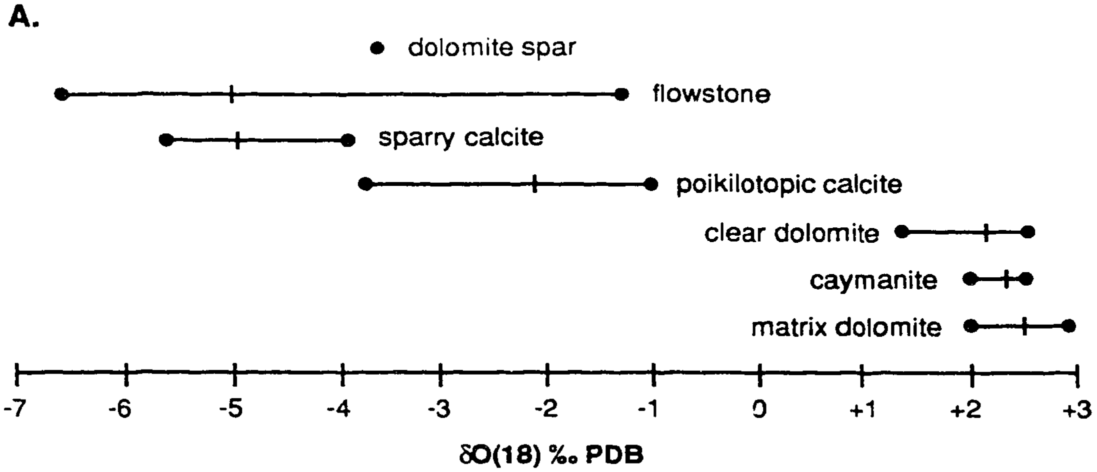
(1) For dolomite, the order of decreasing $\delta^{18}O$ content is matrix dolomite, caymanite, dolomite cement (limpid dolomite), and coarse dolomite spar (Fig.VII.3A).

(2) For calcite, the order of decreasing $\delta^{18}O$ content poikilotopic calcite, sparry calcite, and flowstone (Fig.VII.3A).

(3) The equilibrium oxygen fractionation relationship between calcite and water is well established, whereas the fractionation relationship between dolomite and water at low temperature is equivocal.

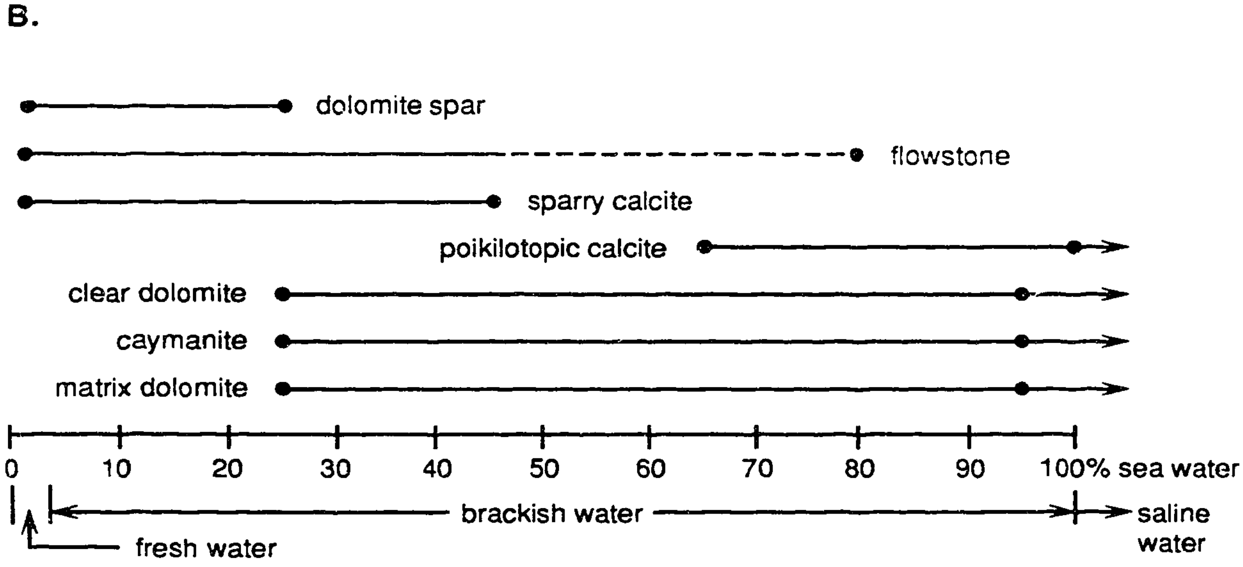
(4) The poikilotopic calcite and dolomite cement having $\Delta^{18}O_{(dolomite\text{-}calcite)}$ values of 2.4 to 6.3‰ PDB are probably not cogenetic phases.

(5) Results of the equilibrium oxygen fractionation between the carbonate minerals and the waters at 22-33°C using different fractionation equations (Fig.VII.3B) conclude



●—● indicates the range of δO(18) values for each mineral phase.
—+— indicates the average δO(18) value.

Fig. VII.3A Summary diagram showing the range of δO(18) values for the various carbonate minerals present in the Bluff Formation.



●—● indicates the range of water salinity in which the mineral phase may precipitate. Interpretation based on average δO(18) values.
—> indicates the salinity range may extend to higher values.
--- indicates the high salinity values (>45%) rarely occur.

Fig. VII.3B Summary diagram showing the range of water salinity in which the various carbonate minerals may precipitate.

that (i) matrix dolomite and caymanite formed in water of 25 to >95% sea water salinity, (ii) calcite spar and flowstone precipitated in fresh to brackish water up to 45% sea water salinity, (iii) poikilotopic calcite precipitated in water of 65 to >100% sea water salinity, (iv) dolomite cement (in association with poikilotopic calcite) formed in water of 25 to >90% sea water salinity, and (v) coarse dolomite spar precipitated in perched, fresh to brackish water up to 25% sea water salinity.

VIII. DIAGENETIC MODELS

The major controlling factors on the diagenetic realms are past tectonic activity that aused uplift and down faulting of the islands and sea level fluctuations. Periods of elatively high sea level stand were characterized by coral reef development and carbonate eposition. Conversely, periods of relative sea level low stand were characterized by arbonate diagenesis, karst development, and increased erosion. This apparently simple oncept with reference to relative sea level changes is complicated by the fact that at times he islands might be partially submerged. Submarine diagenetic textures are rare in the Bluff Formation. Pleydell (1987), however, documented the occurrence of minor amounts f submarine textures such as micrite and isopachous cements. Numerous cycles of arbonate deposition and diagenesis have made the interpretation of the diagenetic ignatures present in the rocks of the Bluff Formation a challenge.

A. STRATIGRAPHIC SETTING

In Pedro Castle Quarry on Grand Cayman, Jones and Hunter (1989) documented a istinct disconformity which they used to divide the Bluff Formation into the lower Cayman Member and the upper Pedro Castle Member. On the basis of paleontological data nd by comparison with sea level curves constructed by Vail *et al.* (1977), Hallam (1984), nd Haq *et al.* (1989), it is apparent that the disconformity separates Oligocene and Miocene strata (Jones and Hunter, 1989).

Correlation of the coral fauna in the Cayman Member with the Caribbean wide Antiguan coral fauna (Vaughan, 1919; Thomas, 1942; Cooke *et al.*, 1943; Woodring, 957) suggests that the Cayman Member is early late Oligocene in age (Jones and Hunter, 989). The assignment of an age for the Pedro Castle Member is less confident because of he lack of biostratigraphic markers (Jones and Hunter, 1989). Nevertheless, Jones and Hunter (1989) suggest that the Pedro Castle Member may be middle Miocene in age. The ronshore Formation that unconformably overlies the Bluff Formation is of late Pleistocene

age (approximately 125,000 years old), based on conventional U-series dating of four coral samples from the upper part of the formation (Woodroffe *et al.*, 1983).

As far as carbonate diagenesis is concerned, it is apparent that the major regressions in late Oligocene to early Miocene and in late Miocene to early Pliocene times would have had considerable impact on the diagenetic alteration of the carbonate sediments of the Bluff Formation. Furthermore, the sea level fluctuations during the Pliocene and Pleistocene epoch would have led to additional diagenetic modifications of the rocks.

B. SEQUENCE OF DIAGENETIC EVENTS

Integration of available stratigraphic, sedimentological and diagenetic information in the Bluff Formation does not permit a definitive interpretation on the sequence and timing of the diagenetic events. Two models can be invoked to satisfy the available data. On the basis of petrographic and geochemical data, Pleydell (1987), Jones (1989a), and Pleydell *et al.* (in preparation) proposed that pervasive dolomitization of the Bluff Formation was a single event involving sea water as the diagenetic fluid. This model is herein called 'Paragenetic Model I' (Fig. VIII.1). This study, however, suggests an alternative interpretation of the geochemical data. Based on the re-evaluation of the geochemical information, mineralogical, petrographic, and circumstantial evidence, this study proposes that dolomitization of the Bluff Formation was achieved through two separate events by mixed meteoric-marine water. The latter model is herein termed 'Paragenetic Model II' (Fig. VIII.1).

Paragenetic Model I

The following sequence of major depositional and diagenetic events (Fig. VIII.1) is summarized from Pleydell (1987), Jones (1989a), Jones and Hunter (1989), Pleydell *et al.* (1989), and from personal discussion with Jones (1989).

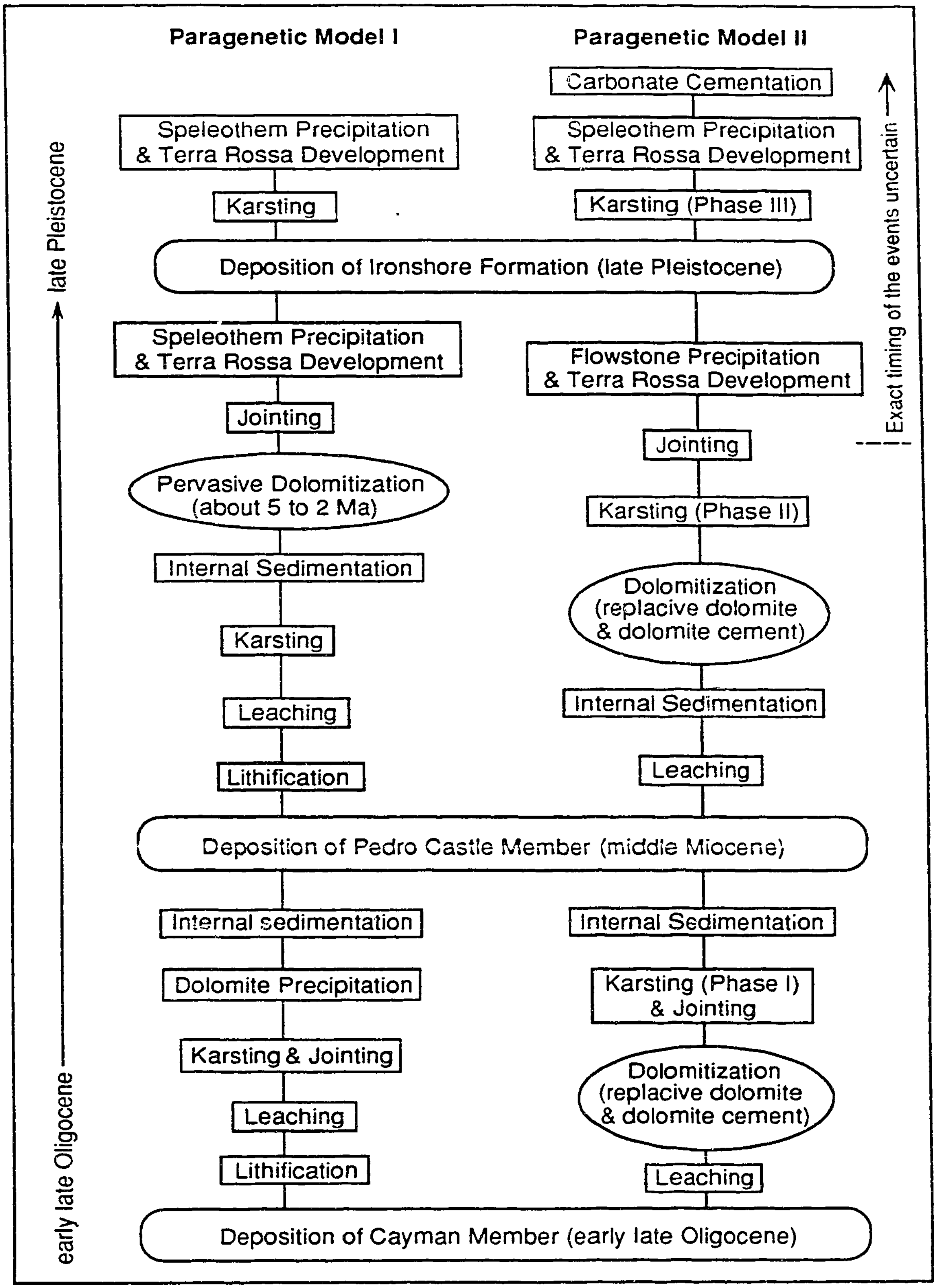


Fig. VIII.1 Sequence of events associated with Paragenetic Model I and II.

(1) Deposition of carbonate sediments of the Cayman Member until early late Oligocene (approximately 30 Ma).

(2) Major regression in late Oligocene with resultant subaerial exposure.

(3) Lithification of carbonate sediments.

(4) Leaching of aragonitic skeletal components, which may have been contemporaneous with lithification of carbonate sediments.

(5) Karst development, and jointing of lithified carbonates.

(6) Precipitation of cavity lining clear dolomite.

(7) Internal sedimentation of fine grained carbonate (caymanite) and skeletal sands during the early Miocene transgression.

(8) Decoration of seafloor (disconformable surface) with a diverse fauna of boring sponges, worms, and bivalves.

(9) Deposition of carbonate sediments of the Pedro Castle Member during middle Miocene (approximately 16 Ma).

(10) Major regression in late Miocene.

(11) Lithification of carbonate sediments.

(11) Leaching of aragonitic skeletal components.

(12) Karst development on the Cayman and Pedro Castle members.

(13) Internal sedimentation of fine grained carbonate and skeletal sands.

(14) Pervasive dolomitization of the Cayman and Pedro Castle members and cavity fills in late Pliocene (approximately 5 to 2 Ma).

(15) Development of joints and fissures.

(16) Precipitation of flowstone and development of terra rossa.

(17) Deposition of carbonate sediments of the Ironshore Formation during late Pleistocene (approximately 125,000 a).

(18) Karst development on dolostones of the Bluff Formation and speleothem precipitation in some caves.

Paragenetic Model II

This study suggests the following sequence of major depositional and diagenetic events (Fig. VIII.1). The depositional history of the Bluff Formation is that of Jones (1989a) and Jones and Hunter (1989).

(1) Deposition of carbonate sediments of the Cayman Member during late Oligocene time (approximately 30 Ma).

(2) Major regression in late Oligocene time with resultant island emergence and meteoric influence.

(3) Leaching of aragonitic skeletal components.

(4) Replacive dolomitization of metastable carbonates and precipitation of dolomite in intergranular space and fossil molds, probably occurring during or shortly after aragonite dissolution.

(5) Jointing and Phase I karst development.

(6) Internal sedimentation of fine grained carbonate (caymanite) and skeletal sands, probably during the early Miocene transgression.

(7) Decoration of the seafloor (disconformable surface) with a diverse fauna of boring sponges, worms, and bivalves.

(8) Deposition of carbonate sediments of the Pedro Castle Member during middle Miocene (approximately 16 Ma).

(9) Major regression in late Miocene with resultant island emergence and meteoric influence.

(10) Leaching of aragonitic skeletal components.

(11) Influx of a small amount of fine grained carbonate and skeletal sands into the fossil molds of the Pedro Castle Member and possibly into the cavities and caves of the Cayman Member.

(12) Replacive dolomitization of metastable carbonate sediments of the Pedro Castle Member and internal sediments in both members, and recrystallization (increase in cation-ordering and stoichiometry) of previously formed dolomites.

(13) Phase II karst development.

(14) Precipitation of flowstone and development of terra rossa.

(15) Extensive joint development.

(16) Deposition of carbonate sediments of the Ironshore Formation during late Pleistocene (approximately 125,000 a).

(17) Phase III karst development (joint controlled) and speleothem precipitation in some caves.

(18) Precipitation of dolomite and calcite cement in cavities that were not occluded by internal sediments and/or speleothemic calcite.

The above sequence is not meant to imply that each diagenetic process was a discrete, separate event. Instead, processes such as dolomitization and recrystallization were probably ongoing events that lasted until the sediments were completely dolomitized and recrystallized to the stable forms.

IX. DIAGENETIC INTERPRETATION OF THE BLUFF FORMATION I: MATRIX DOLOMITIZATION

Dolomitization or replacement of calcium carbonate by dolomite has continued to receive great interest because dolostones form important reservoirs for hydrocarbon (e.g. Thomas and Glaister, 1960; Yan and Zhai, 1980; Watson, 1982) and are host rocks for base-metal deposits (e.g. Kyle, 1983; Force *et al.*, 1986; Buelter and Guillemette, 1988). Recent reviews show that no concensus exists regarding the diagenetic environments and fluid compositions that are responsible for massive dolomitization of thick limestone sequences (Morrow, 1982a, 1982b; Land, 1980, 1983a, 1985; Machel and Mountjoy, 1986, 1987; Hardie, 1987). In addition to the inability to produce dolomitization in the laboratory under low temperature setting, the problem is compounded by the complexity of the cation disordering and cation nonstoichiometry of dolomite.

In light of the present day hydrogeological and hydrochemical information and petrographic and geochemical data, this study attempts to examine the conditions that led to the pervasive dolomitization of the Bluff Formation in terms of the chemical equilibria, chemical kinetics, timing, fluid, and mechanism of dolomitization.

A. CHEMICAL EQUILIBRIA OF DOLOMITIZATION

The replacement of calcium carbonate by dolomite is commonly expressed by

$$2CaCO_3 + Mg^{2+} = CaMg(CO_3)_2 + Ca^{2+} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1)$$

which represents a mole for mole replacement reaction. This process has been used to account for the formation and redistribution of porosity in dolostone reservoir rocks (Murray, 1960). If the CO_3^{2-} ion is brought to the site of dolomitization from an outside source, porosity destruction occurs according to the following reaction (Murray, 1960; Lippman, 1973):

$$CaCO_3 + Mg^{2+} + CO_3^{2-} = CaMg(CO_3)_2 \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (2)$$

This process of overdolomitization involves a volume gain of 75% to 88% (aragonite or calcite replacement). Such a replacement process is inconsistent with the petrographic fabrics of the Bluff Formation which have a fairly high effective porosity.

A volume for volume replacement (Friedman and Sanders, 1967) rather than a mole for mole replacement probably occurred during the dolomitization of the Bluff Formation as exemplified by the retention of the original skeletal structure such as red algae and foraminifera. Morrow (1982a) proposed that for a volume for volume reaction, the net dolomitization is

$$(2-x)CaCO_3 + Mg^{2+} + xCO_3^{2-} = CaMg(CO_3)_2 + (1-x)Ca^{2+} \text{ ....} (3)$$

where the coefficient x is 0.11 and 0.25 for aragonite and calcite respectively.

At three phase equilibrium (at a particular temperature and pressure), calcite and dolomite are in equilibrium with the solution according to the following reactions:

$$CaCO_3 = Ca^{2+} + CO_3^{2-} \text{ ....} (4)$$

$$CaMg(CO_3)_2 = Ca^{2+} + Mg^{2+} + CO_3^{2-} \text{ ....} (5)$$

Stoessell (1987) showed that the equilibrium constant for the dolomitization reaction (Kcd) of equation (3) is

$$Kcd = \frac{Kc^{2-x}}{Kd} = \frac{[Ca^{2+}]}{[Mg^{2+}]}\left(\frac{1}{Kc^{x}}\right) \text{ ....} (6)$$

where Kc and Kd are the solubility constants for calcite and dolomite respectively according to equations (4) and (5) and $[Ca^{2+}]$ and $[Mg^{2+}]$ are the activities of calcium and magnesium ions in solution. The relationship shown in equation (6) suggests that the activity of CO_3^{2-} is not a factor according to concepts of chemical equilibrium.

On the basis of ground water data in the Floridan aquifer, Hanshaw *et al.* (1971) showed that a Mg/Ca activity ratio close to 1 is indicative of a three phase equilibrium system between calcite, dolomite and the solution. Using the thermodynamic properties of carbonate minerals tabulated by Carpenter (1980), Hardie (1987) demonstrated the importance of cation order-disorder in the evaluation of the Mg/Ca activity ratio. For fully

ordered dolomite, the activity ratio of Mg/Ca is the lowest at 0.10, whereas for disordered dolomite, the ratio is 3.31 (Hardie, 1987). A ratio of 1.0 is only applicable for partly ordered dolomite. The Mg/Ca activity ratio required for dolomitization, therefore, must be used with extreme caution because it depends strongly on the cation-disordering and nonstoichiometry of the dolomite mineral. If calcite is not present as a discrete phase, there is no constraint on the Mg/Ca ratio which may have any value greater than that necessary for three phase equilibrium. Most brackish and saline ground waters on the Cayman Islands are supersaturated with respect to dolomite and have a Mg/Ca activity ratio greater than 1.0 (Tables IV.7, 8). Therefore, from a thermodynamic standpoint, the brackish to saline ground waters are capable of dolomitizing any limestone sequences.

The matrix dolomite of the Bluff Formation ranges in composition from stoichiometric dolomite with 50 mole % $CaCO_3$ to calcian dolomite with 55 mole % $CaCO_3$ (Pleydell, 1987). Fuchtbauer and Goldschmidt (1965), Lumsden and Chimahusky (1980), Sass and Katz (1982), and Sperber *et al.* (1984) suggest that stoichiometric dolomites are commonly associated with micritic lithologies that are indicative of evaporitic depositional environments. Morrow (1982b) also noted that solutions in evaporative settings have high Mg/Ca ratios and commonly form stoichiometric dolomites. Conversely, at Mg/Ca ratios between 2.5 to 5.1, and at salinity less than sea water, precipitation of calcium rich dolomites is common (Morrow, 1982b). Thus, the nonstoichiometric composition of the matrix dolomite of the Bluff Formation argues against a hypersaline dolomitization setting. This contention is further supported by the lack of evaporites in the rocks of the Bluff Formation.

Sperber *et al.* (1984) suggest that complete replacement of calcium carbonate by dolomite requires a continuous influx of magnesium ions. In such open systems, the generalized reaction is

$$CaCO_3 + (0.45\text{-}0.50)Mg^{2+} = Ca_{0.55\text{-}0.50}Mg_{0.45\text{-}0.50}(CO_3)_2 + (0.45\text{-}0.50)Ca^{2+}$$

Therefore, the stoichiometry of the matrix dolomite in the Bluff Formation suggests that the pervasive dolomitization probably occurred in an open system with a sufficient supply of Mg^{2+}.

B. CHEMICAL KINETICS OF DOLOMITIZATION

Some insights concerning the kinetic factors on dolomitization of calcium carbonate have been obtained from experimental works done under hydrothermal conditions (Katz and Matthews, 1977; Matthews and Katz, 1977; Gaines, 1980; Baker and Kastner, 1981; Bullen and Sibley, 1984; Morrow and Ricketts, 1988; Sibley *et al.*, 1988). High temperature experimental conditions were used because dolomite synthesized under earth-surface conditions form only metastable phases.

Dolomitization is a multi-step process involving dissolution of calcium carbonate (aragonite and calcite) and precipitation of dolomite from the solution (Katz and Matthews, 1977; Matthews and Katz, 1977; Gaines, 1980; Baker and Kastner, 1981; Bullen and Sibley, 1984; Sibley *et al.*, 1988). The replacement process proceeds through an intermediate phase(s) of magnesian calcite or calcium rich dolomite which, in turn, converts to dolomite (Katz and Matthews, 1977; Baker and Kastner, 1981; Bullen and Sibley, 1984; Morrow and Ricketts, 1988; Sibley *et al.*, 1988). Katz and Matthews (1977) also concluded that on a submicroscopic scale, the intermediate phases are formed in reaction zones surrounding the replacing grains or crystals, which are not in equilibrium with the bulk solution. On the basis of partitioning models of Sr^{2+} and Mg^{2+} and oxygen isotope data, the reaction zones in the transformation of aragonite to low-magnesian calcite were calculated to occupy <4% of the total solution volume (Katz and Matthews, 1977; Matthews and Katz, 1977).

Gaines (1980) suggested that nucleation of the dolomite phase is the major factor in reaction kinetics. In addition to the normal nucleation and growth stages that are well established for crystal growth, Sibley *et al.* (1988) noted an induction stage. The induction

stage refers to nucleation and growth of dolomite to a detectable limit (Sibley *et al.*, 1988). It is a critical part of the calcite-to-dolomite transformation because it is the slowest step in the overall replacement (Sibley *et al.*, 1988). Rate of dolomite replacement is, therefore, related to the kinetic effects on the length of the induction period.

In low temperature diagenetic environments, physico-chemical parameters that kinetically affect the rate of dolomitization include (1) hydration of Mg^{2+}, (2) molar Mg/Ca ratio, (3) salinity, (4) sulfate reduction, (5) concentration of HCO_3^-, and (6) organic materials.

In aqueous solutions, Mg^{2+} is strongly bound by water with a much higher hydration energy than Ca^{2+} (Lippman, 1973; Lahann, 1978; Hanshaw and Back, 1979). The hydrated Mg^{2+} must be dehydrated (removal of the water molecules from the hydrated ions) before it can be incorporated into the crystal lattice of dolomite. Gaines (1980) demonstrated that Li^{2+} acts as a catalyst for dehydrating Mg^{2+}, and hence, accelerates the dolomitization process. Fe^{2+} probably enhances dolomitization in a similar manner (Gaines, 1980).

The induction stage of dolomitization increases with decreasing molar Mg/Ca ratio (Sibley *et al.*, 1988); therefore, the rate of dolomitization increases with increasing Mg/Ca ratio of the solution. Sibley *et al.* (1988) further demonstrated that a higher Mg/Ca ratio increases the stoichiometry of the dolomite and that the intermediate product is more calcium rich at low Mg/Ca ratio. Baker and Kastner (1981) noted that the molar Mg/Ca ratios for the calcite-dolomite phase boundary lie between 0.57 and 1.06. Gaines (1980) showed that an increase in the transformation rate of dolomite with increasing Mg/Ca ratio occurs only within the dolomite stability field and, because at high ratios, the replacement proceeds to form magnesite.

The reaction rate increases significantly with increasing salinity (Gaines, 1980) due to a reduction in the induction stage (Sibley *et al.*, 1988). Folk and Land (1975) postulated that micritic dolomite, which is commonly calcium rich, forms in hypersaline condition

with a high Mg/Ca ratio. At reduced salinities, with low Mg/Ca ratios close to 1.0, the rate of dolomitization decreases, and the resulting dolomite tends to be limpid, euhedral and more stoichiometric (Folk and Land, 1975). However, Gunatilaka *et al.* (1987) documented the occurrence of calcium poor dolomites in a sabkha environment, where calcium rich dolomites are known to occur in such a setting (Gunatilaka *et al.*, 1984; McKenzie, 1981; Patterson and Kinsman, 1982). Thus, it appears that the effect of salinity on the stoichiometry of dolomite may not be directly correlatable and is probably more complicated than currently perceived.

Under experimental conditions, Baker and Kastner (1981) noted that the presence of even minor amount of SO_4^{2-} in the solution significantly inhibits the rate and degree of calcite-to-dolomite transformation. This inhibition occurs even if the SO_4^{2-} concentration is less than 5% of the sea water content (i.e. about 140 mg/l for the Caribbean sea water). The influence of SO_4^{2-} on dolomitization of calcium carbonate is due to poisoning of surface sites via surface adsorption or to surface precipitation (Baker and Kastner, 1981; Kastner, 1988). Land (1983a) suggested that SO_4^{2-} in solution may reduce the activity of Mg^{2+} by forming a $MgSO_4^{\circ}$ ion pair. However, Morrow and Ricketts (1988) showed that the presence of SO_4^{2-} in solution may inhibit dolomitization by retarding the rate of calcite dissolution, rather than by inhibiting the direct precipitation of dolomite from solution. Therefore, it appears that SO_4^{2-} content is the main kinetic factor in controlling dolomitization instead of the Mg/Ca ratio as suggested by Folk and Land (1975).

Although, according to thermodynamic concepts (equation 6), the dolomitization process is independent of CO_3^{2-} concentration, Morrow (1982a) argued that an increase in the CO_3^{2-} concentration of the solution may promote dolomitization by providing sufficient energy to push aside the hydration shield of Mg^{2+}. This proposition appears to be in agreement with the experimental results of Morrow and Ricketts (1988) and Sibley *et al.* (1988) which showed that higher CO_3^{2-} or HCO_3^- concentrations shorten the induction stage and expedite dolomitization.

Extensive dolomitization is known to occur in organic rich hemipelagic sediments (Baker and Burns, 1985; Burns *et al.*, 1988) and hypersaline sediments (Gunatilaka *et al.*, 1984). Baker and Kastner (1981), Kastner (1983, 1984, 1988), Gunatilaka *et al.* (1984), and Burns *et al.* (1988) concurred that dolomitization in these settings was promoted by an increase in the HCO_3^- content in the pore waters because of sulfate reduction. This process is particularly attractive because it raises the concentration of the dolomitization promoter (HCO_3^-) by reducing the content of the inhibitor (SO_4^{2-}). However, there are numerous examples of dolomites forming in marine conditions that have undergone little or no sulfate reduction (Saller, 1984; Aharon *et al.*, 1987; Mazzullo *et al.*, 1987; Carballo *et al.*, 1987; Mitchell *et al.*, 1987). Gunatilaka *et al.* (1984) and Kastner (1984) suggested that meteoric-sea water mixing may be an effective process in reducing the SO_4^{2-} content in solutions. Therefore, it may be suggested that the schizohaline environment is a favourable setting for dolomitization because of SO_4^{2-} dilution, rather than a result of Mg/Ca ratio decrease as suggested by Folk and Land (1975).

Gaines (1980) showed that organic materials and animal proteins associated with biogenic calcium carbonates inhibit dolomitization. He suggested that this negative kinetic effect can be effectively removed in fresh water diagenetic environments through oxidation.

On the basis of the kinetic aspects of dolomitization, it appears that mixed meteoric-sea water remains a viable medium for dolomitizing any carbonate sequences. However, pervasive dolomitization is probably site specific and only occurs when all the factors for dolomitization such as mineralogical, geological, climatic, and time conditions are favourable.

C. TIMING OF DOLOMITIZATION EVENT(S)

The clear cut evidence that serves to constrain the timing of dolomitization of the Bluff Formation is the absence of dolomite in the Pleistocene Ironshore Formation (Jones *et al.*, 1984). This indicates that the Bluff Formation was dolomitized prior to deposition

of the Ironshore Formation at about 125,000 years ago. Two important points remain to be considered. First, did the pervasive dolomitization occur in a single phase as suggested in Paragenetic Model I or did it occur in two stages as proposed in Paragenetic Model II (Fig. VIII.1). Second, is there any other evidence that can be used to better constrain the timing of the dolomitization event(s).

Aragonite Dissolution

Preferential dissolution of original skeletal aragonite in the molluscs, gastropods and corals was common in the Bluff Formation. Conversely, skeletal components formed of high-magnesian calcite, such as red algae and most foraminifera, have been dolomitized and their textures preserved (Fig. 16a of Lockhart, 1986; Plates 9A, 9F of Pleydell, 1987). Similar dissolution of aragonitic bioclasts has been documented in the Pleistocene Belmont Formation of Bermuda (Land, 1967), the Pleistocene Hope Gate Formation of Jamaica (Land, 1973a), the Pliocene Seroe Domi Formation of Bonaire (Sibley, 1980, 1982), the Pleistocene limestones of Yucatan Peninsula (Ward and Halley, 1985), the Miocene dolostones of Gulf of Suez, Egypt (Coniglio *et al.*, 1988), and the Pliocene Blessing Formation of St. Croix, U.S. Virgin Islands (Gill *et al.*, 1989).

Kinetics

The commonly perceived sequence of carbonate dissolution, in order of decreasing solubility, is magnesian calcite, aragonite and calcite (Chave *et al.*, 1962; Pytkowicz, 1969). This is only observed in solution at or near aragonite saturation state (Walter, 1985). The dissolution rate constants are commonly an inverse function of the grain size (Keir, 1980; Dreiss, 1984; Walter and Morse, 1984). More importantly, experimental studies by Walter (1985) and Walter and Morse (1985) showed that differences in grain microstructures can override thermodynamic constraints and lead to selective dissolution of more stable mineral phase. Furthermore, Walter (1985) concluded that the microstructural

control on dissolution rate is related to the saturation state of the solution. If the solution is undersaturated with respect to all the carbonate mineral phases, the reactive surface area of the grain microstructure controls the relative rate of dissolution (Walter, 1985). In this connection, the preferential dissolution of the aragonitic bioclasts in the Bluff Formation is probably related to their complex microstructures which have large reactive surface areas. For example, branching corals such as *Stylophora* were completely dissolved, whereas some massive corals such as *Montastrea* were partly preserved.

Timing

The selective dissolution phenomenon is due to the fact that aragonite is not thermodynamically stable under earth-surface conditions (Bathurst, 1975; Berner, 1981; Morse, 1983). Thus, aragonitic sediments that are stable when bathed in sea water will dissolve or be transformed to low-magnesian calcite when exposed to fresh water. Subaerial exposure of metastable carbonate sediments of the Bluff Formation undoubtedly occurred during the relative sea level drops in late Oligocene and late Miocene times. Therefore, most of the fossil molds in the Bluff Formation may have been formed in relation to sea level falls.

Studies of Pleistocene limestones led Land (1970), Steinen and Matthews (1973), Pingitore (1976), Longman (1980), and James and Choquette (1984) to conclude that dissolution of biogenic aragonite is much more effective in the fresh water phreatic environment than in the vadose setting. Thus, the extensive dissolution of the aragonitic skeletal components of the Bluff Formation may have occurred in the phreatic diagenetic realm. The preservation of the fossil molds also indicates that aragonite dissolution probably occurred after the sediments had undergone some degree of lithification.

Land (1973a) suggested that aragonite dissolution and dolomitization of the Pleistocene Hope Gate Formation of Jamaica occurred almost contemporaneously because aragonitic fossil molds have void-lining dolomite cement but no calcite cement. A similar

conclusion was drawn by Sibley (1982) in the study of the Pliocene Seroe Domi Formation of Bonaire. The common absence of aragonite in the dolomitized portions of the Pleistocene limestones also led Ward and Halley (1985) to suggest that dolomitization occurred during or shortly after aragonite dissolution. Sibley and Gregg (1987) also suggested that because allochem molds are much more common in dolostones than limestones, the molds probably formed during or after dolomitization. Experimental dolomitization of calcareous skeletal components also suggested that dolomitization and aragonite dissolution are near contemporaneity (Bullen and Sibley, 1984).

Aragonite dissolution and dolomitization appear to be closely related in some dolomitized limestone sequences (Land, 1973a; Sibley, 1982; Ward and Halley, 1985; Coniglio *et al.*, 1988). In other dolomitic limestone sequences, the relationship between aragonite dissolution and dolomite replacement is not clear. Examples cited in the Pleistocene coral terraces on Barbados (Humphrey, 1988), the Pliocene Blessing Formation on St. Croix, U.S. Virgin Islands (Gill *et al.*, 1989), and the Eocene to Miocene Gambier Limestone on South Australia (James and Bone, 1989) do not suggest any particular relationship between aragonite dissolution and dolomite replacement in the sequences.

In the case of the Bluff Formation, the rocks are completely dolomitized; therefore, it is difficult to establish the timing of aragonite dissolution with respect to dolomitization using petrographic analysis. However, it is important to note that in all the partially or completely dolomitized Tertiary and Pleistocene limestone sequences, aragonite dissolution is common (Land, 1973a; Sibley, 1982; Jones *et al.*, 1984; Ward and Halley, 1985; Coniglio *et al.*, 1988; Humphrey, 1988; Gill *et al.*, 1989; James and Bone, 1989). Perhaps aragonite dissolution and dolomitization is a kinetic relationship because aragonite dissolution provides additional CO_3^{2-}/HCO_3^- ions for the volume to volume dolomite replacement of the calcium carbonate skeletal materials. Morrow (1982a), Machel and Mountjoy (1986), and Morrow and Ricketts (1988) also suggested that an increase in

CO_3^{2-} favours dolomitization. Because preferential dissolution of most of the aragonite fossils in the Bluff Formation would provide an additional source of CO_3^{2-}, it is suggested that their dissolution probably occurred contemporaneous with dolomite replacement (i.e. Paragenetic Model II). Furthermore, early lithification can also be achieved by dolomite precipitation in the intergranular space during dolomitization.

Mineralogical Considerations

Petrographic studies generally indicate that dolomite has selectively replaced former lime mud (Murray and Lucia, 1967; Cander *et al.*, 1988). This is because substrates with a high surface-to-volume ratio, such as micrite, provide abundant active sites for nucleation (Sibley and Gregg, 1987; Sibley *et al.*, 1988). It has also been noted that aragonite and high magnesian calcite are more susceptible to dolomitization than low magnesian calcite because metastable carbonates have higher standard free energy (Fairbridge, 1957; Sibley, 1980, 1982; Sibley and Gregg, 1987). These observations are consistent with the experimental results obtained by Gaines (1974), Bullen and Sibley (1984), and Sibley *et al.* (1988).

Sibley *et al.* (1988) showed that the mineralogical selectivity of dolomite replacement of calcium carbonate is due to the shorter induction stage for aragonite than for calcite. This shorter induction stage results in the higher dolomitization rate of aragonite than of calcite. Dolomitization of aragonite was also found to proceed at higher SO_4^{2-} concentrations than that of calcite (Baker and Kastner, 1981).

Bullen and Sibley (1984) noted that there is no difference in the dolomitization rate of cryptocrystalline aragonite, high magnesian calcite and low magnesian calcite. They concluded that crystal size rather than mineralogy is the determining factor in the abundance of nucleation sites, and hence, the rate of dolomite formation. Furthermore, the preservation of replacement fabrics is also a function of the crystal size of the original skeletal components. Cryptocrystalline skeletal components such as coralline algae,

echinoids, and foraminifera generally have their microstructures preserved during dolomitization (Bullen and Sibley, 1984). Conversely, microcrystalline fossils such as corals and molluscs commonly lose their microstructures during dolomitization (Bullen and Sibley, 1984).

The matrix dolomite of the Bluff Formation was formed by replacement of precursor calcium carbonate as shown by the dolomitized bioclasts. Mimic replacement (i.e. microstructure preserved) of the high magnesian calcitic skeletal components (e.g. red algae, foraminifera) but not the aragonitic skeletal components (e.g. corals, molluscs) suggests that the allochems had not been transformed to low magnesian calcite prior to dolomitization. This conclusion is consistent with Bullen and Sibley's (1984) experimental results. Although conversion of high magnesian calcite to low magnesian calcite may not lead to destruction of original fossil fabrics (Friedman, 1964; Land, 1967; James and Choquette, 1984), dolomitization of diagenetic low magnesian calcite is kinetically not favourable (Gaines, 1974; Sibley, 1980, 1982; Bullen and Sibley, 1984). In this connection, it is suggested that dolomitization of the Bluff Formation probably occurred prior to the stabilization of the metastable carbonates (i.e. Paragenetic Model II) in a manner similar to that suggested by Land (1973a) for the Pleistocene Hope Gate Formation of Jamaica, Sibley (1982) for the Pliocene Seroe Domi Formation of Bonaire, and Coniglio *et al.* (1988) for the Miocene carbonates of Gulf of Suez, Egypt.

Geochemical Considerations

The Cayman and Pedro Castle members of the Bluff Formation have similar $\delta^{18}O$ contents and $^{87}Sr/^{86}Sr$ ratios (Pleydell, 1987; Jones, 1989a; Pleydell *et al.*, in preparation). This geochemical information led Jones (1989a) and Pleydell *et al.* (in preparation) to suggest that dolomitization of the Bluff Formation (Paragenetic Model I) was a single event at about 5 to 2 million years ago. Therefore, in order for Model II (Fig. VIII.1) to be viable alternative, it must take into account the geochemical data.

Stable Oxygen Isotopes

The stable oxygen isotopic composition of a mineral is controlled by the isotopic composition of the fluid from which the mineral precipitates and the temperature of precipitation (Land, 1980, 1983a; Anderson and Arthur , 1983; Lohmann, 1983). The $\delta^{18}O$ composition of the diagenetic mineral can, therefore, provide useful information on the diagenetic environment.

More than 90% of the $\delta^{18}O$ values of the matrix dolomite of the Oligocene Cayman Member fall between 2.05 and 3.05‰ PDB (Fig. IX.1A), although the values range from 1.4 to 3.0‰ PDB. The low values probably resulted from calcite contamination during the separation procedure. The $\delta^{18}O$ contents of the matrix dolomite of the Miocene Pedro Castle Member are slightly higher, ranging from 2.4 to 3.4 ‰ PDB; however, most of the values are between 2.55 to 3.05 ‰ PDB (Fig. IX.1B). The similar stable oxygen isotopic contents of dolomites from the Cayman Member and the Pedro Castle Member (Fig. IX.1) may have resulted from other diagenetic phenomena rather than the single dolomitization event as suggested by Jones (1989a) and Pleydell *et al.* (in preparation). Similar data could be achieved (1) if the various dolomitization events occurred under similar diagenetic conditions, or (2) if the isotopic signatures of previously formed dolomites were overprinted by later phase diagenetic fluids.

On the basis of the geological history of the Bluff Formation (Jones and Hunter, 1989), it is likely that the two members were subjected to similar diagenetic fluids (i.e. meteoric and sea water) during island emergence in late Oligocene and late Miocene times. However, the isotopic content of the Bluff Formation was probably reset by later phase diagenetic fluids in a manner suggested by Coniglio *et al.* (1988) and Moore *et al.* (1988). It has been noted by numerous workers that stable oxygen isotopic values can be reset by recrystallization as a result of late stage diagenesis (Land, 1980, 1983a, 1985; Machel and Mountjoy, 1986; Hardie, 1987; Longstaffe, 1987). Recrystallization of earlier formed dolomites by later diagenetic fluids was suggested by McKenzie (1981), Coniglio *et al.*

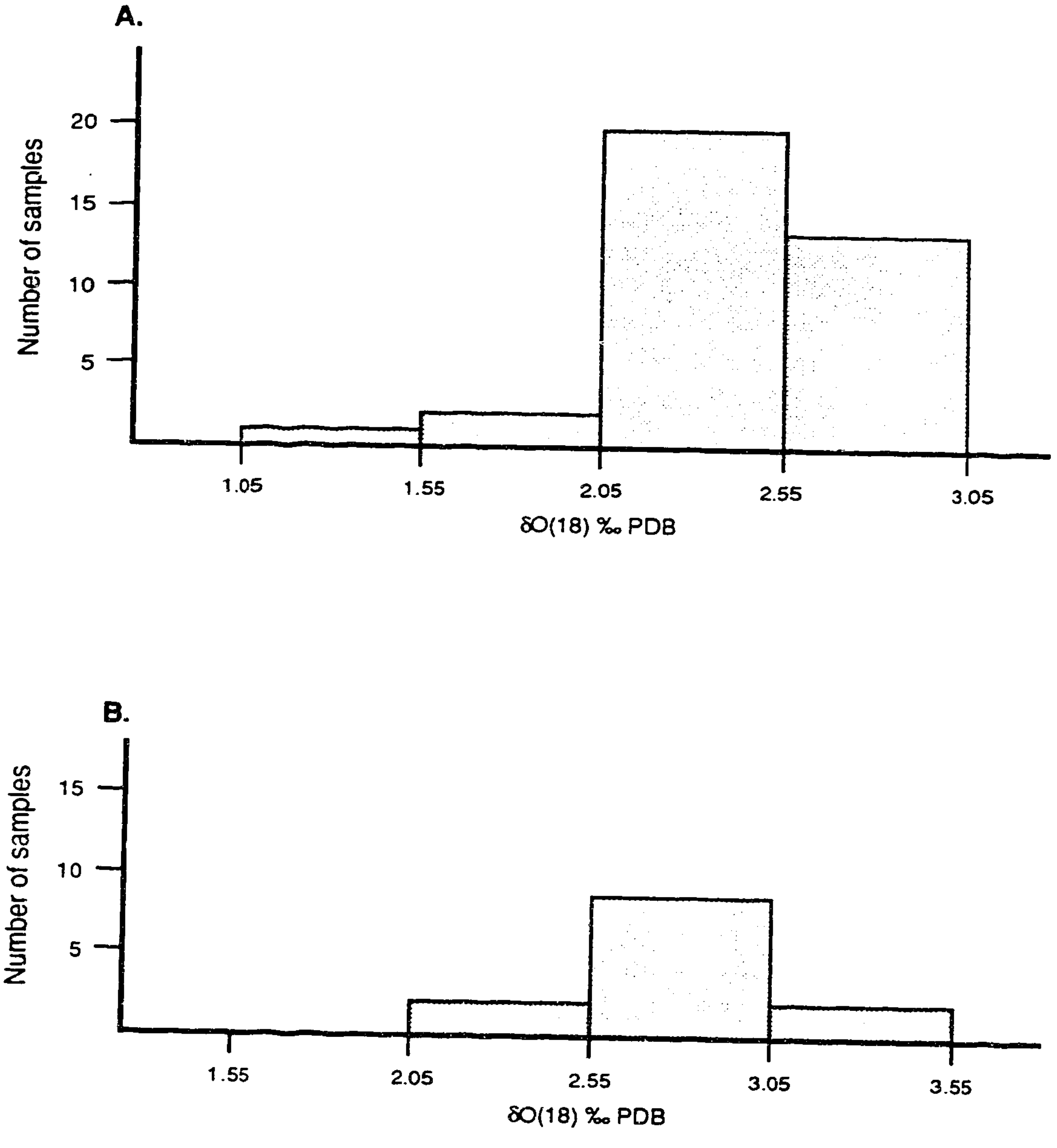


Fig. IX.1 Histograms showing distribution of δO(18) values of (A) Cayman Member dolostone and (B) Pedro Castle dolostone. Isotope data courtesy of Dr. B. Jones.

(1988), and Moore *et al.* (1988) to explain the stable isotopic composition of the dolostones from Holocene, Miocene and Jurassic ages, respectively. Thus, it appears that the stable oxygen isotopic signature of the diagenetic mineral is not a reliable means of differentiating the various stages of dolomitization without other supporting evidence.

Strontium Isotopes

The premise for using Sr isotopic ratio ($^{87}Sr/^{86}Sr$) for age dating is based on the following criteria:

(1) The Sr isotopic composition in sea water is uniform at any given time (Brass, 1976) because the oceanic residence time of Sr ($\sim 10^6$ years) is much longer than the oceanic mixing time ($\sim 10^3$ years).

(2) The Sr contained in marine carbonate, sulfate, and phosphate samples records the $^{87}Sr/^{86}Sr$ values of the sea water from which they were formed.

(3) the Sr isotopic ratio changes slowly over millions of years in a predictable trend (Burke *et al.*, 1982; Koepnick *et al.*, 1985; DePaolo and Ingram, 1985; DePaolo, 1986; Hess *et al.*, 1986; Richter and DePaolo, 1987; Rundberg and Smalley, 1989).

Studies by Saller (1984) on the Eocene strata of Enewetak Atoll and Swart *et al.* (1987) on the Pliocene and Miocene strata of the Bahamas suggest that the Sr isotopic composition may provide the age of dolomitization. This is possible because the isolated geologic location of the Enewetak Atoll and the Bahamas means that the sequence is removed from any source of dolomitizing fluids other than sea water and meteoric water. The contribution of Sr from fresh water is generally negligible relative to that of the sea water (8 ppb vs. 8 ppm; Faure *et al.*, 1967). Therefore, the Sr isotopic content of the dolomite is essentially a measurement of the Sr isotopic composition of the sea water at the time of dolomitization. Thus, the age of the dolomitization event can be obtained from the $^{87}Sr/^{86}Sr$ trend versus time data of Burke *et al.* (1982), Koepnick *et al.* (1985), DePaolo

and Ingram (1985), DePaolo (1986), Hess *et al.* (1986), Richter and DePaolo (1987), and Rundberg and Smalley (1989).

Following the approach of Saller (1984) and Swart *et al.* (1987), Jones (1989a) and Pleydell *et al.* (in preparation) showed that the Sr isotopic data fall in a narrow range (Table IX.1), with an average value of 0.7090. Using the $^{87}Sr/^{86}Sr$ sea water versus time curve of Koepnick *et al.* (1985), the average value suggests that dolomitization of the Bluff Formation was a single event that took place about 5 to 2 Ma (Jones, 1989a; Pleydell *et al.*, in preparation).

The $^{87}Sr/^{86}Sr$ sea water data are relatively well defined for the Cenozoic; nevertheless, Sr isotope versus time curves derived from different sampling sites show variation (cf. Keopnick *et al.*, 1985; DePaolo and Ingram, 1985; DePaolo, 1986; Hess *et al.*, 1986). The variation is probably caused by sample alteration (recrystallization) and uncertainty in biostratigraphic dating (Hess *et al.*, 1986; Richter and DePaolo, 1987; Rundberg and Smalley, 1989; Wardlaw, 1989). According to Koepnick *et al's.* (1985, Figs. 3 and 4) Sr-isotopic sea water curve, the present day sea water is the most radiogenic and has a $^{87}Sr/^{86}Sr$ ratio slightly less than 0.70910. This means that any $^{87}Sr/^{86}Sr$ ratios in excess of 0.70910 are meaningless values; however, a close examination of the Sr isotopic data of the Bluff Formation shows that almost half of the data are above this critical value (Table IX.1). Using the latest Sr isotope versus age trends determined by DePaolo (1986), Hess *et al.* (1986), Richter and DePaolo (1987), and Rundberg and Smalley (1989), the Sr isotopic ratios give a rather different interpretation (Table IX.1). The age of dolomitization of the Bluff Formation may be as early as 9 million years ago (Table IX.1). Although the Pedro Castle Member is presently assigned an age of approximately 16 million years, the actual age of the member is open to debate due to the lack of biostratigraphic markers in dating the sequence (Jones and Hunter, 1989; Jones, 1989a). The Pedro Castle Member may be as young as 9 million years old (I. Hunter, 1989, per. comm.). Furthermore, it is not possible to determine how much of the Pedro Castle strata

Table IX.1 $^{87}Sr/^{86}Sr$ ratios and interpretation of the age of dolomitization for dolostones from the Bluff Formation on Grand Cayman. Sr isotopic data courtesy of Dr. B. Jones.

Sample #	Age	$^{87}Sr/^{86}Sr$	Age[1] Ma	Age[2] Ma
1264	Oligocene	0.709125	NA	2.0±0.5
2002	Oligocene	0.709124	NA	2.0±0.5
2023	Oligocene	0.709062	<1.5	4.0±1.5
		0.709042*	1.5±1.0	4.0±1.5
2036	Oligocene	0.709134	NA	2.0±0.5
2037	Oligocene	0.709106	NA	2.5±0.5
		0.709045*	1.5±1.0	4.0±1.5
3077	Oligocene	0.709070	<1.0	4.0±1.5
3126	Oligocene	0.709000	3.0±2.0	6.0±3.0
3152	Oligocene	0.709000	3.0±2.0	6.0±3.0
2013	Miocene	0.709009	3.0±2.0	6.0±3.0
2018	Miocene	0.708999	3.0±2.0	6.0±3.0
2019	Miocene	0.709115	NA	2.0±0.5
2024	Miocene	0.709060	0.5±1.0	4.0±1.5
2033	Miocene	0.709080	<0.5	3.5±1.5
		0.708983*	3.5±2.0	6.0±3.0
2035	Cavity fill (skeletal grainstone)	0.709331	NA	NA
3167	Cavity fill (caymanite)	0.709140	NA	1.5±0.5

Note:
(1) Sample # refers to the catalogue no. of the Cayman Islands rock collection.
(2) All samples were analyzed at the University of Alberta, Sr isotopic data marked by an asterisk* refer to results determined by the University of Saskatchewan on the same samples.
(3) Age[1] refers to age of dolomitization determined from Sr isotopic sea water curve of Koepnick *et al.* (1985).
(4) Age[2] refers to age of dolomitization determined from Sr isotopic sea water curves of DePaolo (1986), Hess *et al.* (1986), Richter and DePaolo (1987), and Rundberg and Smalley (1989).
(5) NA means that no age can be assigned to the Sr isotopic value because it exceeds the Sr isotopic ratio of the present day sea water.

was lost by erosion, and hence, to determine the age of the missing strata. Based on the older dolomitization age and the uncertainty in the age assignment of the Miocene Pedro Castle Member, it would appear that sediments of the Pedro Castle Member may have been dolomitized early in the diagenetic history, probably in relation to the late Miocene sea level fall at about 10 Ma (Vail *et al.*, 1977; Haq *et al.*, 1987). If this age interpretation is correct, it would suggest that the dolomitization of the Pedro Castle Member occurred prior to the stabilization of the metastable calcium carbonate minerals. Thus, the dolomite fabric of the Miocene Pedro Castle Member resulted from an early dolomitization event. If so, the petrographic fabric of the Oligocene Cayman Member, which is similar to the Miocene Pedro Castle Member, might also have resulted from early dolomitization of metastable carbonate sediments during late Oligocene times.

Another source of uncertainty is shown by the Sr isotopic values obtained from the same samples by two separate laboratories (Table IX.1). The results are generally similar, but there are measurable differences, particularly for sample #2033 (Table IX.1). The $^{87}Sr/^{86}Sr$ ratio determined by the University of Alberta gives an age of 3.5±1.5 Ma whereas the ratio determined by the University of Saskatchewan gives an age of 6.0±3.0 Ma (Table IX.1). This indicates that results obtained from different laboratories may vary.

It is also important to note that the skeletal grainstone and the caymanite samples from the Cayman Member have the highest radiogenic Sr isotopic ratios (Table IX.1), and hence, the youngest dolomitization age. This indicates that the latest dolomitization fluid had penetrated deep into the Oligocene Cayman Member. This young Sr isotopic age is consistent with the Paragenetic Model II which suggests that the caymanite and skeletal sands in the Cayman Member were dolomitized at a later time than the host rock. However, the Sr isotopic value for the skeletal grainstone is questionable because it exceeds the highest point of the $^{87}Sr/^{86}Sr$ curves determined by DePaolo (1986), Hess *et al.* (1986), Richter and DePaolo (1987), and Rundberg and Smalley (1989).

Machel and Mountjoy (1986) noted that Sr isotopic ratios can be reset by recrystallization. Land (1985) also suggested that the radiogenic Sr ratios may indicate fluid that stabilizes a previously formed dolomite. Studies of the Upper Jurassic Smackover dolomites by Moore *et al.* (1988) also suggested that Sr isotopic ratios of the dolomite may have been reset by later-phase recrystallization. Therefore, overprinting of the Sr isotopic ratios of the previously formed dolomites of the Cayman Member may explain the generally uniform Sr isotopic composition of the Bluff Formation. The spread in the dolomitizing age data (2.0±0.5 to 6.0±3.0 Ma; Table IX.1) may indicate the continual equilibration of the previously formed dolomites until late Pliocene and early Pleistocene times. The Sr ratios also suggest that dolomitization is a slow and gradual process.

Recrystallization

The term recrystallization is commonly used to describe any change in the fabric of a mineral (Bathurst 1975). In the context of this study, recrystallization of the matrix dolomite of the Bluff Formation refers to transformation of poorly ordered and/or nonstoichiometric dolomite to ordered and stoichiometric dolomite. Sibley and Gregg (1987) preferred the term neomorphism to recrystallization because such transformation can be considered a change in mineralogy. Changes of the $\delta^{18}O$ contents and $^{87}Sr/^{86}Sr$ ratios probably accompany recrystallization.

Experimental studies by Glover and Sippel (1967) showed that cation-disordered rhombohedral carbonates of dolomitic composition, precipitated at room temperature, slowly transformed to aragonite when left in contact with their supernatant solutions or with pure water. Similarly, Gaines (1974), Katz and Matthews (1977), Baker and Kastner (1981), Bullen and Sibley (1984), and Sibley *et al.* (1988) showed that the initial products of experimental dolomitization was metastable, poorly ordered, calcium rich dolomite which converted to well ordered dolomite with sufficient time.

Land (1980), Sperber *et al.* (1984), and Hardie (1987) noted that any poorly ordered Ca-rich phase formed at or near earth surface will have a large thermodynamic drive to undergo spontaneous ordering as time progresses because of the large order-disorder energies in dolomites. Lumsden and Chimahusky (1980) and Sperber *et al.* (1984) also suggested that dolomite stoichiometry may be strongly time dependent as the rocks are exposed to the ever changing pore fluids after their initial precipitation. The stoichiometry of the dolomites of the Bluff Formation, therefore, may reflect the result of diagenetic stabilization.

Petrographic Considerations

Paragenetic Model I (Fig. VIII.1; Pleydell, 1987; Jones, 1989a; Pleydell *et al.*, in preparation) suggests that dolomitization of the Bluff Formation occurred about 5 to 2 million years ago. If so, the metastable carbonate sediments (aragonite and high magnesian calcite) would have been subjected to extensive meteoric influence in late Oligocene and late Miocene times as a result of relative sea level falls prior to dolomitization. During these periods of subaerial exposure, most of the metastable carbonates would have transformed to low magnesian calcite in a manner similar to that documented for the Pleistocene limestones of Bermuda (Land, 1970), Barbados (Steinen and Matthews, 1973; James, 1974; Pingitore, 1976), and Florida (Martin *et al.*, 1986; Schmoker and Hester 1986). These studies concluded that significant diagenetic modification takes place in the fresh water phreatic zone where the matrix was cemented by microspar and metastable carbonates were inverted to low magnesian calcite or partially dissolved. Because the time for the inversion of aragonite to calcite is in the order of thousands to hundred of thousands of years (Harrison, 1975; Halley and Harris, 1979), it is reasonable to suggest that most carbonate sediments were inverted to low magnesian calcite prior to the Model I dolomitization about 5 to 2 Ma.

Studies of marine shorelines and coral terraces on Barbados (Mesolella *et al.*, 1969; Bender *et al.*, 1973; Steinen *et al.*, 1973), Bahamas (Neumann and Moore, 1975), Bermuda (Harmon *et al.*, 1978), New Guinea (Bloom *et al.*, 1974), and Hawaii (Ku *et al.*, 1974) established that eustatic sea level has changed at least six times during the past 125,000 years. These frequent sea level changes probably resulted in the formation of unstable hydrogeological systems that were not conducive to mineral stabilization of the carbonate sediments. If so, the sediments of the Ironshore Formation were exposed to the marine phreatic and vadose diagenetic zones at different times after their deposition. Furthermore, marine phreatic and vadose diagenetic realms are not active diagenetic environments for mineral stabilization and cementation relative to the fresh water phreatic zone (Land, 1970; Steinen and Matthews, 1973; Longman, 1980; James and Choquette, 1984). This is probably the main reason the Ironshore Formation still contains a high content of aragonite. The Bluff Formation, however, was subaerially exposed over long periods of time (in the order of 10^6 years) as a result of the major regression in late Oligocene to early Miocene and late Miocene to early Pliocene times. These periods of island emergence would have resulted in extensive meteoric influence, particularly in the central part of the islands where marine influence is less severe. Therefore, the lack of diagenetic modification of the Ironshore Formation cannot be used as a direct reference for the study of the diagenesis of the Bluff Formation.

Pleydell (1987) and Jones (1989a) suggested that the petrographic homogeneity of the Bluff Formation is indicative of single stage dolomitization (i.e. Paragenetic Model I). According to Jones and Hunter (1989), Cayman Member was subaerially exposed for about 15 million years prior to deposition of the Pedro Castle Member whereas the Pedro Castle Member was exposed for less than 10 million years prior to dolomitization. Furthermore, the Cayman Member probably experienced an additional phase of subaerial exposure and meteoric diagenesis when the Pedro Castle Member was emerged above sea level. If dolomitization was a single event, the carbonate precursors of the two members

would have to be altered to the same fabric, particularly the crystal size, prior to the pervasive dolomitization in order to form petrographically identical dolostones for the two members. The mineral stabilization and cementation during meteoric diagenesis would certainly make it difficult to preserve the microfabrics of the skeletal components as well as they are preserved.

The finely crystalline to microcrystalline fabrics of the Bluff Formation (Plates VI.1A, 1B) also argue against inversion of metastable carbonates prior to dolomitization because mineral stabilization commonly results in an increase in crystal size (Steinen and Matthews, 1973; Steinen, 1978, 1982; Longman, 1980). Folk (1973) and Morrow (1982b) argued that finely crystalline dolomites are indicative of early replacement. Modern dolomites reported from Jamaica (Mitchell *et al.*, 1987) and Florida (Carballo *et al.*, 1987) have dolomite crystal size similar to that of the Caymanian matrix dolomite. Therefore, based on the petrographic fabrics of the Bluff Formation, it is suggested the dolomites of the Bluff Formation probably formed by early replacement of metastable carbonates as suggested by Paragenetic Model II.

Other Circumstantial Considerations

The following features are circumstantial evidence that assist in supporting the argument for Paragenetic Model II.

Cavity Lining Dolomite Cements

Cavity lining dolomite cement is common in the Oligocene Cayman Member, but it is absent in the Pedro Castle Member (Jones and Hunter, 1989). In the Cayman Member the dolomite cements lining aragonitic fossil molds were subsequently overlain by internal sediments (Plate VI.6F). The internal sediments were probably deposited during the early stages of the marine transgression in early Miocene times prior to deposition of the Pedro Castle Member (Fig. VIII.1; Jones and Hunter, 1989).

In support of Paragenetic Model I, Jones (1989, pers. comm.) suggested that the dolomite crystals were formed in the cavities prior to host rock dolomitization (Fig. VIII.1) and were not affected by later pervasive dolomitization because of their stable form. Void-lining and filling dolomite cement is common in dolostone formations (Beales, 1971). Dolomite cements rooted on limestone are not common, but are reported from the late Pleistocene Falmouth Formation of Jamaica (Land, 1973b) and from the Pleistocene Yucatecan limestones of Yucatan Peninsula (Ward and Halley, 1985). In both sequences, replacive dolomite is present in the matrix, and other forms of meteoric cement such as calcite spar and/or zoned dolomite and calcite are commonly associated with the dolomite cement. There is, however, no petrographic evidence to indicate that precipitation of other types of meteoric cement accompanyed the precipitation of the dolomite cement in the Cayman Member.

Land (1973a, 1973b) suggested that replacive dolomite and dolomite cement were formed at or near contemporaneity in the middle Pleistocene Hope Gate Formation and the late Pleistocene Falmouth Formation of Jamaica. Similarly, Holocene dolomitization of supratidal sediments from Sugarloaf Key, Florida also showed dolomite replacement and contemporaneous dolomite precipitation (Carballo *et al.*, 1987). Experimental dolomitization of calcareous components by Bullen and Sibley (1984) also showed that dolomite cementation accompanies dolomitization of the substrates in some cases. In this connection, it is suggested that the void lining dolomite cements that predated the influx of internal sediments were probably formed at or near contemporaneity with early dolomite replacement of the Cayman Member.

Cave Development

Cave development probably began in late Oligocene times when the Cayman Member was subaerially exposed due to a sea level drop. This early karst development

(Phase I in Fig. VIII.1) is indicated by the filling of caymanite and skeletal sands prior to deposition of the Pedro Castle Member.

Most caves in the Cayman Member were not completely filled by internal sediments, suggesting that the Cayman Member was lithified prior to karst development or it would have been subject to cave collapse. From studies of the Eocene to Miocene Gambier Limestone of southern Australia, James and Bone (1989) presented an example where karst is developed in the soft to friable sediments without significant cementation. In the Gambier Limestone, the original sediments were entirely calcite or Mg-calcite (James and Bone, 1989). Conversely, the original sediments of the Bluff Formation were predominantly aragonite. For aragonitic sediments, leaching or inversion of skeletal aragonite and cementation are common when the sediments are exposed to meteoric diagenetic realm (Longman, 1980; James and Choquette, 1984).

According to Paragenetic Model I (Fig. VIII.1, Jones, 1989a; Pleydell *et al.*, in preparation), lithification of the carbonate sediments was probably accomplished by calcite cementation in the meteoric vadose and phreatic realms. Conversely, in Model II (Fig. VIII.1), it suggests that lithification was achieved by dolomite precipitation in intergranular space at about the same time as early dolomite replacement. There is, however, no petrographic evidence indicating pre-existing meteoric calcite cement. Furthermore, the originally high lime mud (micrite) content of the carbonate sediments of the Cayman Member would have facilitated extensive diagenesis of the sediments when exposed to meteoric phreatic realm. Steinen (197[illegible], 1982) and Lasemi and Sandberg (1984) noted that diagenesis of lime mud in fresh water environments involves rapid stabilization of aragonite and high magnesian calcite to low magnesian calcite and considerable precipitation of microspar in intergranular voids. This diagenetic modification would have resulted in significant loss of primary matrix porosity and in permeability of the carbonate sediments of the Cayman Member, characteristics required for the movement of the dolomitizing fluid and for delivering Mg^{2+} to the site of reaction. In order to form a homogeneous dolostone,

high intergranular porosity and permeability is particularly important. Late dolomitization after extensive meteoric diagenesis and cave development suggests that dolomitizing fluid would flow preferentially along open joints and cave passages. If so, dolomitization fronts would probably develop in the vicinity of the main avenues of fluid flow. Dolomite dikes found in the Precambrian Wyman Formation of northeastern Inyo Mountains of California were postulated by Zenger (1976) to have been formed from dolomitization along fractures. The absence of any recognizable dolomitization fronts in the vicinity of caves suggests that dolomitization of the Cayman Member probably occurred prior to transformation of metastable carbonates and cave development.

Synopsis

The one time dolomitization event (Model I) suggested by Jones (1989a) and Pleydell *et al.* (in preparation) is a simple model that satisfies the geochemical and petrographic data. However, the geochemical data (oxygen and strontium isotopes) do not permit a definitive interpretation on the timing of the dolomitization event(s). On the basis of the cumulative information on aragonite dissolution, mineralogy, petrography, isotope geochemistry and on circumstantial evidence, it is suggested that the Bluff Formation was probably dolomitized in two separate times (Model II). The earlier phase dolomitized the Cayman Member and the later phase dolomitized the Pedro Castle Member and the internal sediments (caymanite and skeletal sands). The second dolomitization event also affected the Cayman Member by resetting the geochemical signatures of previously formed dolomites, probably through increased cation ordering and stoichiometry.

D. HYDROGEOLOGICAL SYSTEM

A fluid-transport mechanism is a basic requirement for dolomitization of calcium carbonate (Hanshaw *et al.*, 1971; Morrow, 1982b; Land, 1983a, 1985; Simms, 1984; Machel and Mountjoy, 1986; Hardie, 1987). For extensive dolomitization to occur, the

diagenetic fluid must have an adequate supply of Mg^{2+} and probably $CO_3{}^{2-}$, and the diagenetic environment must have an active hydrogeological system for delivering the Mg^{2+} and $CO_3{}^{2-}$ to the reaction sites and for carrying away the Ca^{2+}. Land (1985) also suggested that dynamic systems may promote dolomitization by substrate preparation or removal of crystal poisons. This dynamic system is necessary regardless of fluid type. Calcite dissolution-reprecipitation occurs in thin reaction zones surrounding the dissolving grains (Katz and Matthews, 1977); therefore, ion diffusion probably plays an important role on a submicroscopic scale. However, advection (fluid flow) is the dominant mass-transfer process, and it is controlled by the hydrogeological conditions of the aquifer.

Sources of Mg^{2+} and $CO_3{}^{2-}$

Goodell and Garman (1969), and Hanshaw *et al.* (1971) suggested that dissolution of high magnesian calcite and a subsequent downward percolation of the Mg-enriched fluid (solution-cannibalism) can be important dolomitization processes provided that the sediments have a high proportion of magnesian calcite. In the Bluff Formation of the Cayman Islands, high magnesian calcite such red algae, foraminifera and echinoids probably formed less than 10% of the original carbonate sediments. This low proportion suggests that the high magnesian calcite could be only a minor source of Mg^{2+} for dolomitizing the calcium carbonates. The major available source of Mg^{2+} apparently is sea water or its derivatives. An external source of $CO_3{}^{2-}$ is also needed for volume for volume dolomitization with retention of microstructures (Sibley, 1980, 1982; Morrow, 1982a: Sibley *et al.*, 1988). Most of the $CO_3{}^{2-}$ was probably obtained from dissolution of aragonitic skeletal components and from sea water.

Static versus Dynamic System

The following calculation adapted from Hanshaw *et al.* (1971) illustrates the importance of fluid dynamics in the dolomitization of calcium carbonate. For a calcite grain

of 1 ml in volume with 40 % porosity, the number of Ca^{2+} positions is related to the grain porosity by

$$Ca^{2+} = \frac{\rho\ N_A\ (1 - \phi)}{M_c} = 9.7 * 10^{21}$$

where ρ = density of calcite = 2.7 g/cc

N_A = Avogadro's No. = $6.022 * 10^{23}$/mole

ϕ = grain porosity = 0.40

M_c = molecular weight of calcite = 100.09 g

Thus, replacement of one half of the Ca^{2+} by Mg^{2+} requires $4.85 * 10^{21}$ Mg^{2+} ions. Using sea water as the dolomitizing fluid, the number of Mg^{2+} ions in the pore fluid is

$$Mg^{2+} = \frac{C_m\ N_A\ \phi}{M_m\ *\ 10^6} = 1.29 * 10^{19}$$

where C_m = concentration of Mg^{2+} in sea water = 1300 mg/l

M_m = atomic weight of Mg = 24.31 g

The results show that Mg^{2+} ions available in the pores are much lower than that required to replace half of the Ca^{2+} in the calcite grain. This pore fluid obviously cannot result in complete dolomitization if the solution is static. More importantly, the calculation shows that the efficiency of replacement is a function of the rock porosity and Mg^{2+} concentration in the solution. Land (1983a, 1985) also demonstrated that, dependant on the water salinity and rock porosity, several tens (for hypersaline water) to several thousands (for brackish water) of volumes of water are needed to dolomitize a unit volume of limestone. Therefore, pervasive dolomitization can only be accomplished by active, long lasting fluid flow that facilitates continual replenishment and supply of Mg^{2+} to the dolomitization sites and removal of excess Ca^{2+}.

Dolomitization Fluids

Currently, five types of waters have been suggested as dolomitizing fluids in various diagenetic environments. They are (1) hypersaline fluid (Adams and Rhodes, 1960; Deffeyes *et al.*, 1965; Illing *et al.*, 1965; Hsu and Siegenthaler, 1969; Zenger, 1972; Morrow, 1978; McKenzie *et al.*, 1980; Patterson and Kinsman, 1982), (2) subsurface formational fluid related to burial (Jodry, 1969; Mattes and Mountjoy, 1980; Zenger, 1983; Machel, 1984; Gregg, 1985), (3) alkaline continental water (von der Borch, 1976; von der Borch and Lock, 1979; Muir *et al.*, 1980; Botz and von der Borch, 1984), (4) sea water (Fanning *et al.*, 1981; Saller, 1984; Simms, 1984; Compton and Siever, 1986; Aharon *et al.*, 1987; Carballo *et al.*, 1987; Coniglio *et al.*, 1988), and (5) mixed meteoric-marine water (Hanshaw et al., 1971; Badiozamani, 1973; Land, 1973; Randazzo and Hickey, 1977; Choquette and Steinen, 1980; Magaritz *et al.*, 1980; Randazzo and Bloom, 1985; Ward and Halley, 1985; Force *et al.*, 1986; Coniglio *et al.*, 1988; Humphrey, 1988; Searl, 1988).

Hypersaline Fluid

Jones and Ng (1988a) documented the occurrence of minor amounts of anhydrite cement in some cavities of a coastal breccia body formed in the Ironshore Formation. Similar conditions might have developed in the coastal areas of the Bluff Formation during periods of land emergence. Although evidence of significant hypersaline diagenetic fluid is absent, saline water (water having salinity slightly greater than sea water) resulting from the evaporation of surface water is common (cf. beach water, pond water and sea water in Table III.2). Salinity measurements of the main water body of North Sound by Rigby and Roberts (1976) also recorded greater than normal marine salinity (total dissolved solids of up to 42,000 ppm versus 38,000 for sea water salinity) depending on the season. Synsedimentary evaporitic environment is ruled out because of the entirely open marine

fauna. Furthermore, the absence of evidence of former evaporites argues against hypersaline diagenetic conditions.

Deep Formational Fluid (Burial)

Diagenetic fluids related to burial can be precluded in the dolomitization of the Bluff Formation because there is no stratigraphic or petrographic evidence to suggest that the formation has been subjected to deep burial.

Alkaline Continental Fluid

The lack of a large hinterland in the Cayman Islands precludes an influx of alkaline water from a continent as possible diagenetic fluid; it is not analogous to the present day Coorong area of South Australia.

Sea Water

Using the ^{18}O fractionation-temperature equation of Land (1983b), which is essentially the same as Matthews and Katz (1977), Pleydell (1987) attempted to deduce the type of dolomitization fluid based on the $\delta^{18}O$ values of the dolostone of the Bluff Formation. She concluded that dolomitization of the Bluff Formation occurred in normal marine water. At low temperature setting, however, there is much disagreement among the oxygen isotopic fractionation equations (Fig. VII.2) of Northrup and Clayton (1966), O'Neil and Epstein (1966), Sheppard and Schwarcz (1970), Fritz and Smith (1970), and Matthews and Katz (1977). Compounding the problem is the variety in forms of cation-disordered and nonstoichiometric dolomites present in the near surface setting as well as the later phase recrystallization that can reset the isotopic content. Indeed, using the same oxygen isotopic data of Pleydell (1987), the five fractionation relationships indicate dolomitizing fluid varying from 25% to 100% sea water salinity over a temperature range of 22-33°C (Table VII.5).

Although sea water has been indicated as a dolomitizing fluid in numerous carbonate sequences, it commonly requires some form of kinetic booster, such as elevated temperature (e.g. Fanning *et al.*, 1981; Saller, 1984; Aharon *et al.*, 1987), elevated salinity (e.g. Sass and Katz, 1982; Bein and Land, 1983), or sulfate reduction (e.g. Baker and Kastner, 1981; Burns *et al.*, 1988). Similarly, the Pleistocene Ironshore Formation (about 125,000 years old), which is bathed in present day sea water, shows no indication of dolomitization. Therefore, it appears that normal sea water alone is not an effective agent.

Mixed Fresh-Sea Water (Brackish Water)

It has been suggested that dolomitization of the Cayman and Pedro Castle members of the Bluff Formation occurred early in the diagenetic history in relation to the major regressions during late Oligocene and late Miocene times. Island emergence during the major regressions may have provided a land area for the recharge of meteoric water. The selective dissolution of aragonitic skeletal components in association with the contemporaneous dolomitization evidently indicates that there was a certain degree of meteoric influx. The stable oxygen isotopic data of the matrix dolomite (Table VII.1) also indicate that the dolomitizing fluids were probably brackish (25% sea water salinity) to saline water (Table VII.5, Fig. VII.3B). Unfortunately, poor understanding of the isotopic oxygen fractionation between dolomite and the precipitating fluid does not permit further refinement of the salinity range of the diagenetic fluids.

Several lines of evidence appear to suggest that the brackish ground water (Tables III.3, 7, IV.7, 8), particularly the highly brackish type (>15% sea water salinity), are kinetically favourable for dolomitization of the Bluff Formation.

(1) The water has higher salinity than the fresh water even though the latter may also be supersaturated with respect to dolomite.

(2) Molar Mg/Ca ratio of the water is greater than 1.0 and lies within the stability field of dolomite.

(3) The water has higher HCO_3^- content than the sea water, apparently through dissolution of skeletal components in the shallow zones.

(4) The water has lower SO_4^{2-} than the sea water as a result of mixing with fresh water.

(5) The shallow diagenetic environment favours removal of organic materials by oxidation.

Sulfate reduction occurs locally only in the shallow ground water on the Cayman Islands. Only one out of eleven piezometers (Table III.1) indicated SO_4^{2-} reduction with corresponding increase in HCO_3^- content (Fig. III.8). It is important to note that the water that showed sulfate reduction is from the brackish water zone. This also suggests that the brackish water zone is favourable for dolomitization because of reduction of SO_4^{2-} ions and with a corresponding increase in the HCO_3^- content.

The mixed meteoric-marine model, however, has been critically reviewed by Machel and Mountjoy (1986) and Hardie (1987) who concluded that it is not an effective mechanism for dolomitizing a thick limestone sequence. Specifically, Machel and Mountjoy (1986) and Hardie (1987) cited the lack of dolomite formation in present day mixing zone setting such as Bermuda, Barbados, Bahamas, Florida, and Yucatan Peninsula. Instead of causing dolomitization, modern mixing zone waters appear to cause subsurface karstification (Machel and Mountjoy, 1986; Hardie, 1987).

The following points attempt to highlight some of the conditions that have been overlooked in rejecting the mixed water dolomitization model:

(1) Brackish water (commonly known as mixed water) encompasses water of >4% to <100% sea water salinity (Table III.9); therefore, it has a very variable chemical composition (Tables III.3, 6, 7, IV.7, 8). Any discussion of mixed water without defining this complete spectrum of water chemistry and water-rock interaction is futile and can only add to the confusion. Furthermore, mixing can occur at an early stage of land emergence without significant water lens development. The mixing zone is a dynamic regime that has a variable thickness (Figs. II.12, 19) and

chemical properties depending on the types of flow mechanism involved. James and Choquette (1984) also illustrated that the thickness of the mixing zone on Bermuda may exceed the thickness of the fresh water zone, particularly in a karst environment.

Pigott and Land (1986) noted that meteoric influence extends from land to the offshore reef tract at Discovery Bay in Jamaica and provides a mixing zone diagenetic environment in a supposedly marine environment. If this is so, many marine limestones may have been influenced by meteoric water depending on the ground water flow system. Involvement of meteoric waters in deep formation fluids has also been noted by Hitchon and Friedman (1969).

(2) Subsurface karst present in the modern mixing zone does not necessarily mean it is forming at present. Machel and Mountjoy (1987) noted that the mixing zones in most Caribbean islands and the adjacent landmasses have shifted six times during the past 120,000 years due to eustatic sea level changes. Therefore, many subsurface karsts may well be paleokarsts. Major regressions in Late Oligocene, Late Miocene and Pliocene times (Vail *et al.*, 1977; Haq *et al.*, 1987) may also have caused karst development in the Tertiary carbonate sequences.

(3) Hydrogeological conditions should encompass the whole spectrum of surface and subsurface hydrology. On Bermuda, undersaturation of ground water with respect to carbonate minerals is largely due to the influx of CO_2 from surface peat marshes (Plummer *et al.*, 1976). On Barbados, the high topographic relief, the large catchment area, and the presence of an impermeable rock formation beneath the limestone aquifer results in the extremely high efficiency of rain water recharge (Dr. S. Foster, 1988, pers. comm.). This high volume of rain water, laden with CO_2, would greatly influenced the saturation states of the ground water. The Floridan aquifer is in a confined condition (Kohout, 1967); therefore, hydrogeological behaviour of such an aquifer is not comparable to that of unconfined aquifers that

are common on most small limestone islands. The aquifers of the Yucatan Peninsula are fed by a large continental recharge area (Sanford and Konikow, 1989) absent in small islands or atolls. Although all of the examples cited are from carbonate aquifers, they all exhibit different ground water chemistry due to differences in ground water flow systems.

(4) The presence of dolomite in three late Pleistocene raised reef terraces in southeastern Barbados was first documented by Humphrey (1988) after many years of research on the island, indicating that the lack of documentation of dolomite forming in mixing zones may be due to lack of exposures for such studies. On the basis of petrographic, stable isotope, and trace element data, Humphrey (1988) concluded that the dolomites, ranging from trace amounts to 100% in places, were formed in a mixed meteoric-sea water environment. Using a forward modelling technique, Humphrey and Quinn (1989) suggested that mixed water is capable of dolomitizing a thick limestone sequence. Furthermore, pervasive dolomitization is probably site-specific and occurs only in environments where all the conditions are favourable.

(5) The frequent eustatic sea level changes during the Pleistocene times probably produced unstable hydrogeological systems that were not conducive to dolomitization. More importantly, these sea level changes would have caused mineral stabilization and cementation; both would make the sediments/rocks more resistant to dolomitization.

Mechanism of Fluid Flow

At present, the aquifers of the Bluff Formation are characterized by heterogeneous ground water flow because of dolomitization and karstification. During the initial stage of ground water lens development resulting from island emergence, ground water flow through the poorly lithified sediments was probably predominantly intergranular. Furthermore, the fresh water lens was probably poorly developed and at an incipient stage

of formation (Fig. IX.2). However, regardless of the differences in flow characteristics between the pre-dolomitized sediments and the present day dolostone aquifers, the flow regimes of the two hydrogeological systems are probably similar (cf. Figs. II.19, IX.2).

In order for the hydrogeological system to be effective in dolomitizing the sediments/rocks, it is important that the flow regime be operative over a long period of time. Flow mechanisms (Fig. IX.2) that were responsible for delivering the Mg^{2+} and $CO_3{}^{2-}$ for dolomitization of the Bluff Formation probably included (1) downward gravitational flow, (2) downward reflux, (3) upward convection, (4) tidal pumping, and (5) diffusion.

Downward gravitational flow of rain water recharge (Fig. IX.2) is a function of the hydraulic head, which is, in turn, dependent on the rainfall quantity and intensity, land area, topographic relief, and permeability of the sediments/rocks (Figs. II.6, 8, 9, 10). Rain water recharge is important in providing the additional $CO_3{}^{2-}$ through dissolution of calcium carbonate in the vadose and/or phreatic zone, particularly the selective dissolution of aragonitic skeletal components. Dilution of sea water by rain water reduces the thermodynamic drive for dolomitization; however, it significantly reduces the kinetic constraints that inhibit dolomitization through $SO_4{}^{2-}$ dilution, $CO_3{}^{2-}$ increase, and organic oxidation. Furthermore, the lower sea levels in the past also increased the topographic relief of the islands, and hence, the hydraulic head for the ground water flow.

Downward reflux of saline water concentrated by evaporation occurs in shallow water ponds and in shallow carbonate bank/shelf (Fig. IX.2). Reflux of hypersaline brines due to density difference (Adams and Rhodes, 1960) and elevation head differential (Hsu and Siegenthaler, 1969; McKenzie, 1980) have been described for sabkha and hypersaline lagoon settings. Sass and Katz (1982) and Bein and Land (1983) documented downward reflux of sea water to slightly hypersaline fluids on shallow carbonate platforms and broad shelves respectively. Simms (1984) suggested that reflux may occur with sea water of only slightly elevated salinity on modern carbonate platforms. In the case of the Cayman

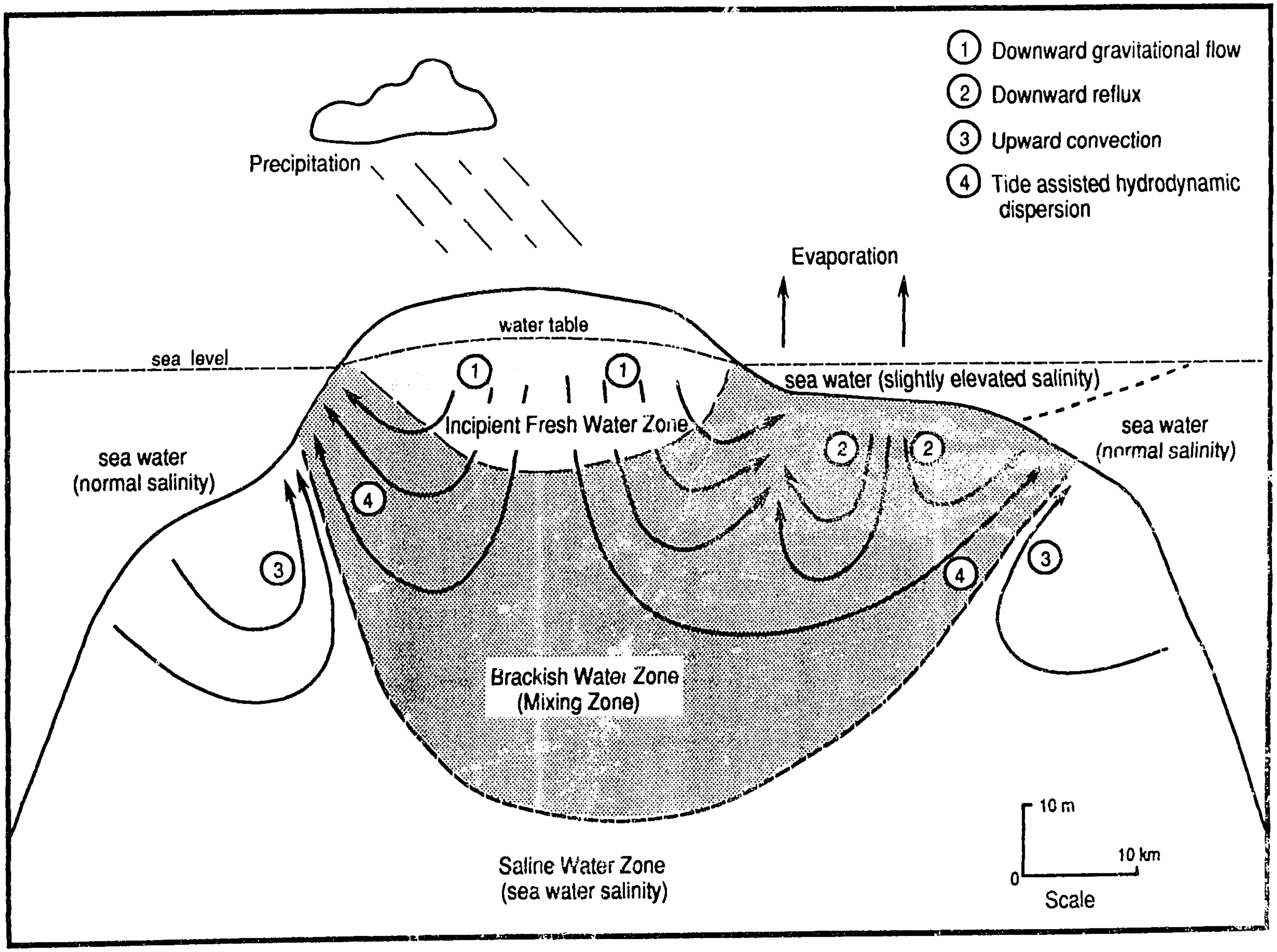


Fig. IX.2 Schematic diagram showing ground water flow regime in an emerging landmass.

Islands, the rain water recharge would have reduced the density of the pore waters and should facilitate this downward flow of sea water and/or saline water.

Upward convection of thermally circulated sea water was originally documented by Kohout (1967) and Kohout *et al.* (1977) in the Floridan aquifer. This thermal convection model, a means of conveying geothermally heated sea water for dolomitization of calcium carbonate, has been proposed for the west coast of Florida (Fanning *et al.*, 1981), Enewetak Atoll (Saller, 1984) and the atoll of Niue Island (Aharon *et al.*, 1987). In these studies, the upward convectional flow of sea water was confirmed by geochemical data. Simms (1984) suggested that convective flow should be present in all steep marginal platforms where there is a strong horizontal pore water density gradient between warm water in platform interiors and surrounding sea water. On the Cayman Islands, it is difficult to determine whether or not there was a heat source at times of dolomitization. The proximity of the Cayman Islands to the mid-oceanic rise, however, suggests the possibility of some forms of heat flow in the past. Fluid density gradient resulting from thermal effect, however, may be caused by the salinity reduction of pore fluids in the aquifers due to rain water recharge on the landward side (Fig. IX.2).

Tidal pumping of Florida Bay sea water has been suggested as the mechanism for the dolomitization of small scale supratidal crusts on Sugarloaf Key of Florida (Carballo *et al.*, 1987). The effect of tidal fluctuation on the ground water system of the Cayman Islands (Figs. II.17, 18) is well exemplified by the thick transition zone (brackish water) developed between the fresh water and the underlying saline water (Figs. II.12, 19). The transition zone of brackish water is formed as a result of tide-generated hydrodynamic dispersion (Fig. IX.2; Cooper, 1964; Kohout, 1964). The ground water table fluctuates in response to semi-diurnal and seasonal tides. The inflow of sea water into the aquifer is a function of the tidal amplitude, and time lag between the sea water and ground water tide (Table II.2). The latter is inversely related to the permeability of the aquifer.

Diffusion of Mg^{2+} from sea water through the sediments is a very slow and ineffective pumping mechanism (Land, 1985; Hardie, 1987). Using a Mg mass balance calculation, Compton and Siever (1986) concluded that Mg^{2+} diffusion from overlying sea water can account for the early diagenetic dolomite (0.5-20% by volume) formed in the uppermost 100 m of the Monterey Formation, Santa Maria basin area of California. Although diffusion alone is probably not able to cause pervasive dolomitization, it is a viable mechanism of supplying Mg^{2+} to the accumulating sediments. These early dolomites may act as seed crystals for pervasive dolomitization at a later stage.

Synopsis

Mixed fresh-marine water, which has fewer kinetic barriers, remains a viable medium for dolomitization. The fresh water recharge also creates density gradients in the flow system to facilitate ground water movement through the sediments/rocks. The diagenetic fluids that caused the pervasive dolomitization of the Bluff Formation were probably sea water that was modified to a certain extent by rain water during an early stage of land emergence in late Oligocene (for the Cayman Member) and late Miocene (for the Pedro castle Member) times. Stable oxygen isotopic results suggest that the degree of meteoric influence ranges from 0 to 75% fresh water by volume depending on the fractionation equations used and temperatures of the diagenetic fluids (Fig. VII.3). The flow mechanism (Fig. IX.2) was similar to that at present, but the fresh water lenses were probably irregularly distributed. It is also important to note that higher land relief in the past, due to lower sea levels, would have facilitated fluid movement through the sediments/rocks by increasing the hydraulic gradient.

Meteorological records on Grand Cayman for the last twenty years have shown appreciable changes in rainfall, temperature, and the amount of sunshine (Figs. II.7, 11). The paleoclimatological regimes might play a role in reducing some of the kinetic constraints so as to promote dolomitization. Kastner (1984, 1988) and Land (1985) also

suggested that the SO_4^{2-} content and the Mg/Ca ratio of sea water might have changed throughout geological time. All of these would have a significant impact on the nature of the mixed water environment.

X. DIAGENETIC INTERPRETATION OF THE BLUFF FORMATION II: KARSTIFICATION

The Bluff Formation has undergone numerous stages of karstification as a result of sea level fluctuations since late Oligocene times (Jones and Smith, 1988). This study (1) identifies the stages of karst development, (2) highlights the chemical equilibria, kinetic concepts and biological effects on carbonate dissolution, and (3) examines the mechanism for karstification.

A. STAGES OF KARSTIFICATION

Jones and Hunter (1989) suggested that the Oligocene Cayman Member of the Bluff Formation was exposed and subjected to karst development during late Oligocene and early Miocene times. Similarly, following regression in late Miocene times, the Miocene Pedro Castle Member and the underlying Oligocene Cayman Member were also subjected to karsting (Jones, 1989a). Frequent fluctuations of sea level in the Caribbean region during late Pleistocene times (Mesolella *et al.*, 1969; Bender *et al.*, 1973; Steinen *et al.*, 1973; Neumann and Moore, 1975; Harmon *et al.*, 1978) means that karst formation has been an ongoing process.

Precise dating of the different stages of karstification is difficult because each stage of karst development further modified the inherited karst features. Stringfield *et al.* (1979) noted that in areas where paleokarst is not too deeply buried, it may be incorporated into present circulation systems such as the artesian aquifer of Tertiary age in southeastern Georgia and Florida. Thus, the present day hydrogeological regime is the end product of numerous past and the present karst processes. It is also difficult to assess the depth of karstification in response to each base (sea) level change because of the overlapping karst effect. Furthermore, changes in the surface and ground water drainage began as soon as the carbonate rocks were elevated above sea level and circulation was established (Stringfield and LeGrand, 1971; Longman, 1980).

Jones and Smith (1988) suggested that some cave formations post-dated dolomitization of the Bluff Formation because the caves cut through dolomitized cavity fills and unaltered speleothemic calcite. The exposures of Miocene Pedro Castle Member give no indication of karst development (Fig. X.1); however, this may simply be due to limited number of outcrops. The different periods of karst development (Fig. VIII.1) on the Bluff Formation can be termed Phase I' (late Oligocene to early Miocene), 'Phase II' (late Miocene to early Pliocene), and 'Phase III' (late Pliocene to late Pleistocene).

Speleothemic precipitation and internal sedimentation may partly or completely fill many caverns and fissures on the Cayman Islands (Lockhart, 1986; Smith, 1987; Jones and Smith, 1988). On the basis of the type and amount of cave fills, the cave systems in the Oligocene Cayman Member of the Bluff Formation can be divided into four categories (Figs. X.1, 2):

(1) Caves filled with completely dolomitized caymanite (colour banded) and/or skeletal grainstone, which may or may not be overlain by undolomitized flowstone and/or terra rossa (Figs. X.1, 2). Examples of Type 1 cave systems include caves exposed in Pedro Castle Quarry on Grand Cayman and caves cut by Faith Caves opposite Faith Hospital on Cayman Brac (Figs. X.2, 3).

(2) Caves filled with undolomitized flowstone and terra rossa but no caymanite (Figs. X.1, 2). Examples of Type 2 cave systems include caves exposed in Pedro Castle Quarry, caves cut by Pirates Caves near Bodden Town on Grand Cayman and caves cut by Great Caves near Pollard Bay on Cayman Brac (Figs. X.2, 3).

(3) Caves partially filled with assorted speleothems such as flowstones, stalactites, stalagmites, terraced rimstones, and cave pisoliths (Fig. X.2). Examples of Type 3 cave system include Old Man Bay Caves near Old Man Bay Village on Grand Cayman, Great Caves near Pollard Bay, Hurricane Caves near Spot Bay and Salt Water Point Caves on Cayman Brac (Fig. X.3).

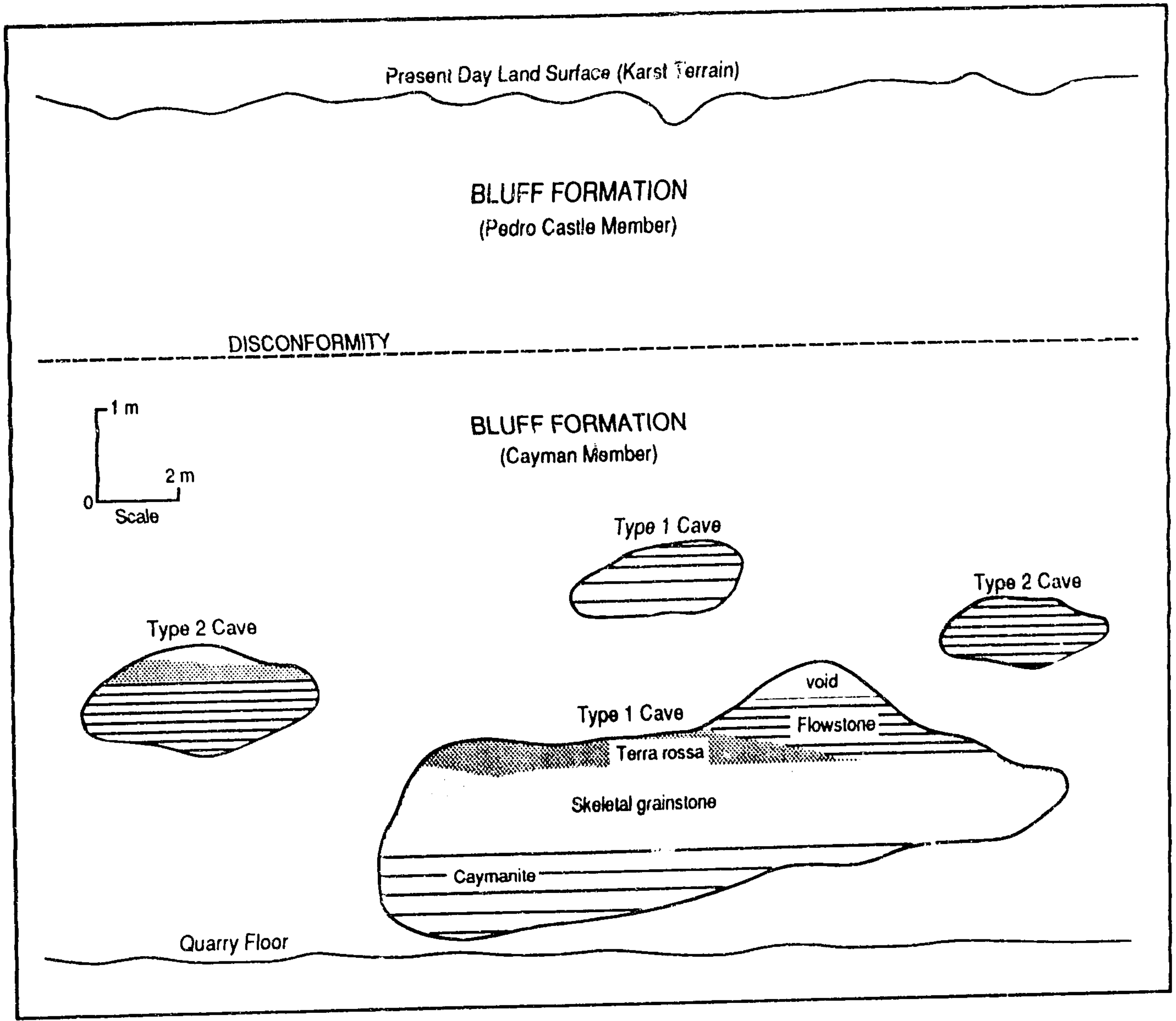


Fig. X.1 Schematic diagram of quarry wall exposure at Pedro Castle Quarry on Grand Cayman showing cavity fills in Type 1 and 2 cave systems.

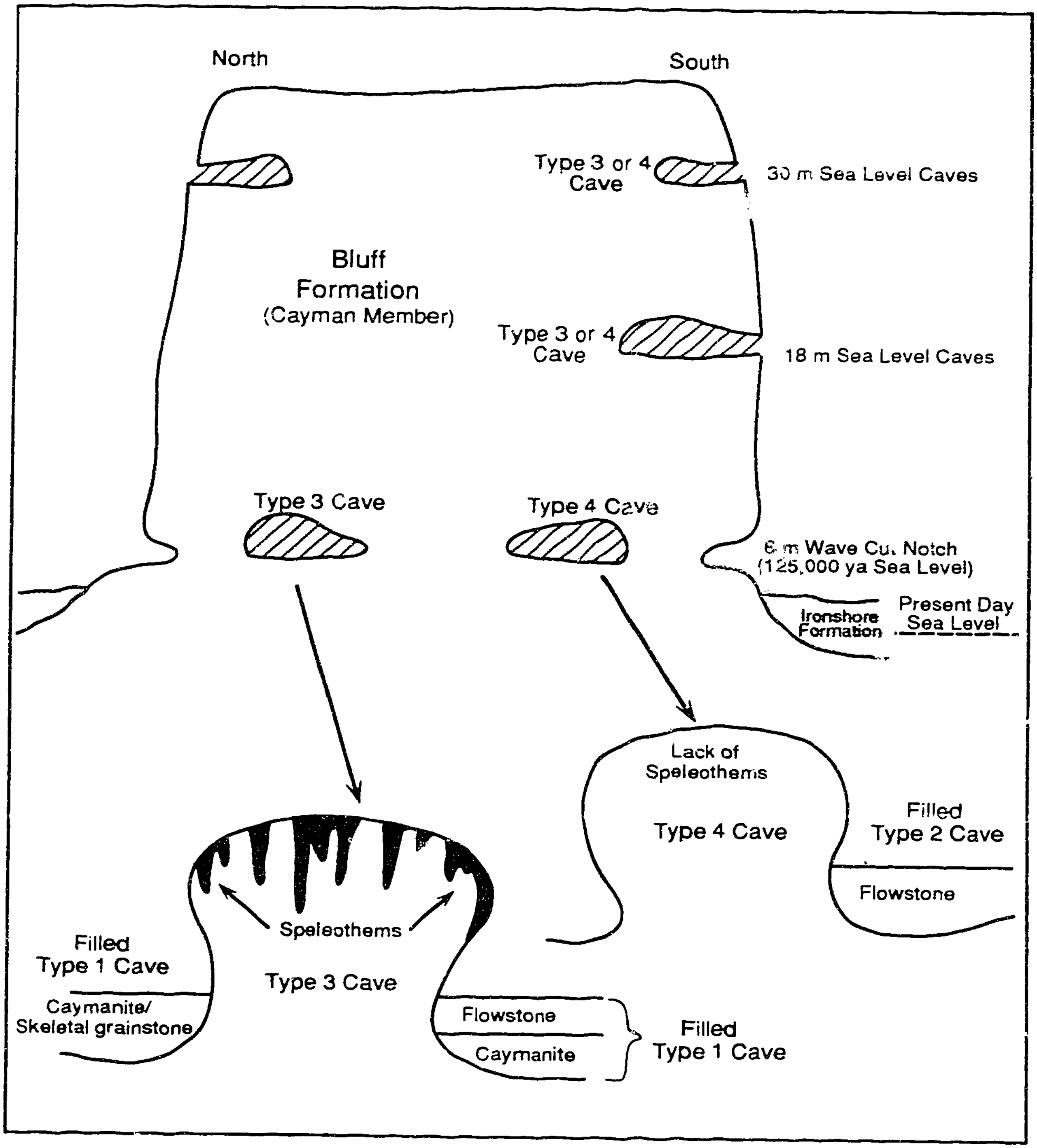


Fig. X.2 Schematic north-south cross-section of Cayman Brac showing the different levels of sea level caves and the four types of cave systems. Diagram not in scale.

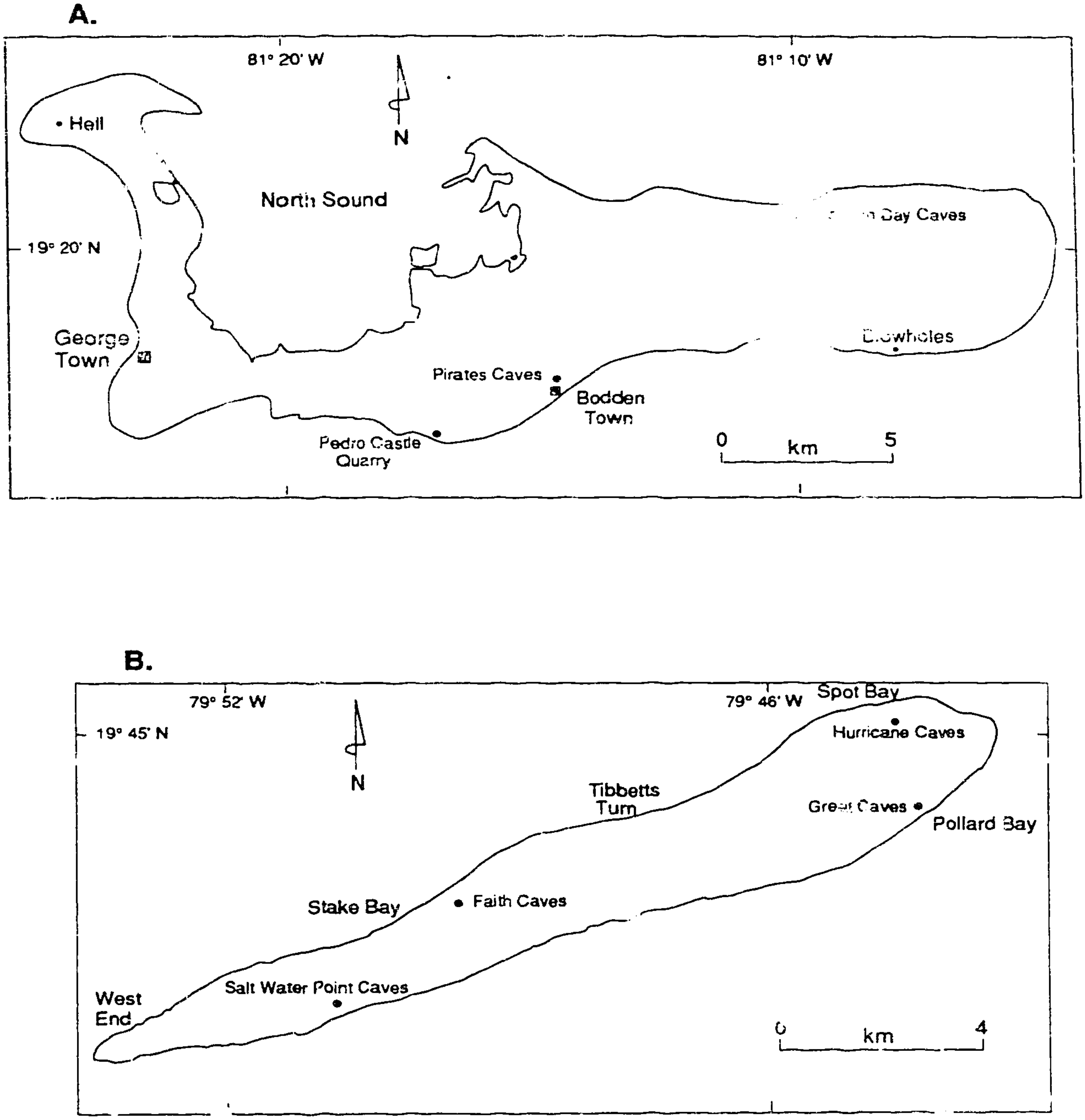


Fig. X.3 Sketch map of (A) Grand Cayman and (B) Cayman Brac showing localities of caves cited in text.

(4) Open caves with no speleothems but commonly floored with terra rossa (Fig. X.2). Examples of Type 4 cave system include Pirates Caves on Grand Cayman and Faith Caves on Cayman Brac (Fig. X.3).

The first two types (Type 1 and 2) of cave are generally less than 20*5 m^2 in vertical section (observed in quarry wall of Pedro Castle Quarry) and do not appear to form extensive cave networks. Conversely, the last two types (Type 3 and 4) commonly measure up to 5*5 m^2 in cross section and form extensive networks of cave passages (in the order of km) and chambers.

Type 1 caves probably formed during late Oligocene to early Miocene times when the Cayman Member was subaerially exposed due to sea level drop. The timing of their formation is inferred from the presence of caymanite fill because Jones and Hunter (1989) noted that caymanite probably entered the cave system prior to the deposition of the middle Miocene Pedro Castle Member (Jones and Hunter, 1989). Thus, the Type 1 caves are related to the 'Phase I' karst development (Fig. VIII.1).

Dating of Type 2 caves is problematic. The absence of dolomitized caymanite suggests that the Type 2 caves might have formed in late Miocene to early Pliocene times when the strata was again exposed in response to sea level drop. If so, the Type 2 cave system might be related to the 'Phase II' karst development (Fig. VIII.1). However, the absence of caymanite may be the result of blockage of solution channels that prevented the influx of internal sediments.

Type 3 and 4 cave systems are clearly younger than Type 1 and 2 caves because they cut through the latter two systems (Fig. X.2; e.g. Old Man Bay Caves and Pirates Caves on Grand Cayman, and Faith Caves and Great Caves on Cayman Brac). They also cut through the undolomitized flowstones in Type 1 and 2 caves suggesting that Type 3 and 4 cave formation were post-dolomitization. The youngest dolomitization age given by the Sr isotopic data (Table IX.1) is 2.0±0.5 Ma, which implies that the caves probably formed

in Pleistocene times. Type 3 and 4 cave systems appear to be genetically related because the two types of cave can be traced along the same horizon on Cayman Brac. Some caves developed at the wave-cut notch about 6 m above present day sea level (Jones and Ng, 1988a, Jones and Smith, 1988). Jones and Smith (1988) also suggested that the wave cut notch probably developed when the carbonate sediments of the Ironshore Formation were deposited about 125,000 years ago (Woodroffe *et al.*, 1983). Thus, it can be postulated that the Type 3 and 4 caves that are associated with the 6 m wave-cut notch probably formed in the late Pleistocene. On Cayman Brac, two other levels of caves, formed at about 18 m (e.g. Great Caves) and 30 m (e.g. Hurricane Caves) above present day sea level, probably belong to the Type 3 and/or 4 categories (Fig. X.2). They are either open or partially filled with speleothems. The horizontal orientation of the cave passages probably indicates former sea level high stands or earlier tectonic uplift of the island. It appears that the latter proposition is more reasonable because eustatic sea levels in the last 125,000 years (Mesolella *et al.*, 1969; Bender *et al.*, 1973; Steinen *et al.*, 1973; Bloom *et al.*, 1974; Ku *et al.*, 1974; Neumann and Moore, 1975; Harmon *et al.*, 1978) were lower than the sea level high stand 125,000 years ago. Thus, it appears that most of the sea level caves are correlated to the 'Phase III' karst development (Fig. VIII.1).

Other evidence of cave development is present in the Oligocene Cayman Member. On Cayman Brac, a cavern 2 m in height, encountered by well B5 (Fig. VI.2) at about 20 m above present sea level, may be correlatable with the sea level cave at about 18 m. Similarly, the perched water lens in well B1 (Fig. VI.2), at about 3.5-10 m above present sea level, may be related to the wave-cut notch at 6 m. Deep well drilling (> 20 m) on the western part of Grand Cayman (Fig. III.2) commonly encountered large caves at about 25-40 m below present sea level, which may correspond with the submerged wave-cut notch at about 21 m below present sea level. Therefore, most of the Type 3 and 4 cave development is probably related to the various levels of sea level high in late Pleistocene.

However, the relationship between sea level elevation and the Type 1 and 2 cave systems is difficult to define.

Cave development in association with the sea or base levels has been noted in many areas. Different levels of cave development effected by changes in Pleistocene sea level were recorded in the Ingleborough district of England (Sweeting. 1950), in Peloponnesus, Greece (Burdon, 1967), on the southern coast of Australia (Jenning, 1963) and on the south coast of Tallahassee, Florida (Stringfield, 1966). Similarly, distinct levels of horizontal cave passages resulting from changes in base level were documented in the southwest Edwards Plateau of Texas (Kastning, 1983) and in Dejiang, Guizhou Province of China (Song *et al.*, 1983).

In addition to the effect of past sea level high stands, the extensive networks of Type 3 and 4 cave systems are probably related to solution features preferentially developed along joints and fractures in a manner suggested by Ford and Ewers (1978) and Ford (1988). If so, a phase of intense joint development probably occurred prior to Type 3 and 4 cave formation but after Type 1 and 2. The lack of extensive networks in Type 1 and 2 caves, however, may be indicative of a different climatic regime or of a much lower sea level in late Oligocene times which exposed the rocks predominantly to the vadose zone.

Jointing is a multi-phase phenomenon (Fig. VIII.1). Joints of different attitudes contained diverse fills. The best example is illustrated by the joint sets exposed near Blowholes on Grand Cayman (Figs. II.14, X.3A). The north northwest - south southeast oriented vertical joints commonly remain open whereas the east northeast - west southwest oriented vertical joints commonly filled with flowstones and terra rossa/terra rossa breccia. Conversely, the gently dipping (about 30° to the north-west), northeast -southwest oriented joints commonly filled with caymanite, terra rossa and/or rarely flowstones. Jones (1989, per. comm.) also noted that the east northeast - west southwest oriented joints exposed on Queen's Road (north coast) on Grand Cayman also contained dolomitized breccia. There appears to be a relation between joint and karst development (Table X.1) in that (1) the

Table X.1 Relationship between joint and karst development based on type of fills.

PHASE	JOINT TYPE & FILL	CAVE TYPE & FILL	RELATIVE TIMING
Phase III Late Pliocene to Late Pleistocene	NNE-SSW/Vertical — Open	Type 4 — Open Type 3 — Assorted Speleothems	Post - Dolomitization
Phase II Late Miocene to Early Pliocene	ENE-WSW/Vertical — Flowstone Terra Rossa	Type 2 — Flowstone Terra Rossa	
Phase I Late Oligocene to Early Miocene	NE-SW/30°NW — Caymanite Flowstone (rare) Terra Rossa	Type 1 — Caymanite Skeletal Grainstone Flowstone Terra Rossa	Pre - Dolomitization

Type 1 cave fills are similar to those in the northeast-southwest trending joints, (2) the Type 2 cave fills are similar to those in the east northeast - west southwest trending joints, and (3) both the Type 4 caves and the north northwest - south southeast trending joints remain open. Thus, the similarity in joint and cavity fills may be an indication of related timing of the phases (Phase I, II, and III) of joint development with that of the karst formation (Fig. VIII.1, Table X.1). This genetic relationship supports the argument that jointing/fracturing is one of the pre-requisite parameters for cave formation, providing avenues for fluid flow, and hence, carbonate dissolution. It is also important to note that filling of joints is an active process that is ongoing at the present time. Some open joints at Hell on Grand Cayman (Fig. X.3A) are presently being filled by swamp sediments.

B. CHEMICAL EQUILIBRIA OF CARBONATE DISSOLUTION

Using chemical equilibrium concepts, speciation calculations of ground waters in the aquifers of the Bluff Formation indicate that the waters in all hydrochemical zones are capable of dissolving or precipitating carbonates, depending on their chemical properties. Some fresh water samples from the Lower Valley lens are undersaturated with respect to both calcite and dolomite (Table IV.5). The low Mg/Ca ratio of the Lower Valley fresh ground water suggests that influx of calcium enriched ground water from the limestone aquifer of the Ironshore Formation and subsequent mixing with the ground water in the Bluff Formation may be the cause of the undersaturation. Furthermore, it has also been demonstrated by artificial injection that rapid rain water recharge through open fractures can cause significant undersaturation at the water table zone (Table IV.19). The shallow water zone is also most likely to receive CO_2 from the respiration of plant roots and organic decay. The corrosiveness of the ground water acts according to the simplified reactions:

$$CO_2 + H_2O = H^+ + HCO_3^-$$

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^-$$

$$CaMg(CO_3)_2 + 2H^+ = Ca^{2+} + Mg^{2+} + 2HCO_3^-$$

In the brackish water (mixed water) zone, undersaturation with respect to carbonate minerals (Table IV.8) probably results from periodic influx of CO_2-ladened water from the surrounding mangrove swamps or from decomposition of organic materials in the aquifers.

C. CHEMICAL KINETICS OF CARBONATE DISSOLUTION

In the ground water systems of the Cayman Islands, the temporal and spatial variation of the ground water chemistry (Tables IV.10, 16, 17, Figs.II.10, III.1, III.5-10) suggests that most of the hydrochemical reactions in the aquifers have not reached thermodynamic equilibrium. Berner (1978) suggested that under earth surface conditions, mineral dissolution is governed by surface chemical reactions. Wigley and Plummer (1976) also demonstrated that the rate of calcite dissolution in natural environments depends on the hydrodynamics of the mineral-water system and the reaction kinetics at the mineral surface.

Weyl (1958) concluded that the rate of limestone dissolution is controlled by diffusion of Ca^{2+} from the surface. Weyl's (1958) results showed that water entering the rocks quickly becomes saturated with respect to calcite, with a saturation length (penetration distance before water reaches calcite saturation state) in the order of a few centimetres. The first comprehensive treatment of solution kinetics of $CaCO_3$ in the H_2O-CO_2 system was the theoretical model of Plummer *et al.* (1978, 1979) where the rate of calcite dissolution (Rc) is given as:

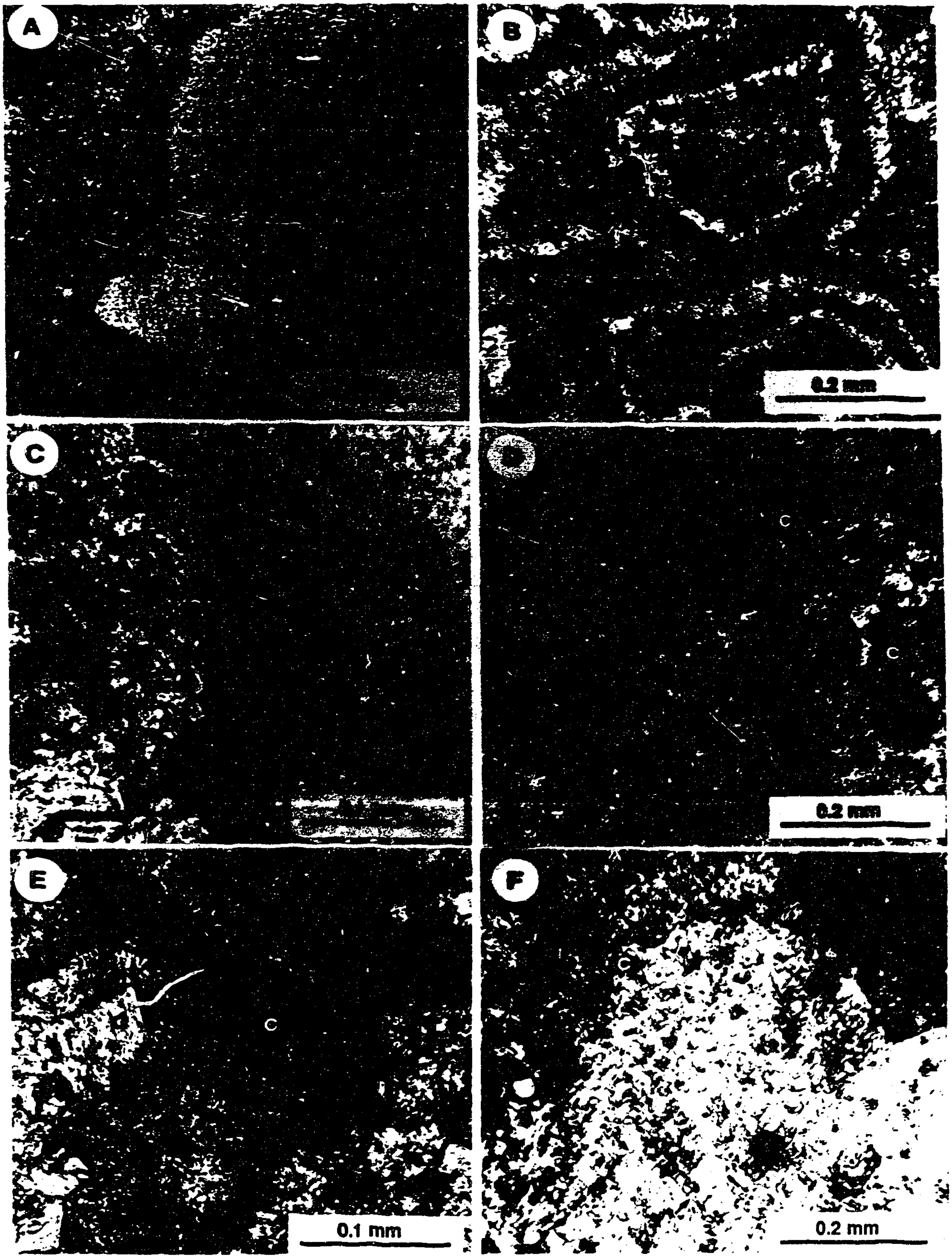
$$Rc = k_1[H^+] + k_2[H_2CO_3] + k_3[H_2O] - k_4[Ca^{2+}][HCO_3^-] \quad \ldots\ldots\ldots\ldots\ldots(1)$$

where k_1, k_2 and k_3 are the forward rate constants which are temperature dependent, k_4 is the backward rate constant depending on both temperature and P_{CO_2}. Three mechanistic reactions for k_1 through k_3 are:

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^-$$

$$CaCO_3 + H_2CO_3 = Ca^{2+} + 2HCO_3^-$$

$$CaCO_3 + H_2O = Ca^{2+} + HCO_3^- + OH^-$$


A
B
0.2 mm
C
D
C
C
0.2 mm
E
C
0.1 mm
F
C
0.2 mm

Some calcite spar cements are zoned with individual zones separated by a thin (1 µm), dark coloured band of clay or organic materials (Plate VI.3E). Rarely, partial dissolution of the sparry calcite also occurs, with preferential dissolution along the cleavage planes (Plate VI.3F).

Alternating Zones of Dolomite and Calcite

Cements composed of alternating zones of dolomite and calcite occur in two forms. The first type consists of alternating zones of about 10 µm thick that are laterally continuous from crystal to crystal (Plates VI.4A, 4B). The calcite band appears to follow the outlines of the preceding dolomite crystals and is subsequently encased by a further zone of dolomite (Plates VI.4A, 4B).

The second type of alternate zoning of dolomite and calcite occurs in a single crystal (Plates VI.4C, 4D). The zoned cements are probably equivalent to the zoned dolomite-calcite cements described by Jones *et al.* (1984). Commonly, the core of the zoned crystals is clear dolomite. In most cases, these zoned crystals were encased by poikilotopic calcite (Plate VI.4D).

Poikilotopic Calcite-Dolomite

Poikilotopic calcite that encases dolomite cement and matrix dolomite produced fabrics comparable to those considered indicative of dedolomite by Shearman *et al.* (1961), Evamy (1967) and Katz (1971). The poikilotopic calcite-dolomite fabrics in the Bluff Formation include (1) hollow zones in dolomite rhombs (Plate VI.5A), (2) calcite zones and cores in dolomite rhombs (Plates VI.5A, 5B, 5C, 5D), and (3) rounded and corroded outlines of dolomite crystals (Plates VI.5B, 5C). Where matrices have two distinct crystal sizes, poikilotopic calcite preferentially replaced the smaller dolomite crystals (Plates VI.5A, 5E).

PLATE VI.4

Photomicrographs of alternating dolomite and calcite cement. All depths are measured from land surface.

(A) and (B) Alternating zones of dolomite (d) and calcite (c) that are laterally continuous from crystal to crystal. Note indistinct intercrystalline boundaries. Rock cutting from West Bay Road well #1 in the highly brackish water zone at a depth of about 12.5 m.

(C) Alternating zones of dolomite (d) and calcite (c) in individual crystals. Rock cutting from Cayman Brac well K1 in the unsaturated zone at a depth of about 9 m.

(D) Alternating zones of dolomite (d) and calcite (c) in individual crystals which were subsequently encased by poikilotopic calcite (pc). Sample from East End core #1.22 in the fresh water zone at a depth of about 5 m.


A
B
0.1 mm
0.1 mm

PLATE VI.5

Photomicrographs of poikilotopic calcite-dolomite fabrics. All depths are measured from land surface.

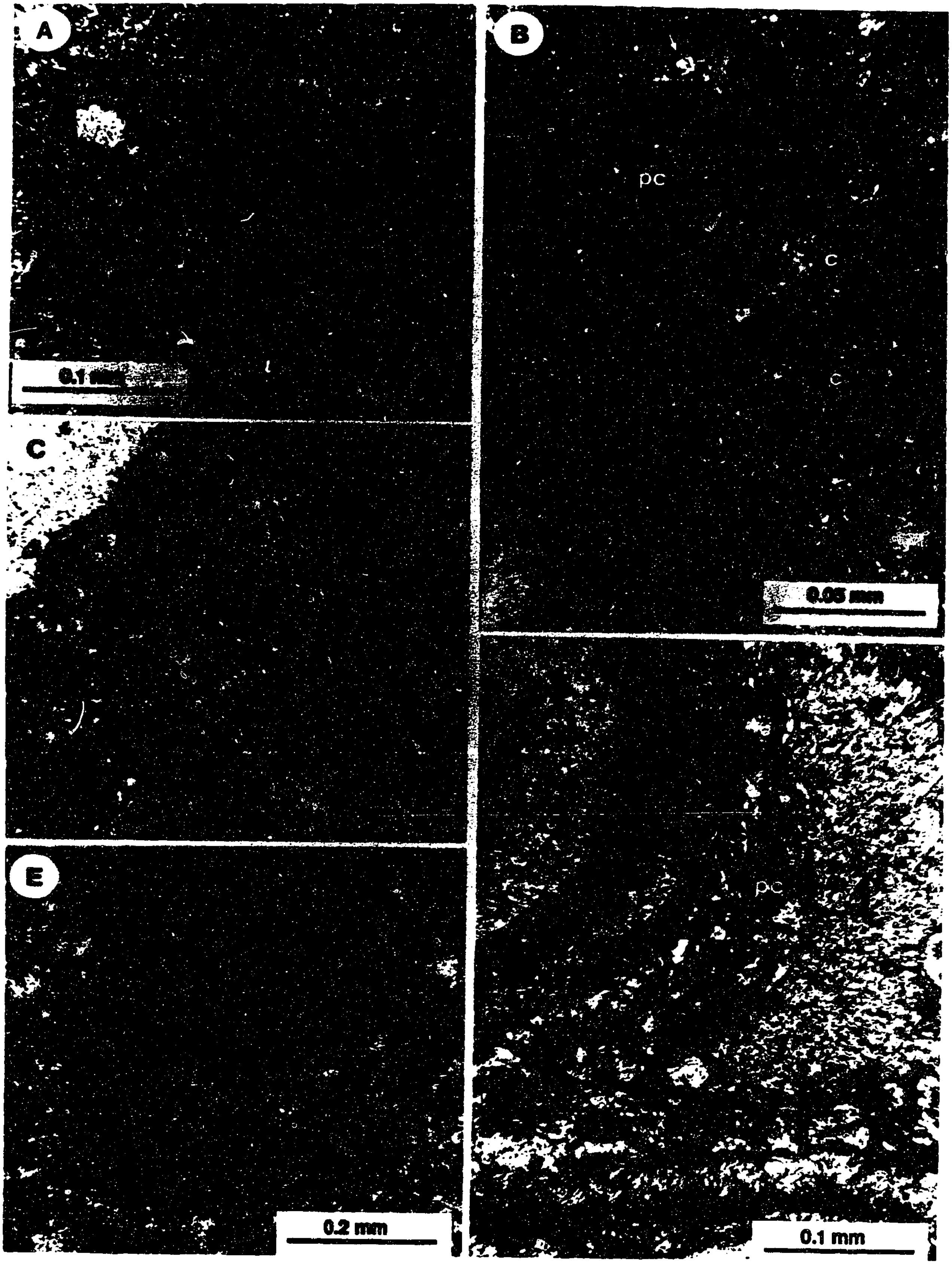
(A) Clear, euhedral dolomite rhombs (d) with hollow cores (h). Rock sample from weathered dolostone outcrop, Lower Valley.

(B) Matrix dolomite crystals (d) with calcite cores and calcite zones (c). Note corroded outline of dolomite (arrows) encased by poikilotopic calcite (pc). Rock sample from Lower Valley trench well at the water table zone at a depth of about 1.5 m.

(C) Dolomite spar (d) replaced and encased by poikilotopic calcite (pc). Rock cutting from Cayman Brac well B2 in the unsaturated zone at a depth of about 9 m.

(D) Dolomite cement zone (arrows) replaced by poikilotopic calcite (pc). Note remnants of dolomite zones (d). Rock cutting from West Bay Road well #1 in the highly brackish water zone at a depth of about 24 m.

(E) Poikilotopic calcite (pc) preferentially replaced smaller sized matrix dolomites (m), leaving coarser euhedral dolomite unreplaced (d). Rock core from Lower Valley well 5-82 in the highly brackish water zone at a depth of about 3 m.


A
0.1 mm
B
pc
c
c
0.05 mm
C
E
0.2 mm
pc
0.1 mm

Internal Sediments

Caymanite is a microcrystalline dolomite characterized by (1) white, orange/red and black colour bands (Fig. 11 of Lockhart, 1986), (2) tightly interlocking anhedral dolomite crystals (Plates VI.6C-6F), (3) angular grains or fragments of dolostone (Plates VI.6C, 6D), (4) geopetal texture (Plates VI. 6E, 6F), and (5) cross bedding, and (6) cut and fill channels (Fig. 12 of Lockhart, 1986). Rare examples a[illegible] contain foraminifera and gastropods.

The laminae of the caymanite, when viewed under the petrographic microscope, show slight differences in the amount of darker-coloured matrix (<0.02 mm) and lighter-coloured angular grains and rock fragments. The grains and fragments are dolostone from 0.02 to 0.50 mm long in thin sections (Plate VI.6C) and up to 50 mm long in field samples. Some angular rock fragments were probably the end result of removal of irregular projections from the underlying bedrock (Plate VI.6D).

Another form of internal sediment is dolomitized skeletal grainstone, which commonly deposited on top of the caymanite. In places, the white coloured grainstone is poorly lithified with high original porosity. The skeletal component is predominantly foraminifera which appear to be leached. Fragments of red algae are also common.

The relationship between the caymanite and other cavity fills include (1) caymanite sedimentation prior to dolomite cementation (Plate VI.6E), (2) dolomite cementation prior to caymanite deposition (Plate VI.6F), (3) sparry calcite precipitation after caymanite sedimentation (Plate VI.6F), (4) flowstone precipitation and terra rossa influx after caymanite sedimentation, and (5) caymanite sedimentation prior to influx of skeletal grainstone.

Terra Rossa

Terra rossa present in the Bluff Formation is formed of organic-rich glaebules embedded in microcrystalline carbonate and clay matrix (Plate VI.6A). The glaebules are

PLATE VI.6

Photomicrographs of cavity fills (terra rossa, caymanite and flowstone). All depths are measured from land surface.

(A) Two phases of terra rossa fill. One phase is characterized by dark, organic rich glaebules (g) embedded in the microcrystalline calcium carbonate matrix, whereas the other phase is characterized by light coloured glaebules. Rock cutting from Cayman Brac well B2 in the unsaturated zone at a depth of about 3 m.

(B) Dolomite cement (d) followed by terra rossa breccia (b). Note the angular dolostone fragments (f) in the terra rossa. Rock cutting from Cayman Brac well B5 in the unsaturated zone at a depth of about 27 m.

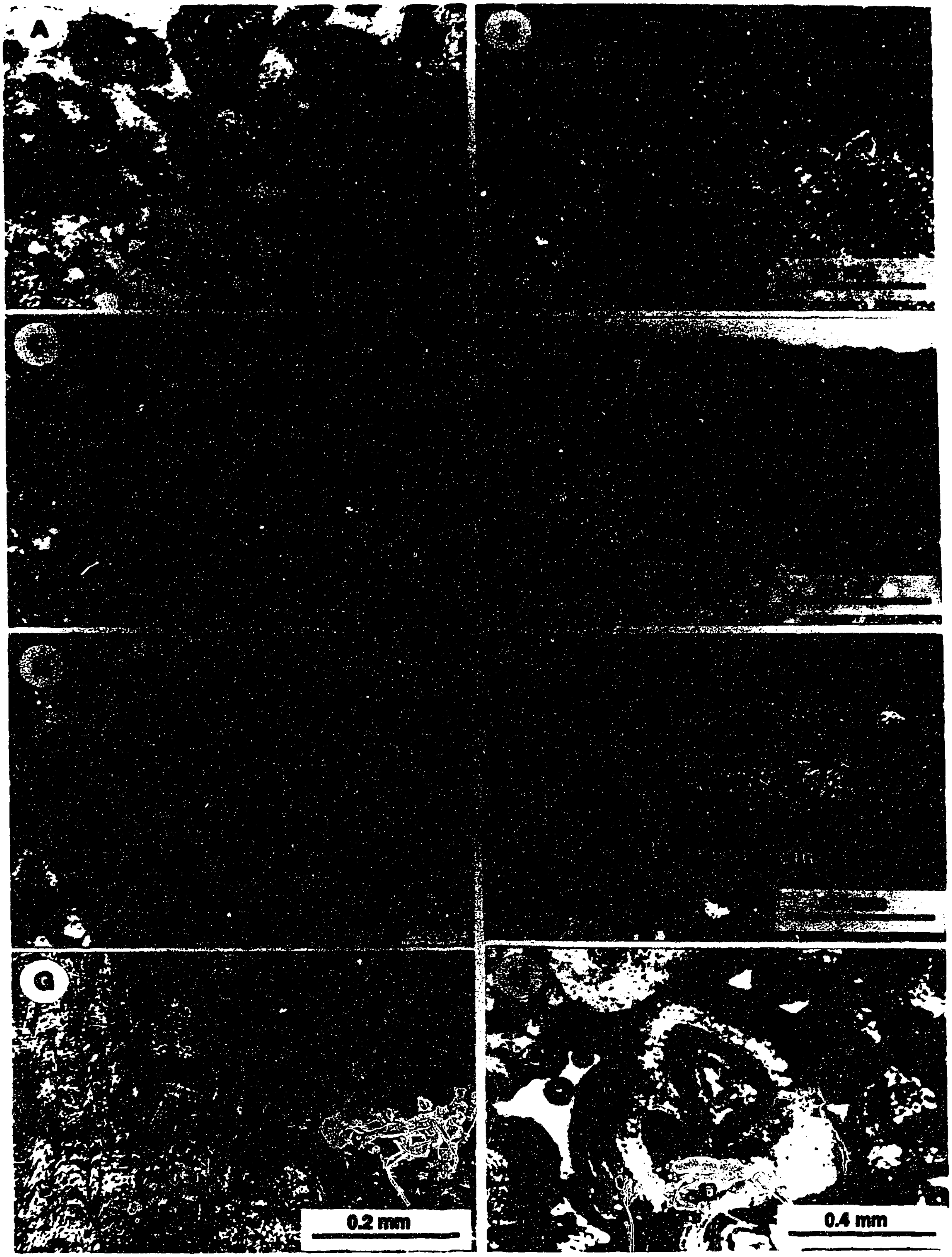
(C) Caymanite sample showing bands resulting from differences in matrix dolomite crystal sizes and content of angular dolostone fragments (f). Sample from East End core #1.15 in the fresh water zone at a depth of about 4 m.

(D) Cavity partially filled by caymanite (cm). Note the angular dolostone fragments (f) apparently ripped from the cavity wall. Sample from East End core #7.22 in the fresh water zone at a depth of about 13 m.

(E) Caymanite (cm) in cavity of coral structure showing geopetal texture, which was followed by euhedral dolomite cement (d). Sample from East End core #5.2 in the fresh water zone at a depth of about 10 m.

(F) Dolomite cementation (d) prior to caymanite sedimentation (cm) with the rest of the cavity subsequently filled by sparry calcite (c). Sample from East End core #3.2 in the fresh water zone at a depth of about 7 m.

(G) and (H) Longitudinal and cross section view of a flowstone sample showing the laminated, columnar calcite crystals (G) and trigonal crystal morphology (H). Note dark inclusion rich growth bands (arrows). Rock cutting from Cayman Brac well B6 in the unsaturated zone at a depth of about 3 m.


A
G
0.2 mm
0.4 mm

made up predominantly of clay minerals with minor calcium carbonate. Terra rossa breccia (Plate VI.6B), which has dolostone fragments embedded in the soil, is common in some cavities and open joints. Commonly, the less well consolidated terra rossa is red in colour whereas the well consolidated terra rossa is brown in colour. However, it is important to note that there are many different colour shades in the consolidated terra rossa. Some cavities were filled by two phases of terra rossa that differ in colour and the amount and size of the glaebules (Plate VI.6A). In places, dolomite cementation preceded the emplacement of terra rossa in the cavity (Plate VI.6B).

Flowstone

Brown, banded flowstone, formed of columnar calcite (Plates VI.6G, 6H), commonly filled cavities, joints and caverns in the Bluff Formation (Lockhart, 1986; Smith, 1987; Jones and Smith, 1988). Locally, flowstone is intercalated with terra rossa.

D. DISTRIBUTION OF THE CARBONATE CEMENTS IN THE PRESENT DAY HYDROCHEMICAL ZONES

A systematic analysis of the carbonate cementation pattern and distribution in each hydrochemical zone should provide insight into the relationship between the cement fabrics and pore fluids. Of particular importance is the late-phase carbonate cements and the present-day ground waters. This relationship is investigated for each of the present day hydrochemical zones in terms of the paragenetic sequence of the cements present in the rocks, and the type and abundance of the last phase of cement.

Fresh Water Zone

There are distinct differences in the diagenetic fabrics of the Bluff Formation between the Lower Valley and East End lens of Grand Cayman. Carbonate cement fabrics

recognized in **individual** cavities of the rocks sampled from the Lower Valley fresh water zone include:

(1) poikilotopic calcite-dolomite near the water table zone, and

(2) sparry calcite cement (voids rarely lined by dolomite cement).

Carbonate cement fabrics recognized in **individual** cavities of the rocks sampled from the East End fresh water zone include:

(1) dolomite cement followed by sparry calcite,

(2) dolomite cement lining voids (not followed by sparry calcite),

(3) alternating zones of dolomite and calcite,

(4) sparry calcite cement only, and

(5) zoned sparry calcite cement.

In the Lower Valley aquifer, the paragenetic sequence of the cements is simple (Fig.VI.3A). The cavities were rarely lined by dolomite cement. Instead, more than 80% of the cavities were lined or filled by calcite as the only cement phase. The poikilotopic calcite-dolomite, which occurs near the water table zone of the Lower Valley lens (Plate VI.5B), is probably related to near surface influences such as rain water infiltration, and evaporation. In the East End aquifer, the cement types indicates the following carbonate cementation sequence (Fig.VI.3B): (1) clear, euhedral dolomite, (2) zoned dolomite, (3) alternating bands of dolomite and calcite, and (4) clear or zoned sparry calcite.

Petrographic studies indicate that the calcite cement is the most common last phase cement in cavities in the fresh water zone of both the Lower Valley and East End lens (Fig.VI.4). Thus, it may be suggested that calcite cement formed in close association with the fresh ground water.

Lightly Brackish Water Zone (<15% sea water salinity)

Like the rocks in the fresh water zone, there are differences in the diagenetic features between those in the Lower Valley and East End lens. Carbonate cement fabrics

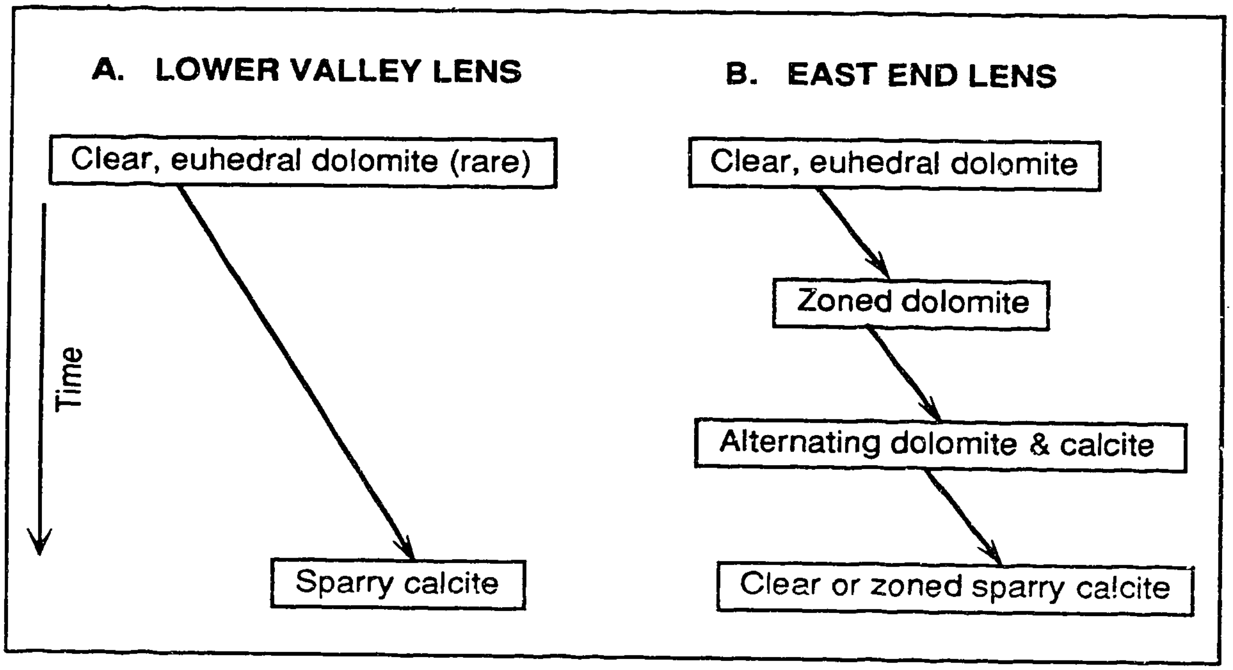


Fig. VI.3 Paragenetic sequence of carbonate cements in the fresh water zone of the (A) Lower Valley and (B) East End aquifers.

LOWER VALLEY	WATER TABLE	EAST END
Poikilotopic calcite-dolomite	Water Table Zone (<1 m)	Sparry calcite
Sparry calcite	Fresh Water Zone Lower Valley lens <10 m East End lens <25 m	
>60% of the cavities have calcite <40% of the cavities have dolomite	Lightly Brackish Water Zone (salinity <15% sea water) Variable Thickness	Dolomite

Fig. VI.4 Types of last carbonate cement phase in the fresh water and lightly brackish water zones of the Lower Valley and East End aquifers.

recognized in **individual** cavities of rocks sampled from the Lower Valley lightly brackish water zone include:

(1) dolomite cement followed by sparry calcite,

(2) dolomite cement with hollow zones or cores, and

(3) sparry calcite cement only.

Carbonate cement fabrics recognized in **individual** cavities of the rocks sampled from the East End lightly brackish water zone:

(1) dolomite cement,

(2) zoned and hollow dolomite, and

(3) open cavities.

In the Lower Valley aquifer, the paragenetic sequence of carbonate cements (Fig.VI.5A) is (1) clear, euhedral dolomite, (2) zoned dolomite (selective leaching of certain zones), and (3) sparry calcite. Approximately 60% of the cavities in the lightly brackish water zone of the Lower Valley lens have calcite as the last phase of cement (Fig.VI.

In the East End lens, calcite cement is not seen in the rocks from the lightly brackish water zone (Fig.VI.5B). All the voids were lined by clear, euhedral dolomite cement or zoned dolomite. Thus, dolomite cement becomes the most common last cement phase in the brackish water zone of the East End lens (Fig.VI.4).

It appears that the brackish water has a much higher potential to precipitate dolomite than the fresh water, particularly in the East End lens. The presence of calcite cement in the rocks of the Lower valley lens but not in those of the East End lens suggests that salinity is probably not the only consideration in carbonate cementation. It appears that the concentrations of the chemical constituents such as Mg^{2+}, Ca^{2+} and HCO_3^- or CO_3^{2-}, and Mg^{2+}/Ca^{2+} ratio (Tables III.3, IV.7) are probably the controlling factors.

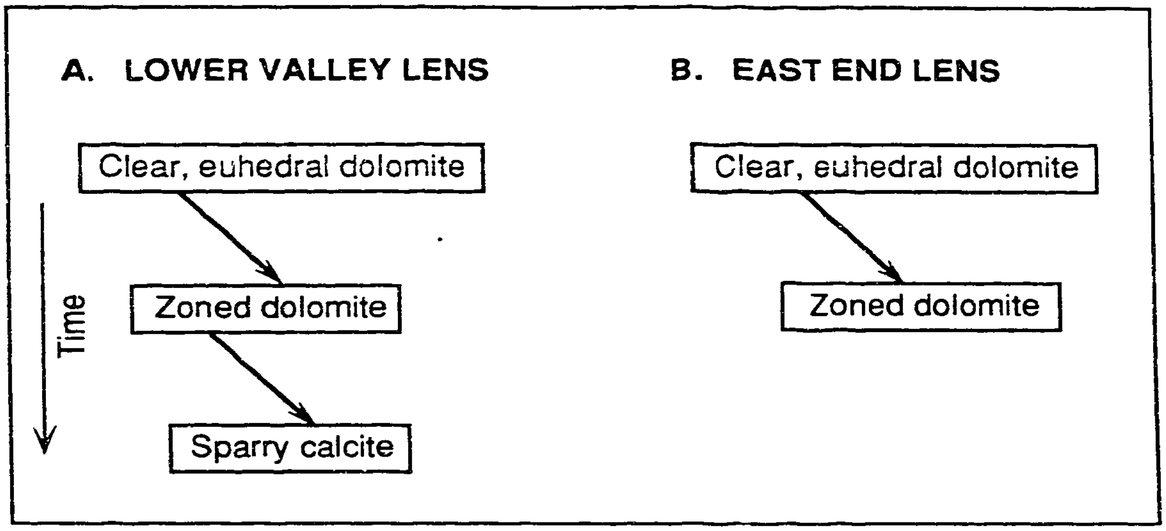


Fig. VI.5 Paragenetic sequence of carbonate cements in the lightly brackish water zone of the (A) Lower Valley and (B) East End aquifers.

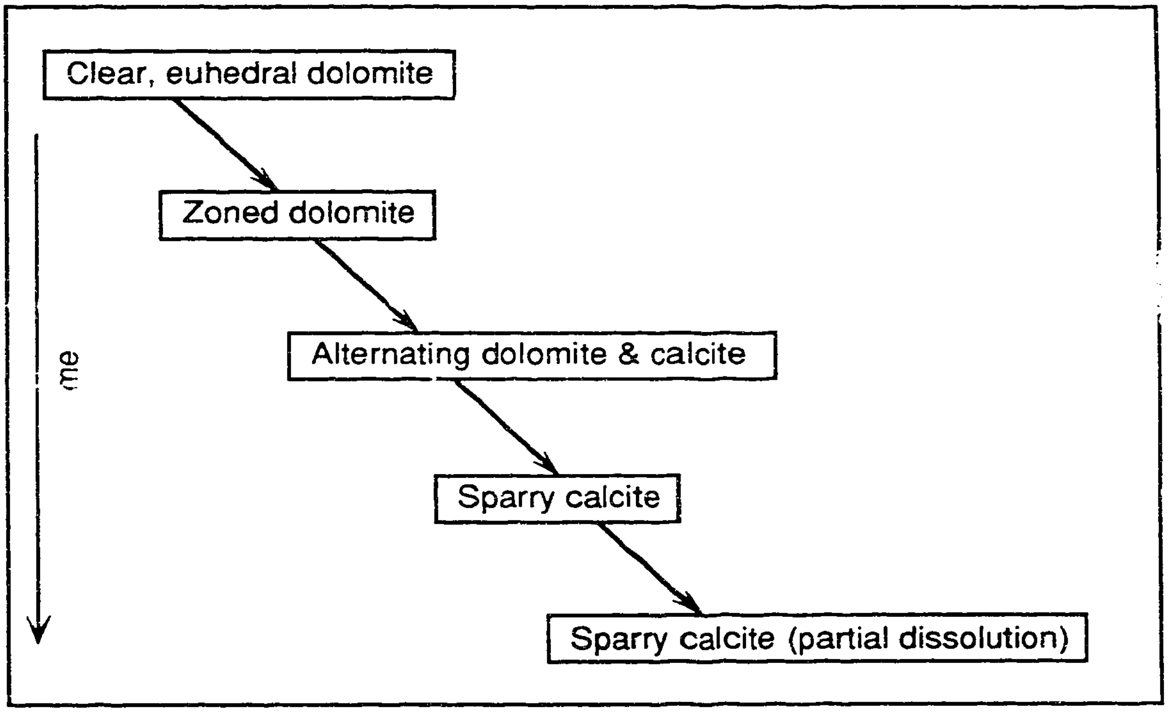


Fig. VI.6 Paragenetic sequence of carbonate cements in the highly brackish water zone.

Highly Brackish Water Zone

Carbonate cement fabrics present in **individual** cavities of the rocks sampled from the highly brackish water zone include:

(1) dolomite cement followed by sparry calcite,

(2) dolomite cement lining voids,

(3) zoned dolomite cement showing selective dissolution of certain zones,

(4) alternating zones of dolomite and calcite cement, and

(5) calcite spar showing partial dissolution.

The paragenetic sequence (Fig.VI.6) comprises (1) clear, euhedral dolomite, (2) zoned dolomite, (3) alternating zones of dolomite and calcite, (4) sparry calcite, and (5) partially dissolved sparry calcite. Most cavities have dolomite as the only cement phase (Fig.VI.7); only 10-20% of the cavities contain some sparry calcite. Therefore, it appears that dolomite is the most common carbonate cement associated with the present-day highly brackish ground water.

Saline Water Zone

Rocks from the saline water zone typically lack calcite cement; however, some 20-30% of the cavities are lined by dolomite cement (Fig.VI.7). Sparry calcite cement is rare. Conversely, about 40-50% of the cavities have no carbonate cements. Rocks in the saline water zone are presently bathed in water that is similar to the sea water in terms of water salinity.

The petrographic data suggest, therefore, that saline water is less favourable for calcite precipitation than fresh water and is also less favourable for dolomite cementation than the brackish water. This phenomenon may be partly related to the presence of inhibitors in the saline water and partly due to the slow ground water flow rate in this zone.

LAST CEMENT PHASE	HYDROCHEMICAL ZONE
Dolomite	Highly Brackish Water (salinity >15% and <100% sea water)
20-30% of the cavities have dolomite 40-50% of the cavities remain open Minor % of the cavities have calcite	Saline Water (salinity ≥100% sea water)

Fig. VI.7 Types of last carbonate cement phase in the highly brackish and saline water zones of the dolostone aquifer. Rock samples from deep wells drilled on the west side of Grand Cayman.

E. AN EXAMPLE OF COMPLEX DIAGENETIC PATTERNS

Rock cuttings, which were collected from the unsaturated (vadose) zone at ten foot intervals from 10 water wells on Cayman Brac (Fig. VI.2, Appendix 1D), provided an excellent opportunity to examining the distribution of diagenetic fabrics over a wide area. Detailed petrographic studies of the rock cuttings indicate a complex distribution of diagenetic fabrics (Fig. VI.8) present in **individual** cavities, which include:

(A) dolomite cement followed by sparry calcite,
(B) dolomite cement lining voids with no calcite cement ,
(C) zoned dolomite cement, dissolution of zones in places,
(D) zoned dolomite cement followed by sparry calcite,
(E) alternating zones of dolomite and calcite,
(F) sparry calcite cement only,
(G) poikilotopic calcite-dolomite,
(H) flowstone,
(I) terra rossa, and
(J) internal sediments (caymanite and skeletal grainstone).

The complicated diagenetic patterns (Fig. VI.8) are a reflection of the complexity of the diagenetic environments. The sediments/rocks were under increasing meteoric influence as Cayman Brac gradually emerged from the sea. The rocks, therefore, record a complete diagenetic history from saline water to brackish water to fresh water to vadose zone. If this is so, the rocks should have been affected by similar pore fluids at the same stratigraphic horizons, and hence, should have similar diagenetic fabrics at those stratigraphic levels. However, the distribution of the diagenetic fabrics (Fig. VI.8) does not seem to display any pattern with respect to a particular aquifer system. This variability in diagenetic signatures probably resulted from the subenvironments created in the joint and karst controlled system of the Bluff Formation, and hence, zones of different fluid chemistry. This feature is important because it demonstrates that samples from the same

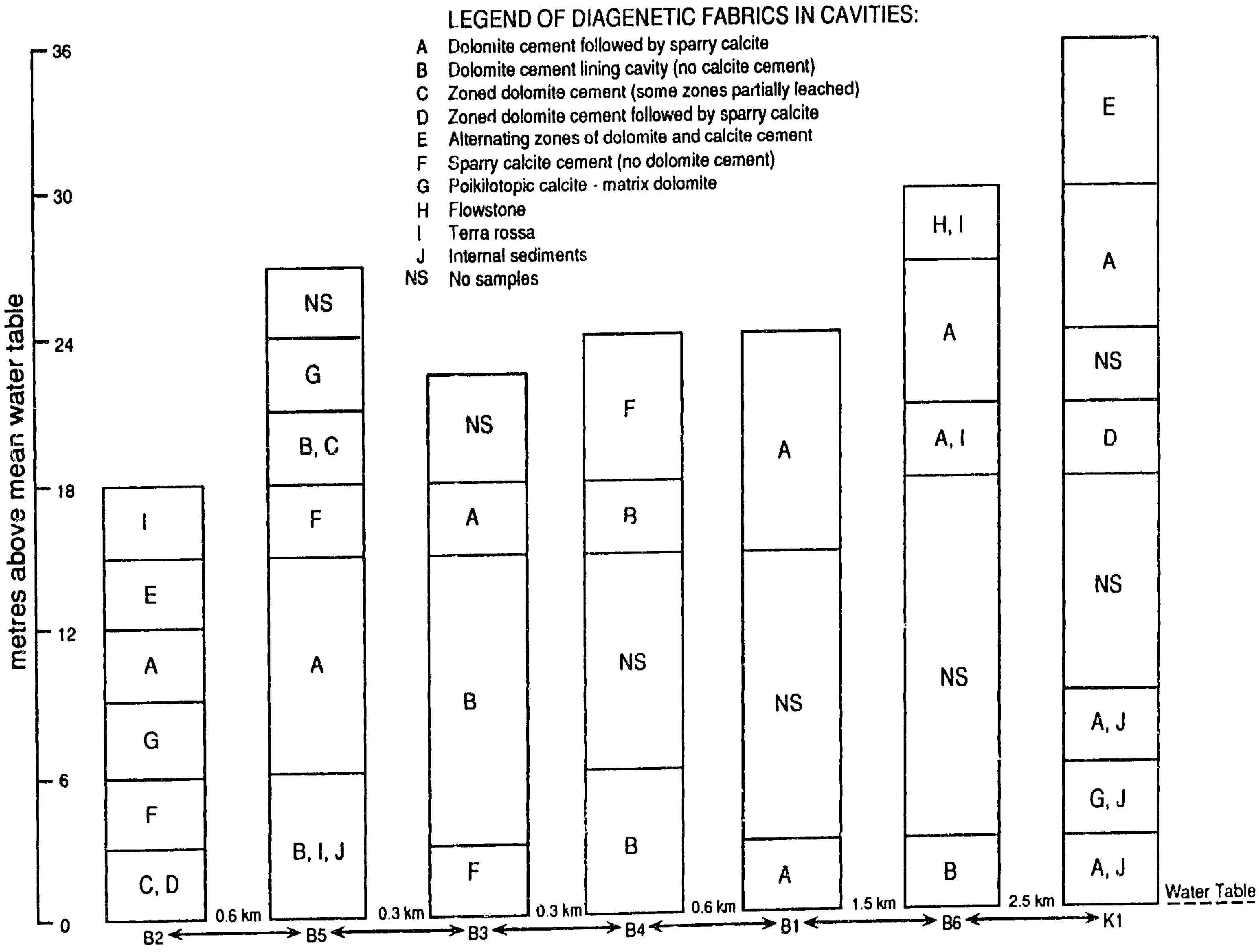


Fig. VI.8 Distribution of the most dominant diagenetic fabrics in the vadose zone of the Bluff Formation on Cayman Brac (refer to Fig. VI.2 for well location).

stratigraphic level of close proximity may have different diagenetic processes due to the heterogeneity of the ground-water flow regime.

It is also important to note that the carbonate cement fabrics in the rocks presently in vadose zones of Cayman Brac (Fig. VI.8) are similar to those in association with the present day hydrochemical regimes of Grand Cayman (Figs. VI.3-7). This suggests that the rocks from the unsaturated zone of Cayman Brac underwent at least one complete cycle of diagenetic environments ranging from marine to meteoric to vadose settings.

F. SYNOPSIS

Detailed petrographic studies of the rocks of the Bluff Formation indicate that:

(1) the Bluff Formation is formed of finely crystalline to microcrystalline dolostone; calcite only occurs as cavity filling and intercrystalline cement or as poikilotopic calcite-dolomite couplet;

(2) the matrix dolomites are characterized by (i) scattered euhedral dolomites up to 40 µm long in microcrystalline dolomite groundmass (5-10 µm), (ii) intercrystalline porosity in leached matrix dolomite, and (iii) poikilotopic calcite encasing corroded matrix dolomites in weathered zones and in the vicinity of the water table in Lower Valley;

(3) paragenetic sequence of carbonate cements commonly is (i) clear and zoned dolomite, (ii) alternating zones of dolomite and calcite as laterally continuous bands from crystal to crystal or within a single crystal, (iii) coarse, unzoned and zoned sparry calcite, (iv) partial dissolution of sparry calcite and zoned dolomite cements, and (v) poikilotopic calcite encasing and infilling leached dolomite cements;

(4) cavity fills other than carbonate cements include terra rossa, flowstone, and internal sediments;

(5) the most important difference in the cement fabrics of the rocks from the two fresh water lenses on Grand Cayman is the rare occurrence of dolomite cement in the

Lower Valley lens although dolomite cement is common in the East End lens; this distinction is probably related to differences in chemical compositions of the two types of ground water which have similar salinity;

(6) the quantity of calcite as last-cement phase decreases from the fresh water to brackish water to saline water zones, and conversely, the abundance of dolomite as last-cement phase increases from the fresh water to brackish water zone;

(7) the rocks in the saline water zone are characterized by minor amounts of dolomite cement and unfilled cavities;

(8) sparry calcite cement is commonly associated with fresh to lightly brackish ground water; dolomite cement is more commonly affiliated with brackish ground water; and

(9) the complex distribution of the diagenetic fabrics of the rocks from the unsaturated zone of Cayman Brac is due to the heterogeneity of the joint and karst controlled aquifer, and hence, is responsible to the variability of fluid chemistry in the subenvironments.

VII. ISOTOPE GEOLOGY

Diagenetic carbonate minerals formed in equilibrium with pore fluids acquire isotopic compositions characteristic of those fluids and the temperature of the diagenetic environment (Hudson, 1977; Savin, 1980; Brand and Veizer, 1981; Anderson and Arthur, 1983; Veizer, 1983; O'Neil, 1986, 1987; Longstaffe, 1987). Thus, where isotopic equilibrium between the carbonate minerals and the diagenetic fluids has been achieved, the isotopic compositions of the diagenetic minerals should provide information about the paleo-environmental conditions. In this context, this study examines the equilibrium fractionation effect of the oxygen isotope between the carbonate minerals and diagenetic fluids, and assesses the salinity of the fluids from which the minerals were precipitated.

A. BASIC PRINCIPLES

Precipitation of carbonate minerals under natural conditions of equilibrium is known to occur (Anderson and Arthur, 1983; Veizer, 1983; O'Neil, 1987). However, carbonate minerals also form under kinetic isotope effects (non-equilibrium) such as biological activity (Keith and Weber, 1965; Weber, 1968; Shackleton *et al.*, 1973) and rapid precipitation or loss of volatiles (Gonfiantini *et al.*, 1968; Hendy, 1971; Turi, 1986; Schwarcz, 1986). Furthermore, the isotopic composition of the diagenetic minerals can be altered by later diagenesis, particularly recrystallization (Land, 1980, 1983b; Longstaffe, 1987; O'Neil, 1987).

The degree of exchange of the oxygen isotope during a reaction is controlled by the oxygen fractionation factor between the carbonate minerals and the diagenetic fluids (Savin, 1980; Brand and Veizer, 1981; Anderson and Arthur, 1983; Land, 1983b; O'Neil, 1986). Oxygen isotopic fractionation between calcite and water has been thoroughly investigated (Anderson and Arthur, 1983; Veizer, 1983). Conversely, the fractionation between dolomite and water is less well established because of the variable stoichiometric

compositions of the dolomite and the inability of dolomite to synthesize under conditions of sedimentary environments (Land, 1980, 1983b, 1985; Hardie, 1987).

Significant isotopic exchange occurs through chemical or mineralogical reactions such as mineral dissolution and precipitation, and recrystallization (Savin, 1980; O'Neil, 1987). Conversely, in low temperature environments, isotopic exchange between the carbonate minerals and water is negligible (Savin, 1980; Anderson and Arthur, 1983; O'Neil, 1987; Welhan, 1987).

B. OXYGEN ISOTOPES OF THE BLUFF FORMATION

The oxygen isotopic data of the rocks and cavity fills of the Bluff Formation used in this study are those determined by Pleydell (1987), Smith (1987), and Jones *et al.* (1989). All isotopic values, which were originally presented in the per mil (‰) notation relative to PDB standard, are converted to the SMOW standard for the temperature dependence equilibrium fractionation calculation. PDB is an oxygen standard for carbonates, derived from the rostrum of *Belemnitella americana* from the Pee Dee Formation of South Carolina, U.S.A. (Craig, 1957; Anderson and Arthur, 1983). The relationship between PDB calcite and SMOW calcite (Anderson and Arthur, 1983) is defined as:

$$\delta^{18}O_{(\text{calcite vs. SMOW})} = 1.03086 * \delta^{18}O_{(\text{calcite vs. PDB})} + 30.86$$

Matrix Dolomite of the Bluff Formation

In order to ensure that the oxygen isotopic compositions are representative of the matrix dolomites, values selected for this study are those that were obtained from dolostone samples of greater than 98% dolomite according to XRD analysis (Pleydell, 1987). The dolomites of the Bluff Formation have a narrow $\delta^{18}O$ range of +2.0 to +3.0‰ PDB and an average value of +2.5‰ (Table VII.1).

Table VII.1 Stable oxygen isotope data of matrix dolomite of the Bluff Formation. Data adapted from Pleydell (1987).

Sample #	**Location**	**$\delta^{18}O$ ‰ SMOW**	**$\delta^{18}O$ ‰ PDB**
801a	High Rock Quarry	+33.2	+2.3
801b	High Rock Quarry	+33.0	+2.1
1209a	High Rock Quarry	+33.7	+2.8
1195	High Rock Quarry	+33.0	+2.1
842	High Rock Quarry	+33.8	+2.9
1242b	Pedro Castle Quarry	+33.5	+2.6
1243b	Pedro Castle Quarry	+33.7	+2.8
1240	Pedro Castle Quarry	+33.2	+2.2
1247	Pedro Castle Quarry	+33.5	+2.5
1230	Blow Hole	+33.1	+2.2
1185	Queen's Road	+33.6	+2.7
1184b	Queen's Road	+32.9	+2.0
1184a	Queen's Road	+32.3	+2.5
1063	Paul Bodden Quarry	+33.6	+2.6
1171	Cayman Kai	+33.9	+2.8
1297c	Cayman Brac	+33.7	+2.8
1297d	Cayman Brac	+33.7	+2.8
Average Stable Oxygen Isotope of Bluff Dolostone		+33.4	+2.5

Note: Sample numbers refer to catalogue numbers of the Cayman Islands rock collection.

Cavity Fills in the Bluff Formation

Cavity fills in the Bluff Formation analysed for the $\delta^{18}O$ content are internal sediments (dolomite) and carbonate mineral precipitates (calcite and dolomite spar, flowstone, and poikilotopic calcite-dolomite).

Dolomite (Caymanite)

The $\delta^{18}O$ contents of the caymanite samples analysed by Pleydell (1987) are similar to those of the dolostone host rocks with an average value of +2.3‰ PDB (Table VII.2). These values are also in agreement with the unpublished data of Collar (1985, per. comm.).

Calcite and Dolomite Spar

Calcite spar cements, their composition confirmed by XRD analysis (Pleydell, 1987), have $\delta^{18}O$ values ranging from -3.9 to -5.6‰ PDB (Table VII.2). One sample of dolomite spar rooted on calcite spar, coarse enough to be isolated for analysis (Pleydell, 1987), has an oxygen isotopic composition of -3.6‰ PDB (Table VII.2). The calcite and dolomite spar cements analysed came from different cavities.

Flowstone

Smith (1987) carried out a detailed examination of stable isotopes of the flowstones collected from different localities of Grand Cayman and Cayman Brac. In an individual flowstone sample, a slight variation in the isotopic content is recorded in each successive calcite layer (Smith, 1987). $\delta^{18}O$ concentrations of the flowstone lie in the -3.0 to -6.5‰ PDB range (Table VII.3). The exceptionally high values of speleothem 1252 (Table VII.3) are due to the presence of a small amount of dolomite (Smith, 1987).

Table VII.2 Stable oxygen isotope data of caymanite, calcite spar and dolomite spar of the Bluff Formation. Data adapted from Pleydell (1987).

Sample #	Location	$\delta^{18}O$ ‰ SMOW	$\delta^{18}O$ ‰ PDB
Dolomite (Caymanite):			
1209d	High Rock Quarry	+33.4	+2.5
1184	Queen's Road	+32.9	+2.0
Average Stable Oxygen Isotopes of Caymanite		+33.2	+2.3
Calcite Spar:			
1223a	East End Quarry	+25.6	-5.1
843	East End Quarry	+25.1	-5.6
1212	High Rock Quarry	+26.8	-3.9
Average Stable Oxygen Isotope of Calcite Spar		+25.8	-4.9
Dolomite Spar:			
1062A	Paul Bodden Quarry	+27.2	-3.6

Note: Sample numbers refer to catalogue numbers of the Cayman Islands rock collection.

Table VII.3 Stable oxygen isotope data of flowstones of the Bluff Formation. Data adapted from Smith (1987).

	$\delta^{18}O$ ‰ SMOW	$\delta^{18}O$ ‰ PDB
Average Stable Oxygen Isotope of Speleothem 1219 (5 calcite layers: max = -5.2‰, min = -5.9‰ PDB)	+25.2	-5.5
Average Stable Oxygen Isotope of Speleothem 726 (6 calcite layers: max = -4.6‰, min = -6.4‰ PDB)	+25.3	-5.4
Average Stable Oxygen Isotope of Speleothem 727 (4 calcite layers: max = -2.3‰, min = -5.0‰ PDB)	+27.1	-3.7
Average Stable Oxygen Isotope of Speleothem 728 (9 calcite layers: max = -3.2‰, min = -5.7‰ PDB)	+25.6	-5.1
Average Stable Oxygen Isotope of Speleothem 730 (4 calcite layers: max = -5.4‰, min = -6.6‰ PDB)	+24.6	-6.1
Average Stable Oxygen Isotope of Speleothem 1250 (8 calcite layers: max = -3.9‰, min = -6.3‰ PDB)	+25.3	-5.4
Average Stable Oxygen Isotope of Speleothem 1252 (6 calcite layers: max = -1.3‰, min = -6.5‰ PDB)	+26.9	-3.9

Note: Speleothem numbers refer to catalogue numbers of the Cayman Islands rock collection.

Poikilotopic Calcite-Dolomite

The $\delta^{18}O$ content of the poikilotopic calcite ranges from -1.0 to -3.7‰ PDB, whereas the $\delta^{18}O$ composition of the associated dolomite cement varies from +1.4 to +2.6‰ PDB (Table VII.4). The limpid dolomite is more depleted in ^{18}O than the matrix dolomite, but is more enriched in ^{18}O than the coarse dolomite spar. (Tables VII.1, 2, 3). Conversely, the poikilotopic calcite is more enriched in ^{18}O than the calcite spar cement and the calcitic flowstone (Tables VII.2, 3, 4).

C. EQUILIBRIUM ISOTOPIC FRACTIONATION OF OXYGEN

The equilibrium isotopic fractionation of oxygen between minerals and water is commonly determined by (1) theoretical calculations, (2) isotopic exchange experiments, and (3) systematic regularities in naturally occurring phases which formed under well-defined geological conditions. Isotopic equilibrium in experimental systems is generally limited to high temperatures where isotopic exchange rates are sufficiently rapid to be monitored in the laboratory. Commonly, the fractionation factors were obtained by extrapolation of partial exchange data (Anderson and Arthur, 1983; O'Neil, 1986; Kyser, 1987). Consequently, fractionation factors determined from various methods are slightly different, particularly when applied to the low temperature range (Savin, 1980; Anderson and Arthur, 1983; Land, 1983b; Kyser, 1987).

The oxygen fractionation factors typically vary with temperature over large temperature ranges according to the relationship (Anderson and Arthur, 1983; Veizer, 1983; O'Neil, 1986; Kyser, 1987):

$$10^3 \ln\alpha = \frac{A}{T^2} + B$$

where α is the fractionation factor, T is in °K, A and B vary between different minerals and methods of determination. The fractionation factor (Fritz and Fontes, 1980b; Anderson and

Table VII.4 Stable oxygen isotope data of poikilotopic calcite and dolomite of the Bluff Formation. Data adapted from Pleydell (1987) and Jones *et al.* (1989).

Sample #	**Location**	**$\delta^{18}O$ ‰ SMOW**	**$\delta^{18}O$ ‰ PDB**
Dolomite Cement (Limpid Dolomite):			
52	High Rock Quarry	+32.3	+1.4
92	High Rock Quarry	+33.6	+2.6
1201b	High Rock Quarry	+33.1	+2.2
1201a	High Rock Quarry	+33.3	+2.4
Average Stable Oxygen Isotope of Dolomite		+33.1	+2.2
Poikilotopic Calcite:			
52	High Rock Quarry	+29.8	-1.1
92	High Rock Quarry	+27.9	-2.9
1201b	High Rock Quarry	+27.0	-3.7
1201a	High Rock Quarry	+29.8	-1.0
283	High Rock Quarry	+27.8	-2.9
1062a	Paul Bodden Quarry	+29.6	-1.2
Average Stable Oxygen Isotope of Calcite		+28.7	-2.1

Note: Sample numbers refer to catalogue numbers of the Cayman Islands rock collection.

Arthur, 1983) between a mineral and the associated water (α_{m-w}) is related to the isotopic composition of the mineral ($\delta^{18}O_m$) and the associated aqueous phase ($\delta^{18}O_w$) by:

$$\alpha_{m-w} = \frac{1000 + \delta^{18}O_m}{1000 + \delta^{18}O_w}$$

O'Neil (1986) argued that the sign and magnitude of α are controlled by (1) temperature, (2) chemical composition (e.g. magnesian calcite versus pure calcite), (3) crystal structure (e.g. aragonite versus calcite), and (4) pressure, although temperature is the dominant factor.

Fractionation between Calcite and Water

The most widely used relationship on the temperature dependence of oxygen isotopic fractionation between calcite and the water phase is that of Craig (1965):

$$t°C = 16.9 - 4.2(\delta_c - \delta_w) + 0.13(\delta_c - \delta_w)^2$$

where δ_c is the $\delta^{18}O$ of CO_2 liberated by reaction with 100‰ phosphoric acid at 25°C and δ_w is that of CO_2 in equilibrium at 25°C with which the calcite was precipitated. δ_c and δ_w are relative to PDB standard. This relationship was based on analysis of $CaCO_3$ (both calcite and aragonite) precipitated by molluscs grown in controlled laboratory experiment or from well-defined natural environments.

Friedman and O'Neil (1977) determined the oxygen isotopic fractionation between inorganically precipitated calcite and water over the temperature range of 0-500°C. Their relationship is:

$$10^3 \ln\alpha_{(calcite\text{-}water)} = \frac{2.78*10^6}{T^2} - 2.89$$

where T is in °K.

The two sets of experimental relationships are in excellent agreement because direct precipitation of calcite under low temperature sedimentary environment permits accurate establishment of the isotopic fractionation between calcite and water. Using a $\delta^{18}O$ value

of -2.8‰ PDB (28.0‰ SMOW) for calcite as an example, the two temperature equations (Craig, 1965; Friedman and O'Neil, 1977) give comparable results (Fig. VII.1). Therefore, in low temperature setting, the $\delta^{18}O$ values of the waters obtained by equilibrium fractionation calculation should be reliable providing the minerals were precipitated under equilibrium condition. Furthermore, the experimental results agree with the fractionation factors calculated by Bottinga (1968) using theoretical considerations.

Fractionation between Dolomite and Water

The relationship between the isotopic fractionation of dolomite and water, and temperature has been determined by a number of investigators using different experimental techniques:

(1) O'Neil and Epstein (1966) obtained the relationship

$$10^3 \ln\alpha_{(\text{dolomite-water})} = \frac{3.34*10^6}{T^2} - 3.34$$

by mineral-CO_2 exchange experiments combined with calcite-water fractionation at 350-400°C,

(2) Northrup and Clayton (1966) obtained the relationship

$$10^3 \ln\alpha_{(\text{dolomite-water})} = \frac{3.2*10^6}{T^2} - 1.50$$

using partial exchange experiments at 300-510°C,

(3) Sheppard and Schwarcz (1970) obtained the relationship

$$10^3 \ln\alpha_{(\text{dolomite-water})} = \frac{3.23*10^6}{T^2} - 3.29$$

by combining empirical fractionations between dolomite and calcite with calcite-water relationship at 100-650°C,

(4) Fritz and Smith (1970) obtained the relationship

$$10^3 \ln\alpha_{(\text{dolomite-water})} = \frac{2.78*10^6}{T^2} + 0.11$$

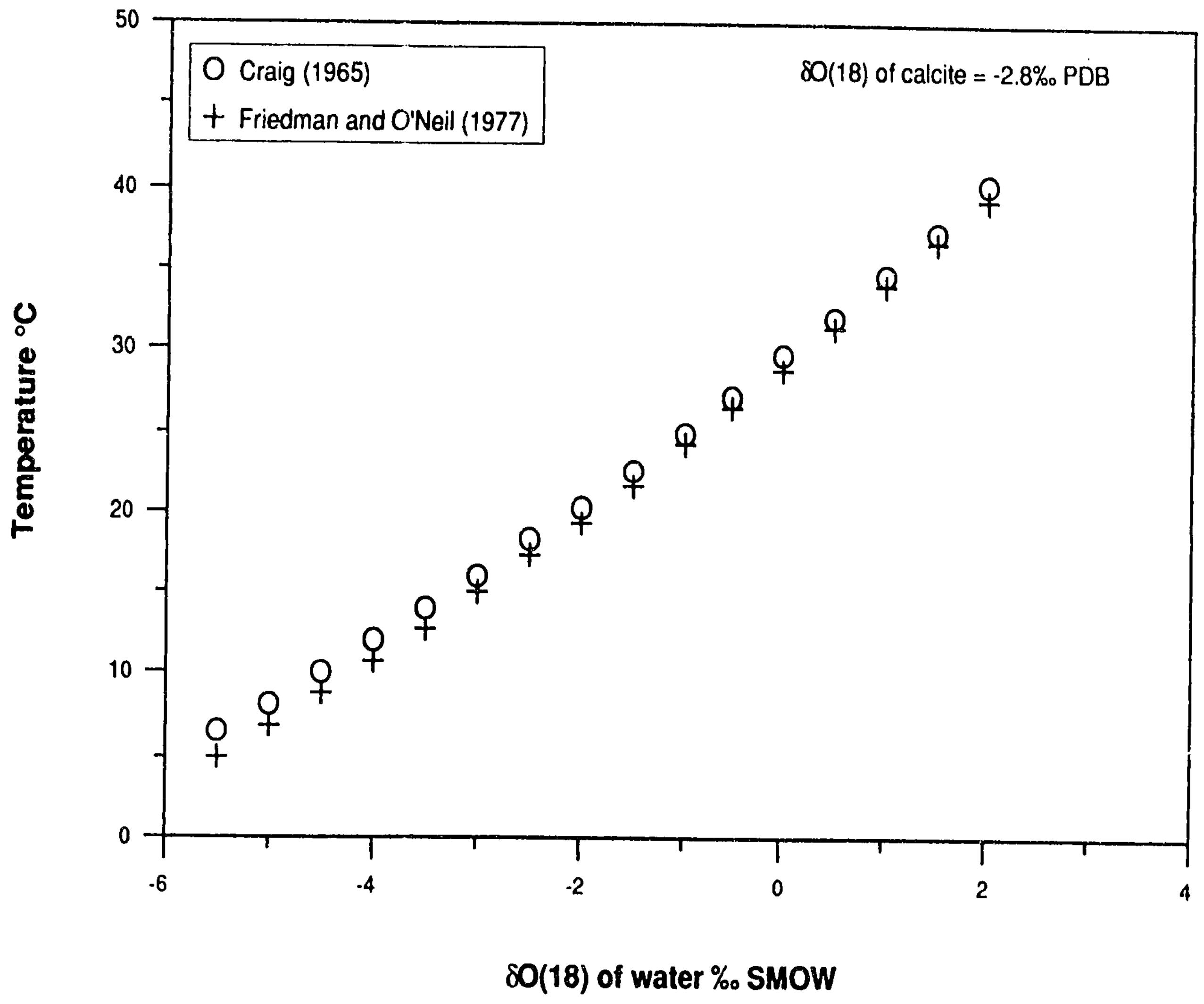


Fig. VII.1 Equilibrium fractionation of oxygen (18) between calcite and water using temperature equations given by Craig (1965) and Friedman and O'Neil (1977).

by carrying out direct precipitation of proto-dolomite (40-45 mole % $MgCO_3$) at 25-78°C, and

(5) Matthews and Katz (1977) obtained the relationship

$$10^3 \ln\alpha_{(\text{dolomite-water})} = \frac{3.06*10^6}{T^2} - 3.24$$

by dolomitization of $CaCO_3$ in apparent isotopic equilibrium with the solution at 252-295°C.

The first four equations were corrected by Land (1983b) to be consistent with Friedman and O'Neil (1977). Using a $\delta^{18}O$ value of +33.4‰ SMOW (+2.5‰ PDB) for dolomite, the equations give significantly different results in the temperature of interest (Fig. VII.2). At 25°C, the $\delta^{18}O$ values of the diagenetic fluids lie between -1.6 to +1.3‰ SMOW (Fig. VII.2). Land (1983b) also noted that at a given $\delta^{18}O$ of dolomite, the range of uncertainty in temperature is 15°C, whereas at a given temperature, the range of uncertainty in $\delta^{18}O$ of water is about 4‰.

The equilibrium fractionation between dolomite and calcite ($\Delta^{18}O$) can be obtained by the difference between $\delta^{18}O_{dolomite}$ and $\delta^{18}O_{calcite}$ for cogenetic dolomite and calcite. Dolomite formed in isotopic equilibrium with calcite in sedimentary environment is enriched in $\delta^{18}O$ by 4 to 7‰ relative to calcite (O'Neil and Epstein, 1966; Northrup and Clayton, 1966). Conversely, the fractionation relationships of Fritz and Smith (1970) and Matthews and Katz (1977) gave $\Delta^{18}O_{(dolomite\text{-}calcite)}$ values in the range of 2 to 4‰. Land (1980, 1983b) also suggested that the equilibrium ^{18}O-fractionation value is probably 3 ± 1‰ at 25°C. In studies of coastal sabkhas of Abu Dhabi, McKenzie (1981) suggested that the naturally occurring dolomite and calcite mixtures have fractionation value of +3.2‰. Hardie (1987), however, suspected that the dolomite studied by McKenzie (1981) might not be formed by replacement.

It is apparent that caution be exercised in accepting the results obtained from these fractionation relationships. This study, therefore, takes into account the results obtained

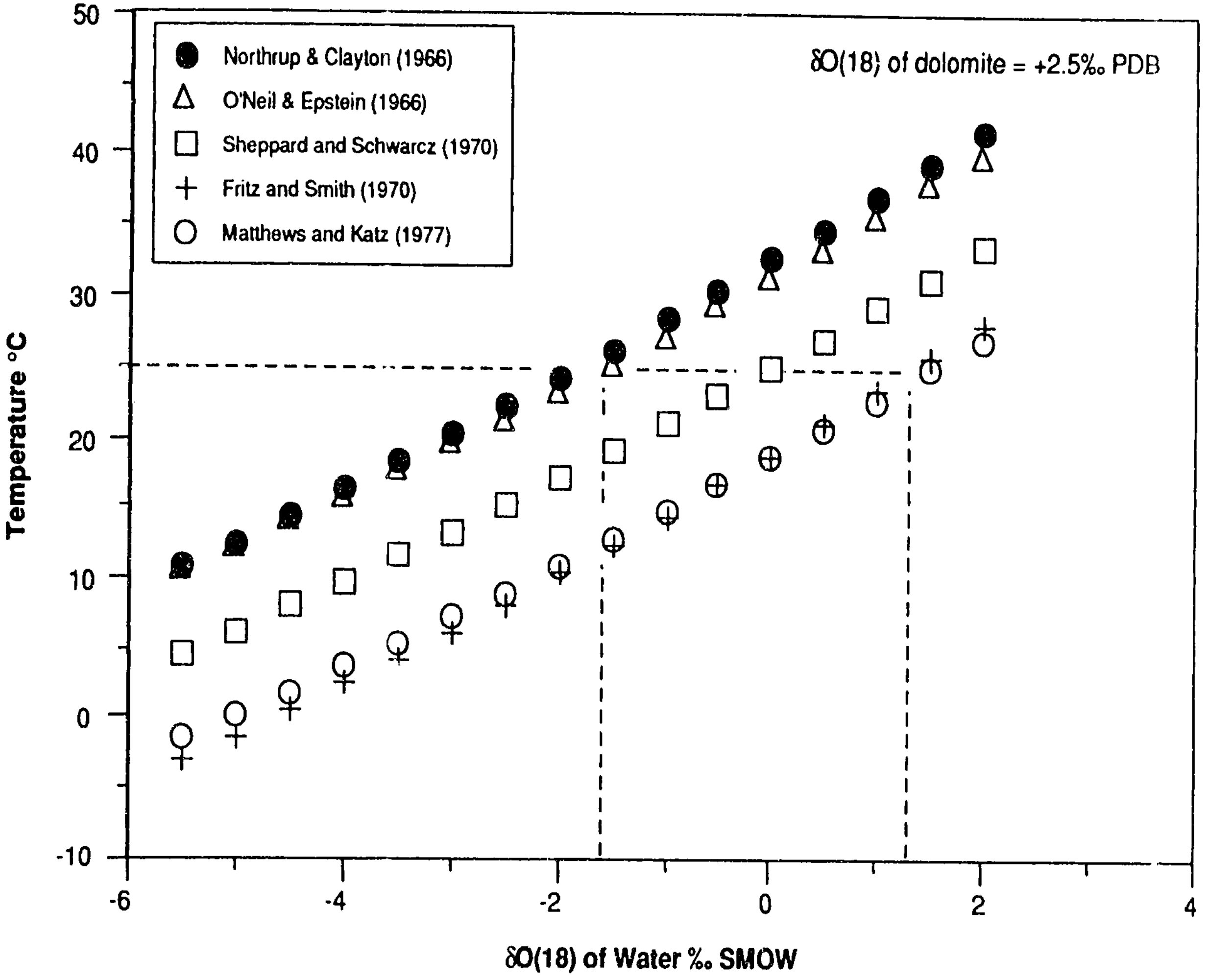


Fig. VII.2 Equilibrium fractionation of oxygen (18) between dolomite and water using five different temperature equations. At 25°C, δO(18) of water differs by about 3‰ depending on the fractionation equations.

from all five equations. Although this conservative approach results in a wide range of $\delta^{18}O$ values in the interpretation of the diagenetic fluids, it avoids the bias resulting from the poor understanding of the fractionation relationship between dolomite and calcite.

D. EQUILIBRIUM FRACTIONATION CALCULATION

Equilibrium fractionation equations of oxygen isotopes allow the evaluation of the relationships of the carbonate minerals, ground water (diagenetic fluid), and the temperature of the aqueous environment in which the minerals formed. The results thus obtained are based on the assumption that the minerals and diagenetic fluids have achieved isotopic equilibrium. Another important assumption is that the diagenetic minerals (dolomite and calcite) have retained the original isotopic signatures since their formation. Unfortunately, there is no assurance that this is the actual situation.

Chemical reactions such as recrystallization, dissolution, and reprecipitation that involve breaking and reforming chemical bonds in the minerals would complicate the interpretation of the results obtained from the equilibrium-fractionation calculation. Furthermore, analytical cross contamination during the separation of calcite and dolomite is possible, particularly when dolomite and calcite are intimately associated with one another as in the case of zoned calcite and dolomite cements.

On the basis of the present day atmospheric and ground water conditions, a temperature range of 22 to 33°C was chosen as the temperatures of the diagenetic fluids for the calculations. Furthermore, because the Cayman Islands are located in low latitudes, it is probable that the ambient temperature in the Tertiary period was similar to that of the present time. The water salinity was determined by the established relationships between the $\delta^{18}O$ content and electrical conductivity (E.C.) of the ground water (Figs. V.2A, 2B, 2C).

Matrix Dolomite of the Bluff Formation

The temperature dependence equilibrium ^{18}O fractionation calculation of dolomite and water is complicated by a variety of temperature equations that were obtained from high temperature experiments (O'Neil and Epstein, 1966; Northrup and Clayton, 1966; Sheppard and Schwarcz, 1970; Matthews and Katz, 1977) or by precipitation of proto-dolomite (Fritz and Smith, 1970). In the temperature range of 22-33°C, the $\delta^{18}O$ values of the fluids are equivalent to waters of 25 to >95% sea water salinity, depending on the equations used (Table VII.5).

The oxygen isotopic composition of the matrix dolomite determined by Pleydell (1987) is the average isotope value of the dolomite crystals in each analysed sample. Therefore, the calculated $\delta^{18}O$ content of the water based on such a bulk $\delta^{18}O$ value of the dolomite may not provide the actual isotopic properties of the dolomitizing fluid(s) if dolomitization occurred in more than a single phase. Land (1983b) suggested that few dolomitized rocks result from a single, short lived event, although it is difficult to recognize single event versus multiple-event dolomitization. Land (1980), however, suggested that inhomogeneities on a single crystal scale are indicative of diagenetic stages.

Caymanite

In the temperature range of 22-33°C, the calculations indicate that the diagenetic fluids that were in association with the caymanite had $\delta^{18}O$ contents ranging from -2.5 to >+1.0‰ SMOW (Table VII.5). These oxygen isotopic compositions correspond to an aqueous phase of 25 to >95% sea water salinity (Table VII.5). This implies that the fluids responsible for the dolomitization of the host rock and the caymanite sediments were of similar salinity, assuming there was no masking of isotopic composition by later phase diagenetic fluids.

Table VII.5 $\delta^{18}O$ and salinity of ground water in equilibrium with different dolomite phases. Temperature range used for the ^{18}O fractionation calculation between dolomite and water is 22 to 33°C.

EQUATION	**N & C**	**O & E**	**S & S**	**F & S**	**M & K**
Matrix Dolomite (Average $\delta^{18}O$ +33.4‰ SMOW):					
$\delta^{18}O$ of water (‰ SMOW)	-2.5 to 0.0	-2.5 to +0.5	-0.5 to +2.0	+1.0 to >+1.0	+1.0 to >+1.0
water salinity (% sea water)	25 to 80	25 to 90	65 to 100	>95	>95
Caymanite (Average $\delta^{18}O$ +33.2‰ SMOW):					
$\delta^{18}O$ of water (‰ SMOW)	-2.5 to 0.0	-2.5 to +0.5	-0.5 to +2.0	+1.0 to >+1.0	+1.0 to >+1.0
water salinity (% sea water)	25 to 80	25 to 90	65 to 100	>95	>95
Limpid Dolomite (Average $\delta^{18}O$ +33.1‰ SMOW):					
$\delta^{18}O$ of water (‰ SMOW)	-2.5 to 0.0	-2.5 to +0.5	-0.5 to +2.0	+0.5 to >+0.5	+1.0 to >+1.0
water salinity (% sea water)	25 to 80	25 to 90	65 to 100	>90	>95
Coarse Dolomite Spar (Average $\delta^{18}O$ +27.2‰ SMOW):					
$\delta^{18}O$ of water (‰ SMOW)	<-5.5	<-5.5 to -5.5	-4.0 to <-4.0	-5.0 to -3.0	-5.0 to -2.5
water salinity	perched/fresh	perched/fresh	fresh	fresh to lightly brackish	fresh to 25% sea water

Note: N&C: Northrup and Clayton, 1966; O&E: O'Neil and Epstein, 1966; S&S: Sheppard and Schwarcz, 1970; F&S: Fritz and Smith, 1970; M&K: Matthews and Katz, 1977.

Calcite Spar

Using the average $\delta^{18}O$ content of the calcite spar (Table VII.2), the temperature calculation shows that the diagenetic fluids had $\delta^{18}O$ values of -3.5 to -1.5‰ SMOW (Table VII.6). These isotopic compositions suggest that the diagenetic fluids that were responsible for the precipitation of the calcite spar were fresh to brackish water up to 45% sea water salinity (Table VII.6).

Dolomite Spar

The coarse dolomite spar was formed in equilibrium with diagenetic fluids having $\delta^{18}O$ compositions of <-5.5 to -2.5‰ SMOW (Table VII.5). At the low $\delta^{18}O$ range (<-5.5‰ SMOW), the associated fluid is perched to fresh water, and at the high $\delta^{18}O$ value (-2.5‰ SMOW), the associated pore fluid is brackish water of 25% sea water salinity.

Flowstone

The oxygen isotopic fractionation calculation between flowstone and water indicates that the flowstones probably precipitated in waters having $\delta^{18}O$ compositions of -5.0 to 0.0‰ SMOW (Table VII.6). These $\delta^{18}O$ values suggest that the diagenetic fluids were fresh to brackish water up to 80% sea water salinity (Table VII.5). The actual precipitating fluids were probably fresh to brackish water up to 45% sea water salinity since the high $\delta^{18}O$ values of the flowstones are due to the presence of detrital dolomite in the flowstone (Smith, 1987).

Disequilibrium precipitation of flowstone, however, has also been known to occur (Hendy, 1971; Schwarcz, 1986). If so, the results obtained from equilibrium calculations become meaningless.

Table VII.6 $\delta^{18}O$ and salinity of ground water in equilibrium with calcite. Temperature range used for the ^{18}O fractionation calculation between calcite and water is 22 to 33°C.

EQUATION	Craig (1965)	Friedman & O'Neil (1977)
Poikilotopic Calcite (Average $\delta^{18}O$ +28.7‰ SMOW):		
$\delta^{18}O$ of water (‰ SMOW)	-0.5 to +1.5	-0.5 to +1.5
water salinity (% sea water)	65 to >100	65 to >100
Calcite Spar (Average $\delta^{18}O$ +25.8‰ SMOW):		
$\delta^{18}O$ of water (‰ SMOW)	-3.5 to -1.5	-3.5 to -1.5
water salinity	fresh water to 45% sea water	fresh water to 45% sea water
Speleothem 726 (Average $\delta^{18}O$ +25.3‰ SMOW):		
$\delta^{18}O$ of water (‰ SMOW)	-4.0 to -2.0	-4.0 to -1.5
water salinity	fresh water to 35% sea water	fresh water to 45% sea water
Speleothem 727 (Average $\delta^{18}O$ +27.1‰ SMOW):		
$\delta^{18}O$ of water (‰ SMOW)	-2.5 to 0.0	-2.0 to 0.0
water salinity (% sea water)	25 to 80	35 to 80
Speleothem 728 (Average $\delta^{18}O$ +25.6‰ SMOW):		
$\delta^{18}O$ of water (‰ SMOW)	-3.5 to -1.5	-3.5 to -1.5
water salinity	fresh water to 45% sea water	fresh water to 45% sea water
Speleothem 730 (Average $\delta^{18}O$ +24.6‰ SMOW):		
$\delta^{18}O$ of water (‰ SMOW)	-5.0 to -2.5	-4.5 to -2.5
water salinity	fresh water to 25% sea water	fresh water to 25% sea water
Speleothem 1219 (Average $\delta^{18}O$ +25.2‰ SMOW):		
$\delta^{18}O$ of water (‰ SMOW)	-4.0 to -2.0	-4.0 to -2.0
water salinity	fresh water to 35% sea water	fresh water to 35% sea water
Speleothem 1250 (Average $\delta^{18}O$ +25.3‰ SMOW):		
$\delta^{18}O$ of water (‰ SMOW)	-4.0 to -2.0	-5.0 to -2.5
water salinity	fresh water to 35% sea water	fresh water to 25% sea water
Speleothem 1252 (Average $\delta^{18}O$ +26.9‰ SMOW):		
$\delta^{18}O$ of water (‰ SMOW)	-2.5 to -0.5	-2.5 to 0.0
water salinity (% sea water)	25 to 65	25 to 80

Poikilotopic Calcite-Dolomite

The diagenetic fluids in equilibrium with the dolomite cement (limpid dolomite) had $\delta^{18}O$ content ranging from -2.5 to >+1.0‰ SMOW (Table VII.5) and the fluids in equilibrium with the poikilotopic calcite had $\delta^{18}O$ composition varying from -0.5 to +1.5‰ SMOW (Table VII.6). Therefore, the diagenetic fluids for the precipitation of the dolomite cement were brackish water of 25 to >90% sea water salinity (Table VII.5), whereas the fluids for the precipitation of the poikilotopic calcite were brackish water of 65 to >100% sea water salinity (Table VII.6). These values suggest that a slight change in the water composition would shift the dolomite formation to calcite or vice versa.

E. SYNOPSIS

Lohmann (1982, 1983) and Meyers and Lohmann (1985) suggest that carbonate minerals precipitated in a progressively more distal phreatic setting commonly display a negative $\delta^{18}O$ trend. The decreasing $\delta^{18}O$ content from dolomite cement to calcite spar probably represents increasing meteoric influence. Detailed studies of the stable isotope geochemistry of the carbonates of the Bluff Formation permit the following conclusions.

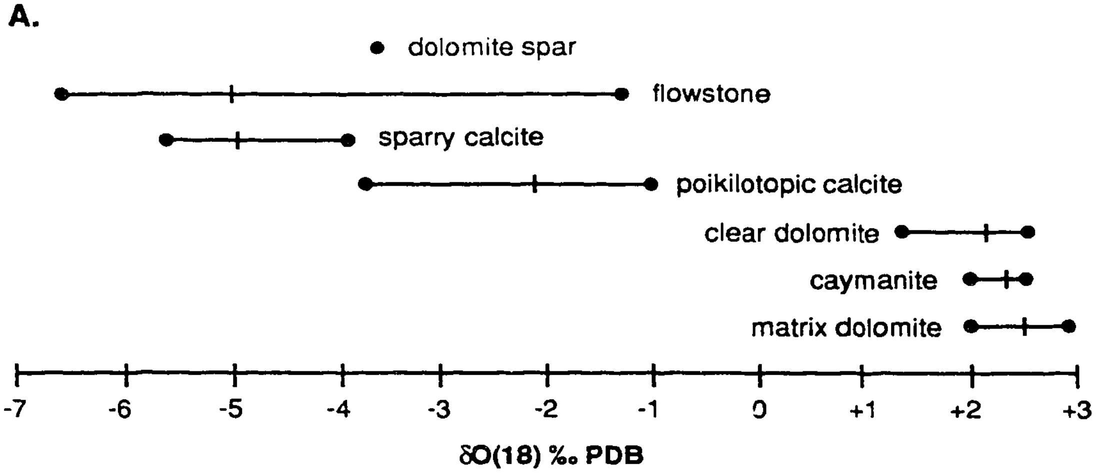
(1) For dolomite, the order of decreasing $\delta^{18}O$ content is matrix dolomite, caymanite, dolomite cement (limpid dolomite), and coarse dolomite spar (Fig.VII.3A).

(2) For calcite, the order of decreasing $\delta^{18}O$ content poikilotopic calcite, sparry calcite, and flowstone (Fig.VII.3A).

(3) The equilibrium oxygen fractionation relationship between calcite and water is well established, whereas the fractionation relationship between dolomite and water at low temperature is equivocal.

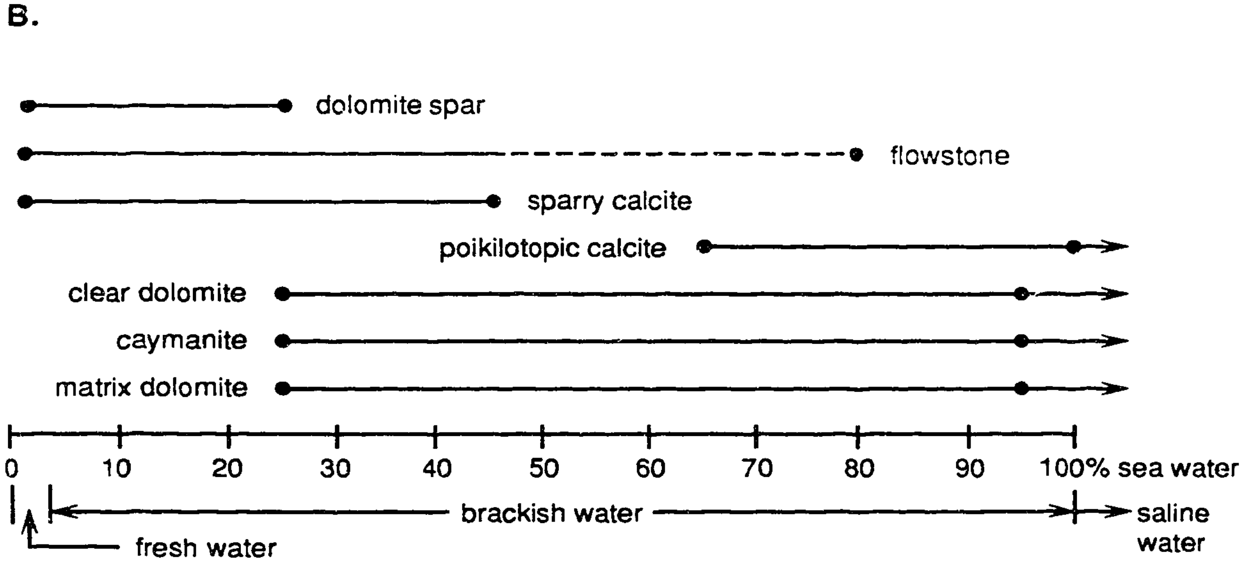
(4) The poikilotopic calcite and dolomite cement having $\Delta^{18}O_{(dolomite\text{-}calcite)}$ values of 2.4 to 6.3‰ PDB are probably not cogenetic phases.

(5) Results of the equilibrium oxygen fractionation between the carbonate minerals and the waters at 22-33°C using different fractionation equations (Fig.VII.3B) conclude



●—● indicates the range of δO(18) values for each mineral phase.
+ indicates the average δO(18) value.

Fig. VII.3A Summary diagram showing the range of δO(18) values for the various carbonate minerals present in the Bluff Formation.



●—● indicates the range of water salinity in which the mineral phase may precipitate. Interpretation based on average δO(18) values.
—➤ indicates the salinity range may extend to higher values.
--- indicates the high salinity values (>45%) rarely occur.

Fig. VII.3B Summary diagram showing the range of water salinity in which the various carbonate minerals may precipitate.

that (i) matrix dolomite and caymanite formed in water of 25 to >95% sea water salinity, (ii) calcite spar and flowstone precipitated in fresh to brackish water up to 45% sea water salinity, (iii) poikilotopic calcite precipitated in water of 65 to >100% sea water salinity, (iv) dolomite cement (in association with poikilotopic calcite) formed in water of 25 to >90% sea water salinity, and (v) coarse dolomite spar precipitated in perched, fresh to brackish water up to 25% sea water salinity.

VIII. DIAGENETIC MODELS

The major controlling factors on the diagenetic realms are past tectonic activity that caused uplift and down faulting of the islands and sea level fluctuations. Periods of relatively high sea level stand were characterized by coral reef development and carbonate deposition. Conversely, periods of relative sea level low stand were characterized by carbonate diagenesis, karst development, and increased erosion. This apparently simple concept with reference to relative sea level changes is complicated by the fact that at times the islands might be partially submerged. Submarine diagenetic textures are rare in the Bluff Formation. Pleydell (1987), however, documented the occurrence of minor amounts of submarine textures such as micrite and isopachous cements. Numerous cycles of carbonate deposition and diagenesis have made the interpretation of the diagenetic signatures present in the rocks of the Bluff Formation a challenge.

A. STRATIGRAPHIC SETTING

In Pedro Castle Quarry on Grand Cayman, Jones and Hunter (1989) documented a distinct disconformity which they used to divide the Bluff Formation into the lower Cayman Member and the upper Pedro Castle Member. On the basis of paleontological data and by comparison with sea level curves constructed by Vail *et al.* (1977), Hallam (1984), and Haq *et al.* (1989), it is apparent that the disconformity separates Oligocene and Miocene strata (Jones and Hunter, 1989).

Correlation of the coral fauna in the Cayman Member with the Caribbean wide Antiguan coral fauna (Vaughan, 1919; Thomas, 1942; Cooke *et al.*, 1943; Woodring, 1957) suggests that the Cayman Member is early late Oligocene in age (Jones and Hunter, 1989). The assignment of an age for the Pedro Castle Member is less confident because of the lack of biostratigraphic markers (Jones and Hunter, 1989). Nevertheless, Jones and Hunter (1989) suggest that the Pedro Castle Member may be middle Miocene in age. The Ironshore Formation that unconformably overlies the Bluff Formation is of late Pleistocene

age (approximately 125,000 years old), based on conventional U-series dating of four coral samples from the upper part of the formation (Woodroffe *et al.*, 1983).

As far as carbonate diagenesis is concerned, it is apparent that the major regressions in late Oligocene to early Miocene and in late Miocene to early Pliocene times would have had considerable impact on the diagenetic alteration of the carbonate sediments of the Bluff Formation. Furthermore, the sea level fluctuations during the Pliocene and Pleistocene epoch would have led to additional diagenetic modifications of the rocks.

B. SEQUENCE OF DIAGENETIC EVENTS

Integration of available stratigraphic, sedimentological and diagenetic information in the Bluff Formation does not permit a definitive interpretation on the sequence and timing of the diagenetic events. Two models can be invoked to satisfy the available data. On the basis of petrographic and geochemical data, Pleydell (1987), Jones (1989a), and Pleydell *et al.* (in preparation) proposed that pervasive dolomitization of the Bluff Formation was a single event involving sea water as the diagenetic fluid. This model is herein called 'Paragenetic Model I' (Fig. VIII.1). This study, however, suggests an alternative interpretation of the geochemical data. Based on the re-evaluation of the geochemical information, mineralogical, petrographic, and circumstantial evidence, this study proposes that dolomitization of the Bluff Formation was achieved through two separate events by mixed meteoric-marine water. The latter model is herein termed 'Paragenetic Model II' (Fig. VIII.1).

Paragenetic Model I

The following sequence of major depositional and diagenetic events (Fig. VIII.1) is summarized from Pleydell (1987), Jones (1989a), Jones and Hunter (1989), Pleydell *et al.* (1989), and from personal discussion with Jones (1989).

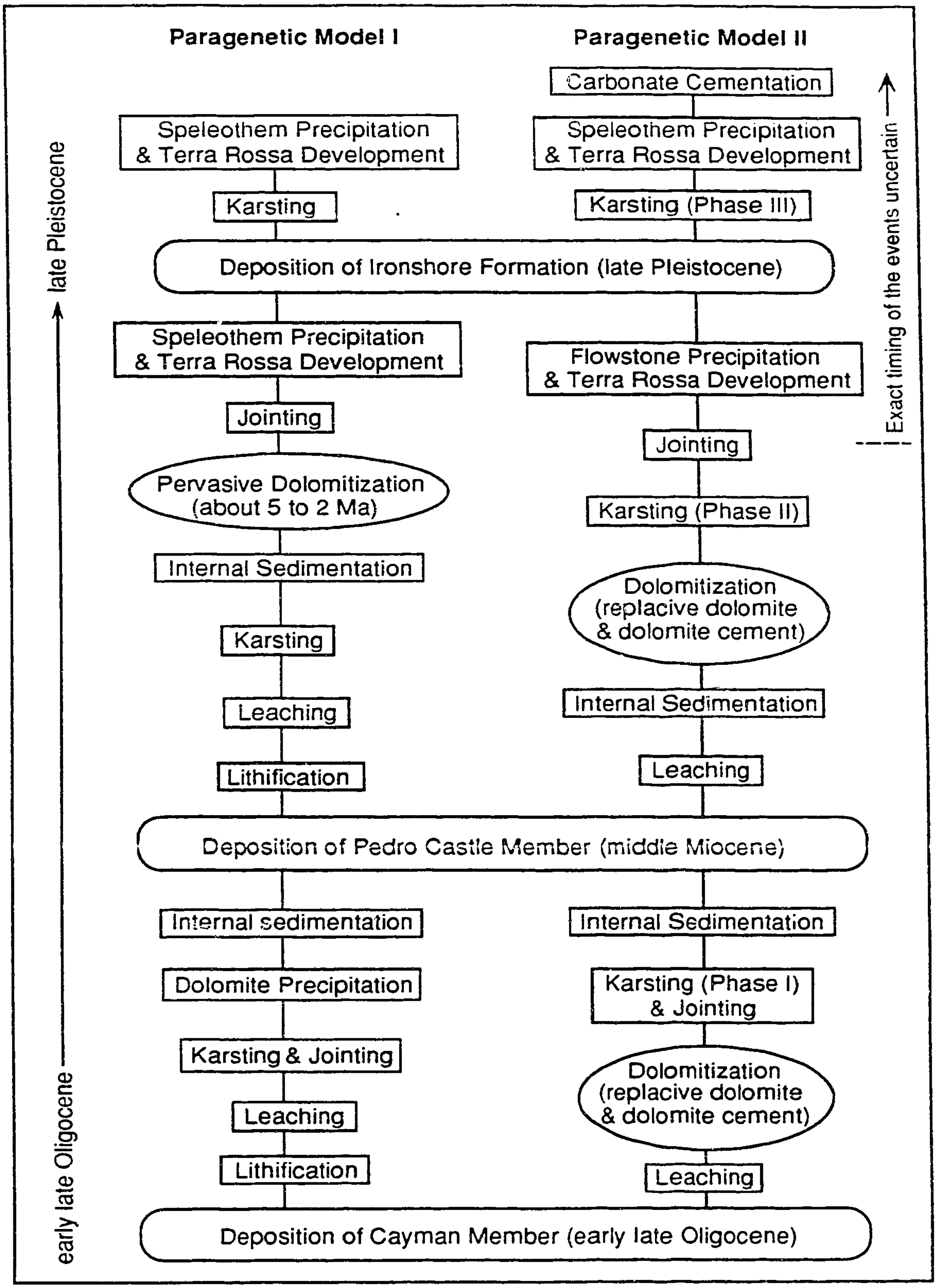


Fig. VIII.1 Sequence of events associated with Paragenetic Model I and II.

(1) Deposition of carbonate sediments of the Cayman Member until early late Oligocene (approximately 30 Ma).

(2) Major regression in late Oligocene with resultant subaerial exposure.

(3) Lithification of carbonate sediments.

(4) Leaching of aragonitic skeletal components, which may have been contemporaneous with lithification of carbonate sediments.

(5) Karst development, and jointing of lithified carbonates.

(6) Precipitation of cavity lining clear dolomite.

(7) Internal sedimentation of fine grained carbonate (caymanite) and skeletal sands during the early Miocene transgression.

(8) Decoration of seafloor (disconformable surface) with a diverse fauna of boring sponges, worms, and bivalves.

(9) Deposition of carbonate sediments of the Pedro Castle Member during middle Miocene (approximately 16 Ma).

(10) Major regression in late Miocene.

(11) Lithification of carbonate sediments.

(11) Leaching of aragonitic skeletal components.

(12) Karst development on the Cayman and Pedro Castle members.

(13) Internal sedimentation of fine grained carbonate and skeletal sands.

(14) Pervasive dolomitization of the Cayman and Pedro Castle members and cavity fills in late Pliocene (approximately 5 to 2 Ma).

(15) Development of joints and fissures.

(16) Precipitation of flowstone and development of terra rossa.

(17) Deposition of carbonate sediments of the Ironshore Formation during late Pleistocene (approximately 125,000 a).

(18) Karst development on dolostones of the Bluff Formation and speleothem precipitation in some caves.

Paragenetic Model II

This study suggests the following sequence of major depositional and diagenetic events (Fig. VIII.1). The depositional history of the Bluff Formation is that of Jones (1989a) and Jones and Hunter (1989).

(1) Deposition of carbonate sediments of the Cayman Member during late Oligocene time (approximately 30 Ma).

(2) Major regression in late Oligocene time with resultant island emergence and meteoric influence.

(3) Leaching of aragonitic skeletal components.

(4) Replacive dolomitization of metastable carbonates and precipitation of dolomite in intergranular space and fossil molds, probably occurring during or shortly after aragonite dissolution.

(5) Jointing and Phase I karst development.

(6) Internal sedimentation of fine grained carbonate (caymanite) and skeletal sands, probably during the early Miocene transgression.

(7) Decoration of the seafloor (disconformable surface) with a diverse fauna of boring sponges, worms, and bivalves.

(8) Deposition of carbonate sediments of the Pedro Castle Member during middle Miocene (approximately 16 Ma).

(9) Major regression in late Miocene with resultant island emergence and meteoric influence.

(10) Leaching of aragonitic skeletal components.

(11) Influx of a small amount of fine grained carbonate and skeletal sands into the fossil molds of the Pedro Castle Member and possibly into the cavities and caves of the Cayman Member.

(12) Replacive dolomitization of metastable carbonate sediments of the Pedro Castle Member and internal sediments in both members, and recrystallization (increase in cation-ordering and stoichiometry) of previously formed dolomites.

(13) Phase II karst development.

(14) Precipitation of flowstone and development of terra rossa.

(15) Extensive joint development.

(16) Deposition of carbonate sediments of the Ironshore Formation during late Pleistocene (approximately 125,000 a).

(17) Phase III karst development (joint controlled) and speleothem precipitation in some caves.

(18) Precipitation of dolomite and calcite cement in cavities that were not occluded by internal sediments and/or speleothemic calcite.

The above sequence is not meant to imply that each diagenetic process was a discrete, separate event. Instead, processes such as dolomitization and recrystallization were probably ongoing events that lasted until the sediments were completely dolomitized and recrystallized to the stable forms.

IX. DIAGENETIC INTERPRETATION OF THE BLUFF FORMATION I: MATRIX DOLOMITIZATION

Dolomitization or replacement of calcium carbonate by dolomite has continued to receive great interest because dolostones form important reservoirs for hydrocarbon (e.g. Thomas and Glaister, 1960; Yan and Zhai, 1980; Watson, 1982) and are host rocks for base-metal deposits (e.g. Kyle, 1983; Force *et al.*, 1986; Buelter and Guillemette, 1988). Recent reviews show that no concensus exists regarding the diagenetic environments and fluid compositions that are responsible for massive dolomitization of thick limestone sequences (Morrow, 1982a, 1982b; Land, 1980, 1983a, 1985; Machel and Mountjoy, 1986, 1987; Hardie, 1987). In addition to the inability to produce dolomitization in the laboratory under low temperature setting, the problem is compounded by the complexity of the cation disordering and cation nonstoichiometry of dolomite.

In light of the present day hydrogeological and hydrochemical information and petrographic and geochemical data, this study attempts to examine the conditions that led to the pervasive dolomitization of the Bluff Formation in terms of the chemical equilibria, chemical kinetics, timing, fluid, and mechanism of dolomitization.

A. CHEMICAL EQUILIBRIA OF DOLOMITIZATION

The replacement of calcium carbonate by dolomite is commonly expressed by

$$2CaCO_3 + Mg^{2+} = CaMg(CO_3)_2 + Ca^{2+} \cdots\cdots\cdots\cdots\cdots\cdots (1)$$

which represents a mole for mole replacement reaction. This process has been used to account for the formation and redistribution of porosity in dolostone reservoir rocks (Murray, 1960). If the CO_3^{2-} ion is brought to the site of dolomitization from an outside source, porosity destruction occurs according to the following reaction (Murray, 1960; Lippman, 1973):

$$CaCO_3 + Mg^{2+} + CO_3^{2-} = CaMg(CO_3)_2 \cdots\cdots\cdots\cdots\cdots\cdots (2)$$

This process of overdolomitization involves a volume gain of 75% to 88% (aragonite or calcite replacement). Such a replacement process is inconsistent with the petrographic fabrics of the Bluff Formation which have a fairly high effective porosity.

A volume for volume replacement (Friedman and Sanders, 1967) rather than a mole for mole replacement probably occurred during the dolomitization of the Bluff Formation as exemplified by the retention of the original skeletal structure such as red algae and foraminifera. Morrow (1982a) proposed that for a volume for volume reaction, the net dolomitization is

$$(2\text{-}x)CaCO_3 + Mg^{2+} + xCO_3^{2-} = CaMg(CO_3)_2 + (1\text{-}x)Ca^{2+} \ldots\ldots(3)$$

where the coefficient x is 0.11 and 0.25 for aragonite and calcite respectively.

At three phase equilibrium (at a particular temperature and pressure), calcite and dolomite are in equilibrium with the solution according to the following reactions:

$$CaCO_3 = Ca^{2+} + CO_3^{2-} \ldots\ldots(4)$$

$$CaMg(CO_3)_2 = Ca^{2+} + Mg^{2+} + CO_3^{2-} \ldots\ldots(5)$$

Stoessell (1987) showed that the equilibrium constant for the dolomitization reaction (Kcd) of equation (3) is

$$Kcd = \frac{Kc^{2-x}}{Kd} = \frac{[Ca^{2+}]}{[Mg^{2+}]}\left(\frac{1}{Kc^{x}}\right) \ldots\ldots(6)$$

where Kc and Kd are the solubility constants for calcite and dolomite respectively according to equations (4) and (5) and $[Ca^{2+}]$ and $[Mg^{2+}]$ are the activities of calcium and magnesium ions in solution. The relationship shown in equation (6) suggests that the activity of CO_3^{2-} is not a factor according to concepts of chemical equilibrium.

On the basis of ground water data in the Floridan aquifer, Hanshaw *et al.* (1971) showed that a Mg/Ca activity ratio close to 1 is indicative of a three phase equilibrium system between calcite, dolomite and the solution. Using the thermodynamic properties of carbonate minerals tabulated by Carpenter (1980), Hardie (1987) demonstrated the importance of cation order-disorder in the evaluation of the Mg/Ca activity ratio. For fully

ordered dolomite, the activity ratio of Mg/Ca is the lowest at 0.10, whereas for disordered dolomite, the ratio is 3.31 (Hardie, 1987). A ratio of 1.0 is only applicable for partly ordered dolomite. The Mg/Ca activity ratio required for dolomitization, therefore, must be used with extreme caution because it depends strongly on the cation-disordering and nonstoichiometry of the dolomite mineral. If calcite is not present as a discrete phase, there is no constraint on the Mg/Ca ratio which may have any value greater than that necessary for three phase equilibrium. Most brackish and saline ground waters on the Cayman Islands are supersaturated with respect to dolomite and have a Mg/Ca activity ratio greater than 1.0 (Tables IV.7, 8). Therefore, from a thermodynamic standpoint, the brackish to saline ground waters are capable of dolomitizing any limestone sequences.

The matrix dolomite of the Bluff Formation ranges in composition from stoichiometric dolomite with 50 mole % $CaCO_3$ to calcian dolomite with 55 mole % $CaCO_3$ (Pleydell, 1987). Fuchtbauer and Goldschmidt (1965), Lumsden and Chimahusky (1980), Sass and Katz (1982), and Sperber *et al.* (1984) suggest that stoichiometric dolomites are commonly associated with micritic lithologies that are indicative of evaporitic depositional environments. Morrow (1982b) also noted that solutions in evaporative settings have high Mg/Ca ratios and commonly form stoichiometric dolomites. Conversely, at Mg/Ca ratios between 2.5 to 5.1, and at salinity less than sea water, precipitation of calcium rich dolomites is common (Morrow, 1982b). Thus, the nonstoichiometric composition of the matrix dolomite of the Bluff Formation argues against a hypersaline dolomitization setting. This contention is further supported by the lack of evaporites in the rocks of the Bluff Formation.

Sperber *et al.* (1984) suggest that complete replacement of calcium carbonate by dolomite requires a continuous influx of magnesium ions. In such open systems, the generalized reaction is

$$CaCO_3 + (0.45\text{-}0.50)Mg^{2+} = Ca_{0.55\text{-}0.50}Mg_{0.45\text{-}0.50}(CO_3)_2 + (0.45\text{-}0.50)Ca^{2+}$$

Therefore, the stoichiometry of the matrix dolomite in the Bluff Formation suggests that the pervasive dolomitization probably occurred in an open system with a sufficient supply of Mg^{2+}.

B. CHEMICAL KINETICS OF DOLOMITIZATION

Some insights concerning the kinetic factors on dolomitization of calcium carbonate have been obtained from experimental works done under hydrothermal conditions (Katz and Matthews, 1977; Matthews and Katz, 1977; Gaines, 1980; Baker and Kastner, 1981; Bullen and Sibley, 1984; Morrow and Ricketts, 1988; Sibley *et al.*, 1988). High temperature experimental conditions were used because dolomite synthesized under earth-surface conditions form only metastable phases.

Dolomitization is a multi-step process involving dissolution of calcium carbonate (aragonite and calcite) and precipitation of dolomite from the solution (Katz and Matthews, 1977; Matthews and Katz, 1977; Gaines, 1980; Baker and Kastner, 1981; Bullen and Sibley, 1984; Sibley *et al.*, 1988). The replacement process proceeds through an intermediate phase(s) of magnesian calcite or calcium rich dolomite which, in turn, converts to dolomite (Katz and Matthews, 1977; Baker and Kastner, 1981; Bullen and Sibley, 1984; Morrow and Ricketts, 1988; Sibley *et al.*, 1988). Katz and Matthews (1977) also concluded that on a submicroscopic scale, the intermediate phases are formed in reaction zones surrounding the replacing grains or crystals, which are not in equilibrium with the bulk solution. On the basis of partitioning models of Sr^{2+} and Mg^{2+} and oxygen isotope data, the reaction zones in the transformation of aragonite to low-magnesian calcite were calculated to occupy <4% of the total solution volume (Katz and Matthews, 1977; Matthews and Katz, 1977).

Gaines (1980) suggested that nucleation of the dolomite phase is the major factor in reaction kinetics. In addition to the normal nucleation and growth stages that are well established for crystal growth, Sibley *et al.* (1988) noted an induction stage. The induction

stage refers to nucleation and growth of dolomite to a detectable limit (Sibley *et al.*, 1988). It is a critical part of the calcite-to-dolomite transformation because it is the slowest step in the overall replacement (Sibley *et al.*, 1988). Rate of dolomite replacement is, therefore, related to the kinetic effects on the length of the induction period.

In low temperature diagenetic environments, physico-chemical parameters that kinetically affect the rate of dolomitization include (1) hydration of Mg^{2+}, (2) molar Mg/Ca ratio, (3) salinity, (4) sulfate reduction, (5) concentration of HCO_3^-, and (6) organic materials.

In aqueous solutions, Mg^{2+} is strongly bound by water with a much higher hydration energy than Ca^{2+} (Lippman, 1973; Lahann, 1978; Hanshaw and Back, 1979). The hydrated Mg^{2+} must be dehydrated (removal of the water molecules from the hydrated ions) before it can be incorporated into the crystal lattice of dolomite. Gaines (1980) demonstrated that Li^{2+} acts as a catalyst for dehydrating Mg^{2+}, and hence, accelerates the dolomitization process. Fe^{2+} probably enhances dolomitization in a similar manner (Gaines, 1980).

The induction stage of dolomitization increases with decreasing molar Mg/Ca ratio (Sibley *et al.*, 1988); therefore, the rate of dolomitization increases with increasing Mg/Ca ratio of the solution. Sibley *et al.* (1988) further demonstrated that a higher Mg/Ca ratio increases the stoichiometry of the dolomite and that the intermediate product is more calcium rich at low Mg/Ca ratio. Baker and Kastner (1981) noted that the molar Mg/Ca ratios for the calcite-dolomite phase boundary lie between 0.57 and 1.06. Gaines (1980) showed that an increase in the transformation rate of dolomite with increasing Mg/Ca ratio occurs only within the dolomite stability field and, because at high ratios, the replacement proceeds to form magnesite.

The reaction rate increases significantly with increasing salinity (Gaines, 1980) due to a reduction in the induction stage (Sibley *et al.*, 1988). Folk and Land (1975) postulated that micritic dolomite, which is commonly calcium rich, forms in hypersaline condition

with a high Mg/Ca ratio. At reduced salinities, with low Mg/Ca ratios close to 1.0, the rate of dolomitization decreases, and the resulting dolomite tends to be limpid, euhedral and more stoichiometric (Folk and Land, 1975). However, Gunatilaka *et al.* (1987) documented the occurrence of calcium poor dolomites in a sabkha environment, where calcium rich dolomites are known to occur in such a setting (Gunatilaka *et al.*, 1984; McKenzie, 1981; Patterson and Kinsman, 1982). Thus, it appears that the effect of salinity on the stoichiometry of dolomite may not be directly correlatable and is probably more complicated than currently perceived.

Under experimental conditions, Baker and Kastner (1981) noted that the presence of even minor amount of SO_4^{2-} in the solution significantly inhibits the rate and degree of calcite-to-dolomite transformation. This inhibition occurs even if the SO_4^{2-} concentration is less than 5% of the sea water content (i.e. about 140 mg/l for the Caribbean sea water). The influence of SO_4^{2-} on dolomitization of calcium carbonate is due to poisoning of surface sites via surface adsorption or to surface precipitation (Baker and Kastner, 1981; Kastner, 1988). Land (1983a) suggested that SO_4^{2-} in solution may reduce the activity of Mg^{2+} by forming a $MgSO_4^{\circ}$ ion pair. However, Morrow and Ricketts (1988) showed that the presence of SO_4^{2-} in solution may inhibit dolomitization by retarding the rate of calcite dissolution, rather than by inhibiting the direct precipitation of dolomite from solution. Therefore, it appears that SO_4^{2-} content is the main kinetic factor in controlling dolomitization instead of the Mg/Ca ratio as suggested by Folk and Land (1975).

Although, according to thermodynamic concepts (equation 6), the dolomitization process is independent of CO_3^{2-} concentration, Morrow (1982a) argued that an increase in the CO_3^{2-} concentration of the solution may promote dolomitization by providing sufficient energy to push aside the hydration shield of Mg^{2+}. This proposition appears to be in agreement with the experimental results of Morrow and Ricketts (1988) and Sibley *et al.* (1988) which showed that higher CO_3^{2-} or HCO_3^- concentrations shorten the induction stage and expedite dolomitization.

Extensive dolomitization is known to occur in organic rich hemipelagic sediments (Baker and Burns, 1985; Burns *et al.*, 1988) and hypersaline sediments (Gunatilaka *et al.*, 1984). Baker and Kastner (1981), Kastner (1983, 1984, 1988), Gunatilaka *et al.* (1984), and Burns *et al.* (1988) concurred that dolomitization in these settings was promoted by an increase in the HCO_3^- content in the pore waters because of sulfate reduction. This process is particularly attractive because it raises the concentration of the dolomitization promoter (HCO_3^-) by reducing the content of the inhibitor (SO_4^{2-}). However, there are numerous examples of dolomites forming in marine conditions that have undergone little or no sulfate reduction (Saller, 1984; Aharon *et al.*, 1987; Mazzullo *et al.*, 1987; Carballo *et al.*, 1987; Mitchell *et al.*, 1987). Gunatilaka *et al.* (1984) and Kastner (1984) suggested that meteoric-sea water mixing may be an effective process in reducing the SO_4^{2-} content in solutions. Therefore, it may be suggested that the schizohaline environment is a favourable setting for dolomitization because of SO_4^{2-} dilution, rather than a result of Mg/Ca ratio decrease as suggested by Folk and Land (1975).

Gaines (1980) showed that organic materials and animal proteins associated with biogenic calcium carbonates inhibit dolomitization. He suggested that this negative kinetic effect can be effectively removed in fresh water diagenetic environments through oxidation.

On the basis of the kinetic aspects of dolomitization, it appears that mixed meteoric-sea water remains a viable medium for dolomitizing any carbonate sequences. However, pervasive dolomitization is probably site specific and only occurs when all the factors for dolomitization such as mineralogical, geological, climatic, and time conditions are favourable.

C. TIMING OF DOLOMITIZATION EVENT(S)

The clear cut evidence that serves to constrain the timing of dolomitization of the Bluff Formation is the absence of dolomite in the Pleistocene Ironshore Formation (Jones *et al.*, 1984). This indicates that the Bluff Formation was dolomitized prior to deposition

of the Ironshore Formation at about 125,000 years ago. Two important points remain to be considered. First, did the pervasive dolomitization occur in a single phase as suggested in Paragenetic Model I or did it occur in two stages as proposed in Paragenetic Model II (Fig. VIII.1). Second, is there any other evidence that can be used to better constrain the timing of the dolomitization event(s).

Aragonite Dissolution

Preferential dissolution of original skeletal aragonite in the molluscs, gastropods and corals was common in the Bluff Formation. Conversely, skeletal components formed of high-magnesian calcite, such as red algae and most foraminifera, have been dolomitized and their textures preserved (Fig. 16a of Lockhart, 1986; Plates 9A, 9F of Pleydell, 1987). Similar dissolution of aragonitic bioclasts has been documented in the Pleistocene Belmont Formation of Bermuda (Land, 1967), the Pleistocene Hope Gate Formation of Jamaica (Land, 1973a), the Pliocene Seroe Domi Formation of Bonaire (Sibley, 1980, 1982), the Pleistocene limestones of Yucatan Peninsula (Ward and Halley, 1985), the Miocene dolostones of Gulf of Suez, Egypt (Coniglio *et al.*, 1988), and the Pliocene Blessing Formation of St. Croix, U.S. Virgin Islands (Gill *et al.*, 1989).

Kinetics

The commonly perceived sequence of carbonate dissolution, in order of decreasing solubility, is magnesian calcite, aragonite and calcite (Chave *et al.*, 1962; Pytkowicz, 1969). This is only observed in solution at or near aragonite saturation state (Walter, 1985). The dissolution rate constants are commonly an inverse function of the grain size (Keir, 1980; Dreiss, 1984; Walter and Morse, 1984). More importantly, experimental studies by Walter (1985) and Walter and Morse (1985) showed that differences in grain microstructures can override thermodynamic constraints and lead to selective dissolution of more stable mineral phase. Furthermore, Walter (1985) concluded that the microstructural

control on dissolution rate is related to the saturation state of the solution. If the solution is undersaturated with respect to all the carbonate mineral phases, the reactive surface area of the grain microstructure controls the relative rate of dissolution (Walter, 1985). In this connection, the preferential dissolution of the aragonitic bioclasts in the Bluff Formation is probably related to their complex microstructures which have large reactive surface areas. For example, branching corals such as *Stylophora* were completely dissolved, whereas some massive corals such as *Montastrea* were partly preserved.

Timing

The selective dissolution phenomenon is due to the fact that aragonite is not thermodynamically stable under earth-surface conditions (Bathurst, 1975; Berner, 1981; Morse, 1983). Thus, aragonitic sediments that are stable when bathed in sea water will dissolve or be transformed to low-magnesian calcite when exposed to fresh water. Subaerial exposure of metastable carbonate sediments of the Bluff Formation undoubtedly occurred during the relative sea level drops in late Oligocene and late Miocene times. Therefore, most of the fossil molds in the Bluff Formation may have been formed in relation to sea level falls.

Studies of Pleistocene limestones led Land (1970), Steinen and Matthews (1973), Pingitore (1976), Longman (1980), and James and Choquette (1984) to conclude that dissolution of biogenic aragonite is much more effective in the fresh water phreatic environment than in the vadose setting. Thus, the extensive dissolution of the aragonitic skeletal components of the Bluff Formation may have occurred in the phreatic diagenetic realm. The preservation of the fossil molds also indicates that aragonite dissolution probably occurred after the sediments had undergone some degree of lithification.

Land (1973a) suggested that aragonite dissolution and dolomitization of the Pleistocene Hope Gate Formation of Jamaica occurred almost contemporaneously because aragonitic fossil molds have void-lining dolomite cement but no calcite cement. A similar

conclusion was drawn by Sibley (1982) in the study of the Pliocene Seroe Domi Formation of Bonaire. The common absence of aragonite in the dolomitized portions of the Pleistocene limestones also led Ward and Halley (1985) to suggest that dolomitization occurred during or shortly after aragonite dissolution. Sibley and Gregg (1987) also suggested that because allochem molds are much more common in dolostones than limestones, the molds probably formed during or after dolomitization. Experimental dolomitization of calcareous skeletal components also suggested that dolomitization and aragonite dissolution are near contemporaneity (Bullen and Sibley, 1984).

Aragonite dissolution and dolomitization appear to be closely related in some dolomitized limestone sequences (Land, 1973a; Sibley, 1982; Ward and Halley, 1985; Coniglio *et al.*, 1988). In other dolomitic limestone sequences, the relationship between aragonite dissolution and dolomite replacement is not clear. Examples cited in the Pleistocene coral terraces on Barbados (Humphrey, 1988), the Pliocene Blessing Formation on St. Croix, U.S. Virgin Islands (Gill *et al.*, 1989), and the Eocene to Miocene Gambier Limestone on South Australia (James and Bone, 1989) do not suggest any particular relationship between aragonite dissolution and dolomite replacement in the sequences.

In the case of the Bluff Formation, the rocks are completely dolomitized; therefore, it is difficult to establish the timing of aragonite dissolution with respect to dolomitization using petrographic analysis. However, it is important to note that in all the partially or completely dolomitized Tertiary and Pleistocene limestone sequences, aragonite dissolution is common (Land, 1973a; Sibley, 1982; Jones *et al.*, 1984; Ward and Halley, 1985; Coniglio *et al.*, 1988; Humphrey, 1988; Gill *et al.*, 1989; James and Bone, 1989). Perhaps aragonite dissolution and dolomitization is a kinetic relationship because aragonite dissolution provides additional CO_3^{2-}/HCO_3^- ions for the volume to volume dolomite replacement of the calcium carbonate skeletal materials. Morrow (1982a), Machel and Mountjoy (1986), and Morrow and Ricketts (1988) also suggested that an increase in

CO_3^{2-} favours dolomitization. Because preferential dissolution of most of the aragonite fossils in the Bluff Formation would provide an additional source of CO_3^{2-}, it is suggested that their dissolution probably occurred contemporaneous with dolomite replacement (i.e. Paragenetic Model II). Furthermore, early lithification can also be achieved by dolomite precipitation in the intergranular space during dolomitization.

Mineralogical Considerations

Petrographic studies generally indicate that dolomite has selectively replaced former lime mud (Murray and Lucia, 1967; Cander *et al.*, 1988). This is because substrates with a high surface-to-volume ratio, such as micrite, provide abundant active sites for nucleation (Sibley and Gregg, 1987; Sibley *et al.*, 1988). It has also been noted that aragonite and high magnesian calcite are more susceptible to dolomitization than low magnesian calcite because metastable carbonates have higher standard free energy (Fairbridge, 1957; Sibley, 1980, 1982; Sibley and Gregg, 1987). These observations are consistent with the experimental results obtained by Gaines (1974), Bullen and Sibley (1984), and Sibley *et al.* (1988).

Sibley *et al.* (1988) showed that the mineralogical selectivity of dolomite replacement of calcium carbonate is due to the shorter induction stage for aragonite than for calcite. This shorter induction stage results in the higher dolomitization rate of aragonite than of calcite. Dolomitization of aragonite was also found to proceed at higher SO_4^{2-} concentrations than that of calcite (Baker and Kastner, 1981).

Bullen and Sibley (1984) noted that there is no difference in the dolomitization rate of cryptocrystalline aragonite, high magnesian calcite and low magnesian calcite. They concluded that crystal size rather than mineralogy is the determining factor in the abundance of nucleation sites, and hence, the rate of dolomite formation. Furthermore, the preservation of replacement fabrics is also a function of the crystal size of the original skeletal components. Cryptocrystalline skeletal components such as coralline algae,

echinoids, and foraminifera generally have their microstructures preserved during dolomitization (Bullen and Sibley, 1984). Conversely, microcrystalline fossils such as corals and molluscs commonly lose their microstructures during dolomitization (Bullen and Sibley, 1984).

The matrix dolomite of the Bluff Formation was formed by replacement of precursor calcium carbonate as shown by the dolomitized bioclasts. Mimic replacement (i.e. microstructure preserved) of the high magnesian calcitic skeletal components (e.g. red algae, foraminifera) but not the aragonitic skeletal components (e.g. corals, molluscs) suggests that the allochems had not been transformed to low magnesian calcite prior to dolomitization. This conclusion is consistent with Bullen and Sibley's (1984) experimental results. Although conversion of high magnesian calcite to low magnesian calcite may not lead to destruction of original fossil fabrics (Friedman, 1964; Land, 1967; James and Choquette, 1984), dolomitization of diagenetic low magnesian calcite is kinetically not favourable (Gaines, 1974; Sibley, 1980, 1982; Bullen and Sibley, 1984). In this connection, it is suggested that dolomitization of the Bluff Formation probably occurred prior to the stabilization of the metastable carbonates (i.e. Paragenetic Model II) in a manner similar to that suggested by Land (1973a) for the Pleistocene Hope Gate Formation of Jamaica, Sibley (1982) for the Pliocene Seroe Domi Formation of Bonaire, and Coniglio *et al.* (1988) for the Miocene carbonates of Gulf of Suez, Egypt.

Geochemical Considerations

The Cayman and Pedro Castle members of the Bluff Formation have similar $\delta^{18}O$ contents and $^{87}Sr/^{86}Sr$ ratios (Pleydell, 1987; Jones, 1989a; Pleydell *et al.*, in preparation). This geochemical information led Jones (1989a) and Pleydell *et al.* (in preparation) to suggest that dolomitization of the Bluff Formation (Paragenetic Model I) was a single event at about 5 to 2 million years ago. Therefore, in order for Model II (Fig. VIII.1) to be viable alternative, it must take into account the geochemical data.

Stable Oxygen Isotopes

The stable oxygen isotopic composition of a mineral is controlled by the isotopic composition of the fluid from which the mineral precipitates and the temperature of precipitation (Land, 1980, 1983a; Anderson and Arthur , 1983; Lohmann, 1983). The $\delta^{18}O$ composition of the diagenetic mineral can, therefore, provide useful information on the diagenetic environment.

More than 90% of the $\delta^{18}O$ values of the matrix dolomite of the Oligocene Cayman Member fall between 2.05 and 3.05‰ PDB (Fig. IX.1A), although the values range from 1.4 to 3.0‰ PDB. The low values probably resulted from calcite contamination during the separation procedure. The $\delta^{18}O$ contents of the matrix dolomite of the Miocene Pedro Castle Member are slightly higher, ranging from 2.4 to 3.4 ‰ PDB; however, most of the values are between 2.55 to 3.05 ‰ PDB (Fig. IX.1B). The similar stable oxygen isotopic contents of dolomites from the Cayman Member and the Pedro Castle Member (Fig. IX.1) may have resulted from other diagenetic phenomena rather than the single dolomitization event as suggested by Jones (1989a) and Pleydell *et al.* (in preparation). Similar data could be achieved (1) if the various dolomitization events occurred under similar diagenetic conditions, or (2) if the isotopic signatures of previously formed dolomites were overprinted by later phase diagenetic fluids.

On the basis of the geological history of the Bluff Formation (Jones and Hunter, 1989), it is likely that the two members were subjected to similar diagenetic fluids (i.e. meteoric and sea water) during island emergence in late Oligocene and late Miocene times. However, the isotopic content of the Bluff Formation was probably reset by later phase diagenetic fluids in a manner suggested by Coniglio *et al.* (1988) and Moore *et al.* (1988). It has been noted by numerous workers that stable oxygen isotopic values can be reset by recrystallization as a result of late stage diagenesis (Land, 1980, 1983a, 1985; Machel and Mountjoy, 1986; Hardie, 1987; Longstaffe, 1987). Recrystallization of earlier formed dolomites by later diagenetic fluids was suggested by McKenzie (1981), Coniglio *et al.*

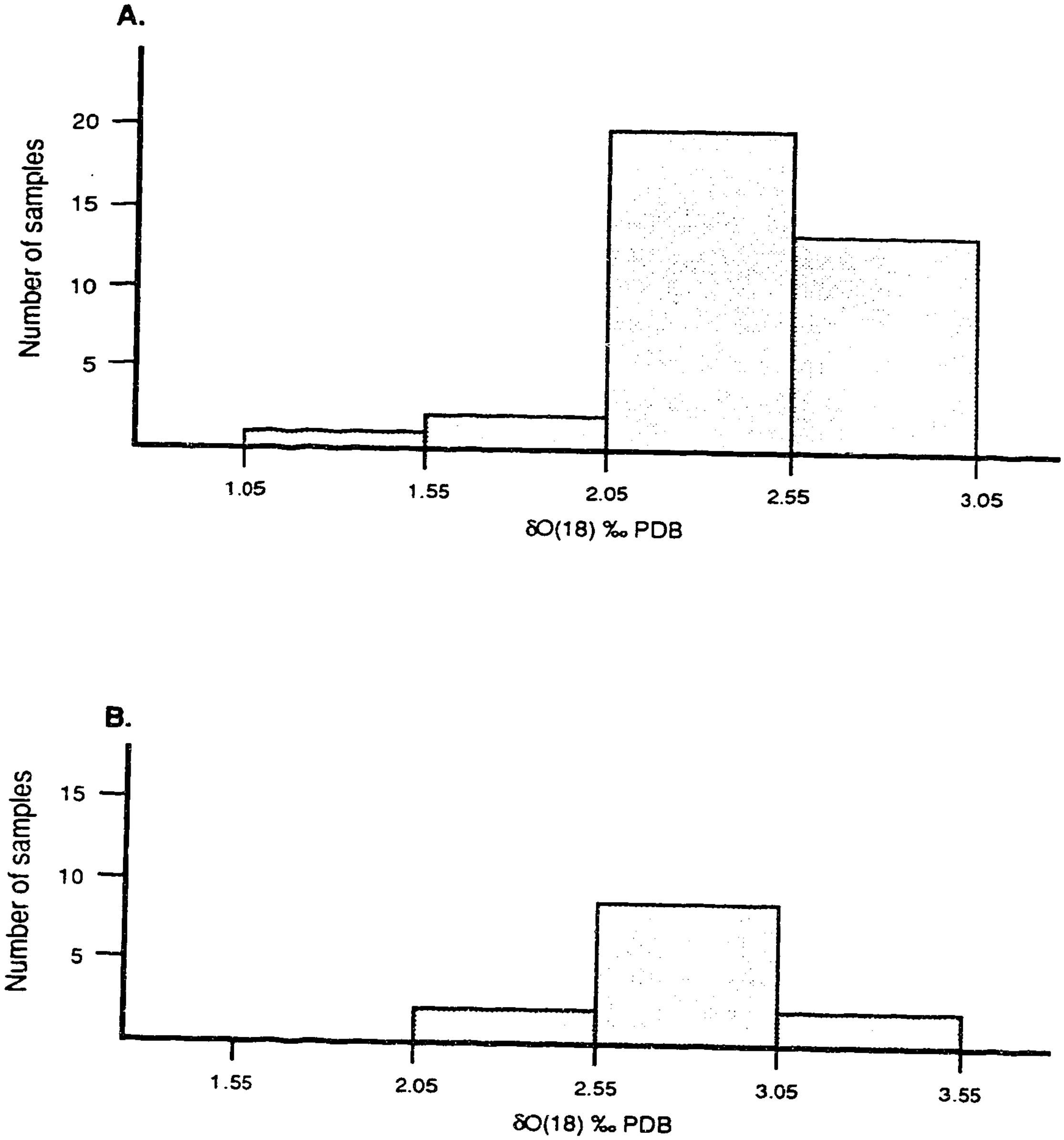


Fig. IX.1 Histograms showing distribution of δO(18) values of (A) Cayman Member dolostone and (B) Pedro Castle dolostone. Isotope data courtesy of Dr. B. Jones.

(1988), and Moore *et al.* (1988) to explain the stable isotopic composition of the dolostones from Holocene, Miocene and Jurassic ages, respectively. Thus, it appears that the stable oxygen isotopic signature of the diagenetic mineral is not a reliable means of differentiating the various stages of dolomitization without other supporting evidence.

Strontium Isotopes

The premise for using Sr isotopic ratio ($^{87}Sr/^{86}Sr$) for age dating is based on the following criteria:

(1) The Sr isotopic composition in sea water is uniform at any given time (Brass, 1976) because the oceanic residence time of Sr (~10^6 years) is much longer than the oceanic mixing time (~10^3 years).

(2) The Sr contained in marine carbonate, sulfate, and phosphate samples records the $^{87}Sr/^{86}Sr$ values of the sea water from which they were formed.

(3) the Sr isotopic ratio changes slowly over millions of years in a predictable trend (Burke *et al.*, 1982; Koepnick *et al.*, 1985; DePaolo and Ingram, 1985; DePaolo, 1986; Hess *et al.*, 1986; Richter and DePaolo, 1987; Rundberg and Smalley, 1989).

Studies by Saller (1984) on the Eocene strata of Enewetak Atoll and Swart *et al.* (1987) on the Pliocene and Miocene strata of the Bahamas suggest that the Sr isotopic composition may provide the age of dolomitization. This is possible because the isolated geologic location of the Enewetak Atoll and the Bahamas means that the sequence is removed from any source of dolomitizing fluids other than sea water and meteoric water. The contribution of Sr from fresh water is generally negligible relative to that of the sea water (8 ppb vs. 8 ppm; Faure *et al.*, 1967). Therefore, the Sr isotopic content of the dolomite is essentially a measurement of the Sr isotopic composition of the sea water at the time of dolomitization. Thus, the age of the dolomitization event can be obtained from the $^{87}Sr/^{86}Sr$ trend versus time data of Burke *et al.* (1982), Koepnick *et al.* (1985), DePaolo

and Ingram (1985), DePaolo (1986), Hess *et al.* (1986), Richter and DePaolo (1987), and Rundberg and Smalley (1989).

Following the approach of Saller (1984) and Swart *et al.* (1987), Jones (1989a) and Pleydell *et al.* (in preparation) showed that the Sr isotopic data fall in a narrow range (Table IX.1), with an average value of 0.7090. Using the $^{87}Sr/^{86}Sr$ sea water versus time curve of Koepnick *et al.* (1985), the average value suggests that dolomitization of the Bluff Formation was a single event that took place about 5 to 2 Ma (Jones, 1989a; Pleydell *et al.*, in preparation).

The $^{87}Sr/^{86}Sr$ sea water data are relatively well defined for the Cenozoic; nevertheless, Sr isotope versus time curves derived from different sampling sites show variation (cf. Keopnick *et al.*, 1985; DePaolo and Ingram, 1985; DePaolo, 1986; Hess *et al.*, 1986). The variation is probably caused by sample alteration (recrystallization) and uncertainty in biostratigraphic dating (Hess *et al.*, 1986; Richter and DePaolo, 1987; Rundberg and Smalley, 1989; Wardlaw, 1989). According to Koepnick *et al's.* (1985, Figs. 3 and 4) Sr-isotopic sea water curve, the present day sea water is the most radiogenic and has a $^{87}Sr/^{86}Sr$ ratio slightly less than 0.70910. This means that any $^{87}Sr/^{86}Sr$ ratios in excess of 0.70910 are meaningless values; however, a close examination of the Sr isotopic data of the Bluff Formation shows that almost half of the data are above this critical value (Table IX.1). Using the latest Sr isotope versus age trends determined by DePaolo (1986), Hess *et al.* (1986), Richter and DePaolo (1987), and Rundberg and Smalley (1989), the Sr isotopic ratios give a rather different interpretation (Table IX.1). The age of dolomitization of the Bluff Formation may be as early as 9 million years ago (Table IX.1). Although the Pedro Castle Member is presently assigned an age of approximately 16 million years, the actual age of the member is open to debate due to the lack of biostratigraphic markers in dating the sequence (Jones and Hunter, 1989; Jones, 1989a). The Pedro Castle Member may be as young as 9 million years old (I. Hunter, 1989, per. comm.). Furthermore, it is not possible to determine how much of the Pedro Castle strata

Table IX.1 $^{87}Sr/^{86}Sr$ ratios and interpretation of the age of dolomitization for dolostones from the Bluff Formation on Grand Cayman. Sr isotopic data courtesy of Dr. B. Jones.

Sample #	Age	$^{87}Sr/^{86}Sr$	Age[1] Ma	Age[2] Ma
1264	Oligocene	0.709125	NA	2.0±0.5
2002	Oligocene	0.709124	NA	2.0±0.5
2023	Oligocene	0.709062	<1.5	4.0±1.5
		0.709042*	1.5±1.0	4.0±1.5
2036	Oligocene	0.709134	NA	2.0±0.5
2037	Oligocene	0.709106	NA	2.5±0.5
		0.709045*	1.5±1.0	4.0±1.5
3077	Oligocene	0.709070	<1.0	4.0±1.5
3126	Oligocene	0.709000	3.0±2.0	6.0±3.0
3152	Oligocene	0.709000	3.0±2.0	6.0±3.0
2013	Miocene	0.709009	3.0±2.0	6.0±3.0
2018	Miocene	0.708999	3.0±2.0	6.0±3.0
2019	Miocene	0.709115	NA	2.0±0.5
2024	Miocene	0.709060	0.5±1.0	4.0±1.5
2033	Miocene	0.709080	<0.5	3.5±1.5
		0.708983*	3.5±2.0	6.0±3.0
2035	Cavity fill (skeletal grainstone)	0.709331	NA	NA
3167	Cavity fill (caymanite)	0.709140	NA	1.5±0.5

Note: (1) Sample # refers to the catalogue no. of the Cayman Islands rock collection.

(2) All samples were analyzed at the University of Alberta, Sr isotopic data marked by an asterisk* refer to results determined by the University of Saskatchewan on the same samples.

(3) Age[1] refers to age of dolomitization determined from Sr isotopic sea water curve of Koepnick *et al.* (1985).

(4) Age[2] refers to age of dolomitization determined from Sr isotopic sea water curves of DePaolo (1986), Hess *et al.* (1986), Richter and DePaolo (1987), and Rundberg and Smalley (1989).

(5) NA means that no age can be assigned to the Sr isotopic value because it exceeds the Sr isotopic ratio of the present day sea water.

was lost by erosion, and hence, to determine the age of the missing strata. Based on the older dolomitization age and the uncertainty in the age assignment of the Miocene Pedro Castle Member, it would appear that sediments of the Pedro Castle Member may have been dolomitized early in the diagenetic history, probably in relation to the late Miocene sea level fall at about 10 Ma (Vail *et al.*, 1977; Haq *et al.*, 1987). If this age interpretation is correct, it would suggest that the dolomitization of the Pedro Castle Member occurred prior to the stabilization of the metastable calcium carbonate minerals. Thus, the dolomite fabric of the Miocene Pedro Castle Member resulted from an early dolomitization event. If so, the petrographic fabric of the Oligocene Cayman Member, which is similar to the Miocene Pedro Castle Member, might also have resulted from early dolomitization of metastable carbonate sediments during late Oligocene times.

Another source of uncertainty is shown by the Sr isotopic values obtained from the same samples by two separate laboratories (Table IX.1). The results are generally similar, but there are measurable differences, particularly for sample #2033 (Table IX.1). The $^{87}Sr/^{86}Sr$ ratio determined by the University of Alberta gives an age of 3.5±1.5 Ma whereas the ratio determined by the University of Saskatchewan gives an age of 6.0±3.0 Ma (Table IX.1). This indicates that results obtained from different laboratories may vary.

It is also important to note that the skeletal grainstone and the caymanite samples from the Cayman Member have the highest radiogenic Sr isotopic ratios (Table IX.1), and hence, the youngest dolomitization age. This indicates that the latest dolomitization fluid had penetrated deep into the Oligocene Cayman Member. This young Sr isotopic age is consistent with the Paragenetic Model II which suggests that the caymanite and skeletal sands in the Cayman Member were dolomitized at a later time than the host rock. However, the Sr isotopic value for the skeletal grainstone is questionable because it exceeds the highest point of the $^{87}Sr/^{86}Sr$ curves determined by DePaolo (1986), Hess *et al.* (1986), Richter and DePaolo (1987), and Rundberg and Smalley (1989).

Machel and Mountjoy (1986) noted that Sr isotopic ratios can be reset by recrystallization. Land (1985) also suggested that the radiogenic Sr ratios may indicate fluid that stabilizes a previously formed dolomite. Studies of the Upper Jurassic Smackover dolomites by Moore *et al.* (1988) also suggested that Sr isotopic ratios of the dolomite may have been reset by later-phase recrystallization. Therefore, overprinting of the Sr isotopic ratios of the previously formed dolomites of the Cayman Member may explain the generally uniform Sr isotopic composition of the Bluff Formation. The spread in the dolomitizing age data (2.0±0.5 to 6.0±3.0 Ma; Table IX.1) may indicate the continual equilibration of the previously formed dolomites until late Pliocene and early Pleistocene times. The Sr ratios also suggest that dolomitization is a slow and gradual process.

Recrystallization

The term recrystallization is commonly used to describe any change in the fabric of a mineral (Bathurst 1975). In the context of this study, recrystallization of the matrix dolomite of the Bluff Formation refers to transformation of poorly ordered and/or nonstoichiometric dolomite to ordered and stoichiometric dolomite. Sibley and Gregg (1987) preferred the term neomorphism to recrystallization because such transformation can be considered a change in mineralogy. Changes of the $\delta^{18}O$ contents and $^{87}Sr/^{86}Sr$ ratios probably accompany recrystallization.

Experimental studies by Glover and Sippel (1967) showed that cation-disordered rhombohedral carbonates of dolomitic composition, precipitated at room temperature, slowly transformed to aragonite when left in contact with their supernatant solutions or with pure water. Similarly, Gaines (1974), Katz and Matthews (1977), Baker and Kastner (1981), Bullen and Sibley (1984), and Sibley *et al.* (1988) showed that the initial products of experimental dolomitization was metastable, poorly ordered, calcium rich dolomite which converted to well ordered dolomite with sufficient time.

Land (1980), Sperber *et al.* (1984), and Hardie (1987) noted that any poorly ordered Ca-rich phase formed at or near earth surface will have a large thermodynamic drive to undergo spontaneous ordering as time progresses because of the large order-disorder energies in dolomites. Lumsden and Chimahusky (1980) and Sperber *et al.* (1984) also suggested that dolomite stoichiometry may be strongly time dependent as the rocks are exposed to the ever changing pore fluids after their initial precipitation. The stoichiometry of the dolomites of the Bluff Formation, therefore, may reflect the result of diagenetic stabilization.

Petrographic Considerations

Paragenetic Model I (Fig. VIII.1; Pleydell, 1987; Jones, 1989a; Pleydell *et al.*, in preparation) suggests that dolomitization of the Bluff Formation occurred about 5 to 2 million years ago. If so, the metastable carbonate sediments (aragonite and high magnesian calcite) would have been subjected to extensive meteoric influence in late Oligocene and late Miocene times as a result of relative sea level falls prior to dolomitization. During these periods of subaerial exposure, most of the metastable carbonates would have transformed to low magnesian calcite in a manner similar to that documented for the Pleistocene limestones of Bermuda (Land, 1970), Barbados (Steinen and Matthews, 1973; James, 1974; Pingitore, 1976), and Florida (Martin *et al.*, 1986; Schmoker and Hester, 1986). These studies concluded that significant diagenetic modification takes place in the fresh water phreatic zone where the matrix was cemented by microspar and metastable carbonates were inverted to low magnesian calcite or partially dissolved. Because the time for the inversion of aragonite to calcite is in the order of thousands to hundred of thousands of years (Harrison, 1975; Halley and Harris, 1979), it is reasonable to suggest that most carbonate sediments were inverted to low magnesian calcite prior to the Model I dolomitization about 5 to 2 Ma.

Studies of marine shorelines and coral terraces on Barbados (Mesolella *et al.*, 1969; Bender *et al.*, 1973; Steinen *et al.*, 1973), Bahamas (Neumann and Moore, 1975), Bermuda (Harmon *et al.*, 1978), New Guinea (Bloom *et al.*, 1974), and Hawaii (Ku *et al.*, 1974) established that eustatic sea level has changed at least six times during the past 125,000 years. These frequent sea level changes probably resulted in the formation of unstable hydrogeological systems that were not conducive to mineral stabilization of the carbonate sediments. If so, the sediments of the Ironshore Formation were exposed to the marine phreatic and vadose diagenetic zones at different times after their deposition. Furthermore, marine phreatic and vadose diagenetic realms are not active diagenetic environments for mineral stabilization and cementation relative to the fresh water phreatic zone (Land, 1970; Steinen and Matthews, 1973; Longman, 1980; James and Choquette, 1984). This is probably the main reason the Ironshore Formation still contains a high content of aragonite. The Bluff Formation, however, was subaerially exposed over long periods of time (in the order of 10^6 years) as a result of the major regression in late Oligocene to early Miocene and late Miocene to early Pliocene times. These periods of island emergence would have resulted in extensive meteoric influence, particularly in the central part of the islands where marine influence is less severe. Therefore, the lack of diagenetic modification of the Ironshore Formation cannot be used as a direct reference for the study of the diagenesis of the Bluff Formation.

Pleydell (1987) and Jones (1989a) suggested that the petrographic homogeneity of the Bluff Formation is indicative of single stage dolomitization (i.e. Paragenetic Model I). According to Jones and Hunter (1989), Cayman Member was subaerially exposed for about 15 million years prior to deposition of the Pedro Castle Member whereas the Pedro Castle Member was exposed for less than 10 million years prior to dolomitization. Furthermore, the Cayman Member probably experienced an additional phase of subaerial exposure and meteoric diagenesis when the Pedro Castle Member was emerged above sea level. If dolomitization was a single event, the carbonate precursors of the two members

would have to be altered to the same fabric, particularly the crystal size, prior to the pervasive dolomitization in order to form petrographically identical dolostones for the two members. The mineral stabilization and cementation during meteoric diagenesis would certainly make it difficult to preserve the microfabrics of the skeletal components as well as they are preserved.

The finely crystalline to microcrystalline fabrics of the Bluff Formation (Plates VI.1A, 1B) also argue against inversion of metastable carbonates prior to dolomitization because mineral stabilization commonly results in an increase in crystal size (Steinen and Matthews, 1973; Steinen, 1978, 1982; Longman, 1980). Folk (1973) and Morrow (1982b) argued that finely crystalline dolomites are indicative of early replacement. Modern dolomites reported from Jamaica (Mitchell *et al.*, 1987) and Florida (Carballo *et al.*, 1987) have dolomite crystal size similar to that of the Caymanian matrix dolomite. Therefore, based on the petrographic fabrics of the Bluff Formation, it is suggested the dolomites of the Bluff Formation probably formed by early replacement of metastable carbonates as suggested by Paragenetic Model II.

Other Circumstantial Considerations

The following features are circumstantial evidence that assist in supporting the argument for Paragenetic Model II.

Cavity Lining Dolomite Cements

Cavity lining dolomite cement is common in the Oligocene Cayman Member, but it is absent in the Pedro Castle Member (Jones and Hunter, 1989). In the Cayman Member the dolomite cements lining aragonitic fossil molds were subsequently overlain by internal sediments (Plate VI.6F). The internal sediments were probably deposited during the early stages of the marine transgression in early Miocene times prior to deposition of the Pedro Castle Member (Fig. VIII.1; Jones and Hunter, 1989).

In support of Paragenetic Model I, Jones (1989, pers. comm.) suggested that the dolomite crystals were formed in the cavities prior to host rock dolomitization (Fig. VIII.1) and were not affected by later pervasive dolomitization because of their stable form. Void-lining and filling dolomite cement is common in dolostone formations (Beales, 1971). Dolomite cements rooted on limestone are not common, but are reported from the late Pleistocene Falmouth Formation of Jamaica (Land, 1973b) and from the Pleistocene Yucatecan limestones of Yucatan Peninsula (Ward and Halley, 1985). In both sequences, replacive dolomite is present in the matrix, and other forms of meteoric cement such as calcite spar and/or zoned dolomite and calcite are commonly associated with the dolomite cement. There is, however, no petrographic evidence to indicate that precipitation of other types of meteoric cement accompanyed the precipitation of the dolomite cement in the Cayman Member.

Land (1973a, 1973b) suggested that replacive dolomite and dolomite cement were formed at or near contemporaneity in the middle Pleistocene Hope Gate Formation and the late Pleistocene Falmouth Formation of Jamaica. Similarly, Holocene dolomitization of supratidal sediments from Sugarloaf Key, Florida also showed dolomite replacement and contemporaneous dolomite precipitation (Carballo *et al.*, 1987). Experimental dolomitization of calcareous components by Bullen and Sibley (1984) also showed that dolomite cementation accompanies dolomitization of the substrates in some cases. In this connection, it is suggested that the void lining dolomite cements that predated the influx of internal sediments were probably formed at or near contemporaneity with early dolomite replacement of the Cayman Member.

Cave Development

Cave development probably began in late Oligocene times when the Cayman Member was subaerially exposed due to a sea level drop. This early karst development

(Phase I in Fig. VIII.1) is indicated by the filling of caymanite and skeletal sands prior to deposition of the Pedro Castle Member.

Most caves in the Cayman Member were not completely filled by internal sediments, suggesting that the Cayman Member was lithified prior to karst development or it would have been subject to cave collapse. From studies of the Eocene to Miocene Gambier Limestone of southern Australia, James and Bone (1989) presented an example where karst is developed in the soft to friable sediments without significant cementation. In the Gambier Limestone, the original sediments were entirely calcite or Mg-calcite (James and Bone, 1989). Conversely, the original sediments of the Bluff Formation were predominantly aragonite. For aragonitic sediments, leaching or inversion of skeletal aragonite and cementation are common when the sediments are exposed to meteoric diagenetic realm (Longman, 1980; James and Choquette, 1984).

According to Paragenetic Model I (Fig. VIII.1, Jones, 1989a; Pleydell *et al.*, in preparation), lithification of the carbonate sediments was probably accomplished by calcite cementation in the meteoric vadose and phreatic realms. Conversely, in Model II (Fig. VIII.1), it suggests that lithification was achieved by dolomite precipitation in intergranular space at about the same time as early dolomite replacement. There is, however, no petrographic evidence indicating pre-existing meteoric calcite cement. Furthermore, the originally high lime mud (micrite) content of the carbonate sediments of the Cayman Member would have facilitated extensive diagenesis of the sediments when exposed to meteoric phreatic realm. Steinen (197[illegible] 1982) and Lasemi and Sandberg (1984) noted that diagenesis of lime mud in fresh w[illegible] [illegible]ironments involves rapid stabilization of aragonite and high magnesian calcite to low magnesian calcite and considerable precipitation of microspar in intergranular voids. This diagenetic modification would have resulted in significant loss of primary matrix porosity and in permeability of the carbonate sediments of the Cayman Member, characteristics required for the movement of the dolomitizing fluid and for delivering Mg^{2+} to the site of reaction. In order to form a homogeneous dolostone,

high intergranular porosity and permeability is particularly important. Late dolomitization after extensive meteoric diagenesis and cave development suggests that dolomitizing fluid would flow preferentially along open joints and cave passages. If so, dolomitization fronts would probably develop in the vicinity of the main avenues of fluid flow. Dolomite dikes found in the Precambrian Wyman Formation of northeastern Inyo Mountains of California were postulated by Zenger (1976) to have been formed from dolomitization along fractures. The absence of any recognizable dolomitization fronts in the vicinity of caves suggests that dolomitization of the Cayman Member probably occurred prior to transformation of metastable carbonates and cave development.

Synopsis

The one time dolomitization event (Model I) suggested by Jones (1989a) and Pleydell *et al.* (in preparation) is a simple model that satisfies the geochemical and petrographic data. However, the geochemical data (oxygen and strontium isotopes) do not permit a definitive interpretation on the timing of the dolomitization event(s). On the basis of the cumulative information on aragonite dissolution, mineralogy, petrography, isotope geochemistry and on circumstantial evidence, it is suggested that the Bluff Formation was probably dolomitized in two separate times (Model II). The earlier phase dolomitized the Cayman Member and the later phase dolomitized the Pedro Castle Member and the internal sediments (caymanite and skeletal sands). The second dolomitization event also affected the Cayman Member by resetting the geochemical signatures of previously formed dolomites, probably through increased cation ordering and stoichiometry.

D. HYDROGEOLOGICAL SYSTEM

A fluid-transport mechanism is a basic requirement for dolomitization of calcium carbonate (Hanshaw *et al.*, 1971; Morrow, 1982b; Land, 1983a, 1985; Simms, 1984; Machel and Mountjoy, 1986; Hardie, 1987). For extensive dolomitization to occur, the

diagenetic fluid must have an adequate supply of Mg^{2+} and probably CO_3^{2-}, and the diagenetic environment must have an active hydrogeological system for delivering the Mg^{2+} and CO_3^{2-} to the reaction sites and for carrying away the Ca^{2+}. Land (1985) also suggested that dynamic systems may promote dolomitization by substrate preparation or removal of crystal poisons. This dynamic system is necessary regardless of fluid type. Calcite dissolution-reprecipitation occurs in thin reaction zones surrounding the dissolving grains (Katz and Matthews, 1977); therefore, ion diffusion probably plays an important role on a submicroscopic scale. However, advection (fluid flow) is the dominant mass-transfer process, and it is controlled by the hydrogeological conditions of the aquifer.

Sources of Mg^{2+} and CO_3^{2-}

Goodell and Garman (1969), and Hanshaw *et al.* (1971) suggested that dissolution of high magnesian calcite and a subsequent downward percolation of the Mg-enriched fluid (solution-cannibalism) can be important dolomitization processes provided that the sediments have a high proportion of magnesian calcite. In the Bluff Formation of the Cayman Islands, high magnesian calcite such red algae, foraminifera and echinoids probably formed less than 10% of the original carbonate sediments. This low proportion suggests that the high magnesian calcite could be only a minor source of Mg^{2+} for dolomitizing the calcium carbonates. The major available source of Mg^{2+} apparently is sea water or its derivatives. An external source of CO_3^{2-} is also needed for volume for volume dolomitization with retention of microstructures (Sibley, 1980, 1982; Morrow, 1982a: Sibley *et al.*, 1988). Most of the CO_3^{2-} was probably obtained from dissolution of aragonitic skeletal components and from sea water.

Static versus Dynamic System

The following calculation adapted from Hanshaw *et al.* (1971) illustrates the importance of fluid dynamics in the dolomitization of calcium carbonate. For a calcite grain

of 1 ml in volume with 40 % porosity, the number of Ca^{2+} positions is related to the grain porosity by

$$Ca^{2+} = \frac{\rho N_A (1 - \phi)}{M_c} = 9.7 * 10^{21}$$

where ρ = density of calcite = 2.7 g/cc

N_A = Avogadro's No. = $6.022 * 10^{23}$/mole

ϕ = grain porosity = 0.40

M_c = molecular weight of calcite = 100.09 g

Thus, replacement of one half of the Ca^{2+} by Mg^{2+} requires $4.85 * 10^{21}$ Mg^{2+} ions. Using sea water as the dolomitizing fluid, the number of Mg^{2+} ions in the pore fluid is

$$Mg^{2+} = \frac{C_m N_A \phi}{M_m * 10^6} = 1.29 * 10^{19}$$

where C_m = concentration of Mg^{2+} in sea water = 1300 mg/l

M_m = atomic weight of Mg = 24.31 g

The results show that Mg^{2+} ions available in the pores are much lower than that required to replace half of the Ca^{2+} in the calcite grain. This pore fluid obviously cannot result in complete dolomitization if the solution is static. More importantly, the calculation shows that the efficiency of replacement is a function of the rock porosity and Mg^{2+} concentration in the solution. Land (1983a, 1985) also demonstrated that, dependant on the water salinity and rock porosity, several tens (for hypersaline water) to several thousands (for brackish water) of volumes of water are needed to dolomitize a unit volume of limestone. Therefore, pervasive dolomitization can only be accomplished by active, long lasting fluid flow that facilitates continual replenishment and supply of Mg^{2+} to the dolomitization sites and removal of excess Ca^{2+}.

Dolomitization Fluids

Currently, five types of waters have been suggested as dolomitizing fluids in various diagenetic environments. They are (1) hypersaline fluid (Adams and Rhodes, 1960; Deffeyes *et al.*, 1965; Illing *et al.*, 1965; Hsu and Siegenthaler, 1969; Zenger, 1972; Morrow, 1978; McKenzie *et al.*, 1980; Patterson and Kinsman, 1982), (2) subsurface formational fluid related to burial (Jodry, 1969; Mattes and Mountjoy, 1980; Zenger, 1983; Machel, 1984; Gregg, 1985), (3) alkaline continental water (von der Borch, 1976; von der Borch and Lock, 1979; Muir *et al.*, 1980; Botz and von der Borch, 1984), (4) sea water (Fanning *et al.*, 1981; Saller, 1984; Simms, 1984; Compton and Siever, 1986; Aharon *et al.*, 1987; Carballo *et al.*, 1987; Coniglio *et al.*, 1988), and (5) mixed meteoric-marine water (Hanshaw et al., 1971; Badiozamani, 1973; Land, 1973; Randazzo and Hickey, 1977; Choquette and Steinen, 1980; Magaritz *et al.*, 1980; Randazzo and Bloom, 1985; Ward and Halley, 1985; Force *et al.*, 1986; Coniglio *et al.*, 1988; Humphrey, 1988; Searl, 1988).

Hypersaline Fluid

Jones and Ng (1988a) documented the occurrence of minor amounts of anhydrite cement in some cavities of a coastal breccia body formed in the Ironshore Formation. Similar conditions might have developed in the coastal areas of the Bluff Formation during periods of land emergence. Although evidence of significant hypersaline diagenetic fluid is absent, saline water (water having salinity slightly greater than sea water) resulting from the evaporation of surface water is common (cf. beach water, pond water and sea water in Table III.2). Salinity measurements of the main water body of North Sound by Rigby and Roberts (1976) also recorded greater than normal marine salinity (total dissolved solids of up to 42,000 ppm versus 38,000 for sea water salinity) depending on the season. Synsedimentary evaporitic environment is ruled out because of the entirely open marine

fauna. Furthermore, the absence of evidence of former evaporites argues against hypersaline diagenetic conditions.

Deep Formational Fluid (Burial)

Diagenetic fluids related to burial can be precluded in the dolomitization of the Bluff Formation because there is no stratigraphic or petrographic evidence to suggest that the formation has been subjected to deep burial.

Alkaline Continental Fluid

The lack of a large hinterland in the Cayman Islands precludes an influx of alkaline water from a continent as possible diagenetic fluid; it is not analogous to the present day Coorong area of South Australia.

Sea Water

Using the ^{18}O fractionation-temperature equation of Land (1983b), which is essentially the same as Matthews and Katz (1977), Pleydell (1987) attempted to deduce the type of dolomitization fluid based on the $\delta^{18}O$ values of the dolostone of the Bluff Formation. She concluded that dolomitization of the Bluff Formation occurred in normal marine water. At low temperature setting, however, there is much disagreement among the oxygen isotopic fractionation equations (Fig. VII.2) of Northrup and Clayton (1966), O'Neil and Epstein (1966), Sheppard and Schwarcz (1970), Fritz and Smith (1970), and Matthews and Katz (1977). Compounding the problem is the variety in forms of cation-disordered and nonstoichiometric dolomites present in the near surface setting as well as the later phase recrystallization that can reset the isotopic content. Indeed, using the same oxygen isotopic data of Pleydell (1987), the five fractionation relationships indicate dolomitizing fluid varying from 25% to 100% sea water salinity over a temperature range of 22-33°C (Table VII.5).

Although sea water has been indicated as a dolomitizing fluid in numerous carbonate sequences, it commonly requires some form of kinetic booster, such as elevated temperature (e.g. Fanning *et al.*, 1981; Saller, 1984; Aharon *et al.*, 1987), elevated salinity (e.g. Sass and Katz, 1982; Bein and Land, 1983), or sulfate reduction (e.g. Baker and Kastner, 1981; Burns *et al.*, 1988). Similarly, the Pleistocene Ironshore Formation (about 125,000 years old), which is bathed in present day sea water, shows no indication of dolomitization. Therefore, it appears that normal sea water alone is not an effective agent.

Mixed Fresh-Sea Water (Brackish Water)

It has been suggested that dolomitization of the Cayman and Pedro Castle members of the Bluff Formation occurred early in the diagenetic history in relation to the major regressions during late Oligocene and late Miocene times. Island emergence during the major regressions may have provided a land area for the recharge of meteoric water. The selective dissolution of aragonitic skeletal components in association with the contemporaneous dolomitization evidently indicates that there was a certain degree of meteoric influx. The stable oxygen isotopic data of the matrix dolomite (Table VII.1) also indicate that the dolomitizing fluids were probably brackish (25% sea water salinity) to saline water (Table VII.5, Fig. VII.3B). Unfortunately, poor understanding of the isotopic oxygen fractionation between dolomite and the precipitating fluid does not permit further refinement of the salinity range of the diagenetic fluids.

Several lines of evidence appear to suggest that the brackish ground water (Tables III.3, 7, IV.7, 8), particularly the highly brackish type (>15% sea water salinity), are kinetically favourable for dolomitization of the Bluff Formation.

(1) The water has higher salinity than the fresh water even though the latter may also be supersaturated with respect to dolomite.

(2) Molar Mg/Ca ratio of the water is greater than 1.0 and lies within the stability field of dolomite.

(3) The water has higher HCO_3^- content than the sea water, apparently through dissolution of skeletal components in the shallow zones.

(4) The water has lower SO_4^{2-} than the sea water as a result of mixing with fresh water.

(5) The shallow diagenetic environment favours removal of organic materials by oxidation.

Sulfate reduction occurs locally only in the shallow ground water on the Cayman Islands. Only one out of eleven piezometers (Table III.1) indicated SO_4^{2-} reduction with corresponding increase in HCO_3^- content (Fig. III.8). It is important to note that the water that showed sulfate reduction is from the brackish water zone. This also suggests that the brackish water zone is favourable for dolomitization because of reduction of SO_4^{2-} ions and with a corresponding increase in the HCO_3^- content.

The mixed meteoric-marine model, however, has been critically reviewed by Machel and Mountjoy (1986) and Hardie (1987) who concluded that it is not an effective mechanism for dolomitizing a thick limestone sequence. Specifically, Machel and Mountjoy (1986) and Hardie (1987) cited the lack of dolomite formation in present day mixing zone setting such as Bermuda, Barbados, Bahamas, Florida, and Yucatan Peninsula. Instead of causing dolomitization, modern mixing zone waters appear to cause subsurface karstification (Machel and Mountjoy, 1986; Hardie, 1987).

The following points attempt to highlight some of the conditions that have been overlooked in rejecting the mixed water dolomitization model:

(1) Brackish water (commonly known as mixed water) encompasses water of >4% to <100% sea water salinity (Table III.9); therefore, it has a very variable chemical composition (Tables III.3, 6, 7, IV.7, 8). Any discussion of mixed water without defining this complete spectrum of water chemistry and water-rock interaction is futile and can only add to the confusion. Furthermore, mixing can occur at an early stage of land emergence without significant water lens development. The mixing zone is a dynamic regime that has a variable thickness (Figs. II.12, 19) and

chemical properties depending on the types of flow mechanism involved. James and Choquette (1984) also illustrated that the thickness of the mixing zone on Bermuda may exceed the thickness of the fresh water zone, particularly in a karst environment.

Pigott and Land (1986) noted that meteoric influence extends from land to the offshore reef tract at Discovery Bay in Jamaica and provides a mixing zone diagenetic environment in a supposedly marine environment. If this is so, many marine limestones may have been influenced by meteoric water depending on the ground water flow system. Involvement of meteoric waters in deep formation fluids has also been noted by Hitchon and Friedman (1969).

(2) Subsurface karst present in the modern mixing zone does not necessarily mean it is forming at present. Machel and Mountjoy (1987) noted that the mixing zones in most Caribbean islands and the adjacent landmasses have shifted six times during the past 120,000 years due to eustatic sea level changes. Therefore, many subsurface karsts may well be paleokarsts. Major regressions in Late Oligocene, Late Miocene and Pliocene times (Vail *et al.*, 1977; Haq *et al.*, 1987) may also have caused karst development in the Tertiary carbonate sequences.

(3) Hydrogeological conditions should encompass the whole spectrum of surface and subsurface hydrology. On Bermuda, undersaturation of ground water with respect to carbonate minerals is largely due to the influx of CO_2 from surface peat marshes (Plummer *et al.*, 1976). On Barbados, the high topographic relief, the large catchment area, and the presence of an impermeable rock formation beneath the limestone aquifer results in the extremely high efficiency of rain water recharge (Dr. S. Foster, 1988, pers. comm.). This high volume of rain water, laden with CO_2, would greatly influenced the saturation states of the ground water. The Floridan aquifer is in a confined condition (Kohout, 1967); therefore, hydrogeological behaviour of such an aquifer is not comparable to that of unconfined aquifers that

are common on most small limestone islands. The aquifers of the Yucatan Peninsula are fed by a large continental recharge area (Sanford and Konikow, 1989) absent in small islands or atolls. Although all of the examples cited are from carbonate aquifers, they all exhibit different ground water chemistry due to differences in ground water flow systems.

(4) The presence of dolomite in three late Pleistocene raised reef terraces in southeastern Barbados was first documented by Humphrey (1988) after many years of research on the island, indicating that the lack of documentation of dolomite forming in mixing zones may be due to lack of exposures for such studies. On the basis of petrographic, stable isotope, and trace element data, Humphrey (1988) concluded that the dolomites, ranging from trace amounts to 100% in places, were formed in a mixed meteoric-sea water environment. Using a forward modelling technique, Humphrey and Quinn (1989) suggested that mixed water is capable of dolomitizing a thick limestone sequence. Furthermore, pervasive dolomitization is probably site-specific and occurs only in environments where all the conditions are favourable.

(5) The frequent eustatic sea level changes during the Pleistocene times probably produced unstable hydrogeological systems that were not conducive to dolomitization. More importantly, these sea level changes would have caused mineral stabilization and cementation; both would make the sediments/rocks more resistant to dolomitization.

Mechanism of Fluid Flow

At present, the aquifers of the Bluff Formation are characterized by heterogeneous ground water flow because of dolomitization and karstification. During the initial stage of ground water lens development resulting from island emergence, ground water flow through the poorly lithified sediments was probably predominantly intergranular. Furthermore, the fresh water lens was probably poorly developed and at an incipient stage

of formation (Fig. IX.2). However, regardless of the differences in flow characteristics between the pre-dolomitized sediments and the present day dolostone aquifers, the flow regimes of the two hydrogeological systems are probably similar (cf. Figs. II.19, IX.2).

In order for the hydrogeological system to be effective in dolomitizing the sediments/rocks, it is important that the flow regime be operative over a long period of time. Flow mechanisms (Fig. IX.2) that were responsible for delivering the Mg^{2+} and CO_3^{2-} for dolomitization of the Bluff Formation probably included (1) downward gravitational flow, (2) downward reflux, (3) upward convection, (4) tidal pumping, and (5) diffusion.

Downward gravitational flow of rain water recharge (Fig. IX.2) is a function of the hydraulic head, which is, in turn, dependent on the rainfall quantity and intensity, land area, topographic relief, and permeability of the sediments/rocks (Figs. II.6, 8, 9, 10). Rain water recharge is important in providing the additional CO_3^{2-} through dissolution of calcium carbonate in the vadose and/or phreatic zone, particularly the selective dissolution of aragonitic skeletal components. Dilution of sea water by rain water reduces the thermodynamic drive for dolomitization; however, it significantly reduces the kinetic constraints that inhibit dolomitization through SO_4^{2-} dilution, CO_3^{2-} increase, and organic oxidation. Furthermore, the lower sea levels in the past also increased the topographic relief of the islands, and hence, the hydraulic head for the ground water flow.

Downward reflux of saline water concentrated by evaporation occurs in shallow water ponds and in shallow carbonate bank/shelf (Fig. IX.2). Reflux of hypersaline brines due to density difference (Adams and Rhodes, 1960) and elevation head differential (Hsu and Siegenthaler, 1969; McKenzie, 1980) have been described for sabkha and hypersaline lagoon settings. Sass and Katz (1982) and Bein and Land (1983) documented downward reflux of sea water to slightly hypersaline fluids on shallow carbonate platforms and broad shelves respectively. Simms (1984) suggested that reflux may occur with sea water of only slightly elevated salinity on modern carbonate platforms. In the case of the Cayman

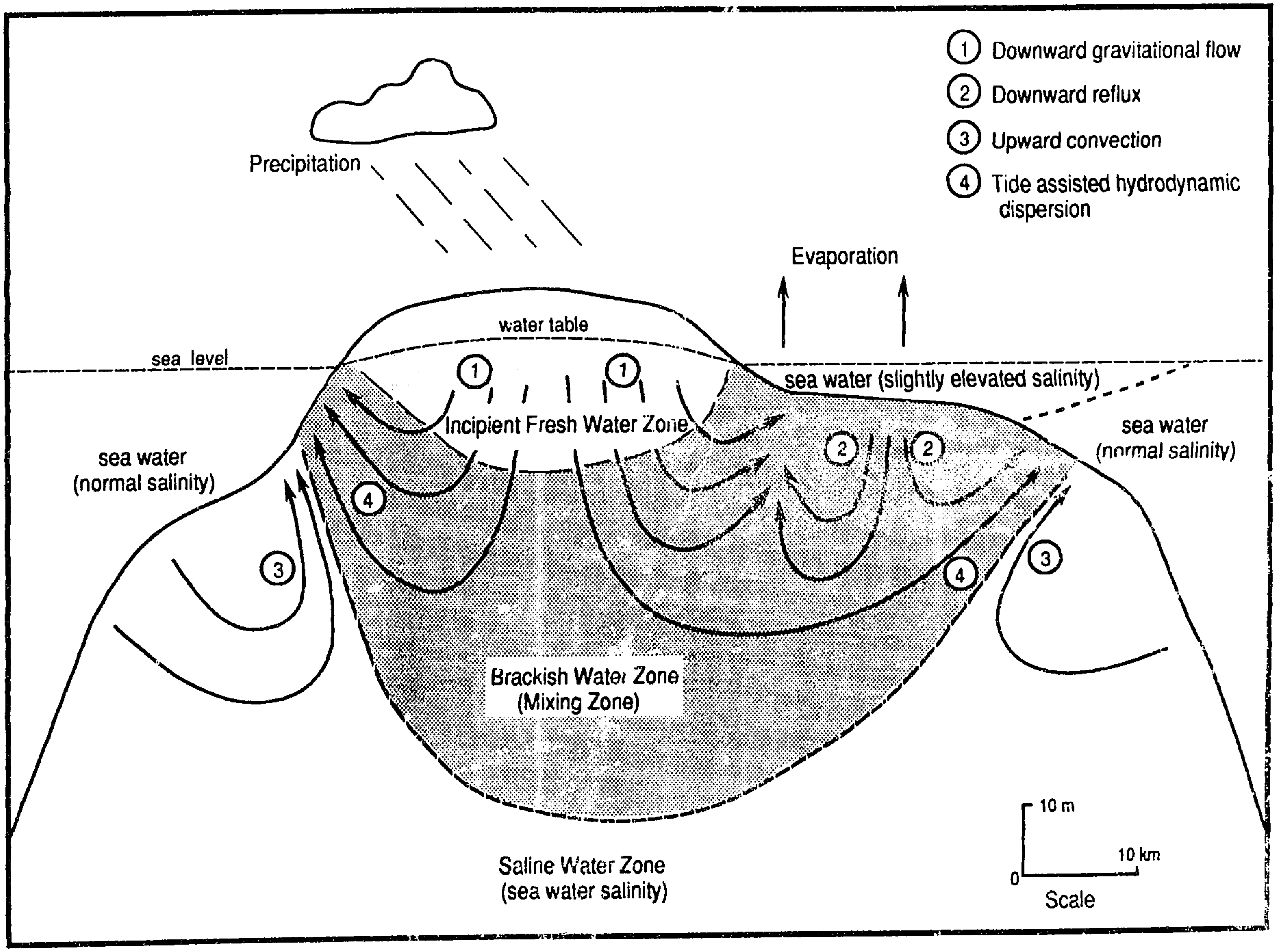


Fig. IX.2 Schematic diagram showing ground water flow regime in an emerging landmass.

Islands, the rain water recharge would have reduced the density of the pore waters and should facilitate this downward flow of sea water and/or saline water.

Upward convection of thermally circulated sea water was originally documented by Kohout (1967) and Kohout *et al.* (1977) in the Floridan aquifer. This thermal convection model, a means of conveying geothermally heated sea water for dolomitization of calcium carbonate, has been proposed for the west coast of Florida (Fanning *et al.*, 1981), Enewetak Atoll (Saller, 1984) and the atoll of Niue Island (Aharon *et al.*, 1987). In these studies, the upward convectional flow of sea water was confirmed by geochemical data. Simms (1984) suggested that convective flow should be present in all steep marginal platforms where there is a strong horizontal pore water density gradient between warm water in platform interiors and surrounding sea water. On the Cayman Islands, it is difficult to determine whether or not there was a heat source at times of dolomitization. The proximity of the Cayman Islands to the mid-oceanic rise, however, suggests the possibility of some forms of heat flow in the past. Fluid density gradient resulting from thermal effect, however, may be caused by the salinity reduction of pore fluids in the aquifers due to rain water recharge on the landward side (Fig. IX.2).

Tidal pumping of Florida Bay sea water has been suggested as the mechanism for the dolomitization of small scale supratidal crusts on Sugarloaf Key of Florida (Carballo *et al.*, 1987). The effect of tidal fluctuation on the ground water system of the Cayman Islands (Figs. II.17, 18) is well exemplified by the thick transition zone (brackish water) developed between the fresh water and the underlying saline water (Figs. II.12, 19). The transition zone of brackish water is formed as a result of tide-generated hydrodynamic dispersion (Fig. IX.2; Cooper, 1964; Kohout, 1964). The ground water table fluctuates in response to semi-diurnal and seasonal tides. The inflow of sea water into the aquifer is a function of the tidal amplitude, and time lag between the sea water and ground water tide (Table II.2). The latter is inversely related to the permeability of the aquifer.

Diffusion of Mg^{2+} from sea water through the sediments is a very slow and ineffective pumping mechanism (Land, 1985; Hardie, 1987). Using a Mg mass balance calculation, Compton and Siever (1986) concluded that Mg^{2+} diffusion from overlying sea water can account for the early diagenetic dolomite (0.5-20% by volume) formed in the uppermost 100 m of the Monterey Formation, Santa Maria basin area of California. Although diffusion alone is probably not able to cause pervasive dolomitization, it is a viable mechanism of supplying Mg^{2+} to the accumulating sediments. These early dolomites may act as seed crystals for pervasive dolomitization at a later stage.

Synopsis

Mixed fresh-marine water, which has fewer kinetic barriers, remains a viable medium for dolomitization. The fresh water recharge also creates density gradients in the flow system to facilitate ground water movement through the sediments/rocks. The diagenetic fluids that caused the pervasive dolomitization of the Bluff Formation were probably sea water that was modified to a certain extent by rain water during an early stage of land emergence in late Oligocene (for the Cayman Member) and late Miocene (for the Pedro castle Member) times. Stable oxygen isotopic results suggest that the degree of meteoric influence ranges from 0 to 75% fresh water by volume depending on the fractionation equations used and temperatures of the diagenetic fluids (Fig. VII.3). The flow mechanism (Fig. IX.2) was similar to that at present, but the fresh water lenses were probably irregularly distributed. It is also important to note that higher land relief in the past, due to lower sea levels, would have facilitated fluid movement through the sediments/rocks by increasing the hydraulic gradient.

Meteorological records on Grand Cayman for the last twenty years have shown appreciable changes in rainfall, temperature, and the amount of sunshine (Figs. II.7, 11). The paleoclimatological regimes might play a role in reducing some of the kinetic constraints so as to promote dolomitization. Kastner (1984, 1988) and Land (1985) also

suggested that the SO_4^{2-} content and the Mg/Ca ratio of sea water might have changed throughout geological time. All of these would have a significant impact on the nature of the mixed water environment.

X. DIAGENETIC INTERPRETATION OF THE BLUFF FORMATION II: KARSTIFICATION

The Bluff Formation has undergone numerous stages of karstification as a result of sea level fluctuations since late Oligocene times (Jones and Smith, 1988). This study (1) identifies the stages of karst development, (2) highlights the chemical equilibria, kinetic concepts and biological effects on carbonate dissolution, and (3) examines the mechanism for karstification.

A. STAGES OF KARSTIFICATION

Jones and Hunter (1989) suggested that the Oligocene Cayman Member of the Bluff Formation was exposed and subjected to karst development during late Oligocene and early Miocene times. Similarly, following regression in late Miocene times, the Miocene Pedro Castle Member and the underlying Oligocene Cayman Member were also subjected to karsting (Jones, 1989a). Frequent fluctuations of sea level in the Caribbean region during late Pleistocene times (Mesolella *et al.*, 1969; Bender *et al.*, 1973; Steinen *et al.*, 1973; Neumann and Moore, 1975; Harmon *et al.*, 1978) means that karst formation has been an ongoing process.

Precise dating of the different stages of karstification is difficult because each stage of karst development further modified the inherited karst features. Stringfield *et al.* (1979) noted that in areas where paleokarst is not too deeply buried, it may be incorporated into present circulation systems such as the artesian aquifer of Tertiary age in southeastern Georgia and Florida. Thus, the present day hydrogeological regime is the end product of numerous past and the present karst processes. It is also difficult to assess the depth of karstification in response to each base (sea) level change because of the overlapping karst effect. Furthermore, changes in the surface and ground water drainage began as soon as the carbonate rocks were elevated above sea level and circulation was established (Stringfield and LeGrand, 1971; Longman, 1980).

Jones and Smith (1988) suggested that some cave formations post-dated dolomitization of the Bluff Formation because the caves cut through dolomitized cavity fills and unaltered speleothemic calcite. The exposures of Miocene Pedro Castle Member give no indication of karst development (Fig. X.1); however, this may simply be due to limited number of outcrops. The different periods of karst development (Fig. VIII.1) on the Bluff Formation can be termed Phase I' (late Oligocene to early Miocene), 'Phase II' (late Miocene to early Pliocene), and 'Phase III' (late Pliocene to late Pleistocene).

Speleothemic precipitation and internal sedimentation may partly or completely fill many caverns and fissures on the Cayman Islands (Lockhart, 1986; Smith, 1987; Jones and Smith, 1988). On the basis of the type and amount of cave fills, the cave systems in the Oligocene Cayman Member of the Bluff Formation can be divided into four categories (Figs. X.1, 2):

(1) Caves filled with completely dolomitized caymanite (colour banded) and/or skeletal grainstone, which may or may not be overlain by undolomitized flowstone and/or terra rossa (Figs. X.1, 2). Examples of Type 1 cave systems include caves exposed in Pedro Castle Quarry on Grand Cayman and caves cut by Faith Caves opposite Faith Hospital on Cayman Brac (Figs. X.2, 3).

(2) Caves filled with undolomitized flowstone and terra rossa but no caymanite (Figs. X.1, 2). Examples of Type 2 cave systems include caves exposed in Pedro Castle Quarry, caves cut by Pirates Caves near Bodden Town on Grand Cayman and caves cut by Great Caves near Pollard Bay on Cayman Brac (Figs. X.2, 3).

(3) Caves partially filled with assorted speleothems such as flowstones, stalactites, stalagmites, terraced rimstones, and cave pisoliths (Fig. X.2). Examples of Type 3 cave system include Old Man Bay Caves near Old Man Bay Village on Grand Cayman, Great Caves near Pollard Bay, Hurricane Caves near Spot Bay and Salt Water Point Caves on Cayman Brac (Fig. X.3).

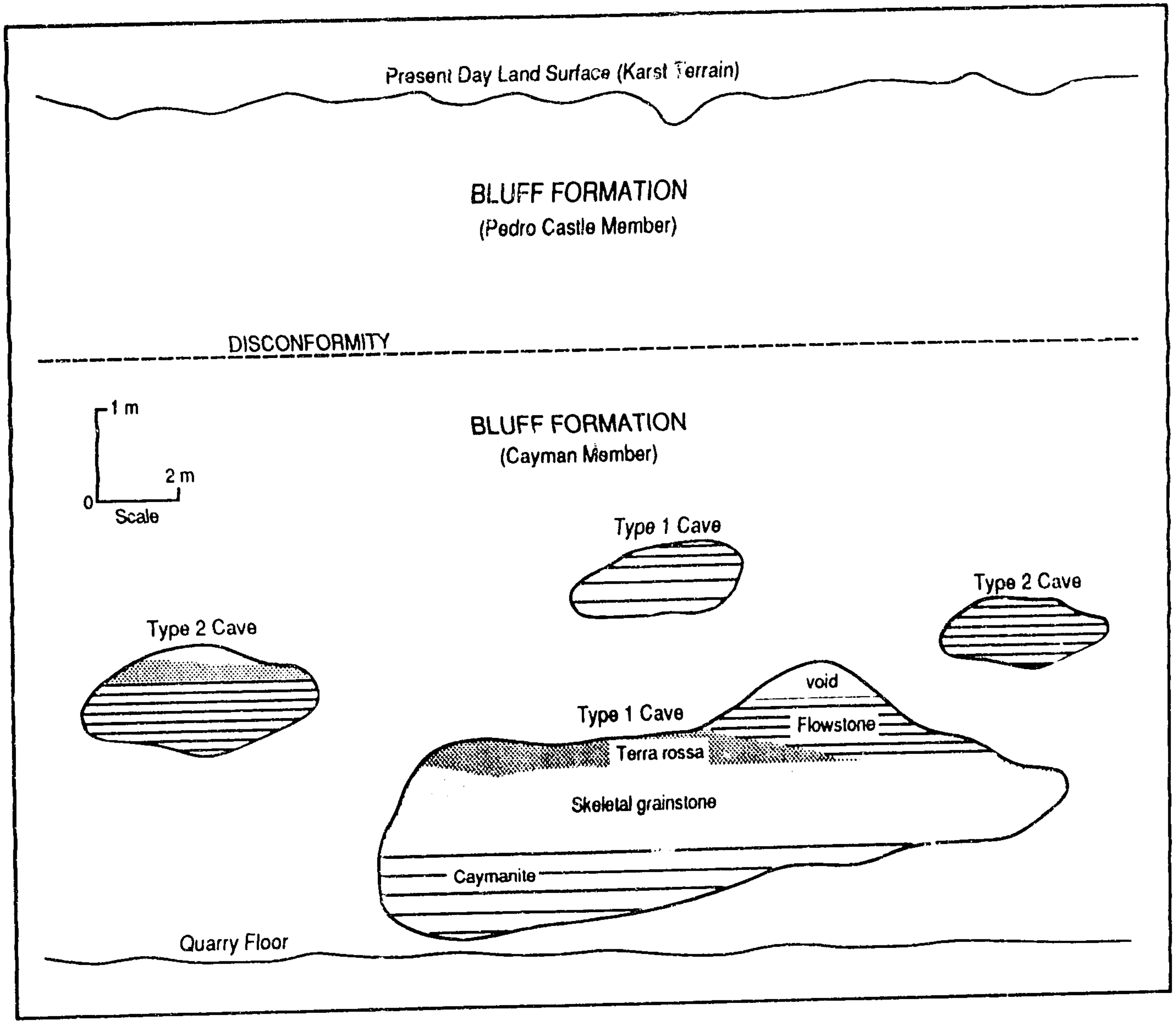


Fig. X.1 Schematic diagram of quarry wall exposure at Pedro Castle Quarry on Grand Cayman showing cavity fills in Type 1 and 2 cave systems.

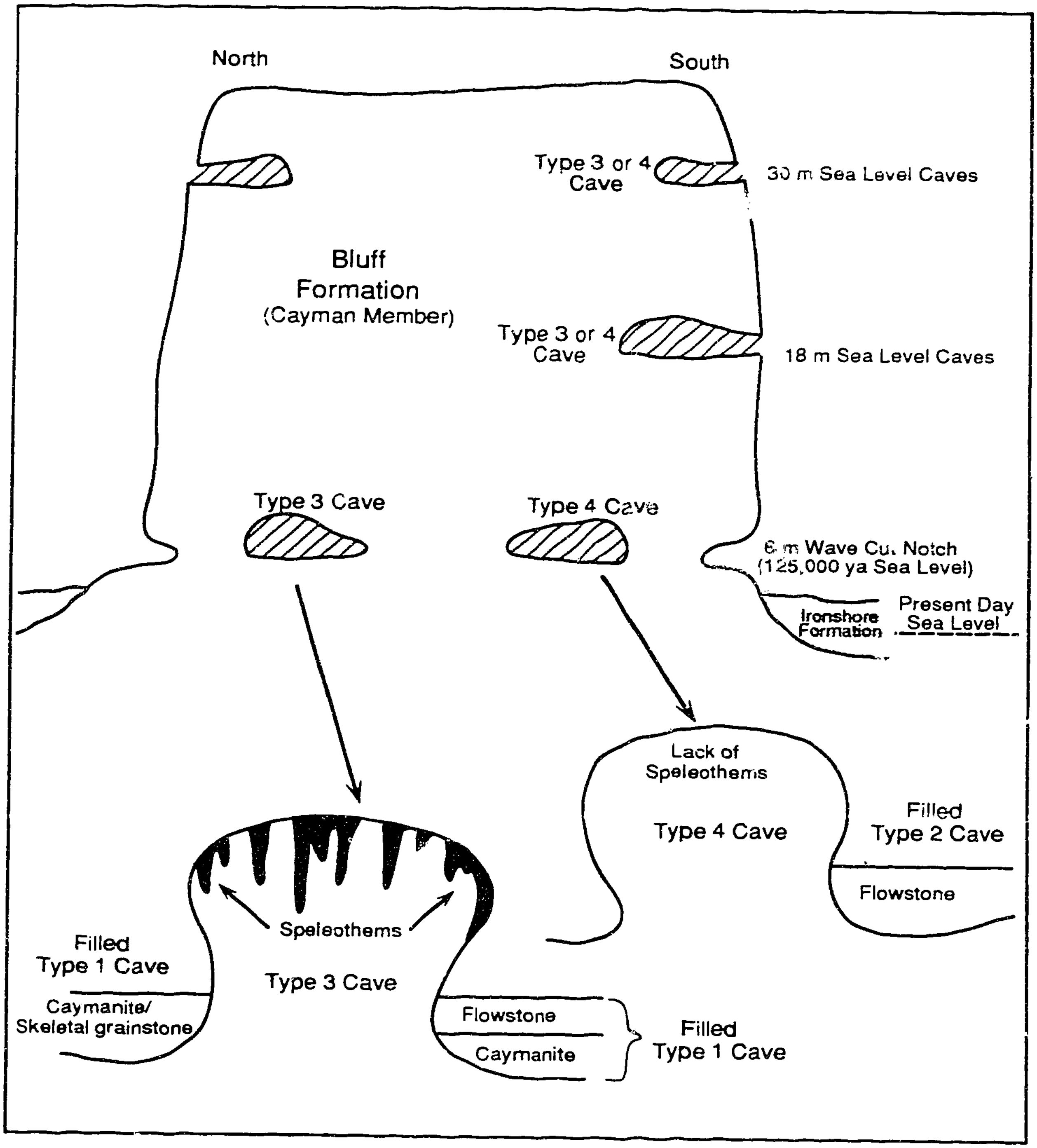


Fig. X.2 Schematic north-south cross-section of Cayman Brac showing the different levels of sea level caves and the four types of cave systems. Diagram not in scale.

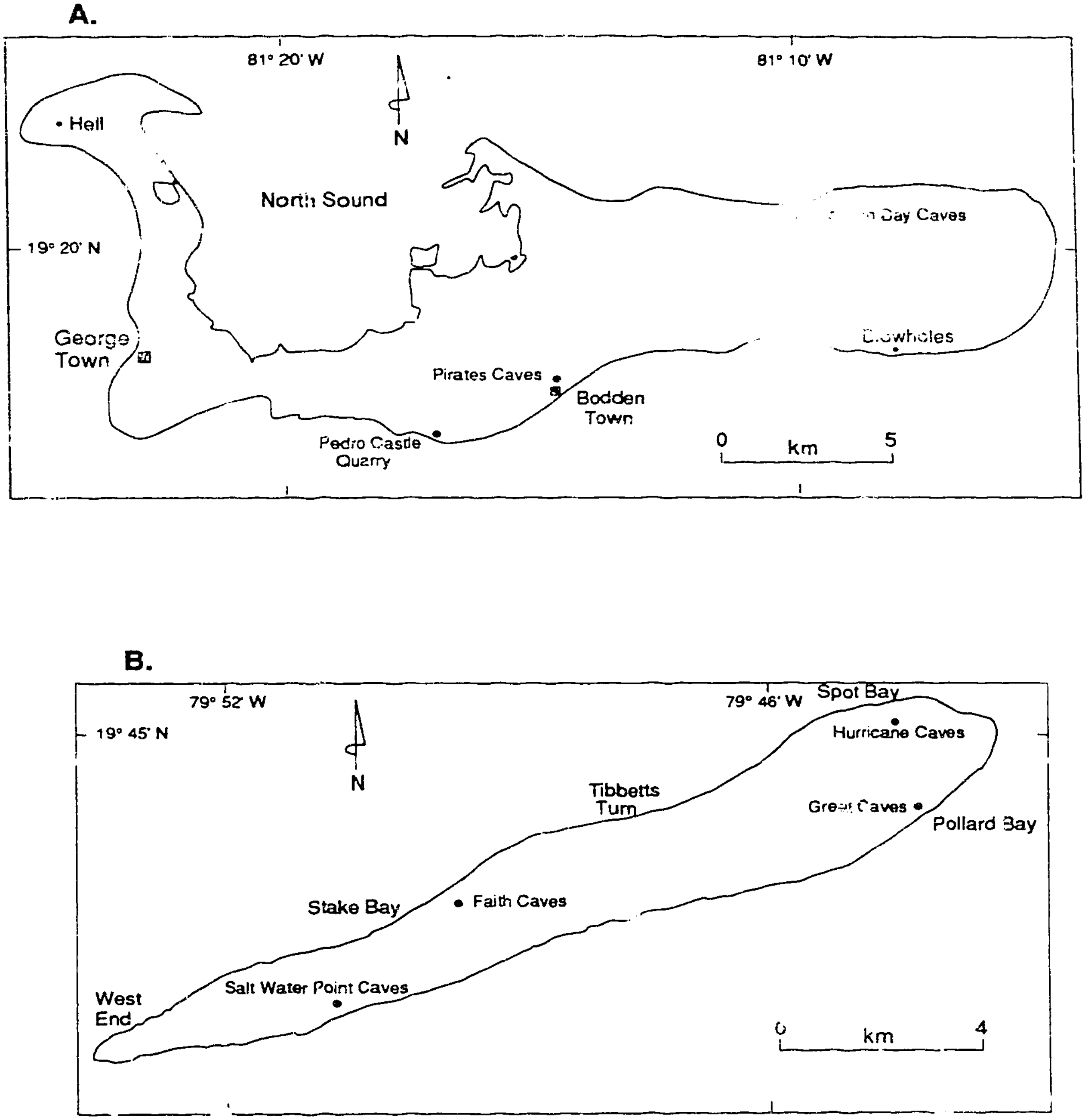


Fig. X.3 Sketch map of (A) Grand Cayman and (B) Cayman Brac showing localities of caves cited in text.

(4) Open caves with no speleothems but commonly floored with terra rossa (Fig. X.2). Examples of Type 4 cave system include Pirates Caves on Grand Cayman and Faith Caves on Cayman Brac (Fig. X.3).

The first two types (Type 1 and 2) of cave are generally less than 20*5 m^2 in vertical section (observed in quarry wall of Pedro Castle Quarry) and do not appear to form extensive cave networks. Conversely, the last two types (Type 3 and 4) commonly measure up to 5*5 m^2 in cross section and form extensive networks of cave passages (in the order of km) and chambers.

Type 1 caves probably formed during late Oligocene to early Miocene times when the Cayman Member was subaerially exposed due to sea level drop. The timing of their formation is inferred from the presence of caymanite fill because Jones and Hunter (1989) noted that caymanite probably entered the cave system prior to the deposition of the middle Miocene Pedro Castle Member (Jones and Hunter, 1989). Thus, the Type 1 caves are related to the 'Phase I' karst development (Fig. VIII.1).

Dating of Type 2 caves is problematic. The absence of dolomitized caymanite suggests that the Type 2 caves might have formed in late Miocene to early Pliocene times when the strata was again exposed in response to sea level drop. If so, the Type 2 cave system might be related to the 'Phase II' karst development (Fig. VIII.1). However, the absence of caymanite may be the result of blockage of solution channels that prevented the influx of internal sediments.

Type 3 and 4 cave systems are clearly younger than Type 1 and 2 caves because they cut through the latter two systems (Fig. X.2; e.g. Old Man Bay Caves and Pirates Caves on Grand Cayman, and Faith Caves and Great Caves on Cayman Brac). They also cut through the undolomitized flowstones in Type 1 and 2 caves suggesting that Type 3 and 4 cave formation were post-dolomitization. The youngest dolomitization age given by the Sr isotopic data (Table IX.1) is 2.0±0.5 Ma, which implies that the caves probably formed

in Pleistocene times. Type 3 and 4 cave systems appear to be genetically related because the two types of cave can be traced along the same horizon on Cayman Brac. Some caves developed at the wave-cut notch about 6 m above present day sea level (Jones and Ng, 1988a, Jones and Smith, 1988). Jones and Smith (1988) also suggested that the wave cut notch probably developed when the carbonate sediments of the Ironshore Formation were deposited about 125,000 years ago (Woodroffe *et al.*, 1983). Thus, it can be postulated that the Type 3 and 4 caves that are associated with the 6 m wave-cut notch probably formed in the late Pleistocene. On Cayman Brac, two other levels of caves, formed at about 18 m (e.g. Great Caves) and 30 m (e.g. Hurricane Caves) above present day sea level, probably belong to the Type 3 and/or 4 categories (Fig. X.2). They are either open or partially filled with speleothems. The horizontal orientation of the cave passages probably indicates former sea level high stands or earlier tectonic uplift of the island. It appears that the latter proposition is more reasonable because eustatic sea levels in the last 125,000 years (Mesolella *et al.*, 1969; Bender *et al.*, 1973; Steinen *et al.*, 1973; Bloom *et al.*, 1974; Ku *et al.*, 1974; Neumann and Moore, 1975; Harmon *et al.*, 1978) were lower than the sea level high stand 125,000 years ago. Thus, it appears that most of the sea level caves are correlated to the 'Phase III' karst development (Fig. VIII.1).

Other evidence of cave development is present in the Oligocene Cayman Member. On Cayman Brac, a cavern 2 m in height, encountered by well B5 (Fig. VI.2) at about 20 m above present sea level, may be correlatable with the sea level cave at about 18 m. Similarly, the perched water lens in well B1 (Fig. VI.2), at about 3.5-10 m above present sea level, may be related to the wave-cut notch at 6 m. Deep well drilling (> 20 m) on the western part of Grand Cayman (Fig. III.2) commonly encountered large caves at about 25-40 m below present sea level, which may correspond with the submerged wave-cut notch at about 21 m below present sea level. Therefore, most of the Type 3 and 4 cave development is probably related to the various levels of sea level high in late Pleistocene.

However, the relationship between sea level elevation and the Type 1 and 2 cave systems is difficult to define.

Cave development in association with the sea or base levels has been noted in many areas. Different levels of cave development effected by changes in Pleistocene sea level were recorded in the Ingleborough district of England (Sweeting. 1950), in Peloponnesus, Greece (Burdon, 1967), on the southern coast of Australia (Jenning, 1963) and on the south coast of Tallahassee, Florida (Stringfield, 1966). Similarly, distinct levels of horizontal cave passages resulting from changes in base level were documented in the southwest Edwards Plateau of Texas (Kastning, 1983) and in Dejiang, Guizhou Province of China (Song *et al.*, 1983).

In addition to the effect of past sea level high stands, the extensive networks of Type 3 and 4 cave systems are probably related to solution features preferentially developed along joints and fractures in a manner suggested by Ford and Ewers (1978) and Ford (1988). If so, a phase of intense joint development probably occurred prior to Type 3 and 4 cave formation but after Type 1 and 2. The lack of extensive networks in Type 1 and 2 caves, however, may be indicative of a different climatic regime or of a much lower sea level in late Oligocene times which exposed the rocks predominantly to the vadose zone.

Jointing is a multi-phase phenomenon (Fig. VIII.1). Joints of different attitudes contained diverse fills. The best example is illustrated by the joint sets exposed near Blowholes on Grand Cayman (Figs. II.14, X.3A). The north northwest - south southeast oriented vertical joints commonly remain open whereas the east northeast - west southwest oriented vertical joints commonly filled with flowstones and terra rossa/terra rossa breccia. Conversely, the gently dipping (about 30° to the north-west), northeast -southwest oriented joints commonly filled with caymanite, terra rossa and/or rarely flowstones. Jones (1989, per. comm.) also noted that the east northeast - west southwest oriented joints exposed on Queen's Road (north coast) on Grand Cayman also contained dolomitized breccia. There appears to be a relation between joint and karst development (Table X.1) in that (1) the

Table X.1 Relationship between joint and karst development based on type of fills.

PHASE	JOINT TYPE & FILL	CAVE TYPE & FILL	RELATIVE TIMING
Phase III Late Pliocene to Late Pleistocene	NNE-SSW/Vertical — Open	Type 4 — Open Type 3 — Assorted Speleothems	Post - Dolomitization
Phase II Late Miocene to Early Pliocene	ENE-WSW/Vertical — Flowstone Terra Rossa	Type 2 — Flowstone Terra Rossa	
Phase I Late Oligocene to Early Miocene	NE-SW/30°NW — *Caymanite* *Flowstone (rare)* *Terra Rossa*	Type 1 — Caymanite Skeletal Grainstone Flowstone Terra Rossa	Pre - Dolomitization

Type 1 cave fills are similar to those in the northeast-southwest trending joints, (2) the Type 2 cave fills are similar to those in the east northeast - west southwest trending joints, and (3) both the Type 4 caves and the north northwest - south southeast trending joints remain open. Thus, the similarity in joint and cavity fills may be an indication of related timing of the phases (Phase I, II, and III) of joint development with that of the karst formation (Fig. VIII.1, Table X.1). This genetic relationship supports the argument that jointing/fracturing is one of the pre-requisite parameters for cave formation, providing avenues for fluid flow, and hence, carbonate dissolution. It is also important to note that filling of joints is an active process that is ongoing at the present time. Some open joints at Hell on Grand Cayman (Fig. X.3A) are presently being filled by swamp sediments.

B. CHEMICAL EQUILIBRIA OF CARBONATE DISSOLUTION

Using chemical equilibrium concepts, speciation calculations of ground waters in the aquifers of the Bluff Formation indicate that the waters in all hydrochemical zones are capable of dissolving or precipitating carbonates, depending on their chemical properties. Some fresh water samples from the Lower Valley lens are undersaturated with respect to both calcite and dolomite (Table IV.5). The low Mg/Ca ratio of the Lower Valley fresh ground water suggests that influx of calcium enriched ground water from the limestone aquifer of the Ironshore Formation and subsequent mixing with the ground water in the Bluff Formation may be the cause of the undersaturation. Furthermore, it has also been demonstrated by artificial injection that rapid rain water recharge through open fractures can cause significant undersaturation at the water table zone (Table IV.19). The shallow water zone is also most likely to receive CO_2 from the respiration of plant roots and organic decay. The corrosiveness of the ground water acts according to the simplified reactions:

$$CO_2 + H_2O = H^+ + HCO_3^-$$

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^-$$

$$CaMg(CO_3)_2 + 2H^+ = Ca^{2+} + Mg^{2+} + 2HCO_3^-$$

In the brackish water (mixed water) zone, undersaturation with respect to carbonate minerals (Table IV.8) probably results from periodic influx of CO_2-ladened water from the surrounding mangrove swamps or from decomposition of organic materials in the aquifers.

C. CHEMICAL KINETICS OF CARBONATE DISSOLUTION

In the ground water systems of the Cayman Islands, the temporal and spatial variation of the ground water chemistry (Tables IV.10, 16, 17, Figs.II.10, III.1, III.5-10) suggests that most of the hydrochemical reactions in the aquifers have not reached thermodynamic equilibrium. Berner (1978) suggested that under earth surface conditions, mineral dissolution is governed by surface chemical reactions. Wigley and Plummer (1976) also demonstrated that the rate of calcite dissolution in natural environments depends on the hydrodynamics of the mineral-water system and the reaction kinetics at the mineral surface.

Weyl (1958) concluded that the rate of limestone dissolution is controlled by diffusion of Ca^{2+} from the surface. Weyl's (1958) results showed that water entering the rocks quickly becomes saturated with respect to calcite, with a saturation length (penetration distance before water reaches calcite saturation state) in the order of a few centimetres. The first comprehensive treatment of solution kinetics of $CaCO_3$ in the H_2O-CO_2 system was the theoretical model of Plummer *et al.* (1978, 1979) where the rate of calcite dissolution (Rc) is given as:

$$Rc = k_1[H^+] + k_2[H_2CO_3] + k_3[H_2O] - k_4[Ca^{2+}][HCO_3^-] \quad \ldots\ldots\ldots\ldots\ldots(1)$$

where k_1, k_2 and k_3 are the forward rate constants which are temperature dependent, k_4 is the backward rate constant depending on both temperature and P_{CO_2}. Three mechanistic reactions for k_1 through k_3 are:

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^-$$

$$CaCO_3 + H_2CO_3 = Ca^{2+} + 2HCO_3^-$$

$$CaCO_3 + H_2O = Ca^{2+} + HCO_3^- + OH^-$$

At pH <~5, the k_1 term dominates the rate equation. At higher pH when P_{CO_2} >0.1 atm, the k_2 term becomes dominant. At high pH when PCO_2 <0.1 atm, the k_3 term dominates.

Using the rate model of Plummer *et al.* (1978, 1979), Dreybrodt (1981a) calculated that the saturation length is on the order of a few metres. Although this result showed that the dissolution rate increases substantially from that of Weyl (1958), cave passages of 1 m in diameter still require a few million years to develop (Dreybrodt, 1981a). Some caves, developed in the Oligocene Cayman Member of the Bluff Formation (along the 6 m high wave cut notch, Fig. X.3), were clearly formed at the time of the 125,000 year sea level high stand. Thus, the time required for large cave development is much less than that deduced from the kinetic models. Furthermore, the kinetic model is not in agreement with the sea level high stand of the order of a few thousand years during the Pleistocene epoch (Harmon *et al.*, 1981; Aharon, 1983; Matthews, 1984).

The net rate of dissolution for dolomite (Rd) was defined by Busenberg and Plummer (1982) as:

$$Rd = k_1[H^+]^n + k_2[H_2CO_3]^n + k_3[H_2O]^n - k_4[HCO_3^-]^n \quad \text{.........................(2)}$$

where n is 0.5 at temperatures below 45°C. The forward-reaction mechanisms comprise the reaction of the $CaCO_3$ component and then the $MgCO_3$ component of dolomite with the bulk solution H^+, H_2CO_3, and H_2O.

The actual dissolution rate of carbonate minerals is difficult to determine from laboratory experiments because of the presence of impurities and micro-organisms in natural conditions (Berner, 1978). If an impurity contains a chemical constituent that is present in the reactant (e.g. Ca^{2+} in $CaCO_3$), the solubility of the reactant could increase due to increase in ionic strength, or could decrease due to the common ion effect (Freeze and Cherry, 1979; Plummer *et al.*, 1979). Furthermore, Plummer *et al.* (1979) and Morse (1983, 1986) noted that trace impurities, such as PO_4^{3-} and organics, cause large changes in dissolution rates without significantly altering the thermodynamic properties of the system. These adsorbed impurities commonly act as strong inhibitors of crystal dissolution

(Berner, 1978; Morse, 1983, 1986). Similar inhibitors may be present in the natural waters on the Cayman Islands and exert similar influence on the dissolution of the carbonate minerals.

D. BIOLOGICAL EFFECTS ON CARBONATE DISSOLUTION

There is considerable information concerning the role that micro-organisms play in carbonate diagenesis (e.g. Schroeder, 1972; Folk *et al.*, 1973, 1985; Schneider, 1977; Krumbein, 1979; Chafetz and Folk, 1984; Viles and Spencer, 1986; Jones, 1987, 1988, in press; Jones and Pemberton, 1987a, 1987b; Pleydell, 1987; Smith, 1987; Squair, 1988). Phytokarst, characterized by a black coating on jagged pinnacles, is formed by boring filamentous algae (Folk *et al.*, 1973; Viles and Spencer, 1986; Jones, in press). Detailed studies of the phytokarst on Grand Cayman suggest that the biological processes operative on the rocks is governed, in part, by the hardness of the substrate (Jones, in press).

Extensive dissolution of spar calcite mediated by fungi was experimentally demonstrated by Jones and Pemberton (1987a, 1987b). More importantly, Jones and Pemberton (1987a) suggested that under the mediation of fungi, dissolution of calcite occurs via surface reaction controlled kinetic processes without the intervention of vast quantities of fluid. Jones (1988) noted that root borings, in addition to being a source of carbon dioxide through plant-root respiration, also provide avenues for water flow and sites where micro-organisms thrive.

Most studies of the role of micro-organisms in carbonate diagenesis on Grand Cayman are related to the vadose (e.g. Folk *et al.*, 1973; Jones, 1987, 1988, in press; Viles and Spencer, 1986) and intertidal settings (Jones and Goodbody, 1982, 1984; Viles and Spencer, 1986). The effect of micro-organisms on carbonate diagenesis in the phreatic zone is not known. Perhaps micro-organisms can enhance or counteract the effect of chemical inhibitors on carbonate minerals dissolution. Detailed investigation in this aspect is required to understand the role micro-organisms play in the phreatic zone.

E. MECHANISM OF KARSTIFICATION

On the Cayman Islands, some caves were developed after host rock dolomitization (Type 3 and 4 cave system; Jones and Smith, 1988) regardless of the differences in defining the timing of dolomitization events suggested by Paragenetic Model I (Jones, 1989a; Pleydell *et al.*, in preparation) or Model II (this study). Busenberg and Plummer (1982) noted that water-clear dolomite of hydrothermal origin dissolves at slower rates than cloudy dolomite crystals of sedimentary origin. More importantly, Busenberg and Plummer (1982) demonstrated that at pH values greater than 6.0, it takes weeks or months to dissolve detectable amount of dolomite, although calcite dissolved readily under similar conditions. Using Middle Ordovician rock samples from central Pennsylvanian, Rauch and White (1977) also concluded that dolostones dissolve at much slower rates than limestones in laboratory-controlled experiments.

The significant differences in the dissolution rates between calcite and dolomite may be one of the controlling factors in explaining the scarcity on the Cayman Islands of large-scale tropical karst features that are common in other carbonate terrains in the Caribbean region (e.g. Jennings, 1971; Sweeting, 1972; Monroe, 1976; Squair, 1988). However, other important parameters such as joint and fracture density, rainfall quantity and intensity, and topographic relief would have significant impact on the hydraulic gradient of the ground water system. The fact that the largest caves on Grand Cayman and Cayman Brac formed after dolomitization of the Bluff Formation (Type 3 and 4 caves; Jones and Smith, 1988) suggests that climatic conditions and density and openness of joints probably were more dominant in controlling the extent of karsting than was lithology.

Mixing of fresh ground water and sea water (Hanshaw *et al.*, 1971; Badiozamani, 1973; Plummer, 1975; Bogli, 1980; Palmer, 1984; Back *et al.*, 1986) and of carbonate waters of different compositions (Wigley and Plummer, 1976) generates unsaturated solutions capable of dissolving calcium carbonate. Incorporating the mixed water dissolution concept with the kinetic model of Plummer *et al.* (1978, 1979), Dreybrodt

(1981b) calculated that the dissolution rate of calcite is in the order of 0.01 mm/year. Thus, the time required for cave development (a few metres in diameter) in limestone sequences is in the order of thousands of years. Dreybrodt's (1981b) data supports the effectiveness of carbonate dissolution of the mixed water model. However, Ford (1988) argued that such mixing is physically unfeasible unless the rock mass has very high effective porosity.

In the study of karst development on Grand Cayman, Jones and Smith (1988) suggested that mixing corrosion, which occurs in the mixing zone, was probably responsible for the development of major caves on the island. A similar mechanism was proposed for the karst features formed on the Bahamas (Palmer, 1984; Mylroie, 1984), and the Yucatan Peninsula (Hanshaw and Back, 1980; Back *et al.*, 1986).

Combining the geochemical mixing theory with the hydrodynamics of fresh and sea water mixing zones in a coupled reaction-transport model, Sanford and Konikow (1989) concluded that significant porosity develops when a large flux of fresh water is present. However, on small islands, mixing corrosion is less effective because of low fluid flow (Sanford and Konikow, 1989). They also noted that dissolution occurs primarily on the fresher portions of the mixing zone - one near the toe of the mixing zone, and one near the top and closer to the coast where velocities are greater. In contrast, based on field observations along the Caribbean coast of the Yucatan Peninsula and petrographic study, Stoessell *et al.* (1989) showed that aragonite dissolves preferentially throughout the modern mixing zone, particularly in the saline portion. This conclusion is inconsistent with the modelling results of Sanford and Konikow (1989). Using water samples collected from the submarine caves of the Yucatan Peninsula, Stoessell *et al.* (1989) also showed that the coastal mixing zone is undersaturated with respect to calcite up to 90% sea water. Therefore, it appears that carbonate dissolution can occur over a wide range of mixing composition. The controlling factors are probably the ground water flow hydraulics and flow regime in the aquifer.

On the Cayman Islands, there is no geological boundary to define the base of the mixing zone: therefore, according to Sanford and Konikows' (1989) study, porosity enhancement is most favourable near the coast at the discharge zone where flow rate is high. High flow rate at the discharge zone has also been suggested by Chidley and Lloyd (1977b). This appears to be the situation on the Cayman Islands, where cave development tends to be locally extensive along the coast. Therefore, the level of karstification on the Bluff Formation of Cayman Islands is predominantly controlled by water table/sea level elevation, whereas the cave geometry is controlled by jointing and climatic conditions.

F. SYNOPSIS

Karstification of the Bluff Formation occurred in at least three distinct phases. As a result four different cave systems were formed. Phase I karst developed in late Oligocene to early Miocene times when the Oligocene Cayman Member was subaerially exposed in relation to the major sea level drop in late Oligocene. In association with the Phase I karstification is the Type 1 cave system which is characterized by dolomitized colour-banded caymanite fill.

Phase II karst developed in late Miocene to early Pliocene times as a result of the major marine regression in late Miocene. Type 2 cave systems, which have no caymanite fill but abundant flowstone deposits, might form during Phase II karstification.

Phase III karst developed in late Pliocene to late Pleistocene times, particularly in the latter period. Type 3 and 4 cave systems, characterized by extensive networks of cave passages and assorted forms of speleothem (in type 3 caves), formed during phase III karstification after the Bluff Formation was completely dolomitized. The extensive cave network is probably related to extensive joint development prior to karstification. suggesting that the presence of joint systems and climatic regimes are the dominant controlling factors rather than the lithology.

The horizontal orientation of some of the caves and their connection to the wave cut notches, particularly Type 3 and 4, suggest that cave development is directly related to past sea level high stands. The concentration of caves along the coastlines further suggests that the cave development probably occurred at the ground water discharge points where flow velocity is high and mixing between ground water and sea water occurs.

XI. DIAGENETIC INTERPRETATION OF THE BLUFF FORMATION III: POROSITY DESTRUCTION

Porosity destruction in the rocks of the Bluff Formation includes processes of (1) calcite cementation, (2) dolomite cementation, (3) alternating dolomite and calcite cementation, (4) poikilotopic calcite-dolomite formation, (5) speleothemic calcite precipitation, (6) internal sedimentation, and (7) terra rossa deposition. The aim of this study is to examine the fluid conditions in which these diagenetic fabrics formed. Chemical kinetics are discussed where appropriate because they control the cement morphology.

A. CALCITE CEMENTATION

Precipitation of calcium carbonate may result from evaporation (e.g. Moore, 1973), degassing of CO_2 (e.g. Hanor, 1978), temperature change (e.g. Langmuir, 1971), and mixing of chemically dissimilar waters (e.g. Runnells, 1969). Many studies on carbonate diagenesis have used cement type and texture for the recognition of diagenetic environments (e.g. Bricker, 1971; Bathurst, 1975; Folk, 1974; Folk and Land, 1975; Longman, 1980; Flugel, 1982; James and Choquette, 1983, 1984; Harris *et al.*, 1985). Chafetz *et al.* (1985) noted, however, that the relationship between cement morphology and fluid composition is difficult to establish. For example, low magnesian calcite is known to form in meteoric waters (e.g. Folk and Land, 1975; James and Choquette, 1984), as well as in deep sea marine environment (Schlager and James, 1978). Likewise the morphology of high magnesian calcite can range from micritic, to fibrous, to bladed, to sparry (Pierson and Shinn, 1985; Aissaoui, 1988). The inherent difficulties in monitoring precipitation reactions, the complexities of fluid composition in natural environments and the biological factors complicate the understanding of mechanisms of carbonate precipitation.

Kinetics of Mineral Precipitation

Mineral precipitation from aqueous solution involves two processes, nucleation and crystal growth. Nucleation refers to the initial formation of a new phase, where there is a free energy barrier to the formation to this phase (Jackson, 1979). The ease of nucleation increases with increasing levels of supersaturation (Nielsen, 1964; Berner, 1980). At a low level of supersaturation, crystals grow on a limited number of nuclei and lead to the development of large crystals (Berner, 1980, 1981).

Crystal growth involves the transportation of ions to and from the surface of a crystal and chemical reactions occurring at the crystal surface (Berner, 1980, 1981; Morse, 1983). The former process (transport controlled) is a function of hydrodynamic conditions whereas the latter process (surface reaction controlled) is governed by the built-in steps and kinks on the crystal's surface. Blockage of these growth sites by foreign ions can greatly retard the rate of crystal growth.

By adding well defined seed crystals to a stable supersaturated solution, Reddy and Nancollas (1971) and Nancollas and Reddy (1971) demonstrated that the rate of calcite precipitation is a function of the saturation state of the solution with respect to calcite. The calcite dissolution rate model of Plummer *et al.* (1978, 1979; equation 1) is also applicable in describing the kinetics of calcite precipitation. According to Plummer *et al.* (1978, 1979), CO_2 is outgassed from solution during crystal growth. Dreybrodt (1980) also concluded that the production of CO_2 and its diffusion away from the surface is the rate-determining step in calcite precipitation. Therefore, mineral precipitation is controlled by the hydrodynamic state and the saturation rate of the solution. Conversely, crystal morphology is a function of the degree of supersaturation of the solution and the presence of foreign ions adsorbed on the crystal surface.

Controlling Parameters

The relationship between the morphologic and fabric criteria and the environment of cementation has been investigated by Thortenson *et al.* (1972), Badiozamani *et al.* (1977), Reddy (1977), Ricketts (1980), Cailleau *et al.* (1982), Walter (1986) and Burton and Walter (1987). Although the experiments employed either outgassing of CO_2 from bicarbonate solution or seeding in order to speed up the precipitation process, the results suggest that calcite cementation in natural environments is easily achieved provided conditions are favourable. In those experiments, significant cementation was commonly obtained in a short time span (a few days to a few months). Rapid rates of calcite crystallization were also demonstrated by Jones and Kahle (1986) by mixing Na_2CO_3 with $Ca(NO_3)_2$ to produce dendritic crystals in less than 2 minutes.

The following conclusions can be drawn from experimental studies (Thortenson *et al.*, 1972; Badiozamani *et al.*, 1977; Reddy, 1977; Ricketts, 1980; Cailleau *et al.*, 1982; Walter, 1986; Burton and Walter, 1987):

(1) Cement in the vadose zone is commonly formed of micron-sized crystals, whereas cement in the phreatic zone is comprised of relatively coarse crystals (Thortenson *et al.*, 1972).

(2) Cement formed in the vadose zone is characterized by void lining and grain contact behaviour (Thortenson *et al.*, 1972). Void lining cement, however, can also form in the phreatic zone (Badiozamani *et al.*, 1977).

(3) Small, needle type crystals of aragonite form in solutions containing Mg^{2+} (Badiozamani *et al.*, 1977), particularly when Mg^{2+}/Ca^{2+} ratios are greater than 2.0 (Ricketts, 1980; Cailleau *et al.*, 1982).

(4) Crystal size varies directly with temperature and NaCl content, but inversely with the concentration of the solution (Badiozamani *et al.*, 1977).

(5) During crystal growth, the degree of supersaturation decreases resulting in the formation of different cement types (Cailleau *et al.*, 1982).

(6) Crystal morphology is generally a function of the temperature and the supersaturation state of the solutions, crystal structure, and substrate defects (Badiozamani *et al.*, 1977; Ricketts, 1980; Cailleau *et al.*, 1982).

(7) Foreign ions and organic matter may lower the rate of crystal growth and cause modifications in crystal size and morphology. For example, PO_4^{3-} adsorbed on the crystal faces inhibits crystal growth rate (Reddy, 1977), whereas Mg^{2+} forms complexes with HCO_3^- and CO_3^{2-} ions (Cailleau *et al.*, 1982).

(8) High SO_4^{2-}, low PO_4^{3-} solutions favour precipitation of aragonite; low SO_4^{2-}, high PO_4^{3-} solutions favour precipitation of calcite (Walter, 1986).

(9) Precipitation rates of calcite decrease with increase in Mg^{2+} and SO_4^{2-} concentrations in solutions (Walter, 1986).

(10) Low temperature favours precipitation of low-magnesian calcite (Burton and Walter, 1987).

It is apparent that in a relatively stable diagenetic environment of uniform ground water temperature (seasonal variation less than 5°C) like that of the Cayman Islands, salinity and the presence of Mg^{2+} are the major factors controlling crystal morphology. Folk (1974, 1978) argued that the incorporation of the small Mg^{2+} ions in the calcite crystal lattice inhibits crystal growth on c-axis faces, and hence, favours precipitation of acicular crystal form. Folk and Land (1975) further suggested that sparry calcite precipitation occurs in meteoric waters or dilute subsurface waters with Mg/Ca ratios ranging from 1:1 to 1:10. Lahann (1978), however, suggested that it is the difficulty in dewatering the substituted Mg^{2+} that determines the calcite growth rate. The Mg^{2+} ions also form complexes with HCO_3^- and CO_3^{2-}, reducing the availability of free carbonate ions for crystal growth (Cailleau *et al.*, 1982). Furthermore, Lahann (1978) proposed that crystal morphology is controlled by the Ca^{2+}/CO_3^{2-} ratio of the solution in such a way that equant calcite crystals precipitate from water with a low Ca^{2+}/CO_3^{2-} ratio. Given and Wilkinson (1985) also suggested that the amount of CO_3^{2-} at the growth sites is the principal parameter in determining crystal morphology, composition, and mineralogy of calcium carbonate cement.

Calcification of algae, fungi and bacteria is common in the Bluff Formation (Jones and Kahle, 1986; Jones, 1987, 1988; Pleydell, 1987; Squair, 1988). The role of micro-organisms in mediating the growth of sparry calcite is not known; however, the ease of calcification of these micro-flora suggests that they may play an important role in controlling the kinetics of surface nucleation for crystal growth.

Timing of Calcite Cementation in the Bluff Formation

Petrographic studies of rock samples collected from all hydrochemical zones indicate that calcite is commonly the last phase of cementation. Sparry calcite was precipitated (1) after clear dolomite cement (Plates VI.3A-3E), (2) after caymanite (Plate VI.6F), (3) after flowstone (Fig. 2A in Jones and Kahle, 1985), and (4) as intercrystalline cement (Plate VI.1E). The relationship between the occurrence of calcite cement and the present day ground water regime (Figs. VI.4, 7) suggests that most sparry calcite is a recent cement and it is related to the present day hydrochemical conditions.

Conditions of Calcite Cementation in the Bluff Formation

Speciation calculations for ground waters from the Cayman Islands indicate that almost all the fresh to saline waters are supersaturated with respect to calcite (Tables IV.5-8). Thus, according to thermodynamic considerations, calcite precipitation should be common throughout the full spectrum of hydrochemical zones. Stable oxygen isotopic data, however, suggest that calcite spar was formed in fresh to brackish water with up to 45% sea water salinity (Table VII.6, Fig. VII.3B).

Sparry calcite is (1) the most common last phase cement in the rocks collected from the present day fresh and lightly brackish water zone (Figs. VI.3-5), and (2) more common in the rocks of the Lower Valley lens than in the East End lens (Figs. VI.3-5). The decrease in the abundance of late phase sparry calcite with increasing salinity (Figs. VI.4, 7) is in agreement with the general premise that Mg^{2+} and CO_3^{2-} are the controlling factors. As salinity of the ground water increases, Mg^{2+} ion generally increases whereas CO_3^{2-} ion decreases (cf. Tables III.3-8). Both trends would lead to less favourable conditions for calcite growth (Folk, 1974, 1978; Lahann, 1978; Given and Wilkinson, 1985). Furthermore, the hydrodynamic state of the ground water in the saline zone is slow relative to the dynamic shallow zone (fresh to brackish water); therefore, the effectiveness of CO_2 diffusion from the reaction sites is also reduced. The number of foreign ions that might act as inhibitors to crystal growth also increases with increasing salinity towards the sea water composition (Morse, 1986). If so, the rate of calcite precipitation also decreases in the high salinity zone.

Fresh ground water in the Lower Valley lens has a significantly lower Mg^{2+} content, with molar Mg/Ca ratios generally less than 0.5 (Tables III.4, IV.5). The more common occurrence of sparry calcite in the fresh water zone of the Lower Valley than in the East End lens is consistent with the differences in chemical properties between the two lenses. Equilibrium speciation calculations for the fresh water in the Lower Valley lens shows that most of the water samples are supersaturated with respect to calcite, whereas fewer than half of these samples (out of 31) are supersaturated with respect to dolomite (Table IV.5). Conversely, fresh ground water from the East End lens is supersaturated with respect to calcite and dolomite for all the samples analysed (Table IV.6). Therefore, calcite is the dominant carbonate mineral precipitating in the fresh water and lightly brackish water zones, particularly in the Lower Valley ground water where the Mg/Ca ratio is low (Figs.VI.3-5). The chemical characteristics of the ground water seem to be in agreement with the petrographic evidence and stable isotopic interpretation. Zoned sparry calcite marked by thin laminae of insoluble residues (Plate VI.3E) indicates a hiatus between each additional zone of calcite growth. The cessation of calcite growth was probably due to depletion of Ca^{2+} and CO_3^{2-} in the pore fluids.

B. DOLOMITE CEMENTATION

Dolomite does not precipitate at temperature less than 100°C (Lippman, 1973; Deelman, 1975; Land, 1980); this suggests that dolomite formation is governed by chemical kinetics. Unfortunately, dolomite solution equilibrium is not adequately known (Hsu, 1963; Hardie, 1987). Furthermore, geochemical techniques cannot resolve the controversy concerning the conditions appropriate for dolomite precipitation in low temperature sedimentary environments (Land, 1980, 1985; Morrow, 1982a, 1982b; Machel and Mountjoy, 1986; Hardie, 1987).

Kinetics of Dolomite Precipitation

Berner (1978, 1981) suggests that the precipitation of minerals with low solubility, such as calcite and dolomite, is governed by surface reaction. It can be argued, therefore, that chemical reactions occurring on crystal surfaces control the precipitation of dolomite. Unlike dissolution kinetics of calcite (equation 1), which also applicable in describing calcite precipitation (Plummer *et al.*, 1978, 1979), the dissolution kinetics of dolomite (equation 2) do not fully describe the backward-reaction mechanisms (Busenberg and Plummer, 1982). Although the backward reactions involve positively charged surface sites with adsorbed HCO_3^-, Busenberg and Plummer (1982) suggested that the reversible dolomite-solution equilibrium probably takes an extremely long time to achieve at temperatures less than 45°C.

The high energy required to dehydrate the very strongly bonded water molecules from the Mg^{2+} prior to incorporation into the crystal structure is probably the main factor controlling dolomite formation (Lippman, 1973; Hanshaw and Back, 1979; Morrow, 1982a). Deelman (1975) argued that dolomite is formed by successive addition of $CaCO_3$ and $MgCO_3$ layers. This unique arrangement requires a considerable change in energy content as each $CaCO_3$ layer is succeeded by a $MgCO_3$ sheet (Deelman, 1975).

Timing of Dolomite Cementation in the Bluff Formation

At least two generations of clear dolomite cement are present. The first generation is commonly the first phase void-lining cement emplaced prior to the influx of internal sediments (Plate VI.6F); the second generation of clear dolomite cement was precipitated on top of the sediments (Plate VI.6E). It is apparent the first generation probably formed during late Oligocene to early Miocene times prior to the deposition of the caymanite sediments in early middle Miocene times. Jones and Hunter (1989) noted that dolomite cement occurs in the Oligocene Cayman Member but not the Miocene Pedro Castle Member. In cavities where only one generation of dolomite cement is present (Plates VI.3B, 3C), it is difficult to determine the timing of the dolomite cementation.

Dolomite commonly occurs as a void-lining cement emplaced prior to the precipitation of sparry calcite in most cavities (Plates VI.3B, 3C). Furthermore, petrographic studies suggest that dolomite cement is the most common last-cement phase in the brackish water zone (Figs. VI.5-7). This indicates that some of the dolomite cements are probably associated with the present-day hydrochemical regime.

Conditions of Dolomite Cementation in the Bluff Formation

Clear euhedral dolomite is a common void-lining cement in the Bluff Formation. Dolomite cement is also common in many carbonate formations, for example, the Pleistocene Hope Gate Formation of Jamaica (Land, 1973), the Pliocene Seroe Domi Formation of Bonaire (Sibley, 1980), the Pleistocene Great Abaco carbonate of Bahamas (Kaldi and Gilman, 1982), the Pleistocene Yucatecan Formation of Yucatan Peninsula (Ward and Halley, 1985) and the Pleistocene limestones of Barbados (Humphrey, 1988). It has been interpreted that all of the dolomite cements in these carbonate sequences have formed in mixed meteoric-marine environments.

The morphology of the clear euhedral dolomite cements found in cavities of the Bluff Formation (Plates VI.2A-2D, VI.6B, 6F) resembles that described in other carbonate sequences in the Caribbean region: therefore, the dolomite cement probably formed in mixed water environments. Folk and Land (1975) and Jones *et al.* (1984) also suggested that the dolomite cement in the Cayman examples was formed in a mixed meteoric-sea water diagenetic realm. The clarity and coarse texture of the dolomite cement in the Bluff Formation suggests that the pore fluids were supersaturated with respect to dolomite, were of low salinity, and contained an adequate supply of Ca^{2+}, Mg^{2+} and CO_3^{2-} ions.

Inclusions concentrated in the cores of dolomite crystals are common in the Bluff Formation, giving the dolomite crystals a cloudy centre and clear rims appearance (Plates VI.1A, 1B). This feature is particularly prominent in the coarser, euhedral crystals scattered in the microcrystalline dolomite groundmass (Plate VI.1B). The inclusions probably consist of calcite, similar to dolomites of other carbonate sequences (Murray, 1964; Folk and Siedlecka, 1974; Sibley, 1980, 1982; Ward and Halley, 1985; Cander *et al.*, 1988). Folk and Siedlecka (1974) studied the late Paleozoic rocks from Bear Islands of Svalbard and suggested that the clear rim was precipitated from a more dilute solution which was undersaturated with respect to calcite. Similarly, petrographic analyses of the Pliocene Seroe Domi dolomites on Bonaire led Sibley (1980) to suggest that the cloudy-centred clear-rimmed fabric is due to evolution of pore fluids during dolomitization, the evolution ranging from a state of near calcite saturation (i.e. formation of cloudy core) to a state of calcite undersaturation (i.e. formation of clear rim). Similar diagenetic conditions were probably responsible for the dolomite fabrics of the Bluff Formation. The clear, euhedral dolomite (Plate VI.1A) probably formed under the same conditions as the clear rim. In this connection, the cloudy-centre, clear-rimmed dolomites may be formed by crystal growth on previously formed dolomites.

Thermodynamic considerations indicate that most waters from all of the hydrochemical zones in the dolostone aquifer of the Bluff Formation are supersaturated with respect to dolomite (Tables IV.5-8). Therefore, theoretically, the ground waters are capable of precipitating dolomite in all zones. Furthermore, the Mg/Ca ratios, which are inconsistent with the ionic strength of the solutions (Table IV.9), suggest that precipitation and/or dissolution of carbonate minerals may be occurring in the dolostone aquifer. Folk and Land (1975) suggested that solutions of high salinity induce rapid crystallization, and therefore, form microcrystalline textures. Sibley (1980) also noted that dolomite crystals are difficult to nucleate, and hence, are composed of few crystals. Although it is open to debate whether or not the mixed fresh-sea water zone is the site for massive dolomitization, it is generally agreed that dolomite cementation occurs in the mixing zone (Land, 1983a, 1985; Machel and Mountjoy, 1986; Hardie, 1987). In the Bluff Formation, there is a decrease in the content of dolomite cement from the slightly brackish to saline water zones (Figs. VI.4, 7). It is, therefore, suggested that dolomite cement in the Bluff Formation probably formed in the brackish water (mixing) zone. Stable isotopic values also indicate that the diagenetic fluids for dolomite cementation are brackish (25% sea water salinity) to saline water (Table VII.6, Fig.VII.3B).

The sharp boundaries in the zoned dolomites (Plates VI.2C, 2D, 3C) probably indicate sequential crystal growth without intervening periods of dissolution. Detailed analysis of syntaxial overgrowths on dolomite crystals that line the walls of near-surface vadose cavities in dolostones of the Bluff Formation led Jones (1989b) to suggest that the overgrowths were formed by sequentially coalescing smaller crystals. Jones (1989b) further suggested that the overgrowths were probably formed from thin films of supersaturated fluid that left from evaporation. A similar sequential crystal growth phenomenon probably occurred in the phreatic zone although in a slightly different manner. When the ions in the pore fluids were depleted by the crystal growth, the pore solutions changed from supersaturation to saturation with respect to dolomite. The next stage of growth probably began when the ions were replenished by new fluids. Another indication of ionic depletion is the fact that dolomite cements do not completely occlude the cavities. The cessation of dolomite growth, therefore, also indicates that the hydraulic system was not effective in delivering the new ions to the cavities, probably an indication of partially closed subenvironments in the heterogeneous aquifer. Perhaps the precipitation was so slow that the crystals ceased to grow because of a change in diagenetic environment due to external factors, such as eustatic sea level fluctuation.

C. ALTERNANT DOLOMITE AND CALCITE CEMENTATION

Banded cements with alternating dolomite and calcite occur in cavities of the Bluff Formation (Plates VI.4A, 4B); they have also been documented in the Yucatecan dolomites of the Yucatan Peninsula (Ward and Halley, 1985) and in the dolomite sequence of the Mururoa Atoll (Aissaoui, 1988). Jones *et al.* (1984) also described a cement of similar fabric in the microstalactitic cement in the Bluff Formation.

Mechanism of Alternant Dolomite and Calcite Cementation

Jones *et al.* (1984) suggested that dolomite/calcite banding in the microstalactites is an original fabric that recorded ever-changing pore water chemistry. An alternative interpretation, not favoured by Jones *et al.* (1984), suggests that the original zonation was formed of alternating low and high magnesian calcite, and the high magnesian calcite was subsequently dolomitized. Aissaoui (1988) argued that the alternating dolomite/calcite cement is formed by preferential dolomitization of high magnesian fibrous and/or blade calcite zones which left the high magnesian calcite spar unaltered.

Conditions of Alternant Dolomite and Calcite Cementation in the Bluff Formation

There are several lines of evidence to suggest that the alternating zones of dolomite and calcite described correspond to successive cementation by dolomite and calcite and they are not the result of diagenetic alteration. Firstly, the zones are of uniform thickness and laterally continuous (Plates VI.4A, 4B). Secondly, the zones are marked by euhedral outlines (Plates VI.4A, 4B). Lastly, each successive zone followed the contour of the previous growth bands (Plates VI.4A, 4B). This alternating growth of dolomite and calcite cement probably represents period of ionic depletion followed by subsequent ionic replenishment of the pore solutions. During cement growth in the cavities, the degree of supersaturation of the pore solutions with respect to the precipitating mineral will decrease. It is possible that this decrease in ionic concentration may lead to the formation of another mineral variety or complete cessation of cement growth. The fact that clear dolomite commonly forms the first zone of the alternating cement (Plates VI.4A, 4B) suggests that the precipitating pore fluid was probably slightly brackish in composition.

Similar, successive growth may be used to explain the intracrystalline zonation of dolomite and calcite (Plates VI.4C, 4D). Katz (1968, 1971) suggested that calcite zones may be formed by preferential dedolomitization of calcian dolomite zones. However, Jones *et al.* (1989) argued that the calcite zones in dolomite rhombs of the Bluff Formation were formed by differential leaching of unstable dolomite zones, formed under high salinity conditions, followed by calcite precipitation. All three hypothesis can explain the formation of alternating calcite and dolomite zones in dolomite rhombs. However, in cases where poikilotopic calcite encasing the zoned dolomite-calcite is in optical continuity with the calcite zone (Plates VI.5B-5E), the explanation put forward by Jones *et al.* (1989) is the most probable one.

D. POIKILOTOPIC CALCITE-DOLOMITE FORMATION

The term poikilotopic calcite-dolomite fabric, proposed by Jones *et al.* (1989), is used in this study to describe dolomite crystals that are hollow, partly filled by calcite, and/or encased by sparry calcite (Plates VI.1D, VI.5A-5E). These fabrics have characteristics similar to those suggested by Shearman *et al.* (1961), Evamy (1967), Folkman (1969), Katz (1971), and Longman and Mench (1978) for dedolomite.

Mechanism of Poikilotopic Calcite-Dolomite Formation

Through experimental work and petrographic studies, five mechanisms have been proposed to explain the process of dedolomitization:

(1) Dedolomitization is promoted by waters having a high Ca/Mg ratio, a low temperature (<50°C) and a low P_{CO_2} (de Groot, 1967).

(2) Dedolomitization involves dolomite calcium sulfate reaction (Shearman *et al.*, 1961; Evamy, 1963; Goldberg, 1967; Folkman, 1969). Yanateva (1955, reviewed by Chilingar, 1956) demonstrated that $CaSO_4$ is an active agent only at low P_{CO_2}.

(3) Dedolomitization is the result of the interaction between the physico-chemical changes of the interstitial water and the original composition of dolomite (Katz, 1968, 1971); Al-Hashimi and Hemingway, 1973; Frank, 1981; Land and Prezbindowski, 1981).

(4) Dedolomitization requires significant Ca^{2+} concentration and is not due to the presence of aqueous SO_4^{2-} (Back *et al.*, 1983; Stoessell *et al.*, 1987).

(5) Dedolomitization evolves through a series of distinct, time separated processes that comprise preferential dissolution of the less stable zones followed by calcite precipitation (Jones *et al.*, 1989).

There is no petrographic evidence to indicate the presence of former evaporites in the Bluff Formation; therefore, the reaction mechanism involving dolomite and calcium sulfate can be eliminated. The poikilotopic calcite-dolomite commonly found in rocks collected from the weathered zones and along joints suggests that the diagenetic fabric was probably formed in near-surface conditions similar to those suggested by de Groot (1967). Dedolomites related to weathering surfaces have been noted by Goldberg (1967), Folkman (1969), Chafetz (1972), and Al-Hashimi and Hemingway (1973). Yanateva (1955), Shearman *et al.* (1961), Evamy (1967), and Back *et al.* (1983) suggested that dedolomites are formed by concomitant dolomite dissolution and calcite precipitation.

Jones *et al.* (1989) suggested that the poikilotopic calcite-dolomite fabric evolved through dissolution of dolomite cement or matrix dolomite followed by precipitation of large calcite crystals. Thus, the fabric can evolve through a series of distinct, time-separated processes (Jones *et al.*, 1989). The fact that the calcite zones in the dolomite crystals and the poikilotopic calcite are in optical continuity attests that the two calcites are genetically related. Thus, the poikilotopic calcite-dolomite fabric identified in this study (Plates VI.5A-5E) was probably formed in a manner akin to that proposed by Jones *et al.* (1989).

The fact that the equilibrium fractionation, $\Delta^{18}O_{(dolomite\text{-}calcite)}$ values of the poikilotopic calcite-dolomite lie between 2.4 and 6.3‰ PDB (Table VII.4), values not in agreement with the generally observed range of 3 ± 1‰ PDB for coexisting dolomite and calcite (Land, 1983b), suggests that the limpid dolomite and poikilotopic calcite were probably not cogenetic phases. The differences in $\delta^{13}C$ between dolomite and poikilotopic calcite (Jones *et al.*, 1989) also suggest that the two carbonate minerals were not genetically related.

Conditions of Poikilotopic Calcite-Dolomite Formation in the Bluff Formation

Stable oxygen isotopic data of the poikilotopic calcite-dolomite from the Bluff Formation suggest that the precipitating fluids of calcite range from highly brackish to saline (Table VII.5, Fig.VII. 3). Dissolution of unstable dolomite zones probably occurred during periodic influxes of CO_2-charged rain water, which is most effective at the water table zone or along joints. Shallow ground waters, particularly in the fresh water zone of the Lower Valley lens, are commonly supersaturated with respect to calcite and have a low Mg/Ca ratio (Table IV.5). They are, therefore, most favourable for precipitating calcite (Fig. VI.5). Furthermore, at the water table zone, rain water recharge would have caused undersaturation of the ground water with respect to dolomite, and hence, dolomite dissolution prior to the precipitation of the calcite. This is in general agreement with the occurrence of poikilotopic calcite-dolomite in the Bluff Formation.

E. SPELEOTHEMIC CALCITE FORMATION

The precipitation of speleothemic calcite is typically regarded as an abiogenic process (e.g. Thraikill, 1976; White, 1976; Folk and Assereto, 1976; Kendall and Broughton, 1978). The common presence of algae, fungi and bacteria in many caves, however, suggests that the formation of speleothem and travertine may, to some extent, be biogenically controlled (e.g. Caumartin, 1963; Lefevre and Laporte, 1969; Draganov, 1977; Chafetz and Folk, 1984; Folk *et al.*, 1985). Studies on Caymanian speleothems by Jones and Motyka (1987), Smith (1987) and Jones and MacDonald (1989) also demonstrate that micro-organisms probably played an important role in controlling the morphology and composition of the speleothems.

Kinetics of Speleothem Formation

Although speleothemic calcite forms in the vadose zone, the kinetics of calcite precipitation given by Reddy and Nancollas (1971), Nancollas and Reddy (1971), and Plummer *et al.* (1978, 1979) remain applicable. Accordingly, Dreybrodt (1980, 1981c) calculated that the speleothemic growth rate is in the order of 0.01-1 mm/year which is in agreement with the observed growth rate of 0.05-0.1 mm/year in temperate regions (Harmon *et al.*, 1975). With an increase of temperature from 10° to 25°C, speleothemic growth rate was shown to increase two fold (Dreybrodt, 1980). Other important factors are the concentration and supply of Ca^{2+} and CO_3^{2-} ions (Dreybrodt, 1980).

Timing of Speleothem Formation in the Bluff Formation

Dating of speleothems is commonly performed by the Uranium-series dating technique (Gascoyne *et al.*, 1978; Crew *et al.*, 1984). Growth layers in the flowstones of the Bluff Formation are marked by insoluble residues, possibly of clay minerals (Plates VI.6G, 6H), that might be ideal for dating the flowstones. However, Woodroffe *et al.* (1983) and Jones and Smith (1988) noted that the lack of felsic igneous rocks on and around the Cayman Islands leads to a scarcity of uranium in the geochemical cycle for absolute age dating. Nevertheless, the fact that all the speleothems still retain their original calcite mineralogy suggests that speleothem precipitation succeeded dolomitization. Flowstones formed in the Type 1 and 2 caves are older than the speleothems precipitated in the Type 3 caves because the flowstone was cut by the Type 3 cave systems. Because the Type 3 caves probably formed in late Pleistocene times (approximately 125,000 years ago) it is possible to suggest that the flowstones precipitated in the Type 1 and Type 2 caves are probably 2.0±0.5 my to 125,000 years old. Conversely, the speleothems precipitated in the Type 3 caves are probably less than 125,000 years old.

Conditions of Speleothem Formation in the Bluff Formation

Water containing carbonic acid obtained from hydration of atmospheric CO_2, organic decomposition and plant respiration is capable of dissolving calcite and dolomite in the bedrock along its flow path. When this water finally reaches a cave with a lower partial pressure of CO_2 than in the solution, CO_2 degasses from the water and a supersaturated solution of $CaCO_3$ results. In the caves on the Cayman Islands, the high relative humidity and stable temperature in the present day cave environment suggests that evaporation probably has minimal effect on speleothemic formation. Around cave entrances or areas open to surface atmospheric conditions, evaporation may be significant. Stable oxygen isotopic data suggest that the speleothems probably precipitated from waters of similar salinity to those responsible for calcite cementation (Table VII.6, Fig.VII.3B; Smith, 1987). It is important to note that the stable isotopic data suggests that flowstones may also form from brackish water of salinity up to 45% sea water (Table VII.6, Fig. VII.3B), which contradicts the general perception that speleothems are indicative of fresh water environments.

Smith (1987) suggested that the Ca^{2+} and CO_3^{2-} ions necessary for speleothem precipitation were probably derived from the dissolution of the overlying dolostones of the Bluff Formation or from limestones of the Ironshore Formation. The fact that the Type 3 and 4 cave systems formed by dissolving the dolostone bedrock suggests that dolomite was probably the main source of $CaCO_3$ for the speleothemic formation.

F. INTERNAL SEDIMENTATION

Caymanite is a common cavity fill in the Bluff Formation. Some cavities were partly or completely filled with skeletal sands (predominantly foraminifera and fragments of red algae), which are locally interlayered with the caymanite. The anhedral dolomite crystals, angular dolostone fragments, and sedimentary structures of the caymanite (Plates VI.6C-6F) unequivocally suggest that the sediments were of detrital origin. The physical features of the caymanite deposits are similar to vadose calcite sediments or mineral deposits found in the Permian Townsend carbonate mound of New Mexico (Dunham, 1969), the Ordovician limestones of Australia (Semeniuk, 1971), the Carboniferous limestones of Peak District in England (Ford *et al.*, 1977) and the Type 4 internal sediments in the Jurassic carbonates of Burgundy and Frond (Aissaoui and Purser, 1983). Ford (1988) also noted that internal sediments in caves are common and that transportation and deposition can be highly energetic.

Origin of the Internal Sediments

The presence of normal marine skeletal components (foraminifera and red algae) in the grainstone led Jones and Hunter (1989) to suggest that the skeletal sands were deposited during the early part of a marine transgression. The origin of the caymanite sediments is less certain. Assuming that the caymanite was formed from swamp sediments

(Folk and McBride, 1976; Collar, 1985, pers. comm.; Lockhart, 1986), one important point that needs to be addressed is the original mineral composition of the sediment. Analyses of sediments collected from a swamp at Hell in West Bay of Grand Cayman showed that only 5% of the bulk weight is dolomite (I. Collar, 1985, pers. comm.), the other 95% is calcite and aragonite. Collar (1985, pers. comm.) proposed that the dolomites were selectively transported into the cavities due to their small grain size (<5 µm in length). The fact that individual laminae are composed of different grain sizes strongly suggests that the model of Collar (1985, pers. comm.) is not a functional mechanism. Furthermore, SEM examination of sediments from the Hell swamp (Lockhart, 1986) and from Colliers Pond in East End (this study) showed little resemblance to the grains in the caymanite. The small amount of dolomite in the swamp sediments were probably derived from (1) wind blown sediments, (2) weathering of the dolostone by rain water, and (3) dolostone bedrock in a manner similar to the fungi mediated micritization of calcite spar (Jones and Pemberton, 1987a, 1987b). It is, therefore, suggested that the original caymanite sediments were of predominantly calcitic compositions. Stable oxygen isotopic values of the caymanite suggest that the calcitic sediments were subsequently dolomitized in fluids of high salinity which ranged from 25 to 100% sea water salinity (Table VII.5, Fig.VII.3B).

Timing of Internal Sedimentation

The absolute timing of the deposition of caymanite is difficult to determine; nevertheless, examination of the various geological relationships suggests the following:

(1) Caymanite (red, orange, black and white coloured) is common in the Oligocene Cayman Member of the Bluff Formation, but the coloured components rarely occur in the middle Miocene Pedro Castle Member (Jones and Hunter, 1989). This suggests that most caymanite was associated with a transgression that led to deposition of the Pedro Castle Member, probably during the land emergence in late Oligocene times.

(2) At least one phase of karstification and jointing occurred prior to caymanite deposition because some joints and caves were filled by caymanite. The karst development (Phase I; Fig. VIII.1) was probably due to the sea level drop in late Oligocene times.

(3) Caymanite postdated one generation of void-lining dolomite cement (Plate VI.6F). This also suggests that caymanite was deposited after dolomitization of the host rock, if void-lining dolomite occurred concurrently with dolomitization, as suggested in paragenetic model II.

(4) Caymanite predated the second generation dolomite cement which was precipitated on top of the caymanite (Plate VI.6E).

(5) Undolomitized flowstone and sparry calcite (Plate VI.6F) precipitated after caymanite deposition. This suggests that caymanite was dolomitized prior to the formation of flowstone and sparry calcite.

Mechanism of Internal Sedimentation

Folk and McBride (1976) and Lockhart (1986) suggested that caymanite was formed from materials washed from swamps into the cavities and caverns via the well-developed joint system during seasonal storms. Lockhart (1986) noted that caymanite appears to occur predominantly in coastal exposures; however, recent data obtained from well drilling indicates that caymanite also occurs in the interior of the islands. Therefore, the occurrence of caymanite is probably governed by the availability of the sediments and the joint system.

The multiple cycles of caymanite formation is best illustrated by the distinct laminations (Plate VI.6C) and cut and filled channels. Therefore, the detrital sediments were probably intermittently washed into the cavities and caverns or deposited from stagnant pond waters in the caverns. The interm[illegible]henomenon of the internal sedimentation is also indicated by dessication cracks present in some caymanite layers. The presence of (1) erosional features and cross-bedding, (2) large angular fragments (Plate VI.6C), and (3) fragments probably removed from irregular projections on cavity walls (Plate VI.6D) suggests that sedimentation occurred under high-stage flow conditions. The sediments may also have entered cavities that were in the phreatic zone.

The variation in grain size of sediments in the same layer (Plate VI.6C) indicates that the sediments were transported in steady turbulent flow in a manner suggested by Bridge (1981). Gales (1984) also suggested that finer sediment can deposit simultaneously with the coarser sediment where flow expansion resulted in a sudden reduction in flow competence such as at the exit to the phreatic zone. A similar mode of flow and transport was probably responsible for the caymanite sedimentation in the Bluff Formation. Caymanite fill in vertical or steeply dipping open joints commonly shows highly contorted laminae that are subparallel to the attitude of the joints. The fact that the sediments were maintained at such a high angle suggests that the sediment flow was probably in a form of high-viscosity fluid and that it underwent rapid lithification.

G. TERRA ROSSA DEPOSITION

Terra rossa is a common cavity fill in the Bluff Formation (Jones *et al.*, 1984; Jones and Smith, 1988; Squair, 1988). The presence of terra rossa at various stratigraphic levels suggests that the soils probably entered the cavities and caverns via the well developed joint and karst systems in a manner similar to the transport of caymanite. Terra rossa derived from the weathering of limestones in karst areas have been identified in the Pleistocene limestones of South Florida (Perkins, 1977), the Triassic Calcare Rosso Limestone of Italy (Assereto and Folk, 1980), the Lower Carboniferous carbonates of South Wales (Riding and Wright, 1981) and the Upper Paleozoic carbonate strata in southwestern New Mexico (Chafetz, 1982). Conversely, Isphording (1974) suggested that the terra rossa on the Yucatan Peninsula were derived from deposits not indigenous of the region. The origin of the terra rossa in the Bluff Formation, however, is not clear.

H. SYNOPSIS

Superposition of the cavity-filling cements and internal sediments allows the construction of a generalized paragenetic sequence for the diagenetic fabrics (Fig. XI.1). It appears that most of the carbonate cements and speleothems were precipitated in late Pleistocene to recent times. There is no evidence in the rock fabrics suggesting pre-dolomitization calcite cementation or speleothem formation.

The following conditions are concluded for the formation of the cements and sediments:

(1) Calcite cement morphology is not a reliable criterion in the recognition of diagenetic environments because of the complexity of the natural environments. On the Cayman Islands, the abundance of sparry calcite cement decreases from the fresh to brackish to saline water zones. Calcite cementation is favoured in waters having low salinity, low molar Mg^{2+}/Ca^{2+} ratio, and high CO_3^{2-} concentration.

(2) Clear euhedral dolomite was probably precipitated from brackish pore fluids (i) supersaturated with respect to dolomite, (ii) containing a sufficient supply of Ca^{2+}, Mg^{2+}, and CO_3^{2-} ions, and (iii) less saline than the sea water. The sequential dolomite growth indicated by the sharp boundaries between individual zone may have resulted from (i) depletion of ions in the pore fluid and subsequent ion replenishment in a partially closed subenvironment in the aquifer, and (ii) a change in external factors, such as eustatic sea level fluctuation.

(3) The alternating growth of dolomite and calcite probably represents periods of ion depletion leading to formation of another mineral variety. The original pore fluid was probably brackish water because dolomite was also the first cement zone.

(4) Poikilotopic calcite and dolomite were formed by dolomite dissolution and subsequent calcite cementation. This fabric is commonly associated with near surface environments such as joint surfaces. at weathered seams, and at the water table zone.

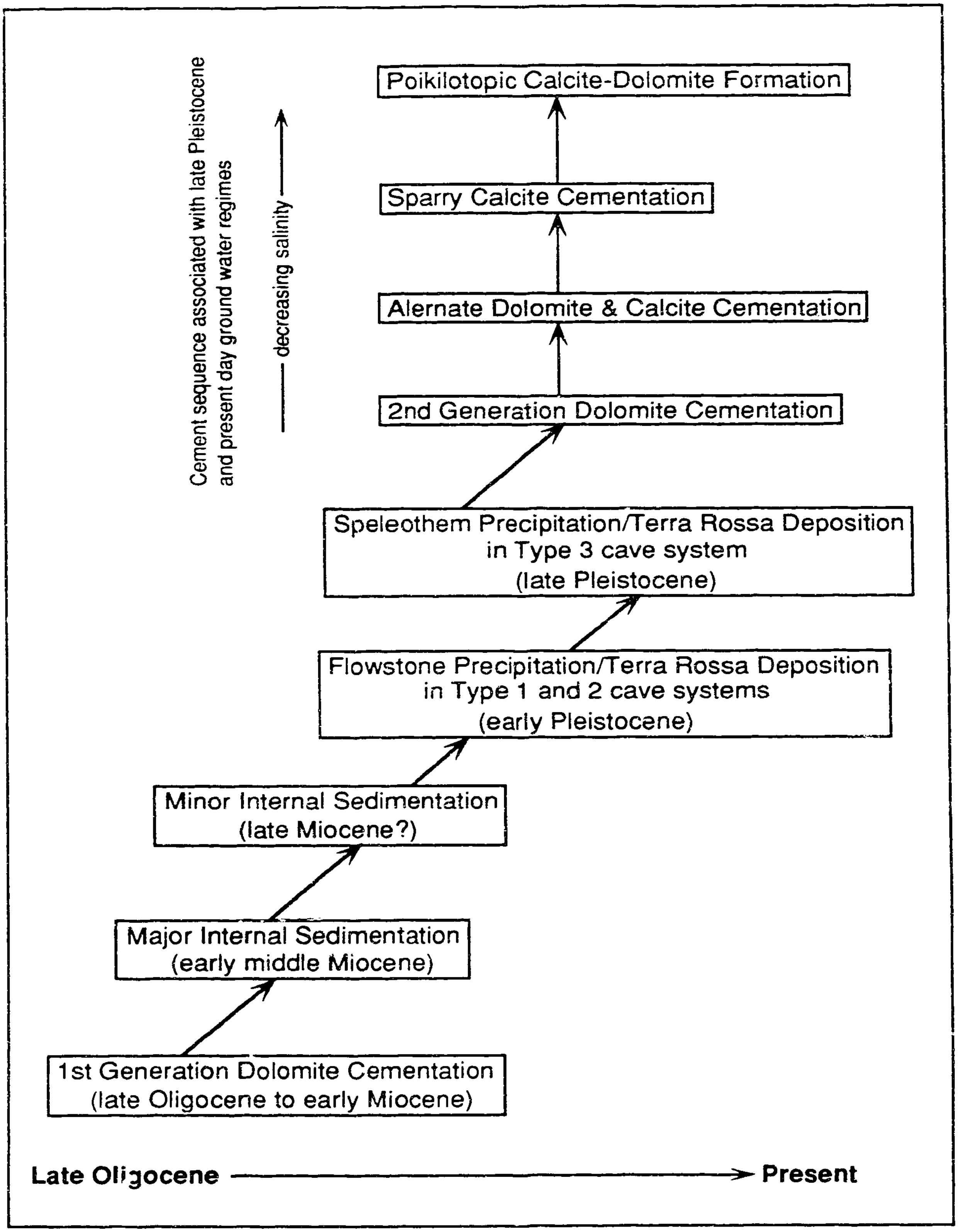


Fig. XI.1 Generalized paragenetic sequence of cavity filling cements and internal

(5) Formation of speleothemic calcite in the vadose zone is controlled by (i) the supply of Ca^{2+} and CO_3^{2-} ions, (ii) evaporation in areas open to the atmosphere, and (iii) micro-organisms such as algae, fungi, and bacteria.

(6) Caymanite sediments were probably derived from calcitic swamp sediments that washed into the underground cave system during periodic storm periods. The overlapping grain size distribution in the laminae indicates that the sediments were transported in steady turbulent flow and deposited when flow competency was reduced, such as the exits to the phreatic tube. The presence of normal marine skeletal components in the skeletal grainstone suggests that the grainstone was marine in origin.

(7) Terra rossa was a late cavity fill that entered the subterranean system in a manner similar to that of the caymanite sedimentation.

XII. CONCLUSIONS

Studies of ancient carbonate sequences rarely, if ever, allow the concomitant investigation of the pore solutions that were responsible for the post-depositional modifications of the rock fabrics. Conversely, diagenetic study of the Oligocene-Miocene Bluff Formation of the Cayman Islands permits the investigation of the source of pore fluids and an assessment of the present day water-rock interactions. The integration of diagenetic fabrics of the rocks with hydrogeological, hydrochemical, and isotopic geochemical data leads to the following conclusions:

(1) The major fresh water lenses, developed in the Bluff Formation, are characterized by (i) unconfined conditions, (ii) small size and thickness, (iii) irregular lens geometry, (iv) thick transition zone, (v) direct hydraulic connection with the surrounding ocean, and (vi) rapid rates of recharge and discharge.

(2) The rocks of the Bluff Formation are characterized by secondary porosity in the form of fossil molds, open joints, fissures, solution channels and caverns formed as a result of preferential dissolution, tectonic fracturing and karst development. The permeable zones (i) provide direct hydraulic connections between ground water and the surrounding ocean, (ii) facilitate the mixing of ground water between individual aquifers, and (iii) create many possible subenvironments such as open, closed, or partially closed conditions within the unconfined aquifer.

(3) It is fundamental to the study of carbonate diagenesis that the hydrochemical zones such as fresh, brackish, and saline water be properly defined on the basis of the water salinity and chemical properties. The ground water present on the Cayman Islands is divided into perched water, fresh water (<600 mg/l Cl^-), brackish water (>600 to <19,000 mg/l Cl^-), Type I saline water (>19,000 mg/l Cl^-, variable chemical compositions) and Type II saline water (>19,000 mg/l Cl^-, almost constant chemical compositions) hydrochemical zone. Similar hydrochemical

zonation can be applied to other studies to avoid confusion among different workers.

(4) Even though all the major fresh water lenses are developed in the Bluff Formation, they show distinct spatial and temporal variation in water chemistry and stable isotopes due to different degrees of external influences and water-rock interactions. This is further complicated by the formation of subenvironments caused by jointing and karsting. Variations in ground water chemistry from area to area and from time to time are common and these variations must be considered in establishing the relationship between carbonate cements and pore fluids.

(5) Ground waters of the Cayman Islands are formed from various combinations of rain water, sea water, ground water of variable chemical constituents from different aquifers, and surface water from swamps and ponds. This means that it is unrealistic to use the generalized mixing model between fresh ground water and sea water in interpreting the actual ground water composition in the aquifers.

(6) Chemical equilibrium calculations indicate that most of the fresh, brackish and saline ground waters on the Cayman Islands are supersaturated with respect to calcite and dolomite, and hence, are capable of precipitating calcite and dolomite. Representative equilibrium calculations in a ground water-carbonate aquifer system like that of the Cayman Islands require consideration of (i) the ion complexing, (ii) field pH and temperature measurements, (iii) tidal fluctuation, (iv) the recharge process, and (v) disturbance due to human activities.

(7) In addition to the evidence from fluctuation in water levels and salinity in response to rainfall, the δ^2H and $\delta^{18}O$ contents of the rain water shows that ground water recharge on the Cayman Islands occurs predominantly during rainfall of high intensity. The isotopic compositions of the fresh and lightly brackish ground water are controlled by evaporation and cluster about a $\Delta\delta^2H/\Delta\delta^{18}O$ slope of 5.91.

Conversely, the dominant factor in controlling the isotopic compositions of the highly brackish ground water is mixing between fresh and saline ground water.

(8) The Bluff Formation has been affected by numerous cycles of sea level change since the deposition of the Cayman Member in Oligocene times. As a result, the rocks of the Bluff Formation have been subjected to various diagenetic regimes in response to the successive cycles of emergence and submergence. The different types of pore fluids would have a profound effect on the diagenetic modification of the rocks because they have variable chemical properties.

(9) Superposition of cavity filling carbonate cements indicate the following paragenetic sequence: (i) clear and zoned dolomite, (ii) alternating zones of dolomite and calcite as laterally continuous bands from crystal to crystal or within a single crystal, (iii) coarse, unzoned and zoned sparry calcite, (iv) partial dissolution of sparry calcite and zoned dolomite cements, and (v) poikilotopic calcite encasing and infilling leached dolomite cements.

(10) Other cavity fills include caymanite, skeletal grainstone, terra rossa and flowstone. The caymanite and skeletal grainstone are completely dolomitized; the terra rossa and flowstone remain as calcium carbonate. Caymanite sedimentation postdated the first generation of dolomite precipitation and predated the second generation dolomite. Terra rossa and flowstone was commonly deposited on top of caymanite in the same cavities.

(11) The distribution of carbonate cements in the present day hydrochemical zones indicates that (i) there is a decreasing quantity of calcite as last-phase cement from the fresh water to brackish water to saline water zone, (ii) the abundance of dolomite as last-phase cement increases from the fresh water to brackish water zone, and (iii) the rocks in the saline water zone are characterized by minor dolomite cement and unfilled cavities.

(12) The relationship between the last phase carbonate cements and present day pore fluids suggests that sparry calcite cement is commonly associated with fresh to lightly brackish ground water and dolomite cement is commonly affiliated with brackish ground water. However, ground waters of similar salinity may have different chemical compositions. Although the waters from the two fresh water lenses have similar salinity, dolomite cement is rare in the Lower Valley lens, whereas dolomite cement is common in the East End lens.

(13) The equilibrium oxygen fractionation relationship between calcite and water is well established, whereas the fractionation relationship between dolomite and water at low temperature is equivocal. However, the $\delta^{18}O$ content of the carbonate minerals provides a useful constraint on the diagenetic conditions. In this study, the relationship between the $\delta^{18}O$ and the salinity of the ground water is established for the direct interpretation of the nature of the diagenetic fluids from which the carbonate minerals precipitated.

(14) Results of the equilibrium oxygen fractionation between the carbonate minerals and the waters at 22-33°C using five different fractionation equations indicate that (i) matrix dolomite and caymanite were formed in water of 25 to >95% sea water salinity, (ii) calcite spar and flowstone were precipitated in fresh to brackish water up to 45% sea water salinity, (iii) poikilotopic calcite was precipitated in water of 65 to >100% sea water salinity, (iv) dolomite cement (in association with poikilotopic calcite) was formed in water of 25 to >90% sea water salinity, and (v) coarse dolomite spar was precipitated in perched, fresh to brackish water up to 25% sea water salinity.

(15) Two paragenetic models can be invoked to satisfy the available petrographic and geochemical data. A relatively simple model (Model I) proposed that pervasive dolomitization of the Bluff Formation was a single event involving sea water as the diagenetic fluid. This study suggests an alternative interpretation of the

geochemical data. The geochemical data (stable oxygen and radioactive strontium isotopes) do not permit a definitive interpretation on the timing of the dolomitization event(s). On the basis of the cumulative information on aragonite dissolution, petrography, isotope geochemistry, and other circumstantial evidence, it is suggested that the Bluff Formation was probably dolomitized by two separate events (Model II). The earlier event dolomitized the Oligocene Cayman Member, whereas the later event dolomitized the Miocene Pedro Castle Member and the internal sediments (caymanite and skeletal grainstone). The second dolomitization event also affected the Cayman Member by resetting the geochemical signatures of previously formed dolomites, probably through increased cation ordering and stoichiometry.

(16) The dolomitizing fluid was probably sea water that was modified to a certain extent by rain water during the early stages of land emergence in late Oligocene (for the Cayman Member) and late Miocene (for the Pedro castle Member) times. Stable oxygen isotopic results (Table VII.5) suggest that the degree of meteoric influence ranged from 0 to 75% fresh water by volume depending on the fractionation equations used and temperatures of the diagenetic fluids.

(17) The fresh water recharge created density gradient in the flow system, and hence, facilitated ground water movement through the sediments/rocks. The flow mechanism, which included downward gravitational flow, downward reflux, upward convection and tidal pumping. is similar to that of the present day. It is also important to note that higher land relief in the past because of lower sea levels would have increased the hydraulic gradient for fluid movement. Furthermore, changes in climatic regimes, such as rainfall intensity and duration and atmospheric temperature, would have a significant impact on the nature of the mixed water diagenetic environment.

(18) Karstification of the Bluff Formation occurred in at least three distinct phases. Phase I karst developed in late Oligocene to early Miocene times when the Oligocene Cayman Member was subaerially exposed due to the major sea level drop in late Oligocene. Phase II karst developed in late Miocene to early Pliocene times as a result of the major marine regression in late Miocene. Phase III karst developed in late Pliocene to late Pleistocene times in response to frequent sea level fluctuations. On the basis of the amount and variety of cave fills, the cave systems in the Bluff Formation can be categorized into four types. The similarity between the joint fills and the cave fills also indicates that joints of different attitudes probably developed in relation to different phases of karstification.

(19) The horizontal orientation of some of the caves and their connection to the wave cut notches suggest that cave development is directly related to past sea level high stands. Most of the caves probably developed at the ground water discharge points where flow velocity is high and mixing between ground water and sea water occurs. The fact that the Phase III karst developed after the Bluff Formation was completely dolomitized attests that lithology is not the dominant factor in controlling the degree of karstification. The extensive network of cave passages formed during the Phase III karstification might be related to intense jointing prior to karstification. Furthermore, the high density of speleothems in some of the caves developed during Phase III karstification suggests that past climatic regimes were probably much wetter than those today.

(20) Chemical equilibrium of water-rock reactions in the joint and karst controlled shallow carbonate aquifers are difficult to achieve; therefore, kinetic concepts are needed to understand the diagenetic processes that are operative in such a hydrogeological setting. In addition, cement morphology is not a reliable criterion in the recognition of diagenetic environments because of the complexity of the natural environments.

(21) The following conditions are suggested for the formation of the diagenetic fabrics that are responsible for the reduction of the porosity of the Bluff Formation.

(i) Calcite cementation took place in waters with low salinity, low molar Mg^{2+}/Ca^{2+} ratio, and high CO_3^{2-} concentration.

(ii) Clear euhedral dolomite was precipitated from pore fluids that contained a sufficient supply of Ca^{2+}, Mg^{2+}, and CO_3^{2-} ions and were supersaturated with respect to dolomite.

(iii) The alternating growth of dolomite and calcite was the probable result of periodic ion depletion which led to the formation of another mineral type. The depletion of ions might be indicative of partially closed subenvironments in the aquifers or a change of diagenetic environment such as eustatic sea level fluctuation.

(iv) Poikilotopic calcite and dolomite were formed by dolomite dissolution and subsequent calcite cementation. This fabric is commonly associated with near surface environments such as along joint surfaces, at weathered seams, and at the water table zone.

(v) Precipitation of speleothemic calcite in the vadose zone is controlled by the supply of Ca^{2+} and CO_3^{2-} ions and activities of micro-organisms such as algae, fungi, and bacteria.

(vi) Caymanite sediments were probably derived from calcitic swamp sediments that washed into the underground cave system during periodic storm periods. The overlapping grain size distribution in the laminae indicates that the sediments were transported in steady turbulent flow and deposited when flow competency was reduced, such as exits to the phreatic tube. The skeletal grainstone of marine origin probably entered the cavities and caverns during early stages of marine transgression. Terra rossa, which was a late cavity fill, probably entered the subterranean system in a mode similar to that of the caymanite sedimentation.

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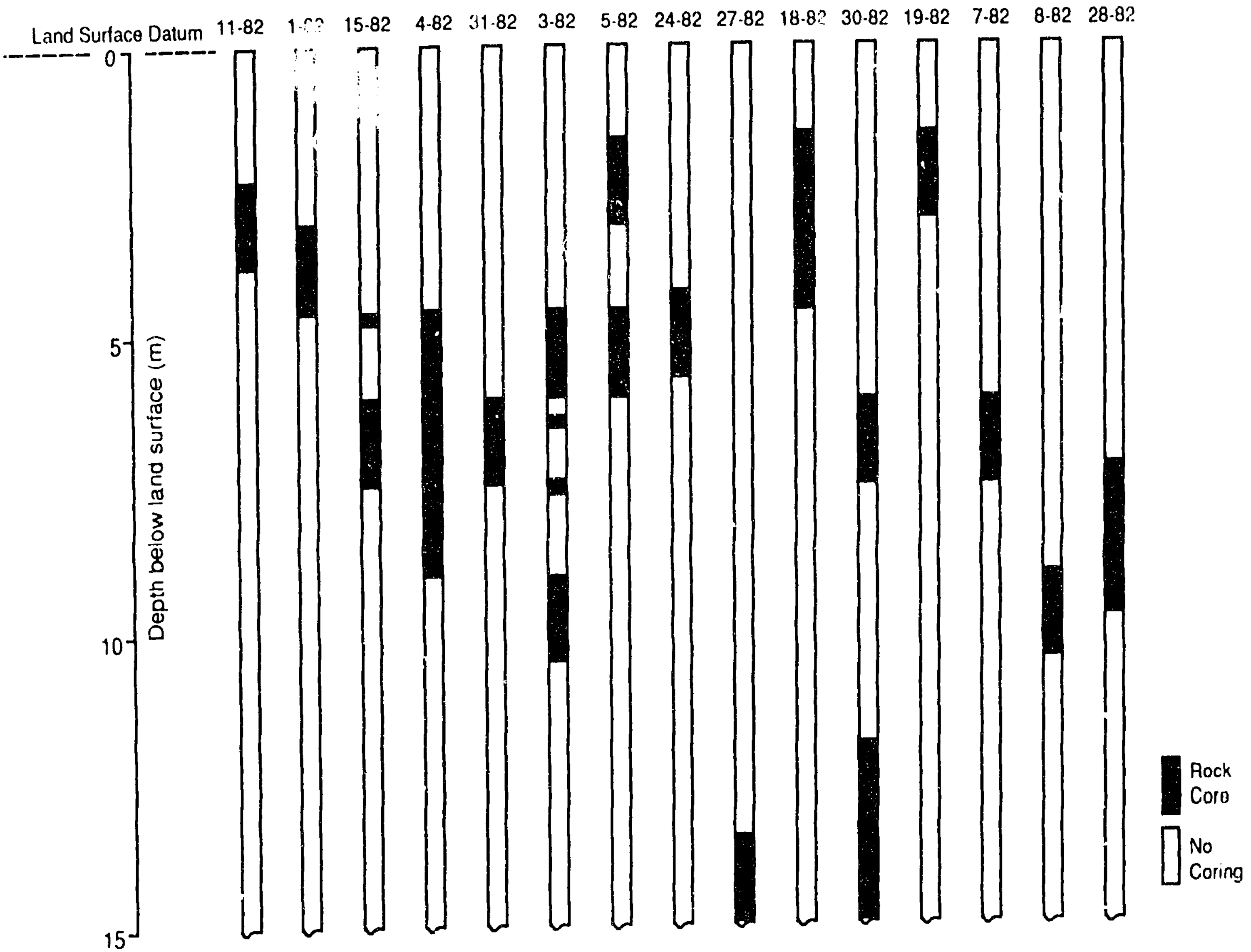
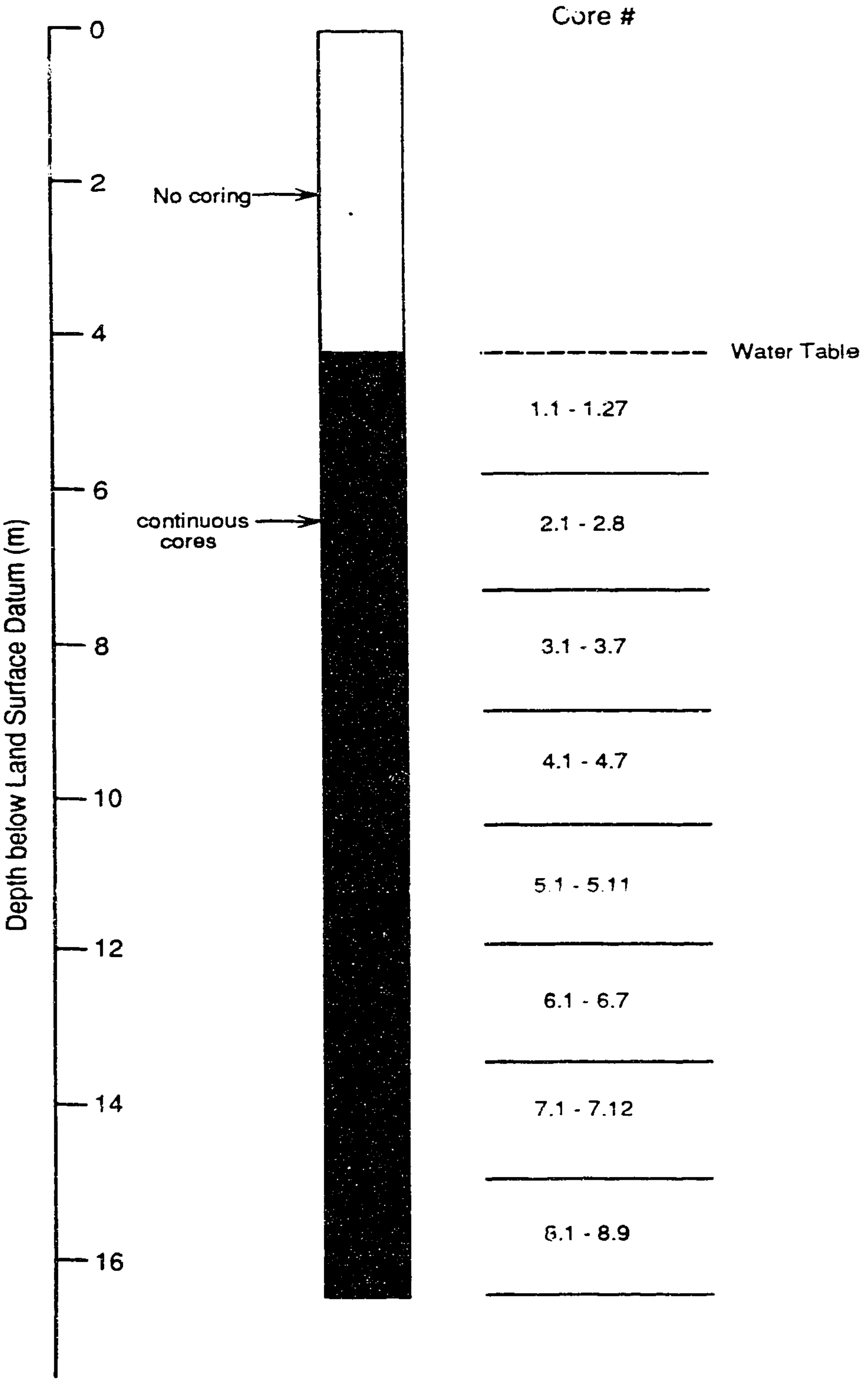
XIV. APPENDICES

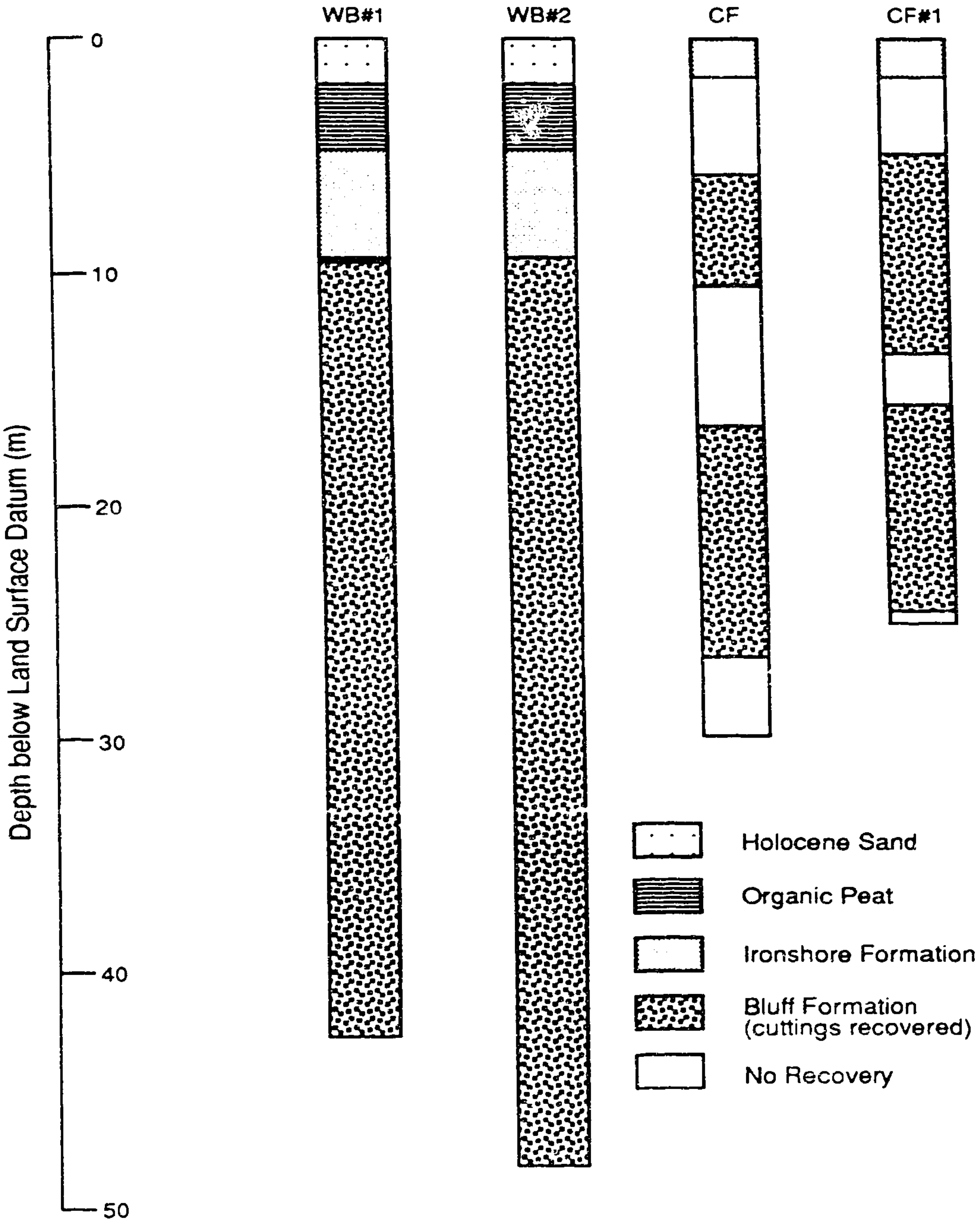
Schematic logs of wells showing rock cores and cuttings of the Bluff Formation used in this study.



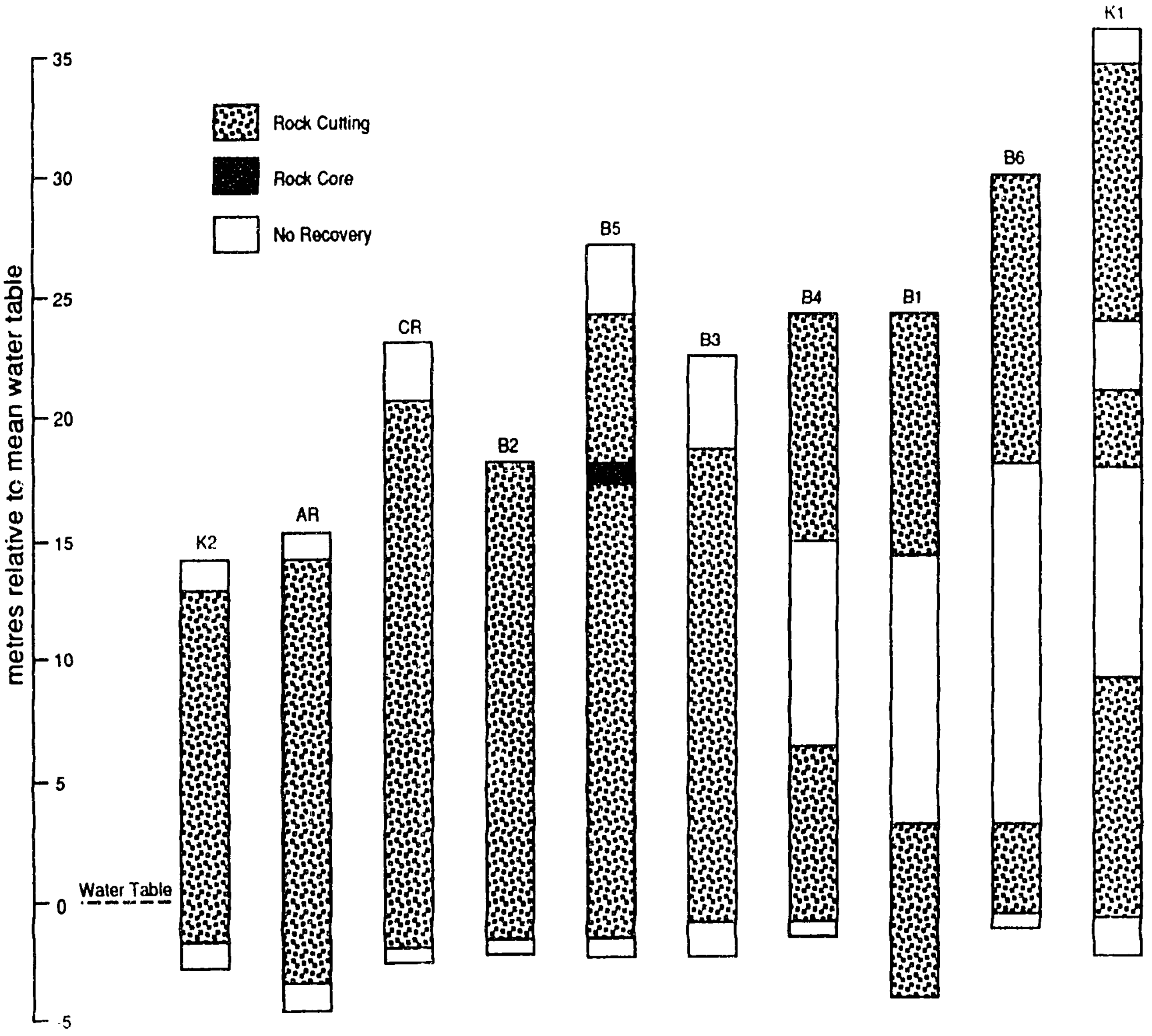
Appendix 1A. Schematic logs of Lower Valley wells showing depth of rock cores recovered. Well location shown on Fig. VI.1. Total depth of wells not known.



Appendix 1B. Schematic log of well 3-84 at East End well field showing depth of cores recovered and core numbers. Well location shown on Fig. II.4.



Appendix 1C. Schematic logs of deep wells located on the western part of Grand Cayman. Well location shown on Fig. III.2.



Appendix 1D. Schematic logs of Cayman Brac wells showing depth of cuttings and core recovered. Well location shown on Fig. VI.2

At pH <~5, the k_1 term dominates the rate equation. At higher pH when P_{CO_2} >0.1 atm, the k_2 term becomes dominant. At high pH when PCO_2 <0.1 atm, the k_3 term dominates.

Using the rate model of Plummer *et al.* (1978, 1979), Dreybrodt (1981a) calculated that the saturation length is on the order of a few metres. Although this result showed that the dissolution rate increases substantially from that of Weyl (1958), cave passages of 1 m in diameter still require a few million years to develop (Dreybrodt, 1981a). Some caves, developed in the Oligocene Cayman Member of the Bluff Formation (along the 6 m high wave cut notch, Fig. X.3), were clearly formed at the time of the 125,000 year sea level high stand. Thus, the time required for large cave development is much less than that deduced from the kinetic models. Furthermore, the kinetic model is not in agreement with the sea level high stand of the order of a few thousand years during the Pleistocene epoch (Harmon *et al.*, 1981; Aharon, 1983; Matthews, 1984).

The net rate of dissolution for dolomite (Rd) was defined by Busenberg and Plummer (1982) as:

$$Rd = k_1[H^+]^n + k_2[H_2CO_3]^n + k_3[H_2O]^n - k_4[HCO_3^-]^n \text{ ....(2)}$$

where n is 0.5 at temperatures below 45°C. The forward-reaction mechanisms comprise the reaction of the $CaCO_3$ component and then the $MgCO_3$ component of dolomite with the bulk solution H^+, H_2CO_3, and H_2O.

The actual dissolution rate of carbonate minerals is difficult to determine from laboratory experiments because of the presence of impurities and micro-organisms in natural conditions (Berner, 1978). If an impurity contains a chemical constituent that is present in the reactant (e.g. Ca^{2+} in $CaCO_3$), the solubility of the reactant could increase due to increase in ionic strength, or could decrease due to the common ion effect (Freeze and Cherry, 1979; Plummer *et al.*, 1979). Furthermore, Plummer *et al.* (1979) and Morse (1983, 1986) noted that trace impurities, such as PO_4^{3-} and organics, cause large changes in dissolution rates without significantly altering the thermodynamic properties of the system. These adsorbed impurities commonly act as strong inhibitors of crystal dissolution

(Berner, 1978; Morse, 1983, 1986). Similar inhibitors may be present in the natural waters on the Cayman Islands and exert similar influence on the dissolution of the carbonate minerals.

D. BIOLOGICAL EFFECTS ON CARBONATE DISSOLUTION

There is considerable information concerning the role that micro-organisms play in carbonate diagenesis (e.g. Schroeder, 1972; Folk *et al.*, 1973, 1985; Schneider, 1977; Krumbein, 1979; Chafetz and Folk, 1984; Viles and Spencer, 1986; Jones, 1987, 1988, in press; Jones and Pemberton, 1987a, 1987b; Pleydell, 1987; Smith, 1987; Squair, 1988). Phytokarst, characterized by a black coating on jagged pinnacles, is formed by boring filamentous algae (Folk *et al.*, 1973; Viles and Spencer, 1986; Jones, in press). Detailed studies of the phytokarst on Grand Cayman suggest that the biological processes operative on the rocks is governed, in part, by the hardness of the substrate (Jones, in press).

Extensive dissolution of spar calcite mediated by fungi was experimentally demonstrated by Jones and Pemberton (1987a, 1987b). More importantly, Jones and Pemberton (1987a) suggested that under the mediation of fungi, dissolution of calcite occurs via surface reaction controlled kinetic processes without the intervention of vast quantities of fluid. Jones (1988) noted that root borings, in addition to being a source of carbon dioxide through plant-root respiration, also provide avenues for water flow and sites where micro-organisms thrive.

Most studies of the role of micro-organisms in carbonate diagenesis on Grand Cayman are related to the vadose (e.g. Folk *et al.*, 1973; Jones, 1987, 1988, in press; Viles and Spencer, 1986) and intertidal settings (Jones and Goodbody, 1982, 1984; Viles and Spencer, 1986). The effect of micro-organisms on carbonate diagenesis in the phreatic zone is not known. Perhaps micro-organisms can enhance or counteract the effect of chemical inhibitors on carbonate minerals dissolution. Detailed investigation in this aspect is required to understand the role micro-organisms play in the phreatic zone.

E. MECHANISM OF KARSTIFICATION

On the Cayman Islands, some caves were developed after host rock dolomitization (Type 3 and 4 cave system; Jones and Smith, 1988) regardless of the differences in defining the timing of dolomitization events suggested by Paragenetic Model I (Jones, 1989a; Pleydell *et al.*, in preparation) or Model II (this study). Busenberg and Plummer (1982) noted that water-clear dolomite of hydrothermal origin dissolves at slower rates than cloudy dolomite crystals of sedimentary origin. More importantly, Busenberg and Plummer (1982) demonstrated that at pH values greater than 6.0, it takes weeks or months to dissolve detectable amount of dolomite, although calcite dissolved readily under similar conditions. Using Middle Ordovician rock samples from central Pennsylvanian, Rauch and White (1977) also concluded that dolostones dissolve at much slower rates than limestones in laboratory-controlled experiments.

The significant differences in the dissolution rates between calcite and dolomite may be one of the controlling factors in explaining the scarcity on the Cayman Islands of large-scale tropical karst features that are common in other carbonate terrains in the Caribbean region (e.g. Jennings, 1971; Sweeting, 1972; Monroe, 1976; Squair, 1988). However, other important parameters such as joint and fracture density, rainfall quantity and intensity, and topographic relief would have significant impact on the hydraulic gradient of the ground water system. The fact that the largest caves on Grand Cayman and Cayman Brac formed after dolomitization of the Bluff Formation (Type 3 and 4 caves; Jones and Smith, 1988) suggests that climatic conditions and density and openness of joints probably were more dominant in controlling the extent of karsting than was lithology.

Mixing of fresh ground water and sea water (Hanshaw *et al.*, 1971; Badiozamani, 1973; Plummer, 1975; Bogli, 1980; Palmer, 1984; Back *et al.*, 1986) and of carbonate waters of different compositions (Wigley and Plummer, 1976) generates unsaturated solutions capable of dissolving calcium carbonate. Incorporating the mixed water dissolution concept with the kinetic model of Plummer *et al.* (1978, 1979), Dreybrodt

(1981b) calculated that the dissolution rate of calcite is in the order of 0.01 mm/year. Thus, the time required for cave development (a few metres in diameter) in limestone sequences is in the order of thousands of years. Dreybrodt's (1981b) data supports the effectiveness of carbonate dissolution of the mixed water model. However, Ford (1988) argued that such mixing is physically unfeasible unless the rock mass has very high effective porosity.

In the study of karst development on Grand Cayman, Jones and Smith (1988) suggested that mixing corrosion, which occurs in the mixing zone, was probably responsible for the development of major caves on the island. A similar mechanism was proposed for the karst features formed on the Bahamas (Palmer, 1984; Mylroie, 1984), and the Yucatan Peninsula (Hanshaw and Back, 1980; Back *et al.*, 1986).

Combining the geochemical mixing theory with the hydrodynamics of fresh and sea water mixing zones in a coupled reaction-transport model, Sanford and Konikow (1989) concluded that significant porosity develops when a large flux of fresh water is present. However, on small islands, mixing corrosion is less effective because of low fluid flow (Sanford and Konikow, 1989). They also noted that dissolution occurs primarily on the fresher portions of the mixing zone - one near the toe of the mixing zone, and one near the top and closer to the coast where velocities are greater. In contrast, based on field observations along the Caribbean coast of the Yucatan Peninsula and petrographic study, Stoessell *et al.* (1989) showed that aragonite dissolves preferentially throughout the modern mixing zone, particularly in the saline portion. This conclusion is inconsistent with the modelling results of Sanford and Konikow (1989). Using water samples collected from the submarine caves of the Yucatan Peninsula, Stoessell *et al.* (1989) also showed that the coastal mixing zone is undersaturated with respect to calcite up to 90% sea water. Therefore, it appears that carbonate dissolution can occur over a wide range of mixing composition. The controlling factors are probably the ground water flow hydraulics and flow regime in the aquifer.

On the Cayman Islands, there is no geological boundary to define the base of the mixing zone; therefore, according to Sanford and Konikows' (1989) study, porosity enhancement is most favourable near the coast at the discharge zone where flow rate is high. High flow rate at the discharge zone has also been suggested by Chidley and Lloyd (1977b). This appears to be the situation on the Cayman Islands, where cave development tends to be locally extensive along the coast. Therefore, the level of karstification on the Bluff Formation of Cayman Islands is predominantly controlled by water table/sea level elevation, whereas the cave geometry is controlled by jointing and climatic conditions.

F. SYNOPSIS

Karstification of the Bluff Formation occurred in at least three distinct phases. As a result four different cave systems were formed. Phase I karst developed in late Oligocene to early Miocene times when the Oligocene Cayman Member was subaerially exposed in relation to the major sea level drop in late Oligocene. In association with the Phase I karstification is the Type 1 cave system which is characterized by dolomitized colour-banded caymanite fill.

Phase II karst developed in late Miocene to early Pliocene times as a result of the major marine regression in late Miocene. Type 2 cave systems, which have no caymanite fill but abundant flowstone deposits, might form during Phase II karstification.

Phase III karst developed in late Pliocene to late Pleistocene times, particularly in the latter period. Type 3 and 4 cave systems, characterized by extensive networks of cave passages and assorted forms of speleothem (in type 3 caves), formed during phase III karstification after the Bluff Formation was completely dolomitized. The extensive cave network is probably related to extensive joint development prior to karstification. suggesting that the presence of joint systems and climatic regimes are the dominant controlling factors rather than the lithology.

The horizontal orientation of some of the caves and their connection to the wave cut notches, particularly Type 3 and 4, suggest that cave development is directly related to past sea level high stands. The concentration of caves along the coastlines further suggests that the cave development probably occurred at the ground water discharge points where flow velocity is high and mixing between ground water and sea water occurs.

XI. DIAGENETIC INTERPRETATION OF THE BLUFF FORMATION III: POROSITY DESTRUCTION

Porosity destruction in the rocks of the Bluff Formation includes processes of (1) calcite cementation, (2) dolomite cementation, (3) alternating dolomite and calcite cementation, (4) poikilotopic calcite-dolomite formation, (5) speleothemic calcite precipitation, (6) internal sedimentation, and (7) terra rossa deposition. The aim of this study is to examine the fluid conditions in which these diagenetic fabrics formed. Chemical kinetics are discussed where appropriate because they control the cement morphology.

A. CALCITE CEMENTATION

Precipitation of calcium carbonate may result from evaporation (e.g. Moore, 1973), degassing of CO_2 (e.g. Hanor, 1978), temperature change (e.g. Langmuir, 1971), and mixing of chemically dissimilar waters (e.g. Runnells, 1969). Many studies on carbonate diagenesis have used cement type and texture for the recognition of diagenetic environments (e.g. Bricker, 1971; Bathurst, 1975; Folk, 1974; Folk and Land, 1975; Longman, 1980; Flugel, 1982; James and Choquette, 1983, 1984; Harris *et al.*, 1985). Chafetz *et al.* (1985) noted, however, that the relationship between cement morphology and fluid composition is difficult to establish. For example, low magnesian calcite is known to form in meteoric waters (e.g. Folk and Land, 1975; James and Choquette, 1984), as well as in deep sea marine environment (Schlager and James, 1978). Likewise the morphology of high magnesian calcite can range from micritic, to fibrous, to bladed, to sparry (Pierson and Shinn, 1985; Aissaoui, 1988). The inherent difficulties in monitoring precipitation reactions, the complexities of fluid composition in natural environments and the biological factors complicate the understanding of mechanisms of carbonate precipitation.

Kinetics of Mineral Precipitation

Mineral precipitation from aqueous solution involves two processes, nucleation and crystal growth. Nucleation refers to the initial formation of a new phase, where there is a free energy barrier to the formation to this phase (Jackson, 1979). The ease of nucleation increases with increasing levels of supersaturation (Nielsen, 1964; Berner, 1980). At a low level of supersaturation, crystals grow on a limited number of nuclei and lead to the development of large crystals (Berner, 1980, 1981).

Crystal growth involves the transportation of ions to and from the surface of a crystal and chemical reactions occurring at the crystal surface (Berner, 1980, 1981; Morse, 1983). The former process (transport controlled) is a function of hydrodynamic conditions whereas the latter process (surface reaction controlled) is governed by the built-in steps and kinks on the crystal's surface. Blockage of these growth sites by foreign ions can greatly retard the rate of crystal growth.

By adding well defined seed crystals to a stable supersaturated solution, Reddy and Nancollas (1971) and Nancollas and Reddy (1971) demonstrated that the rate of calcite precipitation is a function of the saturation state of the solution with respect to calcite. The calcite dissolution rate model of Plummer *et al.* (1978, 1979; equation 1) is also applicable in describing the kinetics of calcite precipitation. According to Plummer *et al.* (1978, 1979), CO_2 is outgassed from solution during crystal growth. Dreybrodt (1980) also concluded that the production of CO_2 and its diffusion away from the surface is the rate-determining step in calcite precipitation. Therefore, mineral precipitation is controlled by the hydrodynamic state and the saturation rate of the solution. Conversely, crystal morphology is a function of the degree of supersaturation of the solution and the presence of foreign ions adsorbed on the crystal surface.

Controlling Parameters

The relationship between the morphologic and fabric criteria and the environment of cementation has been investigated by Thortenson *et al.* (1972), Badiozamani *et al.* (1977), Reddy (1977), Ricketts (1980), Cailleau *et al.* (1982), Walter (1986) and Burton and Walter (1987). Although the experiments employed either outgassing of CO_2 from bicarbonate solution or seeding in order to speed up the precipitation process, the results suggest that calcite cementation in natural environments is easily achieved provided conditions are favourable. In those experiments, significant cementation was commonly obtained in a short time span (a few days to a few months). Rapid rates of calcite crystallization were also demonstrated by Jones and Kahle (1986) by mixing Na_2CO_3 with $Ca(NO_3)_2$ to produce dendritic crystals in less than 2 minutes.

The following conclusions can be drawn from experimental studies (Thortenson *et al.*, 1972; Badiozamani *et al.*, 1977; Reddy, 1977; Ricketts, 1980; Cailleau *et al.*, 1982; Walter, 1986; Burton and Walter, 1987):

(1) Cement in the vadose zone is commonly formed of micron-sized crystals, whereas cement in the phreatic zone is comprised of relatively coarse crystals (Thortenson *et al.*, 1972).

(2) Cement formed in the vadose zone is characterized by void lining and grain contact behaviour (Thortenson *et al.*, 1972). Void lining cement, however, can also form in the phreatic zone (Badiozamani *et al.*, 1977).

(3) Small, needle type crystals of aragonite form in solutions containing Mg^{2+} (Badiozamani *et al.*, 1977), particularly when Mg^{2+}/Ca^{2+} ratios are greater than 2.0 (Ricketts, 1980; Cailleau *et al.*, 1982).

(4) Crystal size varies directly with temperature and NaCl content, but inversely with the concentration of the solution (Badiozamani *et al.*, 1977).

(5) During crystal growth, the degree of supersaturation decreases resulting in the formation of different cement types (Cailleau *et al.*, 1982).

(6) Crystal morphology is generally a function of the temperature and the supersaturation state of the solutions, crystal structure, and substrate defects (Badiozamani *et al.*, 1977; Ricketts, 1980; Cailleau *et al.*, 1982).

(7) Foreign ions and organic matter may lower the rate of crystal growth and cause modifications in crystal size and morphology. For example, PO_4^{3-} adsorbed on the crystal faces inhibits crystal growth rate (Reddy, 1977), whereas Mg^{2+} forms complexes with HCO_3^- and CO_3^{2-} ions (Cailleau *et al.*, 1982).

(8) High SO_4^{2-}, low PO_4^{3-} solutions favour precipitation of aragonite; low SO_4^{2-}, high PO_4^{3-} solutions favour precipitation of calcite (Walter, 1986).

(9) Precipitation rates of calcite decrease with increase in Mg^{2+} and SO_4^{2-} concentrations in solutions (Walter, 1986).

(10) Low temperature favours precipitation of low-magnesian calcite (Burton and Walter, 1987).

It is apparent that in a relatively stable diagenetic environment of uniform ground water temperature (seasonal variation less than 5°C) like that of the Cayman Islands, salinity and the presence of Mg^{2+} are the major factors controlling crystal morphology. Folk (1974, 1978) argued that the incorporation of the small Mg^{2+} ions in the calcite crystal lattice inhibits crystal growth on c-axis faces, and hence, favours precipitation of acicular crystal form. Folk and Land (1975) further suggested that sparry calcite precipitation occurs in meteoric waters or dilute subsurface waters with Mg/Ca ratios ranging from 1:1 to 1:10. Lahann (1978), however, suggested that it is the difficulty in dewatering the substituted Mg^{2+} that determines the calcite growth rate. The Mg^{2+} ions also form complexes with HCO_3^- and CO_3^{2-}, reducing the availability of free carbonate ions for crystal growth (Cailleau *et al.*, 1982). Furthermore, Lahann (1978) proposed that crystal morphology is controlled by the Ca^{2+}/CO_3^{2-} ratio of the solution in such a way that equant calcite crystals precipitate from water with a low Ca^{2+}/CO_3^{2-} ratio. Given and Wilkinson (1985) also suggested that the amount of CO_3^{2-} at the growth sites is the principal parameter in determining crystal morphology, composition, and mineralogy of calcium carbonate cement.

Calcification of algae, fungi and bacteria is common in the Bluff Formation (Jones and Kahle, 1986; Jones, 1987, 1988; Pleydell, 1987; Squair, 1988). The role of micro-organisms in mediating the growth of sparry calcite is not known; however, the ease of calcification of these micro-flora suggests that they may play an important role in controlling the kinetics of surface nucleation for crystal growth.

Timing of Calcite Cementation in the Bluff Formation

Petrographic studies of rock samples collected from all hydrochemical zones indicate that calcite is commonly the last phase of cementation. Sparry calcite was precipitated (1) after clear dolomite cement (Plates VI.3A-3E), (2) after caymanite (Plate VI.6F), (3) after flowstone (Fig. 2A in Jones and Kahle, 1985), and (4) as intercrystalline cement (Plate VI.1E). The relationship between the occurrence of calcite cement and the present day ground water regime (Figs. VI.4, 7) suggests that most sparry calcite is a recent cement and it is related to the present day hydrochemical conditions.

Conditions of Calcite Cementation in the Bluff Formation

Speciation calculations for ground waters from the Cayman Islands indicate that almost all the fresh to saline waters are supersaturated with respect to calcite (Tables IV.5-8). Thus, according to thermodynamic considerations, calcite precipitation should be common throughout the full spectrum of hydrochemical zones. Stable oxygen isotopic data, however, suggest that calcite spar was formed in fresh to brackish water with up to 45% sea water salinity (Table VII.6, Fig. VII.3B).

Sparry calcite is (1) the most common last phase cement in the rocks collected from the present day fresh and lightly brackish water zone (Figs. VI.3-5), and (2) more common in the rocks of the Lower Valley lens than in the East End lens (Figs. VI.3-5). The decrease in the abundance of late phase sparry calcite with increasing salinity (Figs. VI.4, 7) is in agreement with the general premise that Mg^{2+} and CO_3^{2-} are the controlling factors. As salinity of the ground water increases, Mg^{2+} ion generally increases whereas CO_3^{2-} ion decreases (cf. Tables III.3-8). Both trends would lead to less favourable conditions for calcite growth (Folk, 1974, 1978; Lahann, 1978; Given and Wilkinson, 1985). Furthermore, the hydrodynamic state of the ground water in the saline zone is slow relative to the dynamic shallow zone (fresh to brackish water); therefore, the effectiveness of CO_2 diffusion from the reaction sites is also reduced. The number of foreign ions that might act as inhibitors to crystal growth also increases with increasing salinity towards the sea water composition (Morse, 1986). If so, the rate of calcite precipitation also decreases in the high salinity zone.

Fresh ground water in the Lower Valley lens has a significantly lower Mg^{2+} content, with molar Mg/Ca ratios generally less than 0.5 (Tables III.4, IV.5). The more common occurrence of sparry calcite in the fresh water zone of the Lower Valley than in the East End lens is consistent with the differences in chemical properties between the two lenses. Equilibrium speciation calculations for the fresh water in the Lower Valley lens shows that most of the water samples are supersaturated with respect to calcite, whereas fewer than half of these samples (out of 31) are supersaturated with respect to dolomite (Table IV.5). Conversely, fresh ground water from the East End lens is supersaturated with respect to calcite and dolomite for all the samples analysed (Table IV.6). Therefore, calcite is the dominant carbonate mineral precipitating in the fresh water and lightly brackish water zones, particularly in the Lower Valley ground water where the Mg/Ca ratio is low (Figs.VI.3-5). The chemical characteristics of the ground water seem to be in agreement with the petrographic evidence and stable isotopic interpretation. Zoned sparry calcite marked by thin laminae of insoluble residues (Plate VI.3E) indicates a hiatus between each additional zone of calcite growth. The cessation of calcite growth was probably due to depletion of Ca^{2+} and CO_3^{2-} in the pore fluids.

B. DOLOMITE CEMENTATION

Dolomite does not precipitate at temperature less than 100°C (Lippman, 1973; Deelman, 1975; Land, 1980); this suggests that dolomite formation is governed by chemical kinetics. Unfortunately, dolomite solution equilibrium is not adequately known (Hsu, 1963; Hardie, 1987). Furthermore, geochemical techniques cannot resolve the controversy concerning the conditions appropriate for dolomite precipitation in low temperature sedimentary environments (Land, 1980, 1985; Morrow, 1982a, 1982b; Machel and Mountjoy, 1986; Hardie, 1987).

Kinetics of Dolomite Precipitation

Berner (1978, 1981) suggests that the precipitation of minerals with low solubility, such as calcite and dolomite, is governed by surface reaction. It can be argued, therefore, that chemical reactions occurring on crystal surfaces control the precipitation of dolomite. Unlike dissolution kinetics of calcite (equation 1), which also applicable in describing calcite precipitation (Plummer *et al.*, 1978, 1979), the dissolution kinetics of dolomite (equation 2) do not fully describe the backward-reaction mechanisms (Busenberg and Plummer, 1982). Although the backward reactions involve positively charged surface sites with adsorbed HCO_3^-, Busenberg and Plummer (1982) suggested that the reversible dolomite-solution equilibrium probably takes an extremely long time to achieve at temperatures less than 45°C.

The high energy required to dehydrate the very strongly bonded water molecules from the Mg^{2+} prior to incorporation into the crystal structure is probably the main factor controlling dolomite formation (Lippman, 1973; Hanshaw and Back, 1979; Morrow, 1982a). Deelman (1975) argued that dolomite is formed by successive addition of $CaCO_3$ and $MgCO_3$ layers. This unique arrangement requires a considerable change in energy content as each $CaCO_3$ layer is succeeded by a $MgCO_3$ sheet (Deelman, 1975).

Timing of Dolomite Cementation in the Bluff Formation

At least two generations of clear dolomite cement are present. The first generation is commonly the first phase void-lining cement emplaced prior to the influx of internal sediments (Plate VI.6F); the second generation of clear dolomite cement was precipitated on top of the sediments (Plate VI.6E). It is apparent the first generation probably formed during late Oligocene to early Miocene times prior to the deposition of the caymanite sediments in early middle Miocene times. Jones and Hunter (1989) noted that dolomite cement occurs in the Oligocene Cayman Member but not the Miocene Pedro Castle Member. In cavities where only one generation of dolomite cement is present (Plates VI.3B, 3C), it is difficult to determine the timing of the dolomite cementation.

Dolomite commonly occurs as a void-lining cement emplaced prior to the precipitation of sparry calcite in most cavities (Plates VI.3B, 3C). Furthermore, petrographic studies suggest that dolomite cement is the most common last-cement phase in the brackish water zone (Figs. VI.5-7). This indicates that some of the dolomite cements are probably associated with the present-day hydrochemical regime.

Conditions of Dolomite Cementation in the Bluff Formation

Clear euhedral dolomite is a common void-lining cement in the Bluff Formation. Dolomite cement is also common in many carbonate formations, for example, the Pleistocene Hope Gate Formation of Jamaica (Land, 1973), the Pliocene Seroe Domi Formation of Bonaire (Sibley, 1980), the Pleistocene Great Abaco carbonate of Bahamas (Kaldi and Gilman, 1982), the Pleistocene Yucatecan Formation of Yucatan Peninsula (Ward and Halley, 1985) and the Pleistocene limestones of Barbados (Humphrey, 1988). It has been interpreted that all of the dolomite cements in these carbonate sequences have formed in mixed meteoric-marine environments.

The morphology of the clear euhedral dolomite cements found in cavities of the Bluff Formation (Plates VI.2A-2D, VI.6B, 6F) resembles that described in other carbonate sequences in the Caribbean region: therefore, the dolomite cement probably formed in mixed water environments. Folk and Land (1975) and Jones *et al.* (1984) also suggested that the dolomite cement in the Cayman examples was formed in a mixed meteoric-sea water diagenetic realm. The clarity and coarse texture of the dolomite cement in the Bluff Formation suggests that the pore fluids were supersaturated with respect to dolomite, were of low salinity, and contained an adequate supply of Ca^{2+}, Mg^{2+} and CO_3^{2-} ions.

Inclusions concentrated in the cores of dolomite crystals are common in the Bluff Formation, giving the dolomite crystals a cloudy centre and clear rims appearance (Plates VI.1A, 1B). This feature is particularly prominent in the coarser, euhedral crystals scattered in the microcrystalline dolomite groundmass (Plate VI.1B). The inclusions probably consist of calcite, similar to dolomites of other carbonate sequences (Murray, 1964; Folk and Siedlecka, 1974; Sibley, 1980, 1982; Ward and Halley, 1985; Cander *et al.*, 1988). Folk and Siedlecka (1974) studied the late Paleozoic rocks from Bear Islands of Svalbard and suggested that the clear rim was precipitated from a more dilute solution which was undersaturated with respect to calcite. Similarly, petrographic analyses of the Pliocene Seroe Domi dolomites on Bonaire led Sibley (1980) to suggest that the cloudy-centred clear-rimmed fabric is due to evolution of pore fluids during dolomitization, the evolution ranging from a state of near calcite saturation (i.e. formation of cloudy core) to a state of calcite undersaturation (i.e. formation of clear rim). Similar diagenetic conditions were probably responsible for the dolomite fabrics of the Bluff Formation. The clear, euhedral dolomite (Plate VI.1A) probably formed under the same cond[illegible] the clear rim. In this connection, the cloudy-centre, clear-rimmed dolomites may be formed by crystal growth on previously formed dolomites.

Thermodynamic considerations indicate that most waters from all of the hydrochemical zones in the dolostone aquifer of the Bluff Formation are supersaturated with respect to dolomite (Tables IV.5-8). Therefore, theoretically, the ground waters are capable of precipitating dolomite in all zones. Furthermore, the Mg/Ca ratios, which are inconsistent with the ionic strength of the solutions (Table IV.9), suggest that precipitation and/or dissolution of carbonate minerals may be occurring in the dolostone aquifer. Folk and Land (1975) suggested that solutions of high salinity induce rapid crystallization, and therefore, form microcrystalline textures. Sibley (1980) also noted that dolomite crystals are difficult to nucleate, and hence, are composed of few crystals. Although it is open to debate whether or not the mixed fresh-sea water zone is the site for massive dolomitization, it is generally agreed that dolomite cementation occurs in the mixing zone (Land, 1983a, 1985; Machel and Mountjoy, 1986; Hardie, 1987). In the Bluff Formation, there is a decrease in the content of dolomite cement from the slightly brackish to saline water zones (Figs. VI.4, 7). It is, therefore, suggested that dolomite cement in the Bluff Formation probably formed in the brackish water (mixing) zone. Stable isotopic values also indicate that the diagenetic fluids for dolomite cementation are brackish (25% sea water salinity) to saline water (Table VII.6, Fig.VII.3B).

The sharp boundaries in the zoned dolomites (Plates VI.2C, 2D, 3C) probably indicate sequential crystal growth without intervening periods of dissolution. Detailed analysis of syntaxial overgrowths on dolomite crystals that line the walls of near-surface vadose cavities in dolostones of the Bluff Formation led Jones (1989b) to suggest that the overgrowths were formed by sequentially coalescing smaller crystals. Jones (1989b) further suggested that the overgrowths were probably formed from thin films of supersaturated fluid that left from evaporation. A similar sequential crystal growth phenomenon probably occurred in the phreatic zone although in a slightly different manner. When the ions in the pore fluids were depleted by the crystal growth, the pore solutions changed from supersaturation to saturation with respect to dolomite. The next stage of growth probably began when the ions were replenished by new fluids. Another indication of ionic depletion is the fact that dolomite cements do not completely occlude the cavities. The cessation of dolomite growth, therefore, also indicates that the hydraulic system was not effective in delivering the new ions to the cavities, probably an indication of partially closed subenvironments in the heterogeneous aquifer. Perhaps the precipitation was so slow that the crystals ceased to grow because of a change in diagenetic environment due to external factors, such as eustatic sea level fluctuation.

C. ALTERNANT DOLOMITE AND CALCITE CEMENTATION

Banded cements with alternating dolomite and calcite occur in cavities of the Bluff Formation (Plates VI.4A, 4B); they have also been documented in the Yucatecan dolomites of the Yucatan Peninsula (Ward and Halley, 1985) and in the dolomite sequence of the Mururoa Atoll (Aissaoui, 1988). Jones *et al.* (1984) also described a cement of similar fabric in the microstalactitic cement in the Bluff Formation.

Mechanism of Alternant Dolomite and Calcite Cementation

Jones *et al.* (1984) suggested that dolomite/calcite banding in the microstalactites is an original fabric that recorded ever-changing pore water chemistry. An alternative interpretation, not favoured by Jones *et al.* (1984), suggests that the original zonation was formed of alternating low and high magnesian calcite, and the high magnesian calcite was subsequently dolomitized. Aissaoui (1988) argued that the alternating dolomite/calcite cement is formed by preferential dolomitization of high magnesian fibrous and/or blade calcite zones which left the high magnesian calcite spar unaltered.

Conditions of Alternant Dolomite and Calcite Cementation in the Bluff Formation

There are several lines of evidence to suggest that the alternating zones of dolomite and calcite described correspond to successive cementation by dolomite and calcite and they are not the result of diagenetic alteration. Firstly, the zones are of uniform thickness and laterally continuous (Plates VI.4A, 4B). Secondly, the zones are marked by euhedral outlines (Plates VI.4A, 4B). Lastly, each successive zone followed the contour of the previous growth bands (Plates VI.4A, 4B). This alternating growth of dolomite and calcite cement probably represents period of ionic depletion followed by subsequent ionic replenishment of the pore solutions. During cement growth in the cavities, the degree of supersaturation of the pore solutions with respect to the precipitating mineral will decrease. It is possible that this decrease in ionic concentration may lead to the formation of another mineral variety or complete cessation of cement growth. The fact that clear dolomite commonly forms the first zone of the alternating cement (Plates VI.4A, 4B) suggests that the precipitating pore fluid was probably slightly brackish in composition.

Similar, successive growth may be used to explain the intracrystalline zonation of dolomite and calcite (Plates VI.4C, 4D). Katz (1968, 1971) suggested that calcite zones may be formed by preferential dedolomitization of calcian dolomite zones. However, Jones *et al.* (1989) argued that the calcite zones in dolomite rhombs of the Bluff Formation were formed by differential leaching of unstable dolomite zones, formed under high salinity conditions, followed by calcite precipitation. All three hypothesis can explain the formation of alternating calcite and dolomite zones in dolomite rhombs. However, in cases where poikilotopic calcite encasing the zoned dolomite-calcite is in optical continuity with the calcite zone (Plates VI.5B-5E), the explanation put forward by Jones *et al.* (1989) is the most probable one.

D. POIKILOTOPIC CALCITE-DOLOMITE FORMATION

The term poikilotopic calcite-dolomite fabric, proposed by Jones *et al.* (1989), is used in this study to describe dolomite crystals that are hollow, partly filled by calcite, and/or encased by sparry calcite (Plates VI.1D, VI.5A-5E). These fabrics have characteristics similar to those suggested by Shearman *et al.* (1961), Evamy (1967), Folkman (1969), Katz (1971), and Longman and Mench (1978) for dedolomite.

Mechanism of Poikilotopic Calcite-Dolomite Formation

Through experimental work and petrographic studies, five mechanisms have been proposed to explain the process of dedolomitization:

(1) Dedolomitization is promoted by waters having a high Ca/Mg ratio, a low temperature (<50°C) and a low P_{CO_2} (de Groot, 1967).

(2) Dedolomitization involves dolomite calcium sulfate reaction (Shearman *et al.*, 1961; Evamy, 1963; Goldberg, 1967; Folkman, 1969). Yanateva (1955, reviewed by Chilingar, 1956) demonstrated that $CaSO_4$ is an active agent only at low P_{CO_2}.

(3) Dedolomitization is the result of the interaction between the physico-chemical changes of the interstitial water and the original composition of dolomite (Katz, 1968, 1971); Al-Hashimi and Hemingway, 1973; Frank, 1981; Land and Prezbindowski, 1981).

(4) Dedolomitization requires significant Ca^{2+} concentration and is not due to the presence of aqueous SO_4^{2-} (Back *et al.*, 1983; Stoessell *et al.*, 1987).

(5) Dedolomitization evolves through a series of distinct, time separated processes that comprise preferential dissolution of the less stable zones followed by calcite precipitation (Jones *et al.*, 1989).

There is no petrographic evidence to indicate the presence of former evaporites in the Bluff Formation; therefore, the reaction mechanism involving dolomite and calcium sulfate can be eliminated. The poikilotopic calcite-dolomite commonly found in rocks collected from the weathered zones and along joints suggests that the diagenetic fabric was probably formed in near-surface conditions similar to those suggested by de Groot (1967). Dedolomites related to weathering surfaces have been noted by Goldberg (1967), Folkman (1969), Chafetz (1972), and Al-Hashimi and Hemingway (1973). Yanateva (1955), Shearman *et al.* (1961), Evamy (1967), and Back *et al.* (1983) suggested that dedolomites are formed by concomitant dolomite dissolution and calcite precipitation.

Jones *et al.* (1989) suggested that the poikilotopic calcite-dolomite fabric evolved through dissolution of dolomite cement or matrix dolomite followed by precipitation of large calcite crystals. Thus, the fabric can evolve through a series of distinct, time-separated processes (Jones *et al.*, 1989). The fact that the calcite zones in the dolomite crystals and the poikilotopic calcite are in optical continuity attests that the two calcites are genetically related. Thus, the poikilotopic calcite-dolomite fabric identified in this study (Plates VI.5A-5E) was probably formed in a manner akin to that proposed by Jones *et al.* (1989).

The fact that the equilibrium fractionation, $\Delta^{18}O_{(\text{dolomite-calcite})}$ values of the poikilotopic calcite-dolomite lie between 2.4 and 6.3‰ PDB (Table VII.4), values not in agreement with the generally observed range of 3 ± 1‰ PDB for coexisting dolomite and calcite (Land, 1983b), suggests that the limpid dolomite and poikilotopic calcite were probably not cogenetic phases. The differences in $\delta^{13}C$ between dolomite and poikilotopic calcite (Jones *et al.*, 1989) also suggest that the two carbonate minerals were not genetically related.

Conditions of Poikilotopic Calcite-Dolomite Formation in the Bluff Formation

Stable oxygen isotopic data of the poikilotopic calcite-dolomite from the Bluff Formation suggest that the precipitating fluids of calcite range from highly brackish to saline (Table VII.5, Fig.VII. 3). Dissolution of unstable dolomite zones probably occurred during periodic influxes of CO_2-charged rain water, which is most effective at the water table zone or along joints. Shallow ground waters, particularly in the fresh water zone of the Lower Valley lens, are commonly supersaturated with respect to calcite and have a low Mg/Ca ratio (Table IV.5). They are, therefore, most favourable for precipitating calcite (Fig. VI.5). Furthermore, at the water table zone, rain water recharge would have caused undersaturation of the ground water with respect to dolomite, and hence, dolomite dissolution prior to the precipitation of the calcite. This is in general agreement with the occurrence of poikilotopic calcite-dolomite in the Bluff Formation.

E. SPELEOTHEMIC CALCITE FORMATION

The precipitation of speleothemic calcite is typically regarded as an abiogenic process (e.g. Thraikill, 1976; White, 1976; Folk and Assereto, 1976; Kendall and Broughton, 1978). The common presence of algae, fungi and bacteria in many caves, however, suggests that the formation of speleothem and travertine may, to some extent, be biogenically controlled (e.g. Caumartin, 1963; Lefevre and Laporte, 1969; Draganov, 1977; Chafetz and Folk, 1984; Folk *et al.*, 1985). Studies on Caymanian speleothems by Jones and Motyka (1987), Smith (1987) and Jones and MacDonald (1989) also demonstrate that micro-organisms probably played an important role in controlling the morphology and composition of the speleothems.

Kinetics of Speleothem Formation

Although speleothemic calcite forms in the vadose zone, the kinetics of calcite precipitation given by Reddy and Nancollas (1971), Nancollas and Reddy (1971), and Plummer *et al.* (1978, 1979) remain applicable. Accordingly, Dreybrodt (1980, 1981c) calculated that the speleothemic growth rate is in the order of 0.01-1 mm/year which is in agreement with the observed growth rate of 0.05-0.1 mm/year in temperate regions (Harmon *et al.*, 1975). With an increase of temperature from 10° to 25°C, speleothemic growth rate was shown to increase two fold (Dreybrodt, 1980). Other important factors are the concentration and supply of Ca^{2+} and CO_3^{2-} ions (Dreybrodt, 1980).

Timing of Speleothem Formation in the Bluff Formation

Dating of speleothems is commonly performed by the Uranium-series dating technique (Gascoyne *et al.*, 1978; Carew *et al.*, 1984). Growth layers in the flowstones of the Bluff Formation are marked by insoluble residues, possibly of clay minerals (Plates VI.6G, 6H), that might be ideal for dating the flowstones. However, Woodroffe *et al.* (1983) and Jones and Smith (1988) noted that the lack of felsic igneous rocks on and around the Cayman Islands leads to a scarcity of uranium in the geochemical cycle for absolute age dating. Nevertheless, the fact that all the speleothems still retain their original calcite mineralogy suggests that speleothem precipitation succeeded dolomitization. Flowstones formed in the Type 1 and 2 caves are older than the speleothems precipitated in the Type 3 caves because the flowstone was cut by the Type 3 cave systems. Because the Type 3 caves probably formed in late Pleistocene times (approximately 125,000 years ago) it is possible to suggest that the flowstones precipitated in the Type 1 and Type 2 caves are probably 2.0±0.5 my to 125,000 years old. Conversely, the speleothems precipitated in the Type 3 caves are probably less than 125,000 years old.

Conditions of Speleothem Formation in the Bluff Formation

Water containing carbonic acid obtained from hydration of atmospheric CO_2, organic decomposition and plant respiration is capable of dissolving calcite and dolomite in the bedrock along its flow path. When this water finally reaches a cave with a lower partial pressure of CO_2 than in the solution, CO_2 degasses from the water and a supersaturated solution of $CaCO_3$ results. In the caves on the Cayman Islands, the high relative humidity and stable temperature in the present day cave environment suggests that evaporation probably has minimal effect on speleothemic formation. Around cave entrances or areas open to surface atmospheric conditions, evaporation may be significant. Stable oxygen isotopic data suggest that the speleothems probably precipitated from waters of similar salinity to those responsible for calcite cementation (Table VII.6, Fig.VII.3B; Smith, 1987). It is important to note that the stable isotopic data suggests that flowstones may also form from brackish water of salinity up to 45% sea water (Table VII.6, Fig. VII.3B), which contradicts the general perception that speleothems are indicative of fresh water environments.

Smith (1987) suggested that the Ca^{2+} and CO_3^{2-} ions necessary for speleothem precipitation were probably derived from the dissolution of the overlying dolostones of the Bluff Formation or from limestones of the Ironshore Formation. The fact that the Type 3 and 4 cave systems formed by dissolving the dolostone bedrock suggests that dolomite was probably the main source of $CaCO_3$ for the speleothemic formation.

F. INTERNAL SEDIMENTATION

Caymanite is a common cavity fill in the Bluff Formation. Some cavities were partly or completely filled with skeletal sands (predominantly foraminifera and fragments of red algae), which are locally interlayered with the caymanite. The anhedral dolomite crystals, angular dolostone fragments, and sedimentary structures of the caymanite (Plates VI.6C-6F) unequivocally suggest that the sediments were of detrital origin. The physical features of the caymanite deposits are similar to vadose calcite sediments or mineral deposits found in the Permian Townsend carbonate mound of New Mexico (Dunham, 1969), the Ordovician limestones of Australia (Semeniuk, 1971), the Carboniferous limestones of Peak District in England (Ford *et al.*, 1977) and the Type 4 internal sediments in the Jurassic carbonates of Burgundy and Frond (Aissaoui and Purser, 1983). Ford (1988) also noted that internal sediments in caves are common and that transportation and deposition can be highly energetic.

Origin of the Internal Sediments

The presence of normal marine skeletal components (foraminifera and red algae) in the grainstone led Jones and Hunter (1989) to suggest that the skeletal sands were deposited during the early part of a marine transgression. The origin of the caymanite sediments is less certain. Assuming that the caymanite was formed from swamp sediments

(Folk and McBride, 1976; Collar, 1985, pers. comm.; Lockhart, 1986), one important point that needs to be addressed is the original mineral composition of the sediment. Analyses of sediments collected from a swamp at Hell in West Bay of Grand Cayman showed that only 5% of the bulk weight is dolomite (I. Collar, 1985, pers. comm.), the other 95% is calcite and aragonite. Collar (1985, pers. comm.) proposed that the dolomites were selectively transported into the cavities due to their small grain size (<5 µm in length). The fact that individual laminae are composed of different grain sizes strongly suggests that the model of Collar (1985, pers. comm.) is not a functional mechanism. Furthermore, SEM examination of sediments from the Hell swamp (Lockhart, 1986) and from Colliers Pond in East End (this study) showed little resemblance to the grains in the caymanite. The small amount of dolomite in the swamp sediments were probably derived from (1) wind blown sediments, (2) weathering of the dolostone by rain water, and (3) dolostone bedrock in a manner similar to the fungi mediated micritization of calcite spar (Jones and Pemberton, 1987a, 1987b). It is, therefore, suggested that the original caymanite sediments were of predominantly calcitic compositions. Stable oxygen isotopic values of the caymanite suggest that the calcitic sediments were subsequently dolomitized in fluids of high salinity which ranged from 25 to 100% sea water salinity (Table VII.5, Fig.VII.3B).

Timing of Internal Sedimentation

The absolute timing of the deposition of caymanite is difficult to determine; nevertheless, examination of the various geological relationships suggests the following:

(1) Caymanite (red, orange, black and white coloured) is common in the Oligocene Cayman Member of the Bluff Formation, but the coloured components rarely occur in the middle Miocene Pedro Castle Member (Jones and Hunter, 1989). This suggests that most caymanite was associated with a transgression that led to deposition of the Pedro Castle Member, probably during the land emergence in late Oligocene times.

(2) At least one phase of karstification and jointing occurred prior to caymanite deposition because some joints and caves were filled by caymanite. The karst development (Phase I; Fig. VIII.1) was probably due to the sea level drop in late Oligocene times.

(3) Caymanite postdated one generation of void-lining dolomite cement (Plate VI.6F). This also suggests that caymanite was deposited after dolomitization of the host rock, if void-lining dolomite occurred concurrently with dolomitization, as suggested in paragenetic model II.

(4) Caymanite predated the second generation dolomite cement which was precipitated on top of the caymanite (Plate VI.6E).

(5) Undolomitized flowstone and sparry calcite (Plate VI.6F) precipitated after caymanite deposition. This suggests that caymanite was dolomitized prior to the formation of flowstone and sparry calcite.

Mechanism of Internal Sedimentation

Folk and McBride (1976) and Lockhart (1986) suggested that caymanite was formed from materials washed from swamps into the cavities and caverns via the well-developed joint system during seasonal storms. Lockhart (1986) noted that caymanite appears to occur predominantly in coastal exposures; however, recent data obtained from well drilling indicates that caymanite also occurs in the interior of the islands. Therefore, the occurrence of caymanite is probably governed by the availability of the sediments and the joint system.

The multiple cycles of caymanite formation is best illustrated by the distinct laminations (Plate VI.6C) and cut and filled channels. Therefore, the detrital sediments were probably intermittently washed into the cavities and caverns or deposited from stagnant pond waters in the caverns. The intermittent phenomenon of the internal sedimentation is also indicated by dessication cracks present in some caymanite layers. The presence of (1) erosional features and cross-bedding, (2) large angular fragments (Plate VI.6C), and (3) fragments probably removed from irregular projections on cavity walls (Plate VI.6D) suggests that sedimentation occurred under high-stage flow conditions. The sediments may also have entered cavities that were in the phreatic zone.

The variation in grain size of sediments in the same layer (Plate VI.6C) indicates that the sediments were transported in steady turbulent flow in a manner suggested by Bridge (1981). Gales (1984) also suggested that finer sediment can deposit simultaneously with the coarser sediment where flow expansion resulted in a sudden reduction in flow competence such as at the exit to the phreatic zone. A similar mode of flow and transport was probably responsible for the caymanite sedimentation in the Bluff Formation. Caymanite fill in vertical or steeply dipping open joints commonly shows highly contorted laminae that are subparallel to the attitude of the joints. The fact that the sediments were maintained at such a high angle suggests that the sediment flow was probably in a form of high-viscosity fluid and that it underwent rapid lithification.

G. TERRA ROSSA DEPOSITION

Terra rossa is a common cavity fill in the Bluff Formation (Jones *et al.*, 1984; Jones and Smith, 1988; Squair, 1988). The presence of terra rossa at various stratigraphic levels suggests that the soils probably entered the cavities and caverns via the well developed joint and karst systems in a manner similar to the transport of caymanite. Terra rossa derived from the weathering of limestones in karst areas have been identified in the Pleistocene limestones of South Florida (Perkins, 1977), the Triassic Calcare Rosso Limestone of Italy (Assereto and Folk, 1980), the Lower Carboniferous carbonates of South Wales (Riding and Wright, 1981) and the Upper Paleozoic carbonate strata in southwestern New Mexico (Chafetz, 1982). Conversely, Isphording (1974) suggested that the terra rossa on the Yucatan Peninsula were derived from deposits not indigenous of the region. The origin of the terra rossa in the Bluff Formation, however, is not clear.

H. SYNOPSIS

Superposition of the cavity-filling cements and internal sediments allows the construction of a generalized paragenetic sequence for the diagenetic fabrics (Fig. XI.1). It appears that most of the carbonate cements and speleothems were precipitated in Late Pleistocene to recent times. There is no evidence in the rock fabrics suggesting pre-dolomitization calcite cementation or speleothem formation.

The following conditions are concluded for the formation of the cements and sediments:

(1) Calcite cement morphology is not a reliable criterion in the recognition of diagenetic environments because of the complexity of the natural environments. On the Cayman Islands, the abundance of sparry calcite cement decreases from the fresh to brackish to saline water zones. Calcite cementation is favoured in waters having low salinity, low molar Mg^{2+}/Ca^{2+} ratio, and high CO_3^{2-} concentration.

(2) Clear euhedral dolomite was probably precipitated from brackish pore fluids (i) supersaturated with respect to dolomite, (ii) containing a sufficient supply of Ca^{2+}, Mg^{2+}, and CO_3^{2-} ions, and (iii) less saline than the sea water. The sequential dolomite growth indicated by the sharp boundaries between individual zone may have resulted from (i) depletion of ions in the pore fluid and subsequent ion replenishment in a partially closed subenvironment in the aquifer, and (ii) a change in external factors, such as eustatic sea level fluctuation.

(3) The alternating growth of dolomite and calcite probably represents periods of ion depletion leading to formation of another mineral variety. The original pore fluid was probably brackish water because dolomite was also the first cement zone.

(4) Poikilotopic calcite and dolomite were formed by dolomite dissolution and subsequent calcite cementation. This fabric is commonly associated with near surface environments such as joint surfaces. at weathered seams, and at the water table zone.

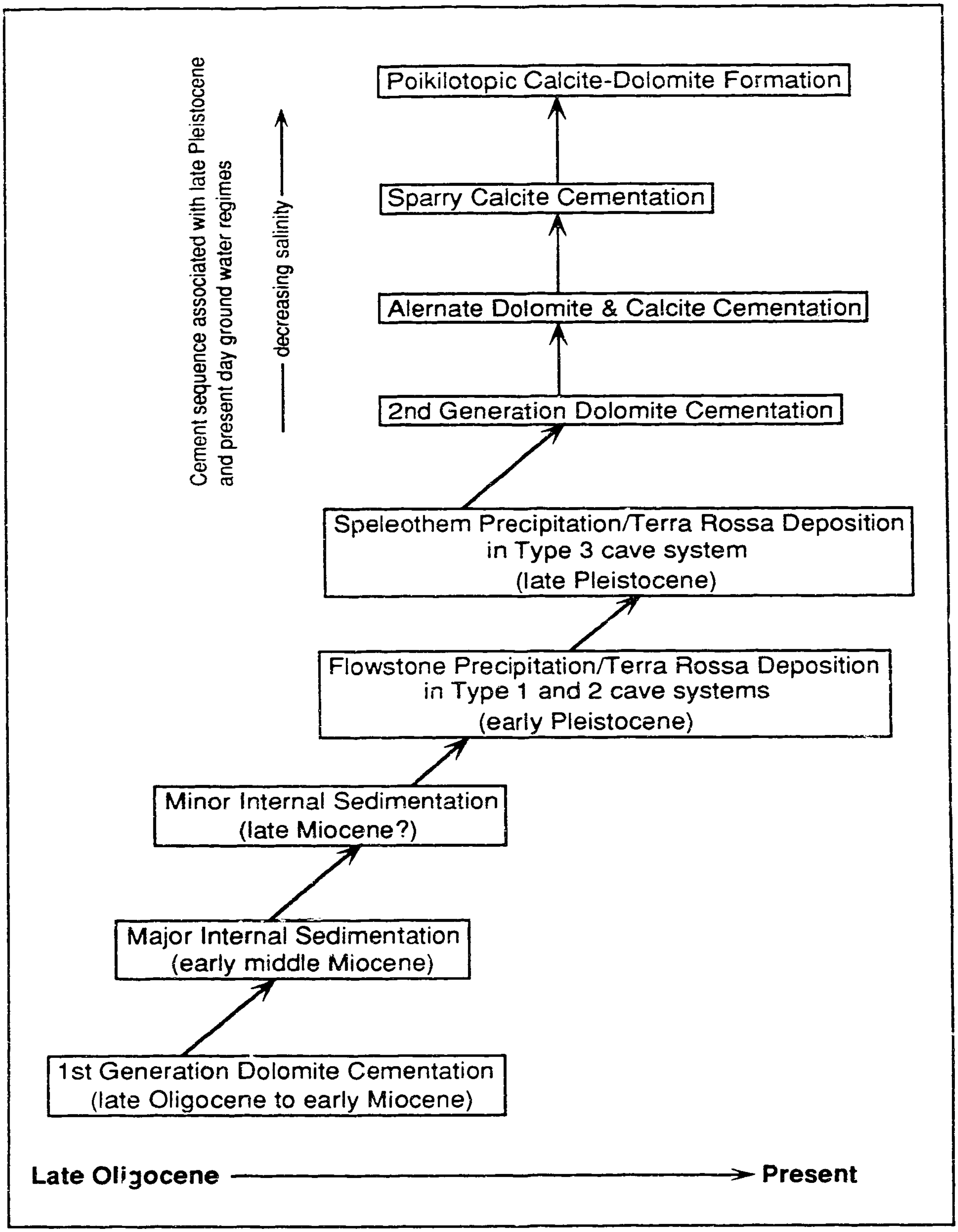


Fig. XI.1 Generalized paragenetic sequence of cavity filling cements and internal

(5) Formation of speleothemic calcite in the vadose zone is controlled by (i) the supply of Ca^{2+} and CO_3^{2-} ions, (ii) evaporation in areas open to the atmosphere, and (iii) micro-organisms such as algae, fungi, and bacteria.

(6) Caymanite sediments were probably derived from calcitic swamp sediments that washed into the underground cave system during periodic storm periods. The overlapping grain size distribution in the laminae indicates that the sediments were transported in steady turbulent flow and deposited when flow competency was reduced, such as the exits to the phreatic tube. The presence of normal marine skeletal components in the skeletal grainstone suggests that the grainstone was marine in origin.

(7) Terra rossa was a late cavity fill that entered the subterranean system in a manner similar to that of the caymanite sedimentation.

XII. CONCLUSIONS

Studies of ancient carbonate sequences rarely, if ever, allow the concomitant investigation of the pore solutions that were responsible for the post-depositional modifications of the rock fabrics. Conversely, diagenetic study of the Oligocene-Miocene Bluff Formation of the Cayman Islands permits the investigation of the source of pore fluids and an assessment of the present day water-rock interactions. The integration of diagenetic fabrics of the rocks with hydrogeological, hydrochemical, and isotopic geochemical data leads to the following conclusions:

(1) The major fresh water lenses, developed in the Bluff Formation, are characterized by (i) unconfined conditions, (ii) small size and thickness, (iii) irregular lens geometry, (iv) thick transition zone, (v) direct hydraulic connection with the surrounding ocean, and (vi) rapid rates of recharge and discharge.

(2) The rocks of the Bluff Formation are characterized by secondary porosity in the form of fossil molds, open joints, fissures, solution channels and caverns formed as a result of preferential dissolution, tectonic fracturing and karst development. The permeable zones (i) provide direct hydraulic connections between ground water and the surrounding ocean, (ii) facilitate the mixing of ground water between individual aquifers, and (iii) create many possible subenvironments such as open, closed, or partially closed conditions within the unconfined aquifer.

(3) It is fundamental to the study of carbonate diagenesis that the hydrochemical zones such as fresh, brackish, and saline water be properly defined on the basis of the water salinity and chemical properties. The ground water present on the Cayman Islands is divided into perched water, fresh water (<600 mg/l Cl^-), brackish water (>600 to <19,000 mg/l Cl^-), Type I saline water (>19,000 mg/l Cl^-, variable chemical compositions) and Type II saline water (>19,000 mg/l Cl^-, almost constant chemical compositions) hydrochemical zone. Similar hydrochemical

zonation can be applied to other studies to avoid confusion among different workers.

(4) Even though all the major fresh water lenses are developed in the Bluff Formation, they show distinct spatial and temporal variation in water chemistry and stable isotopes due to different degrees of external influences and water-rock interactions. This is further complicated by the formation of subenvironments caused by jointing and karsting. Variations in ground water chemistry from area to area and from time to time are common and these variations must be considered in establishing the relationship between carbonate cements and pore fluids.

(5) Ground waters of the Cayman Islands are formed from various combinations of rain water, sea water, ground water of variable chemical constituents from different aquifers, and surface water from swamps and ponds. This means that it is unrealistic to use the generalized mixing model between fresh ground water and sea water in interpreting the actual ground water composition in the aquifers.

(6) Chemical equilibrium calculations indicate that most of the fresh, brackish and saline ground waters on the Cayman Islands are supersaturated with respect to calcite and dolomite, and hence, are capable of precipitating calcite and dolomite. Representative equilibrium calculations in a ground water-carbonate aquifer system like that of the Cayman Islands require consideration of (i) the ion complexing, (ii) field pH and temperature measurements, (iii) tidal fluctuation, (iv) the recharge process, and (v) disturbance due to human activities.

(7) In addition to the evidence from fluctuation in water levels and salinity in response to rainfall, the δ^2H and $\delta^{18}O$ contents of the rain water shows that ground water recharge on the Cayman Islands occurs predominantly during rainfall of high intensity. The isotopic compositions of the fresh and lightly brackish ground water are controlled by evaporation and cluster about a $\Delta\delta^2H/\Delta\delta^{18}O$ slope of 5.91.

Conversely, the dominant factor in controlling the isotopic compositions of the highly brackish ground water is mixing between fresh and saline ground water.

(8) The Bluff Formation has been affected by numerous cycles of sea level change since the deposition of the Cayman Member in Oligocene times. As a result, the rocks of the Bluff Formation have been subjected to various diagenetic regimes in response to the successive cycles of emergence and submergence. The different types of pore fluids would have a profound effect on the diagenetic modification of the rocks because they have variable chemical properties.

(9) Superposition of cavity filling carbonate cements indicate the following paragenetic sequence: (i) clear and zoned dolomite, (ii) alternating zones of dolomite and calcite as laterally continuous bands from crystal to crystal or within a single crystal, (iii) coarse, unzoned and zoned sparry calcite, (iv) partial dissolution of sparry calcite and zoned dolomite cements, and (v) poikilotopic calcite encasing and infilling leached dolomite cements.

(10) Other cavity fills include caymanite, skeletal grainstone, terra rossa and flowstone. The caymanite and skeletal grainstone are completely dolomitized; the terra rossa and flowstone remain as calcium carbonate. Caymanite sedimentation postdated the first generation of dolomite precipitation and predated the second generation dolomite. Terra rossa and flowstone was commonly deposited on top of caymanite in the same cavities.

(11) The distribution of carbonate cements in the present day hydrochemical zones indicates that (i) there is a decreasing quantity of calcite as last-phase cement from the fresh water to brackish water to saline water zone, (ii) the abundance of dolomite as last-phase cement increases from the fresh water to brackish water zone, and (iii) the rocks in the saline water zone are characterized by minor dolomite cement and unfilled cavities.

(12) The relationship between the last phase carbonate cements and present day pore fluids suggests that sparry calcite cement is commonly associated with fresh to lightly brackish ground water and dolomite cement is commonly affiliated with brackish ground water. However, ground waters of similar salinity may have different chemical compositions. Although the waters from the two fresh water lenses have similar salinity, dolomite cement is rare in the Lower Valley lens, whereas dolomite cement is common in the East End lens.

(13) The equilibrium oxygen fractionation relationship between calcite and water is well established, whereas the fractionation relationship between dolomite and water at low temperature is equivocal. However, the $\delta^{18}O$ content of the carbonate minerals provides a useful constraint on the diagenetic conditions. In this study, the relationship between the $\delta^{18}O$ and the salinity of the ground water is established for the direct interpretation of the nature of the diagenetic fluids from which the carbonate minerals precipitated.

(14) Results of the equilibrium oxygen fractionation between the carbonate minerals and the waters at 22-33°C using five different fractionation equations indicate that (i) matrix dolomite and caymanite were formed in water of 25 to >95% sea water salinity, (ii) calcite spar and flowstone were precipitated in fresh to brackish water up to 45% sea water salinity, (iii) poikilotopic calcite was precipitated in water of 65 to >100% sea water salinity, (iv) dolomite cement (in association with poikilotopic calcite) was formed in water of 25 to >90% sea water salinity, and (v) coarse dolomite spar was precipitated in perched, fresh to brackish water up to 25% sea water salinity.

(15) Two paragenetic models can be invoked to satisfy the available petrographic and geochemical data. A relatively simple model (Model I) proposed that pervasive dolomitization of the Bluff Formation was a single event involving sea water as the diagenetic fluid. This study suggests an alternative interpretation of the

geochemical data. The geochemical data (stable oxygen and radioactive strontium isotopes) do not permit a definitive interpretation on the timing of the dolomitization event(s). On the basis of the cumulative information on aragonite dissolution, petrography, isotope geochemistry, and other circumstantial evidence, it is suggested that the Bluff Formation was probably dolomitized by two separate events (Model II). The earlier event dolomitized the Oligocene Cayman Member, whereas the later event dolomitized the Miocene Pedro Castle Member and the internal sediments (caymanite and skeletal grainstone). The second dolomitization event also affected the Cayman Member by resetting the geochemical signatures of previously formed dolomites, probably through increased cation ordering and stoichiometry.

(16) The dolomitizing fluid was probably sea water that was modified to a certain extent by rain water during the early stages of land emergence in late Oligocene (for the Cayman Member) and late Miocene (for the Pedro castle Member) times. Stable oxygen isotopic results (Table VII.5) suggest that the degree of meteoric influence ranged from 0 to 75% fresh water by volume depending on the fractionation equations used and temperatures of the diagenetic fluids.

(17) The fresh water recharge created density gradient in the flow system, and hence, facilitated ground water movement through the sediments/rocks. The flow mechanism, which included downward gravitational flow, downward reflux, upward convection and tidal pumping. is similar to that of the present day. It is also important to note that higher land relief in the past because of lower sea levels would have increased the hydraulic gradient for fluid movement. Furthermore, changes in climatic regimes, such as rainfall intensity and duration and atmospheric temperature, would have a significant impact on the nature of the mixed water diagenetic environment.

(18) Karstification of the Bluff Formation occurred in at least three distinct phases. Phase I karst developed in late Oligocene to early Miocene times when the Oligocene Cayman Member was subaerially exposed due to the major sea level drop in late Oligocene. Phase II karst developed in late Miocene to early Pliocene times as a result of the major marine regression in late Miocene. Phase III karst developed in late Pliocene to late Pleistocene times in response to frequent sea level fluctuations. On the basis of the amount and variety of cave fills, the cave systems in the Bluff Formation can be categorized into four types. The similarity between the joint fills and the cave fills also indicates that joints of different attitudes probably developed in relation to different phases of karstification.

(19) The horizontal orientation of some of the caves and their connection to the wave cut notches suggest that cave development is directly related to past sea level high stands. Most of the caves probably developed at the ground water discharge points where flow velocity is high and mixing between ground water and sea water occurs. The fact that the Phase III karst developed after the Bluff Formation was completely dolomitized attests that lithology is not the dominant factor in controlling the degree of karstification. The extensive network of cave passages formed during the Phase III karstification might be related to intense jointing prior to karstification. Furthermore, the high density of speleothems in some of the caves developed during Phase III karstification suggests that past climatic regimes were probably much wetter than those today.

(20) Chemical equilibrium of water-rock reactions in the joint and karst controlled shallow carbonate aquifers are difficult to achieve; therefore, kinetic concepts are needed to understand the diagenetic processes that are operative in such a hydrogeological setting. In addition, cement morphology is not a reliable criterion in the recognition of diagenetic environments because of the complexity of the natural environments.

(21) The following conditions are suggested for the formation of the diagenetic fabrics that are responsible for the reduction of the porosity of the Bluff Formation.

(i) Calcite cementation took place in waters with low salinity, low molar Mg^{2+}/Ca^{2+} ratio, and high CO_3^{2-} concentration.

(ii) Clear euhedral dolomite was precipitated from pore fluids that contained a sufficient supply of Ca^{2+}, Mg^{2+}, and CO_3^{2-} ions and were supersaturated with respect to dolomite.

(iii) The alternating growth of dolomite and calcite was the probable result of periodic ion depletion which led to the formation of another mineral type. The depletion of ions might be indicative of partially closed subenvironments in the aquifers or a change of diagenetic environment such as eustatic sea level fluctuation.

(iv) Poikilotopic calcite and dolomite were formed by dolomite dissolution and subsequent calcite cementation. This fabric is commonly associated with near surface environments such as along joint surfaces, at weathered seams, and at the water table zone.

(v) Precipitation of speleothemic calcite in the vadose zone is controlled by the supply of Ca^{2+} and CO_3^{2-} ions and activities of micro-organisms such as algae, fungi, and bacteria.

(vi) Caymanite sediments were probably derived from calcitic swamp sediments that washed into the underground cave system during periodic storm periods. The overlapping grain size distribution in the laminae indicates that the sediments were transported in steady turbulent flow and deposited when flow competency was reduced, such as exits to the phreatic tube. The skeletal grainstone of marine origin probably entered the cavities and caverns during early stages of marine transgression. Terra rossa, which was a late cavity fill, probably entered the subterranean system in a mode similar to that of the caymanite sedimentation.

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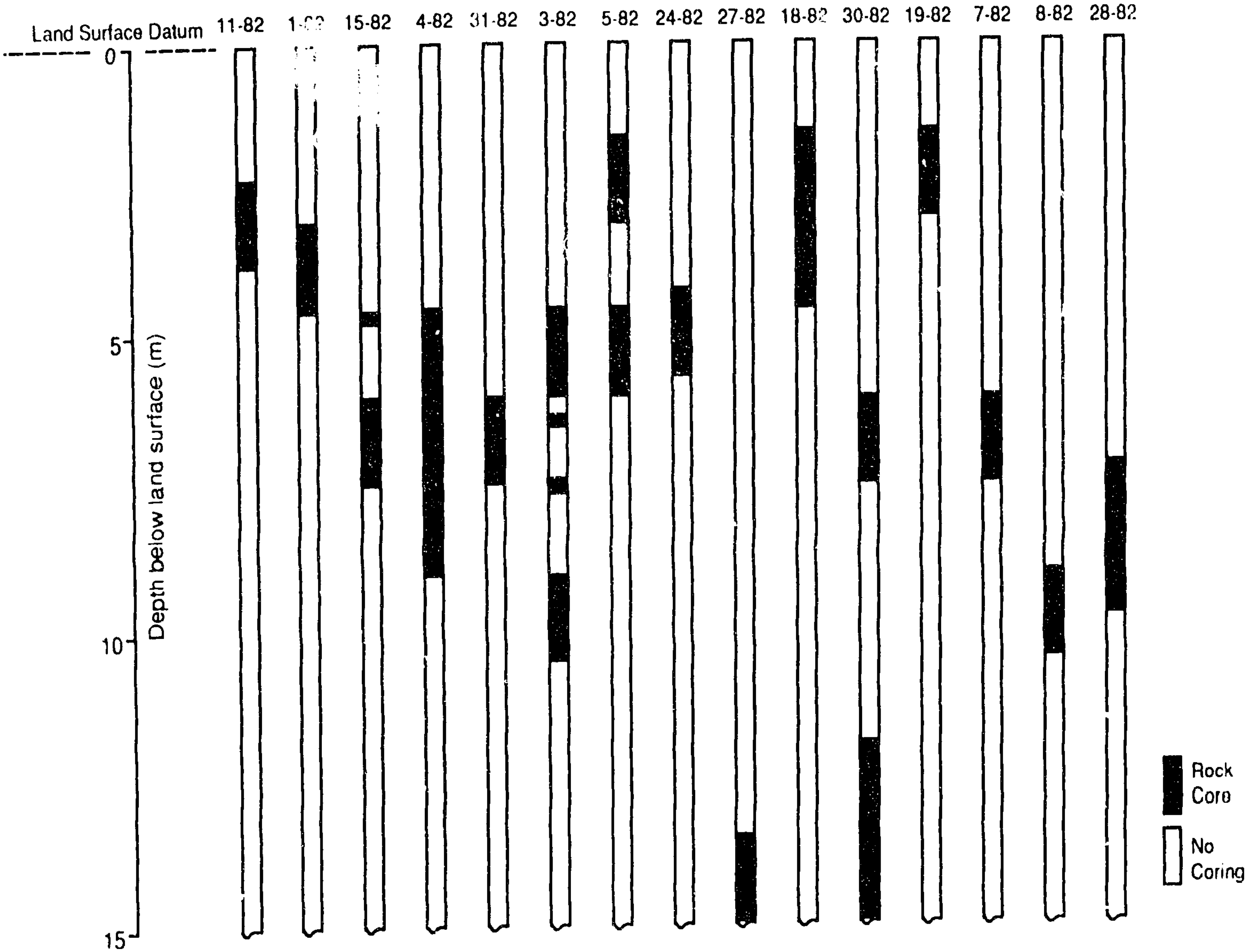
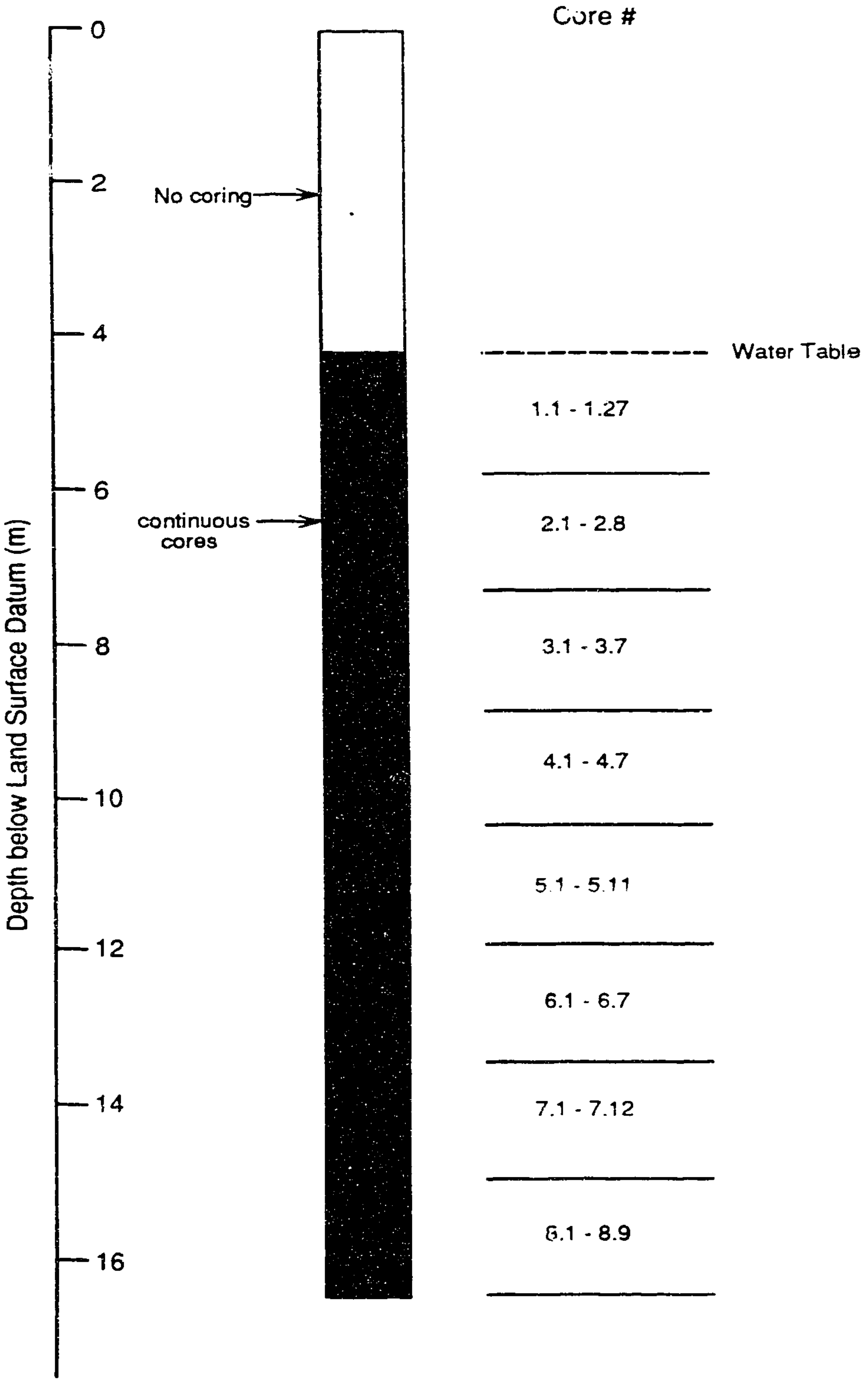
XIV. APPENDICES

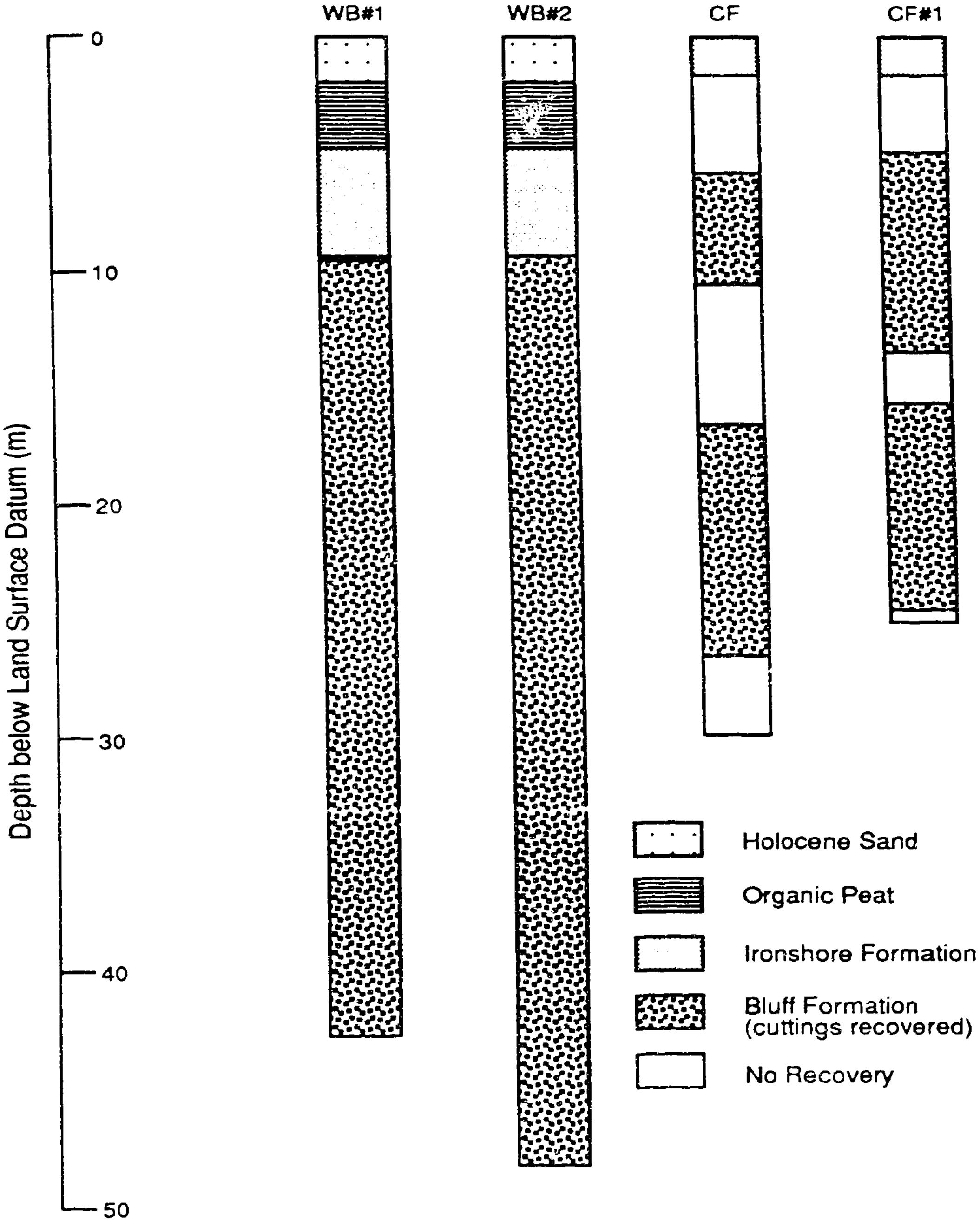
Schematic logs of wells showing rock cores and cuttings of the Bluff Formation used in this study.



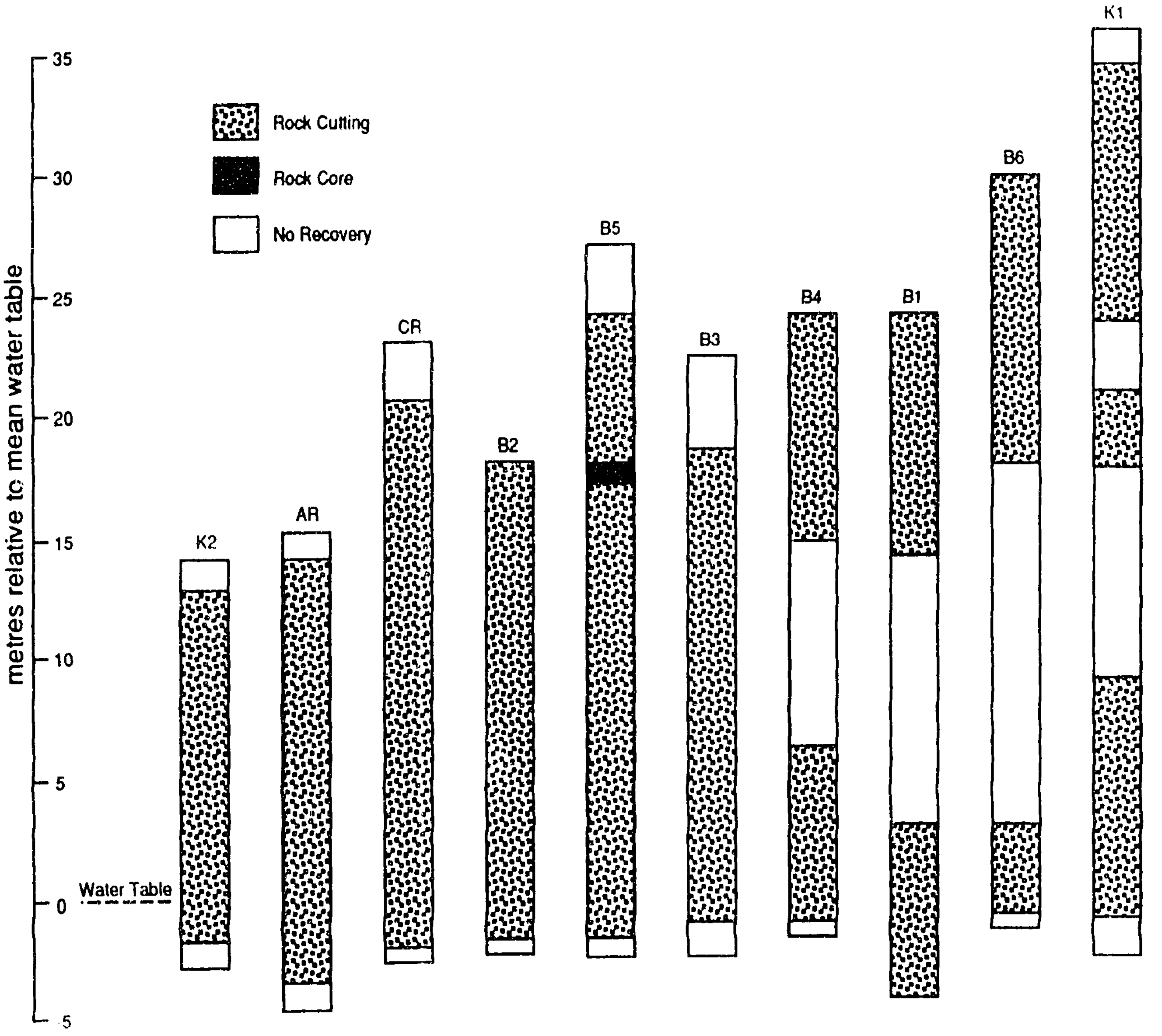
Appendix 1A. Schematic logs of Lower Valley wells showing depth of rock cores recovered. Well location shown on Fig. VI.1. Total depth of wells not known.



Appendix 1B. Schematic log of well 3-84 at East End well field showing depth of cores recovered and core numbers. Well location shown on Fig. II.4.



Appendix 1C. Schematic logs of deep wells located on the western part of Grand Cayman. Well location shown on Fig. III.2.



Appendix 1D. Schematic logs of Cayman Brac wells showing depth of cuttings and core recovered. Well location shown on Fig. VI.2