Genesis of island dolostones

Min Ren, Brian Jones

Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Alberta, Canada T6G 2E3

Corresponding author: mren@ualberta.ca

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ABSTRACT

Cenozoic "island dolostones" are found on islands throughout the oceans of the world. Due to their geological youth and lack of deep burial, these dolostones provide an opportunity to resolve some of the mysteries surrounding the dolomite problem. In island dolostone bodies, which are of variable size and variable dolomitization, the petrographic and geochemical properties of the dolostones are characterized by geographic and stratigraphic variations. In the larger island-wide dolostone bodies, like those found on Grand Cayman, there are progressive increases in mole %Ca (%Ca_{mean}: 53.9 to 57.6%), depletion of the heavier ^{18}O and ^{13}C isotopes ($\delta^{18}O_{mean}$: 3.6 to 2.1‰ $_{VPDB}$; $\delta^{13}C_{mean}$: 3.1 to 1.4 ‰ $_{VPDB}$), and changes from fabric-retentive to fabric-destructive fabrics and a decrease in the amount of dolomite cement from the coastal areas towards the centers of the islands, similarly on the Little Bahama Bank. These changes define geographically concentric zones that parallel the coastlines and reflect geochemical modification of the dolomitizing fluid through water-rock interactions, mixing with meteoric water, and the changes in the rate and flux of seawater as it flowed from coasts to island interiors. The pattern of dolomitization, however, is not consistent from island to island because geographic and stratigraphic variations, specific to each island, influenced groundwater flow pattern (e.g., geometry and size of the islands; the porosity and permeability of the precursor limestone), the duration of the dolomitization reaction, and other factors. The geographic extent of dolomitization and variation in dolomite stoichiometry of island dolostones may be comparable to the reaction stages established in high-temperature laboratory experiments.

INTRODUCTION

The origin of thick, aerially extensive dolostone bodies, which are common throughout the geological record, is still the subject of much debate (i.e., the "dolomite problem"; Land, 1985; Budd, 1997; Machel, 2004). Resolution of the "dolomite problem" has commonly been addressed by considering "island dolostones" (Budd, 1997) that are integral parts of Cenozoic successions on many islands throughout the oceans of the world. They are prime candidates to address the problem because, unlike most older dolostones, they have not been subjected to deep burial diagenesis, and have originated in environments that can be reasonably inferred from their present-day setting. Even so, many different dolomitization models have been proposed to explain the genesis of these island dolostones including tidal pumping, seepage influx, brine reflux, mixing zone, ocean current pumping, and Kohout convection (see Tucker, 1990, his Fig. 8.31; Budd, 1997, his Fig. 1).

In many cases, suggested origins of island dolostones have been based on isolated successions with emphasis being placed on stratigraphic variations in the various attributes of the dolostones. With the notable exceptions of Vahrenkamp & Swart (1994), Fouke (1994), Gill et al. (1995), and Budd & Mathias (2015), little attention has been given to any geographic variations that may exist in the petrographic and geochemical attributes of these dolostones. Ren & Jones (2017), based on dolostones found in the Cayman Formation (Miocene) on Grand Cayman, clearly demonstrated that geographic variations in dolostone petrography, and dolomite stoichiometry were more pronounced and important than stratigraphic variations. They suggested that this was due to subsurface environmental variations from coastal to inland areas.

Attempts to produce a unified model that explains the pervasive dolomitization of the Cenozoic successions on oceanic islands have been complicated by the fact that the data available from those islands are highly variable and commonly prevent assessment of geographic as opposed to stratigraphic variations in the dolostones. Assessment of available data from "island dolostones" shows that progress on this issue has been hindered by (1) inconsistent data sets, especially in situations where the island dolostones are known only from a limited number of wells and/or localized outcrops, (2) a primary focus on stratigraphic variations with little or no consideration given to geographic variations in the attributes of the dolostones, (3) for individual island dolostones, focus has commonly been on the average level and "commonalities" of their geochemical and/or petrographic data while ignoring the information behind those "differences" and variabilities, and (4) little integration between the attributes of the island dolostones and information obtained from laboratory synthesis experiments. Herein, an attempt is made to evaluate island dolostones from a worldwide perspective with a view of summarizing our current understanding of their genesis. Emphasis is placed on assessing the importance of recognizing geographic variations as well as stratigraphic variations in the petrographic and geochemical (e.g., dolomite stoichiometry, stable isotopes) properties of the dolostones. An attempt is made to integrate experimental information into the interpretation of island dolomitization. In so doing, this paper highlights the shortcomings in current interpretations of island dolostones and outlines the approaches and types of data that are needed to resolve many of the problems that hamper our understanding of their origin.

DATABASE

Cenozoic island dolostones have been found on many islands in the Caribbean Sea, the Atlantic Ocean, Pacific Oceans, Philippine Sea, and South China Sea (Table 1; Fig. 1; see also Budd, 1997, his table 2). The size of these islands ranges from tens of square kilometers (e.g., Cayman Brac) to over a hundred thousand square kilometers (e.g., the Great Bahama Bank).

Island widths range from ~2-3 km (e.g., Kita-daito-jima, Cayman Brac) to over 100 km (the Great Bahama Bank). Most studies of island dolostones have been based on surface and near-surface samples collected from outcrops and well cores to depths of ~100 m, although deeper wells have revealed Cenozoic dolomitization to up to 300 m below present sea level on some Pacific atolls (e.g., Funafuti, Midway; Ladd et al, 1970), to ~600 m on the Great Bahama Bank and the Xisha Islands (e.g., Swart & Melim, 2000; Wang et al., 2015), and 1400 m on Enewetak (e.g., Saller, 1984).

While acknowledging that stratigraphic variations in island dolostones do occur, this study also examines the importance of geographic variations in the dolostones. Accordingly, preference is given to those islands that are characterized by thick, geographically widespread dolostones that have been well characterized by large arrays of stratigraphically and geographically distributed samples. Ideal examples include the surface to subsurface dolostones found on Grand Cayman (Jones, 1989; Jones & Luth, 2002, 2003a, b; Jones, 2004, 2005; Ren & Jones, 2016, 2017), Cayman Brac (MacNeil, 2001; MacNeil & Jones, 2003; Zhao & Jones, 2012a, b), the Little Bahama Bank (Vahrenkamp et al., 1991; Vahrenkamp & Swart, 1994), Kita-daito-jima (Ohde & Elderfield, 1992; Suzuki et al., 2006), and Mururoa (Aissaoui et al., 1986). Examples that are geographically localized or represented by limited numbers of samples are used with caution.

This study is primarily based on data from two sources (Table 1). Data for the Cayman Islands builds on the data that Pleydell et al. (1990), Ng (1990), Willson (1998), Jones et al. (1994a, b), Jones et al., (2001), Jones & Luth (2002, 2003a, b), MacNeil (2002), MacNeil & Jones (2003), Der (2012), Zhao & Jones (2012a, b, 2013), and Ren & Jones (2016, 2017) used in their assessments of the Cayman dolostones. Data for the other islands come from works by

Schlanger et al. (1963), Berner (1965), Deffeyes (1965), Ladd et al. (1970), Chevalier (1973), Land (1973, 1991), Bandoian & Murray (1974), Supko (1977), Sibley (1980, 1982), Rodgers et al. (1982), Saller (1984), Ward & Halley (1984), Aissaoui et al. (1986), Aharon et al. (1987), Swart et al. (1987), Dawans & Swart (1988), Humphrey (1988, 2000), Humphrey & Radjef (1991), Vahrenkamp & Swart (1991, 1994), Hein et al. (1992), Ohde & Elderfield (1992), Beach (1993, 1995), Fouke (1994), Lucia & Major (1994), Machel et al. (1994, 2000), Gill et al. (1995), Wheeler et al. (1999), Swart & Melim (2000), Melim et al. (2002), Suzuki et al. (2006), Wei et al. (2006, 2008), and Wang et al. (2015). Most of these data came from the tables, appendices, and reports in those papers. Where datasets were not supplied, data were extracted from the figures used in the papers (Table 1).

EXTENT OF DOLOMITIZATION

The extent of dolomitization in island carbonates is highly variable. Based on the geographic scale of a dolostone body relative to the size of the island and the dolomite content in the rocks, the bodies are herein divided into: Group A, regional dolostones, and Group B localized dolostones/dolomitic limestones (Table 1). Regional dolostones refers to those dolostone bodies that are formed largely of dolostone and geographically cover at least half of the island. Localized dolostone/dolomitic limestone bodies are those that are stratigraphically and geographically restricted and typically cover less than half of the island and invariably contain limestones that have been only partly dolomitized. The regional dolostones form sub-groups A1, which includes those dolostone bodies where geographic and stratigraphic variations in the properties of the dolomite can be documented from numerous different localities, and A2 that includes those islands where geographic variations cannot be established because the succession is known from only one well.

In general, group A dolostones are less common than those in group B. In group B, the dolostones are more common in the coastal areas than in the center of the island. Budd (1997, p. 33) pointed out that logically "… partial dolomitization should be focused towards the periphery of an island, atoll or platform…". This situation is illustrated by the Cayman Formation on the eastern part of Grand Cayman (Ren & Jones, 2016, 2017) and on the Great Bahama Bank (Beach, 1993, 1995), where limestones and dolostones at the margins grade into limestones in the bank interior.

There is no uniform stratigraphic relationship between the extent of dolomitization and the ages of the formations. On some islands, older, deeper parts of the succession are less dolomitized than younger overlying strata. Examples of this architecture include Cayman Brac, where the partially dolomitized Brac Formation (Oligocene) is overlain by the pervasively dolomitized Cayman Formation; Niue, where the partly dolomitized Lower Dolomites (Late Miocene) are overlain by the pervasively dolomitized Upper Dolomite (Pliocene) (Wheeler et al., 1999); and the Xisha Islands, where the absence of dolomite in the Lower Miocene Xisha Formation contrasts with the pervasively dolomitized rocks in the overlying Middle Miocene Xuande Formation and Upper Miocene Yongle Formation (Wei et al., 2006).

PETROGRAPHY

At island-wide scales, Cenozoic island dolostones range from fabric-retentive to fabric-destructive (e.g., Vahrenkamp & Swart, 1994; Ren & Jones, 2017). The dolostone fabrics, however, have been classified in different ways. Budd (1997), for example, divided island dolostones into mimetic, non-mimetic but texture preserving, and non-mimetic and texture destroying. In contrast, dolostones on the Bahamas Bank (Dawans & Swart, 1984; Vahrenkamp & Swart, 1994), Niue (Wheeler et al., 1999) and Kita-daito-jima (Suzuki et al., 2006) have been classified as crystalline mimetic, crystalline microsucrosic, crystalline non-mimetic, and microsucrosic dolomites.

Geographic variations are evident in the fabrics of group A1 dolostones, including those found on the Little Bahama Bank, Mururoa, Niue, and Grand Cayman. On those islands, the depositional fabrics of the dolostones are better preserved in the coastal areas than in the interior of the island. In the Cayman Formation on the east end of Grand Cayman, there is a gradual change from fabric retentive fabrics in the coastal areas to fabric destructive fabrics in the interior of the island (Ren & Jones, 2017). Similar transitions are also apparent in the Cayman Formation on the western part of Grand Cayman (Jones & Luth, 2002). In contrast, only fabric retentive dolostones are evident in the Cayman Formation on Cayman Brac, which is only ~3 km wide (Zhao & Jones, 2012a). On the Little Bahama Bank, crystalline mimetic dolomites are more common near the bank margins and there is a gradual change to microsucrosic dolostone inland (Vahrenkamp & Swart, 1994). On some islands, there is a parallel landward decrease in the amount of dolomite cement. This is illustrated on Mururoa (Aissaoui et al., 1986) where void-lining dolomite cement or overgrowths on replacive dolomites (Type 2 dolomite in Aissaoui et al., 1986), is best developed in the hard-crystalline dolostones found around the coast of the island.

For groups A2 and B, the diagenetic fabrics can be related to their geographic and stratigraphic locations. Examples of fabric-retentive textures include those found in the (1) Pliocene dolostones from the coastal area of San Salvador (Dawans & Swart, 1988), (2) Pleistocene dolostones from Hole 2 drilled in the coastal area of Aitutaki (Hein et al., 1992), (3) Upper Miocene dolostones from Xisha Islands (Wei et al., 2008, their Fig. 5; Wang et al., 2015, their Figs. 4, 5), (4) dolostones in the Seroe Domi Formation (Pliocene) on Bonaire and Curacao

(Sibley, 1980; Fouke, 1994), (5) Upper Dolomites (Pliocene) from Niue (Wheeler et al., 1999), and (6) Pedro Castle Formation (Pliocene) from the Cayman Islands (MacNeil & Jones, 2003). These examples show that fabric-retentive dolomites are commonly found in the shallow coastal areas of a regional dolostone body where dolomitizations probably occurred immediately after the sediments were deposited. Dolostones with fabric destructive fabrics are found in the interior of many islands, including those from a well drilled in the interior of Kita-daito-jima (Suzuki et al., 2006), in the incompletely dolomitized limestones in the Oligocene dolostones from the Brac Formation on Cayman Brac (Zhao & Jones, 2012b), in the Lower Dolomites (Miocene) on Niue (Wheeler et al., 1999), in the deep part of the succession on Enewetak (1250 m below surface; Saller et al., 1984), and the Miocene dolostones on San Salvador (110 m below surface; Dawans & Swart, 1988). In all cases, these fabric-destructive dolostones are overlain by dolostones characterized by fabric retentive textures (i.e., Pliocene dolomites above Miocene dolomites from Kita-daito-jima, Upper Dolomite above the Lower Dolomite from Niue, Cayman Formation above Brac Formation from Cayman Islands, and Pliocene dolomites above Miocene dolomites from San Salvador). In general, the distribution of these fabric-destructive dolostone samples indicate that the original depositional fabrics evident in the deeper and/or interior dolostones on the islands are not as well preserved as the overlying younger, coastal dolostones.

In most Cenozoic island dolostones, the dolomite crystals are microcrystalline (< 1 μm) to ~2 mm long (Budd, 1997). In the dolostones from the Cayman Islands and the Bahamas, crystal size is correlated, to some extent, with the diagenetic fabrics (cf., Dawans & Swart, 1988; Vahrenkamp & Swart, 1994; Zhao & Jones, 2012a, b). The fabric destructive dolostones tend to be formed of larger crystals (100–200 μm in the crystalline non-mimetic Bahamian dolostones; 50–1500 μm in the dolostones of the Brac Formation from Cayman Brac) than in the fabric retentive dolostones (10–60 μm of the crystalline mimetic and microsucrosic Bahamian dolomites; 10–20 μm of the dolostones of Cayman Formation from Cayman Brac).

DOLOMITE STOICHIOMETRY

Cenozoic dolomites are invariably nonstoichiometric (Table 2; Figs. 2, 3) with >50% mole %$CaCO_3$ (hereafter referred to as %Ca). Based on the %Ca, many island dolostones contain more than one population of dolomite (e.g., Vahrenkamp & Swart, 1994; Swart & Melim, 2000; Wheeler et al., 1999; Jones et al., 2001; Suzuki et al., 2006). On the Cayman Islands, for example, dolostones are typically formed of low-calcium calcian dolomite (LCD, %Ca <55%) and high-calcium calcian dolomite (HCD, %Ca >55%) (Jones et al., 2001). The LCD and HCD crystals are characterized by different crystal microstructures, submicron growth zones in LCD, and dissolution slots in HCD (Jones, 2013).

In group A1, geographic variations in dolomite stoichiometry are more obvious in the larger island (width > 4 km) dolostone bodies than in the small ones. Examples include the Cayman Formation (Miocene) on Grand Cayman, the Lower and Upper Dolomites (Miocene–Pliocene) on Little Bahama Bank, and the Daito Formation (Pliocene) on Kita-daito-jima (Table 2, group A1; Figs. 2, 3). The increase in average %Ca in these dolostone bodies from the coastal area to the island center can be > 2%. On Grand Cayman, the Cayman Formation was divided into the peripheral, transitional, and interior dolostone zones based on geographic trends in dolomite stoichiometry (Ren & Jones, 2017). For smaller dolostone bodies, like the Cayman Formation on Cayman Brac (width ~2-3 km), the %Ca is relatively constant and all dolostone appears to correspond to the peripheral dolostone zone of the Cayman Formation on Grand Cayman.

Dolostones from single wells on islands that belong to group A2 can provide hints as to the lateral variability in dolomite %Ca when comparison is made with other islands. Two coastal wells on San Salvador and Chenhang Island (Xisha Islands), for example, have more stoichiometric dolomites than the dolomites from a well in the interior of Kita-daito-jima (Table 2). In these situations, the distance from the shoreline seems to be an important factor.

For all bodies in group B, the dolomite in partially dolomitized limestones has a high average %Ca (>54.9%), irrespective of their positions relative to the coast of the island. The dolomite %Ca may be related to the percentage of dolomite in the rocks, as suggested by an overall higher %Ca in dolomites from islands that contain dolomitic limestones solely relative to both dolostones and dolomitic limestones. A negative correlation between the dolomite content and %Ca is also observed in dolomites from the Great Bahama Bank (Swart & Melim, 2000).

STABLE ISOTOPES

Most island dolostones have positive $\delta^{18}O$ values varying from 0 to +5‰, and $\delta^{13}C$ values from 0 to +4‰ (Table 2; Figs. 2, 4). Notable exceptions are those with negative $\delta^{13}C$ values, such as those found in the Seroe Domi Formation on Curacaos (Fouke, 1994) and the Golden Grove dolostones on Barbados (Humphrey, 1988; Machel & Burton, 1994). The oxygen and carbon isotopes, like values of dolomite stoichiometry, are geographically variable on individual islands.

In group A1, oxygen and carbon isotope values of the dolostones generally decrease towards the centers of islands. This systematic variation is evident in dolostones from the Cayman Formation on Grand Cayman, the Daito Formation on Kita-daito-jima, the Lower and Upper Dolomites on Little Bahama Bank, and the Pliocene dolostones on Mururoa (Table 2; Figs. 2, 4B). For each dolostone body, there is no overlap in the dolomite isotope values between the peripheral and interior samples, and there is a positive co-variation between the $\delta^{18}O$ and $\delta^{13}C$ values (Fig. 4B).

Dolostones in group B show no particular relationship between isotope values and locations of samples or with dolomite %Ca (Table 2; Fig. 2). Within individual dolostone bodies, available data suggest that the partially dolomitized limestones typically have lower $\delta^{18}O$ and $\delta^{13}C$ values than samples formed entirely of dolomite, as demonstrated by the Cayman Formation from Grand Cayman and the Brac Formation from Cayman Brac (Zhao & Jones, 2012b) (Fig. 2). Partly dolomitized island carbonates, however, do not necessarily have lower dolomite $\delta^{18}O$ and $\delta^{13}C$ values than those that have been completely dolomitized. The high variability in the dolomite isotope values between islands and formations reflects the complexity of the factors controlling their incorporation. Despite this, comparison between dolostone bodies shows that most of those with high or low $\delta^{18}O$ have correspondingly high or low $\delta^{13}C$ values (Table 2; Fig. 2).

CASE STUDY: COMPARISONS BETWEEN THE CENOZOIC DOLOSTONES OF GRAND CAYMAN AND CAYMAN BRAC

The carbonate succession on the Cayman Islands comprises the Oligocene Brac Formation (> 30 m thick), the Miocene Cayman Formation (~100–140 m thick), and the Pliocene Pedro Castle Formation (~15–20 m thick) that belong to the Bluff Group, and the Pleistocene Ironshore Formation (Jones et al., 1994a, b) (Fig. 5). The distribution and attributes of the dolostones in this succession vary from formation to formation and from island to island (Figs. 6-8). As such, they are ideal for comparing dolostones of different ages from islands of different sizes, different morphologies, and different tectonic backgrounds (cf., Jones, 1994).

Some caution must be taken with respect to the geochemical attributes of the finely crystalline dolostones that are found in the Cayman Formation and Pedro Castle Formation. The constituent crystals, typically < 50 µm long and commonly < 25 µm long, are commonly formed of zones of LCD and HCD (Fig. 8) that are commonly < 10 µm thick. Given that it is impossible to sample individual crystals and zones at these scales, it is important to realize that all of the geochemical analyses are averages of the all of the zones and/or crystals that contributed to that sample. It is also important to note that this problem applies to all samples of finely crystalline dolostones, irrespective of their age and location.

Extent of dolostones

On Grand Cayman and Cayman Brac, dolostones are present in the Cayman Formation, Brac Formation, and Pedro Castle Formation (e.g., Jones, 1994), with only minor dolomite occurrences (maximum 12% content in rock) in the oldest part of the Ironshore Formation (Unit A) on Grand Cayman (Li & Jones, 2013). With respect to the dolostones in the older formations, the following points are important (Fig. 6):

- On both islands, the Cayman Formation is the most extensively dolomitized part of the succession with ~75% of the formation on Grand Cayman and the entire formation on Cayman Brac consisting of dolostones (cf., Jones, 1994; Jones & Luth, 2002; Der, 2012; Ren & Jones, 2017).
- On Cayman Brac, the Brac Formation is incompletely dolomitized. On the north coast, dolomite is absent apart from scattered rhombs and small pods found in the limestones near the upper boundary (e.g., Jones, 1994). In contrast, on the south coast this formation is formed of coarsely crystalline dolostones that contains isolated pods of limestone (e.g.,

Jones, 1994; Zhao & Jones, 2012b). On Grand Cayman, for example, the Brac Formation found only in the deepest wells, is also incompletely dolomitized.

- On both islands, the Pedro Castle Formation has been variably dolomitized (Jones, 1994; MacNeil & Jones, 2003). On Cayman Brac, dolostones at the base grade upwards into dolomitic limestone and then limestone. Collectively, dolostones form less than half of the formation.

Petrography

The depositional textures of the original limestones are generally better preserved in the dolostones of the Cayman Formation and Pedro Castle Formation (Jones & Luth, 2002; MacNeil & Jones, 2003; Jones, 2005; Ren & Jones, 2017) than those of the Brac Formation that is characterized by fabric-destructive dolomitization (Zhao & Jones, 2012b). In the Cayman Formation, which has been most extensively dolomitized, geographic variation in diagenetic fabrics is evidenced (Fig. 7). Most dolostones in the Cayman Formation and Pedro Castle Formation are formed of finely crystalline dolomite (average 10-30 μm, most < 50 μm long), whereas those in the Brac Formation are formed of crystals up to 1.5 mm long. Dolomite crystals (especially dolomite cement), irrespective of which formation and island they are from, are commonly formed of zoned LCD- HCD (Fig. 8).

Dolomite stoichiometry

Dolostones from the Bluff Group consist of varying proportions of LCD and HCD and variable average %Ca (Table 3; Figs. 6, 8).

- In the Cayman Formation, dolostones range from LCD-dominated dolostones (LCD/HCD > 1), with a low average %Ca in the coastal regions to HCD-dominated dolostones (LCD/HCD < 1) with high average %Ca in the island interior on the east end of Grand Cayman (Table 3).

In contrast, on Cayman Brac, the dolostones in this formation are dominated by LCD and in this respect are equivalent to the peripheral dolostones on Grand Cayman.

- In the Pedro Castle Formation on Grand Cayman, dolostones are formed largely of LCD with an average %Ca <55% (Jones & Luth, 2002). In contrast, on Cayman Brac, the dolostones in this formation are largely HCD with an average %Ca >55% (MacNeil & Jones, 2003).
- The Brac Formation is composed of HCD-dominated dolostones with average %Ca 56.8 ± 0.5% in the pure dolostones and 56.6 ± 0.5% in the partially dolomitized limestones (Table 3).

Stable isotopes

There is no readily identifiable pattern in the oxygen and carbon isotope values in the dolostones from the three formations in the Bluff Group (Table 3). In the Cayman Formation, the isotope values vary by location: (1) dolostones from the interior part of the eastern Grand Cayman are depleted with respect to the heavy isotopes, and (2) the $\delta^{18}O$ and $\delta^{13}C$ values of dolostones from the peripheral area of western part of Grand Cayman and Cayman Brac are lower than those from the peripheral dolostones on the eastern end of Grand Cayman (Table 3). Dolomite from partially dolomitized limestones from the Pedro Castle Formation and Brac Formation have $\delta^{18}O$ and $\delta^{13}C$ values similar to those obtained from the dolomites in the dolomitic limestones in the interior of Grand Cayman (Table 3). In the Brac Formation, the average $\delta^{18}O$ and $\delta^{13}C$ of dolomite from the pure dolostones are 1.1‰ and 0.6‰ higher than those in partially dolomitized limestones (Table 3).

Time of dolomitization

Based on $^{87}Sr/^{86}Sr$ dating and stratigraphy, the carbonate successions on the Cayman Islands appear to have experienced multiple episodes of dolomitization since the Oligocene

(Jones & Luth, 2002, 2003b; MacNeil & Jones, 2003; Zhao & Jones, 2012a, b; Ren & Jones, 2017), as follows:

- The Brac Formation was affected by late Miocene (8–6 Ma) and Pliocene–early Pleistocene (5–1 Ma) phases of dolomitization (Zhao & Jones, 2012a).
- Proposed dates for the dolomitization events that affected the Cayman Formation include late Miocene (8.0–6.0 Ma) and late Pliocene (2.2–1.9 Ma) (Jones & Luth, 2003b), late Miocene (8–6 Ma) and Pliocene–late Pleistocene (5–1 Ma) (Zhao & Jones, 2012a, b), and late Miocene (7.5–5.5 Ma) and late Pliocene–early Pleistocene (3–1.5 Ma) (Ren & Jones, 2017). Dolomitization during the middle Pleistocene may have had a local effect on the formation (Jones & Luth, 2003b).
- Dolomitization of the Pedro Castle Formation occurred during late Pliocene (Jones & Luth, 2003b), possibly 4.4–1.2 Ma (MacNeil & Jones, 2003).
- The dolomite in Unit A of the Ironshore Formation must have formed after the deposition of that unit, which took place ~0.4 Ma according to Vézina et al. (1999).

CONSTRAINTS FROM EXPERIMENTAL DATA

In the laboratory, abiogenic dolomite is invariably synthesized at high temperatures with most being > 175 °C (e.g., Katz & Matthews, 1977; Baker & Kastner, 1981; Bullen & Sibley, 1984; Sibley et al., 1987; Sibley & Bartlett, 1987; Sibley, 1990; Nordeng & Sibley, 1994; Sibley et al., 1994; Kessels et al., 2000; Kaczmarek & Sibley, 2007, 2011, 2014; Gregg et al., 2015; Kaczmarek & Thornton, 2017) (Table 4). Lower-temperature experiments typically produce high magnesium calcite (HMC, mole %Mg > 4%; see Tucker & Wright, 1990) and very high magnesium calcite (VHMC, mole %Mg > 36%; see Sibley, 1994 and reference therein) instead of dolomite. Experiments under ambient (~25 °C) abiogenic conditions have failed to precipitate dolomite (e.g., Land, 1998). Nevertheless, these dolomitization experiments (Table 4) conducted under variable reaction temperatures, reactants, and solution compositions, have produced a wide array of Mg-Ca carbonate precipitates and have provided some valuable insights into natural dolomite formation.

Many dolomite-synthesis experiments have demonstrated that stoichiometric dolomites are produced once the calcite/aragonite reactants have been fully consumed (e.g., Katz & Matthews, 1977; Sibley et al., 1987; Kessels et al., 2000; Kaczmarek & Sibley, 2011). Development of these stoichiometric dolomites, however, typically includes a long induction stage and various intermediate phases (e.g., Katz & Matthews, 1973; Sibley et al., 1987; Sibley, 1990; Kaczmarek & Sibley, 2014). The "induction stage", which is the period prior to the "…nucleation and growth of dolomite to detectable amounts…" (Sibley et al., 1987, p. 1112), is critical to the entire reaction process because it can last for a very long time, especially when the solution has low Mg/Ca ratios (e.g., Kaczmarek & Sibley, 2011, their Table 1). The intermediate products produced during the formative stages are Ca-Mg carbonates with an array of stoichiometric compositions include low-magnesium calcite, high-magnesium calcite, very high-magnesium calcite, and nonstoichiometric, poorly ordered dolomite (Katz & Matthews, 1973; Sibley, 1990; Sibley et al., 1994; Kaczmarek & Sibley, 2011, 2014). Sibley (1990) suggested that dolomitization evolves through three-stages (HMC – Ca-rich, poorly ordered dolomite – stoichiometric, ordered dolomite). Kaczmarek & Sibley (2014) proposed a four-stage reaction model: induction – rapid replacement – first recrystallization – second recrystallization (note that here the recrystallization is referred to as increases in dolomite stoichiometry and cation ordering) (Table 4; Fig. 9B).

Results from high-temperature experiments indicate that the stoichiometry of synthetic dolomites is related to the Mg/Ca ratio of the initial solution and the stage at which the dolomite is synthesized (Table 4; Fig. 9A, B). The Mg/Ca ratio of the solution determines the stoichiometry of the initial dolomite product (Sibley, 1990; Kaczmarek & Sibley, 2011). As the reaction progresses until its last stage (i.e., 95-100% dolomite), the Mg content in the dolomite does not change even though the Mg/Ca ratio of the solution is reduced (Kaczmarek & Sibley, 2011, 2014). During the final stage, dramatic increases in dolomite stoichiometry take place and stoichiometric dolomite is formed when the precursor calcite is fully transformed to dolomite (Kaczmarek & Sibley, 2014; Fig. 9B). Thus, it seems that factors that accelerate the reaction rate or reduce the induction period may promote dolomite stoichiometry. These kinetic-controlling factors include primarily temperature (high), mineralogy (aragonite *versus* calcite), surface area (large), and crystal size of the reactant (small), alkalinity (high), Mg and Ca concentrations (high), and Mg/Ca ratio in the solution (high), and water-rock ratio (high) (e.g., Katz & Matthews, 1973; Baker & Kastner, 1981; Bullen & Sibley, 1984; Sibley et al., 1987; Land, 1998; Sibley et al., 1994; Arvidson & McKenzie, 1999; Kaczmarek & Sibley, 2011; Kaczmarek & Thornton, 2017; Table 4).

DISCUSSION

Studies of island dolostones have produced many important insights into Cenozoic dolomitization processes (cf., Budd, 1997) and led to the development of various dolomitization models and genetic interpretations of island dolostones (e.g., Land, 1973, 1985; Saller, 1984; Dawans & Swart, 1988; Swart & Melim, 2000; Table 1). Given that most studies were based on limited numbers of wells or localized outcrops, many models and genetic interpretations were based on the “average” dolostone properties and/or stratigraphic variations in the petrographic and stable isotopic attributes of the rocks, and little thought was given to geographic variations. Although some demonstrated variations in dolostones at various geographic scales (e.g., Vahrenkamp & Swart, 1994; Fouke, 1994; Gill et al., 1995; Budd and Mathias, 2015), no consensus has been reached with respect to the possible linkages between the geographic variability and the dolomitization processes.

Using subsurface data from dolostones on Grand Cayman, Ren & Jones (2017) demonstrated that the geographic variations in the stoichiometric and geochemical attributes of the dolostones from the coast to the center of a carbonate island are significant and should be incorporated into dolomitization models (i.e., Cayman model). On Grand Cayman, differences in dolostone properties evident over distances of 1–2 km from the coastline are apparent in the (1) composition of the dolomite populations, (2) average %Ca of the dolostones, (3) $\delta^{18}O$ and $\delta^{13}C$ values, and (4) degree of preservation of sedimentary fabrics and percentage of dolomite cement (Fig. 10).

Geographic variations in dolomite stoichiometry and stable isotopes are reflections of the dolomitization process (Ren & Jones, 2017). Thus, after the seawater enters the island at the coastline, its chemical composition is constantly modified by water-rock interactions and by mixing with meteoric water as it flows inland (Fig. 10). If the rate of Mg and ^{18}O consumption during dolomitization is higher than the supply rate of the seawater, then the high Mg/Ca ratio and ^{18}O content of the dolomitizing fluid found in coastal areas of the island cannot be maintained as seawater flows inland. Dolomite stoichiometry and stable isotopes are controlled largely by the chemical compositions of the formative fluids (Folk & Land, 1975; Ward & Halley, 1985; Hardier, 1987; Kaczmarek & Sibley, 2011) and precipitation of dolomite can cause a change in the fluid properties and thereby reduce its capability for dolomitization (e.g., Kaczmarek & Sibley, 2011). This mechanism may be further enhanced by lateral variations in some of the environmental conditions, including for example, a landward decrease in flow rate and possibly, a decrease in groundwater temperature. This negative feedback in the dolomitization system may eventually lead to a situation where dolomitization is no longer possible. Depending on where that limit is, the original limestones in the interior of the island will not be dolomitized. This is the situation, for example, in the Cayman Formation on the eastern part of Grand Cayman (Ren & Jones, 2017).

The possibility that the lateral extent of dolomitization and variations in the geochemical attributes of the Cenozoic dolostones may reflect later diagenetic modifications is not supported by available evidence. There is, for example, no petrographic evidence that post-dolomitization diagenesis has had any significant impact on the Cayman dolostones. Although the metastable HCD may, with time, be altered to LCD (cf., Jones, 2007), there is little evidence that this has taken place in the dolostones on the Cayman Islands. Mazzullo (1992) and Machel (1997) suggested that dolomite recrystallization will lead to increased stoichiometry, increased crystal size, depletion of ^{18}O, decreased Sr and Na concentrations, and homogenization of primary cathodoluminescent crystal zonation. In the Brac Formation on Cayman Brac, the high calcium content (>55%), lack of correlation between %Ca and diagenetic fabrics, no evidence of depletion of ^{18}O and Sr, and the zoned dolomite crystals (Zhao & Jones, 2012b) indicate that those dolostones have not been recrystallized. There is no correlation between the LCD/HCD in dolostones and their ages with the oldest sampled dolostones from the Brac Formation still being composed largely of HCD.

Like the Cayman Formation on Grand Cayman, the regional dolostone bodies on Cayman Brac, the Little Bahama Bank, Kita-daito-jima, and Mururoa have similar geographic variation patterns in many of their properties (Fig. 10). The similarity reveals some key points behind the genesis of regional island dolostones during the Cenozoic: (1) seawater is the source of the dolomitizing fluid, (2) seawater migrates inland from all coastlines of the island, (3) during the landward migration, the seawater changes its chemical composition (due to water-rock interaction and/or mixing with freshwater) and flow rate, and (4) the extent of dolomitization is probably limited by reaction kinetics of dolomitization and seawater supply. Although the general patterns are similar to those proposed for Grand Cayman, they are universally the same. On Cayman Brac, for example, which has a similar geological setting as Grand Cayman, the Cayman Formation has been pervasively dolomitized and there are no limestones in the island interior. There, all the dolostones in the Cayman Formation consist largely of LCD (generally >75%) with an average %Ca <54% and thus resemble the peripheral dolostones on Grand Cayman (Fig. 11A). The differences between these islands reflect island-size with the full width (N-S) of Cayman Brac being comparable to the width of the peripheral dolostone zone on Grand Cayman. For the Little Bahama Bank and Kita-daito-jima the peripheral zones are narrower and the transitional or interior dolostone zones are wider (Fig. 11B) than those found on Grand Cayman. The situations on San Salvador, Kita-daito-jima, and the Xisha Islands are more difficult to assess because each island is represented by only one well. If the locations of the wells are considered relative to the island margin, however, the differences in dolomite stoichiometry seem consistent with the Cayman model. Nevertheless, more data are needed to verify the dolomitization pattern on those islands.

The Cayman model is a conceptual model that cannot, at this time, be precisely quantified. This situation arises for reasons that are inherent to the dolomitization process and reflects differences in the geographic intrusion of the dolomitizing fluids, as is demonstrated by the following considerations.

- On many islands, the pattern of dolomitization is geographically asymmetrical. On Grand Cayman, for example, the inland extent of dolomitization is greater on the northeast corner than elsewhere (Ren & Jones, 2017). Similarly, on Kita-daito-jima, the lateral extent of dolomitization in the Pliocene strata is greater on the east coast than on the west coast. Although the hydrological conditions during dolomitization are unknown, the asymmetry is probably linked directly to the size and location of freshwater lens(es), seawater intrusion pathways, and the overall patterns of groundwater flow.
- The width of dolostone zones varies from island to island (Fig. 11). The gradient of dolomite stoichiometry is related to the distance from the island edge (lateral changes in the average %Ca of dolomites per km, %Ca/km) but varies from island to island. The gradient on Grand Cayman (1.5%Ca/km) is greater than that on Kita-daito-jima (1.1%Ca/km; Figs. 2, 12). On the Little Bahama Bank, which seems to be an "enlarged" version of the Grand Cayman model, the lateral stoichiometric gradient is only 0.1%Ca/km (Figs. 2, 12). These differences may reflect differences in hydrological conditions, the duration of dolomitization(s), and/or sampling density on the islands.
- Dolostones from the same zone with similar stoichiometry can have different stable isotope signatures. The isotopic values of the dolostones from the Cayman Formation on Cayman Brac, for example, are typically ~1‰ lower (on average) than those from the peripheral dolostone zone on Grand Cayman. This means that these two parameters are controlled by different factors and "…have different rock/water ratios in dolomitizing systems…" (Budd, 1997, p. 34). High-temperature experiments have shown that dolomite stoichiometry is

controlled by the chemical compositions of the dolomitizing fluid and the stage of dolomitization reactions (e.g., Kaczmarek & Sibley, 2011, 2014). In contrast, the stable isotopic compositions of island dolostones are primarily controlled by the isotopic composition and temperature of the formative fluid. Likewise, trace elements such as Sr and Mn, and $^{87}Sr/^{86}Sr$ may also show spatial variations in natural dolostones (e.g., Machel, 1988; Qing and Mountjoy, 1992; Machel and Cavell, 1999) but may differ in same dolostone zone on different islands.

The variations in the dolomitization patterns between islands illustrates the dynamic nature of dolomitization and the fact that dolomitization is influenced by many factors. Theoretically, dolomitization can take place once (1) an efficient circulation mechanism has been established whereby seawater can circulated into the island, (2) a fluid with appropriate geochemical properties (e.g., Mg/Ca, pCO_2, T) has been developed, and (3) temporal stability allows the dolomitization process to take place over a long period (e.g., Morrow, 1982; Land, 1985; Machel, 2004). Once these conditions are established, intrinsic factors within the host limestone become important. Such factors include the size and geometry of the island, the extent of the water-rock interaction, the development of a freshwater lens, openness of the dolomitization system that are largely related to bedrock porosity and permeability and their evolution during dolomitization (e.g., Banner and Hanson, 1990). Collectively, these factors affect the flux and geochemistry of the dolomitizing fluid that, in turn, control the mass supply of the reactants and reaction kinetics. Given this multitude of variables, it is not surprising that the dolostones on different islands are petrographically and geochemically variable. It is also important to note that the geographic variations evident in the island dolostones are consistent with the groundwater flow rate from numerical modeling and the conclusions obtained from high-temperature dolomite synthesis experiments (e.g., Wilson et al., 1990; Kaufman, 1994; Whitaker et al., 2004; Sibley, 1990; Kaczmarek & Sibley, 2011, 2014).

The variability evident between Cenozoic dolostones from different oceanic islands has been a major problem in developing models that explain the dolomitizing processes. In scope, island dolostone bodies range from limestones that have only been partially dolomitized with the dolomite typically HCD, to pervasively dolomitized rocks that are characterized by organized geographic zones (Fig. 13). Many Cenozoic island dolostones are localized in extent. Despite their coastal locations, many of these dolostones have very high average %Ca (> 55%), and are therefore more akin to the dolostones found in the interior dolomitic limestone zone of the Cayman model. No peripheral or transitional zones are evident in these formations (Fig. 11C). These variations between localized and pervasive dolomitizations, however, may reflect the development stage of the dolomitizing process and the supply rate and distance that formative fluids have migrated from coastlines.

The evolutionary stages of dolomitization have been illustrated in many high temperature experiments (Katz & Matthews, 1977; Sibley et al., 1987; Sibley, 1990; Sibley et al., 1994; Kaczmarek & Sibley, 2011, 2014). Kaczmarek & Sibley (2014), for example, proposed that dolomitization reaction progresses through induction (no dolomite), replacement (Ca-rich dolomite, stoichiometry and cation ordering remain constant; 0-97% dolomite), primary recrystallization (Ca-rich dolomite, stoichiometry and cation ordering increases; ~95-100% dolomite), and secondary recrystallization (stoichiometric dolomite, cation ordering increases; 100% dolomite) stages. Correlation between the evolutionary stages of the experimental dolomitization and the evolution of the Cenozoic island dolostones is not straightforward. This is due largely to the fact that the stages evident in experimental reactions are practically impossible to recognize in natural settings where dolomitization has taken place under low temperature conditions. Another reason that hinders the correlation is that the relationship between the extent of dolomitization and dolomite stoichiometry (which are the criteria for the experimental stages) is inconsistent in the two settings. In the laboratory, most experiments have shown that stoichiometric dolomite is only achieved when 100% dolomite is formed (Table 4) whereas in nature, 100% dolomitized carbonate contains dominantly Ca-rich dolomite with very rare stoichiometric dolomite (e.g., Lumsden & Chimahusky, 1980). This difference between synthetic and natural dolomites adds further difficulties for applying experimental data to natural dolomitization.

Applying the experimental information directly to island dolomitization is complicated by many factors including (1) the temperatures (> 175 °C) used in the laboratory experiments are significantly higher than the ambient temperatures under which island dolostones formed, (2) the reagent-grade reactants (spar calcite or aragonite) used in most experiments (except Bullen & Sibley, 1984, and Kaczmarek & Thornton, 2017) are very different from the reactants in the original island limestones that are dominated by fossil fragments of variable compositions and sizes, (3) the compositions of the solutions (mostly Mg-Ca-Cl) and Mg/Ca ratios (mostly ~1) used in laboratory experiments are significantly different from the sea water (or slight modified seawater) that mediates island dolomitization, (4) reaction in the dolomite-synthesis experiments take place in confined reaction vessels whereas island dolomitization typically occurs in an open system with constant material exchange with the vast oceans and sea level fluctuations, (5) many of the kinetic-promoting factors, such as high temperature and shortened reaction time in the laboratory to hours to weeks, is practically impossible in natural dolomitization, and (6) microorganisms that may play a role in island dolomitization are not involved in the laboratory experiments. Nevertheless, the laboratory synthesis does provide information that may be applicable to the development of the island dolomites. Bullen & Sibley (1984), for example, demonstrated diagenetic fabrics in synthetic and natural dolostones that are similar, and Kaczmarek & Sibley (2007) showed that the crystal growth mechanisms are probably the same and implied that the synthesized dolomites are analogous to natural dolomites.

There is a possible correlation between the dolomitization pattern that exists spatially in the island dolostone bodies and the evolution of the synthetic dolomite in laboratory (Fig. 9B, C). For many regional island dolostone bodies, including the Cayman Formation on Grand Cayman, the landward increase in dolomite stoichiometry is probably caused by the landward decrease in the groundwater Mg/Ca ratio that is caused by the water-rock interactions and mixing with freshwater as it flows inland through the bedrock. This spatial variation in dolomite stoichiometry may also reflect the different dolomitization stages that individual dolostone zones are at. A possible correlation between dolostone zones and dolomitization reaction stages (following Kaczmarek & Sibley, 2014; Kaczmarek & Thornton, 2017) is that: interior limestone – induction stage, interior dolomitic limestone – rapid replacement stage, transitional dolostone – early primary recrystallization, and peripheral dolostone zone – late primary recrystallization (Fig. 9). For the localized dolomitic limestone bodies with most having isotopic evidence of seawater-mediated dolomitization, the high Ca contents in those dolomites may suggest that the reactions on these islands are possibly still at the rapid replacement stage.

The similarities in dolomite stoichiometry, geochemistry, and diagenetic fabrics between island dolostones throughout the Caribbean Sea and Pacific Ocean has led to the suggestion that they may have developed during Caribbean-wide or even world-wide dolomitization events (e.g., Sibley, 1980; Pleydell et al., 1990; Vahrenkamp et al., 1991; Budd, 1997; Jones & Luth, 2003b).

Most of the pervasively dolomitized bodies, which are typically at shallow depths with many being directly under the present-day island surface, seem to have experienced multiple phases of dolomitization during the late Miocene to Pliocene (dolomitization events C and/or D of Budd, 1997) (Fig. 13). Although there are few common features between the geographically localized dolostone bodies, most of them seem to be younger (Pleistocene and later), older (Eocene), or deeper (typically >100 m burial) than the regional dolostone bodies, and most seem to have experienced only one phase of dolomitization. Pervasive dolomitization such as in the Miocene-Pliocene dolostones from the Bahamas and Miocene dolostones on Cayman Islands may have resulted from longer duration of dolomitization, higher efficiency of seawater circulation, together with favorable atmospheric and seawater compositions including for example, the increased seawater Mg/Ca ratio during late Cenozoic.

The availability of more data from more island dolostones throughout the world provides a basis for improved comparisons that contribute to a better understanding of these complex successions. Despite these advances, the underlying causes of dolomitization in these settings is still open to debate even though it is generally agreed that seawater mediates the process. It is difficult to precisely define the factors that lead to dolomitization in these settings because it is difficult to precisely date the dolomitization “events” and even more difficult to relate those events to oceanic conditions (e.g., temperature, salinity, sea-level positions) and climatic regimes. The precise factors that govern the island dolomitization will remain enigmatic until it becomes possible to precisely integrate all aspects of the processes that control fluid circulation, and/or water-rock interactions, and dolomite growth. As yet, however, the precise factors that “trigger” dolomitization in these settings remain elusive.

CONCLUSIONS

Many Cenozoic island dolostone bodies demonstrate spatial variability in mineral properties. Analysis of these island dolostones from the viewpoint of spatial variation patterns has led to the following important conclusions.

- Regional dolostone bodies found on the Cenozoic islands show landward increase in %Ca, and decreases in $\delta^{18}O$ and $\delta^{13}C$ values, and preservation of precursor fabrics. A full range of peripheral to interior dolostone zones can be recognized in some large-scale dolostone bodies like the Cayman Formation on Grand Cayman.
- The geographic variability within dolostone bodies originates from changes in the chemical compositions of the dolomitizing fluid along the flow paths caused by water-rock interaction and/or mixing with meteoric water.
- Theoretically, a geographically concentric zonation pattern in the geochemical attributes of the dolostones can be applied to the Cenozoic island dolostones where laterally derived seawater was the parent dolomitizing fluid. The variations in the dolomitization patterns between islands attribute to the traits of the islands and the precursor carbonates, and/or the duration of dolomitization(s).
- Localized, incomplete dolomitized bodies contain dolomites with high %Ca and are equivalent to the dolomitic limestone zone of the Cayman model.
- Spatial variability in island dolostones largely conforms to the results obtained from dolomite synthesis experiments. Reaction stages in the experiments may apply to the evolution of island dolostones and explain their spatial variation pattern.

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FIGURE CAPTIONS

Fig. 1. Location of Cenozoic island dolostones.

Fig. 2. Dolomite stoichiometry, stable isotopes, and dolomitization phases of island dolostones (see Fig. 1 for locations). CB = Cayman Brac, GC(W) = Grand Cayman (west), GC(E) = Grand Cayman (east). PD = Peripheral Dolostone, TD = Transitional Dolostone, ID = Interior Dolostone, IL = Interior Dolomitic Limestone. Dolomitization phases after Budd (1997). (*: Dolomitization phase A (late Early Miocene) on the Little Bahama Bank not show.) GB1, WC, GB2, SC, Clino, Unda, DH4, and Fonuakula are wells on the islands. Data source: Cayman Formation, Cayman Islands (Jones & Luth, 2002; Zhao & Jones, 2012a; Ren & Jones, 2017); Mururoa (Aissaoui et al. 1986); Daito Formation, Kita-daito-jima (Suzuki et al., 2006); Little Bahama Bank (Vahrenkamp & Swart, 1994); San Salvador (Supko, 1977); Kita-daito-jima (Suzuki et al., 2006); Xuande Formation, Xisha (Wei et al., 2006); Bonaire [a] (Sibley, 1980); Bonaire [b] (Lucia and Major, 1994); Curacao and Curacao Dol II (Fouke, 1994); Pedro Castle Formation, Cayman Brac (MacNeil, 2002; MacNeil & Jones, 2003); Great Bahama Bank (Swart & Melim, 2000); Aitutaki (Hein et al., 1992); Niue Upper Dolomite (DH4) (Wheeler et al., 1999); Niue Upper Dolomite (Fonuakula) (Aharon et al., 1987); Jamaica (Land, 1973, 1991); Enewetak (Saller, 1984); Niue Lower Dolomite (Wheeler et al., 1999); Yucatan (Ward & Halley, 1984), Barbados (Humphrey, 1988; Machel, 1994), St. Croix (Gill et al., 1995).

Fig. 3. Geometry and size of the dolostone bodies and landward decrease in the dolomite stoichiometry in island dolostones from Cayman Brac (CB, Miocene Cayman Formation), Kita-daito-jima (K-D-J, Pliocene Daito Formation), Grand Cayman (Miocene Cayman Formation), and Little Bahama Bank (Miocene-Pliocene) along line of

section indicated on island. Data source: Cayman Brac (Zhao & Jones, 2012a), Kita-daito-jima (Suzuki et al., 2006), Grand Cayman (Ren & Jones, 2017), and Little Bahama Bank (Vahrenkamp & Swart, 1994).

Fig. 4. Oxygen and Carbon isotopes of (A) the island dolostones, and (B) dolostones from Grand Cayman (Cayman Formation), Daito Formation (Kita-daito-jima), and Mururoa (Pliocene), grouped by their geographic locations. Note geographic trends and overlaps in the isotope values of the formations from the three islands highlighted in panel B. Data source: San Salvador (Supko, 1977), Aitutaki (Hein et al., 1992), Niue [a] (Aharon et al., 1987), Niue [b] Upper Dol. (Wheeler et al., 1999), Niue [b] Lower Dolomite (Wheeler et al., 1999), Bonaire (Lucia and Major, 1994), Curacao Dol I, I', II (Fouke, 1994), Jamaica Hope Gate Formation (Land, 1973, 1991), Yucatan (Ward & Halley, 1984), Enewetak (Saller, 1984), Barbados (Humphrey, 1988; Machel, 1994), St. Croix (Gill et al., 1995), Xisha (Wei et al., 2008); and Daito Formation, Kita-daito-jima (Suzuki et al., 2006), Mururoa (Aissaoui et al. 1986), Cayman Formation, Grand Cayman (Ren & Jones, 2017).

Fig. 5. Stratigraphic succession on Grand Cayman (modified from Jones et al., 1994a).

Fig. 6. Cross sections on Grand Cayman and Cayman Brac showing the spatial variation of the extent of dolomitization, and mineral compositions in the Brac Formation, the Cayman Formation, and the Pedro Castle Formation (from Jones & Luth, 2002; MacNeil & Jones, 2003; Zhao & Jones, 2012a, b; Ren & Jones, 2016, 2017; and unpublished data).

Fig. 7. Thin section photomicrographs showing the characteristics of peripheral dolostones (A-C), transitional dolostones (D, E), and interior dolostones/limestones (F-H) from the Cayman Formation on Grand Cayman. All depths are below ground surface (well tops of wells RWP-2, HRQ-3, and GFN-2 are ~ 0.5 m, 2.9 m, and 3.0 m above sea level, respectively). Thin sections (A-C) have been stained with Alizarin Red S, and samples (D-H) have been impregnated with blue epoxy and half of the thin sections have been stained with Alizarin Red S. *H* = *Halimeda*, g = grain, p = porosity, dcmt = dolomite cement, ccmt = calcite cement, cfs = cavity-filling sediment, *Am* = *Amphistigina*, hd = hollow dolomite. (A) Fabric-retentive dolomitization of *Halimeda* plates, micritized grains, and cavity-filling sediments. RWP-2, 24.4 m. (B) Fabric-retentive dolomitization of *Amphistigina* with chamber-filling dolomite cement. Zoned dolomite cement lining the pores. RWP-2, 94.6 m. (C) Replacive dolomitization of skeletal grains with pores filled with blocky finely crystalline dolomite cement. RWP-2, 3.5 m. (D) Fabric-selective dolomitization of micritized grains. Some (micritized) benthic forams have been completed leached to generate the moldic porosities. Inter-particle pores are filled with very finely – finely crystalline dolomite cement. HRQ-3, 37.0 m. (E) Dolomitization of an intact *Amphistigina* and a partially leached grain with dolomite cement fills pores. HRQ-3, 79.6 m. (F) Finely crystalline dolostone with little fabric preservation. GFN-2, 9.6 m. (G) Hollow dolomite crystals formed by leaching of their interior. Inter-crystalline pores have been filled with calcite cement. GFN-2, 9.6 m. (H) Interior limestone: various components, little cementation, high porosity, and no evidence of dolomitization. GFN-2, 90.7 m.

Fig. 8. SEM photomicrographs of highly polished and etched thin sections (with concentrated HCl) from the Cayman Formation on Grand Cayman. All depths are below ground surface (well tops of wells RTR-1, HRQ-2, and HMB-1 are ~ 1.7 m, 2.9 m, and 4.0 m above sea level, respectively). LCD = low calcium calcian dolomite; HCD = high calcium calcian dolomite. (A) Anhedral – subheral matrix dolomite crystals (upper right)

and cavity filled with zoned euhedral dolomite cement. RTR-1, 8.2 m. (B) Interlocking anhedral – subheral dolomite crystals. HRQ-2, 27.1 m. (C) Cement dolomite crystals showing growth zones with LCD and HCD. HMB-1, 1.1 m. (D) Matrix formed of interlocking zoned dolomite crystals formed of LCD and HCD. HMB-1, 1.1 m.

Fig. 9. Comparison between the dolomite stoichiometry in high-temperature dolomite synthesis experiments that are associated with (A) the Mg/Ca ratios of the initial solutions (modified from Kaczmarek & Sibley, 2011) and (B) reaction stages (modified from Kaczmarek & Sibley, 2014 and Kaczmarek & Thornton, 2017), and (C) dolomite stoichiometry in many regional island dolostone bodies that typically can be divided into spatially distributed dolomitization zones characterized by varying dolomite stoichiometry (exampled by the Cayman Formation on Grand Cayman). HCD: high-calcium dolomite (%Ca > 55%), LCD: low-calcium dolomite (%Ca < 55%).

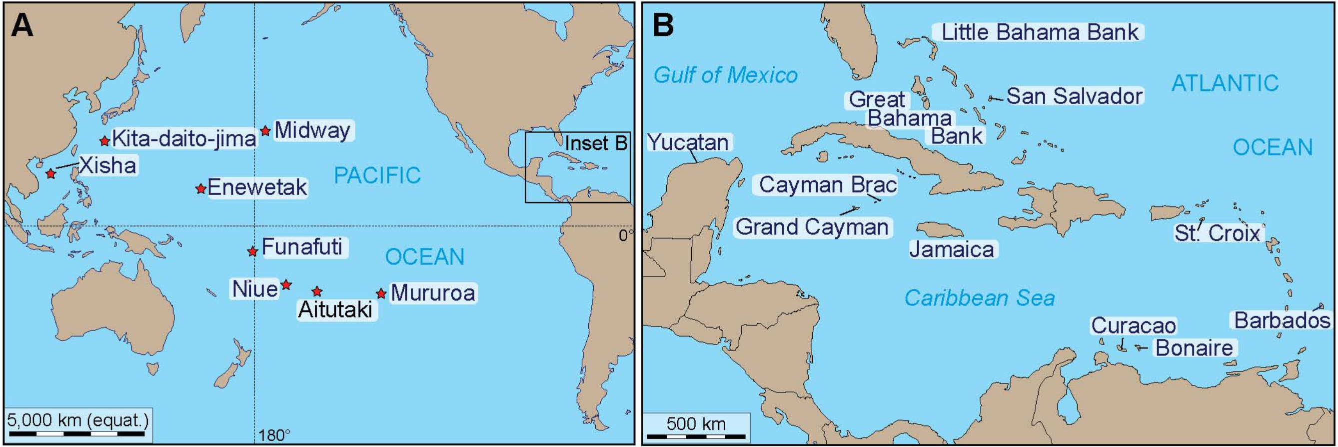
Fig. 10. Dolomitization model showing the lateral variations in various attributes of island dolostones (after Ren & Jones, 2017). See text for discussion.

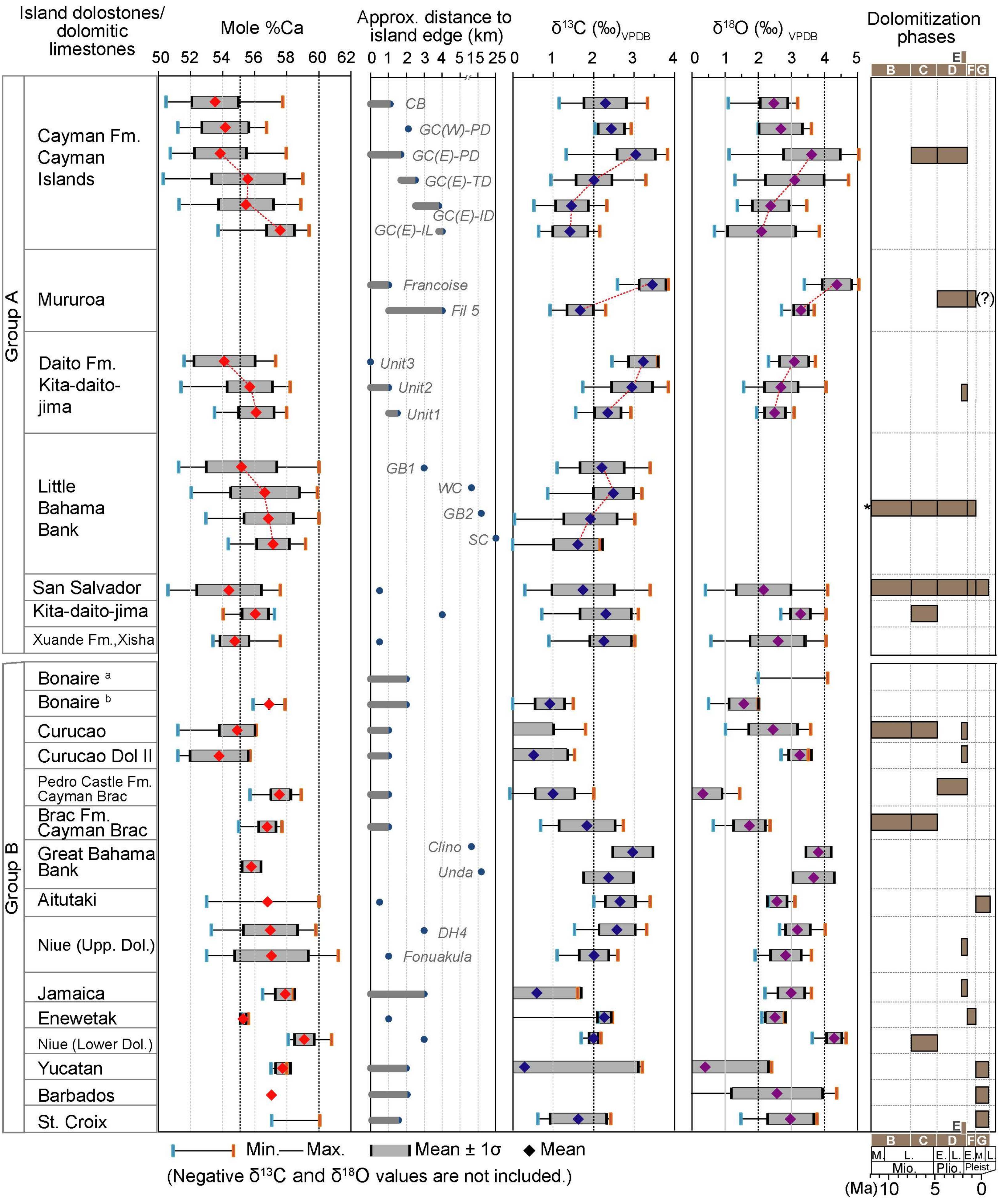
Fig. 11. Schematic diagram showing geographic zones on various islands based primarily on the dolomite stoichiometry including (A, B) on regionally dolomitized islands, and (C) incomplete zones on localized dolomitized islands. (A) Cayman Formation includes PD (Peripheral dolostone), TD (Transitional dolostone), ID (Interior dolostone), and IL (Interior (dolomitic) limestone) on Grand Cayman, and PD only on Cayman Brac defined by the LCD-HCD compositions and %Ca. (B) Possible zones in the Daito Formation, Kita-daito-jima, and Miocene-Pliocene dolostones on the Little Bahama Bank, based on zones recognized in the Cayman model. (C) Localized dolostones in the Pedro Castle Formation, the Brac Formation, and the Hope Gate Formation contain zones that are

equivalent to the interior dolostone/dolomitic limestones zone of the Cayman model. Size of arrows indicating seawater flow directions indicate differences in dolomitization potential.

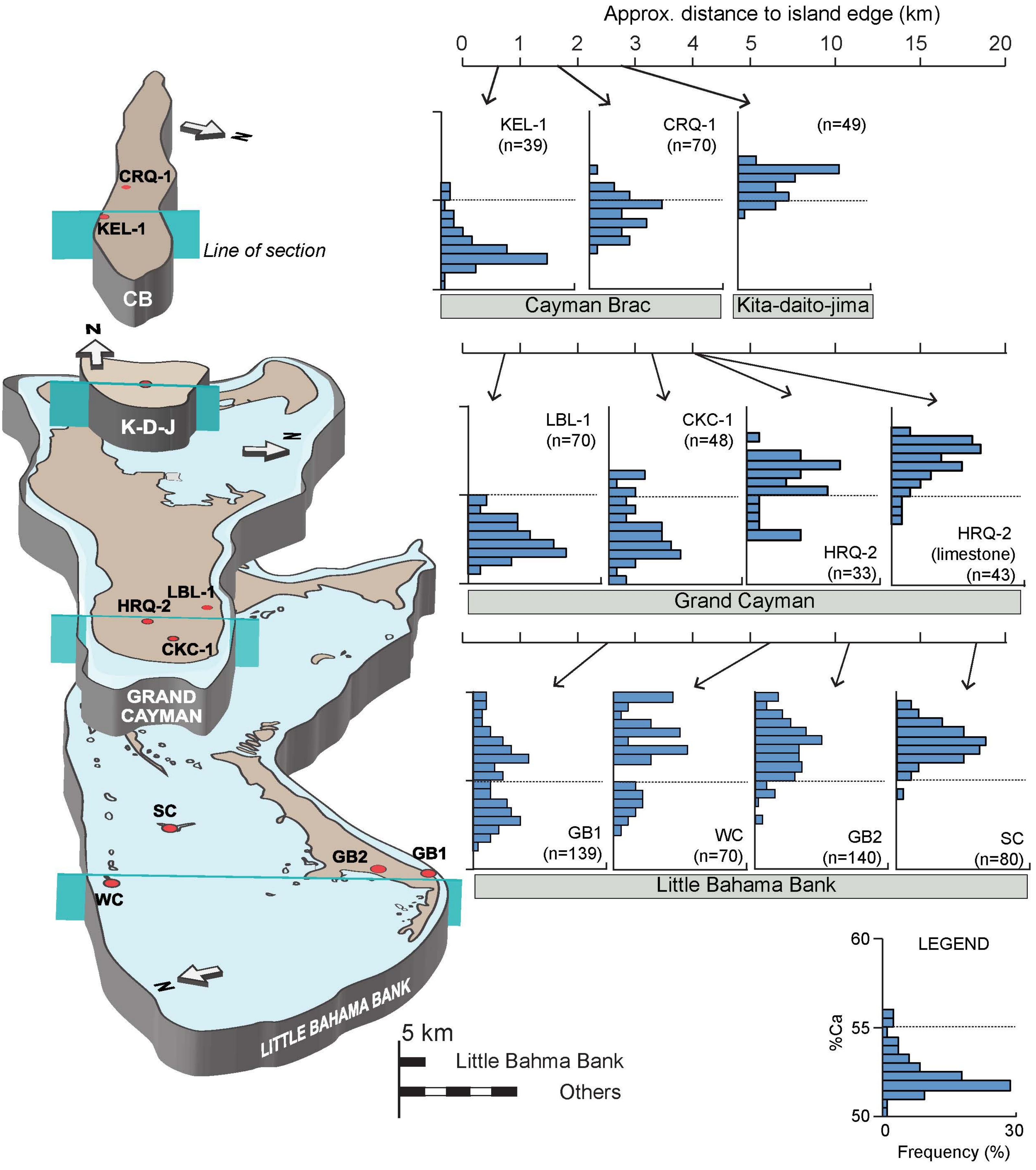
Fig. 12. Increases of the average %Ca in dolomites with distance from the edge of the Little Bahama Bank (Miocene-Pliocene), Grand Cayman (Cayman Formation), and Kita-daito-jima (Daito Formation).

Fig. 13. Cenozoic island carbonate successions showing variation in development stages in terms of the landward extending of the dolomites and the lateral distribution pattern of the dolomite attributes relative to the dolomitization events (as defined by Budd, 1997), and the $^{87}Sr/^{86}Sr$ ratios of the dolostones (dolomitic limestones).

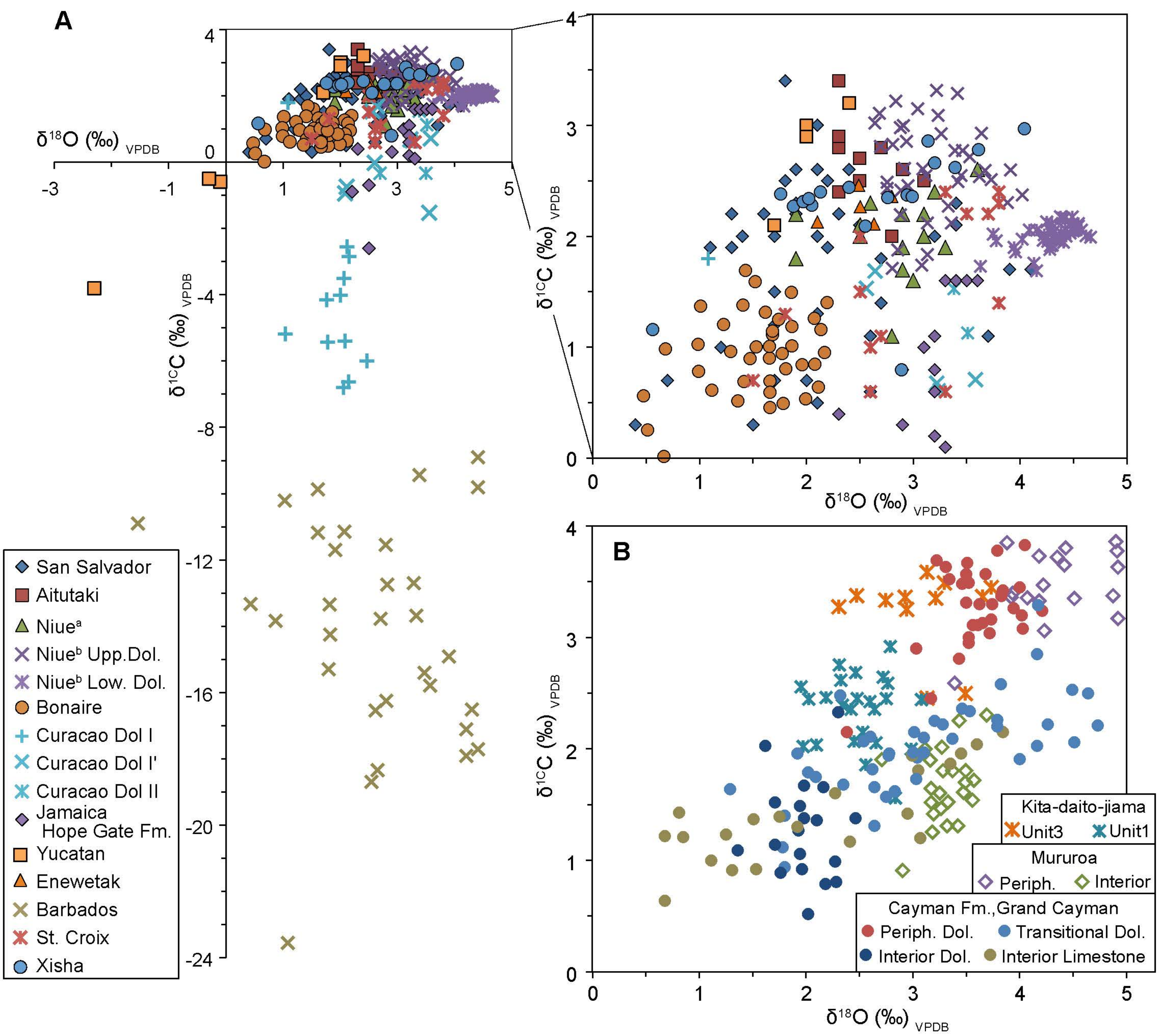

A
Kita-daito-jima
Midway
Xisha
Enewetak
PACIFIC
Inset B
0°
Funafuti
OCEAN
Niue
Aitutaki
Mururoa
5,000 km (equat.)
180°
B
Little Bahama Bank
Gulf of Mexico
Great
Bahama
Bank
San Salvador
ATLANTIC
OCEAN
Yucatan
Cayman Brac
Grand Cayman
Jamaica
St. Croix
Caribbean Sea
Curacao
Bonaire
Barbados
500 km



Island dolostones/ dolomitic limestones
Mole %Ca
Approx. distance to island edge (km)
δ13C (‰)VPDB
δ18O (‰) VPDB
Dolomitization phases
Group A
Group B
Cayman Fm. Cayman Islands
Mururoa
Daito Fm. Kita-daito-jima
Little Bahama Bank
San Salvador
Kita-daito-jima
Xuande Fm.,Xisha
Bonaire a
Bonaire b
Curucao
Curucao Dol II
Pedro Castle Fm. Cayman Brac
Brac Fm. Cayman Brac
Great Bahama Bank
Aitutaki
Niue (Upp. Dol.)
Jamaica
Enewetak
Niue (Lower Dol.)
Yucatan
Barbados
St. Croix
CB
GC(W)-PD
GC(E)-PD
GC(E)-TD
GC(E)-ID
GC(E)-IL
Francoise
Fil 5
Unit3
Unit2
Unit1
GB1
WC
GB2
SC
Clino
Unda
DH4
Fonuakula
B C D E F G
(?)
Min.—Max.
Mean ± 1σ
◆ Mean
(Negative δ13C and δ18O values are not included.)
M. L. E. L. E. M. L.
Mio. Plio. Pleist.
(Ma) 10 5 0



Approx. distance to island edge (km)
0 1 2 3 4 5 10 15 20
KEL-1 (n=39)
CRQ-1 (n=70)
(n=49)
Cayman Brac
Kita-daito-jima
LBL-1 (n=70)
CKC-1 (n=48)
HRQ-2 (n=33)
HRQ-2 (limestone) (n=43)
Grand Cayman
GB1 (n=139)
WC (n=70)
GB2 (n=140)
SC (n=80)
Little Bahama Bank
LEGEND
%Ca
60
55
50
0
30
Frequency (%)
CRQ-1
KEL-1
Line of section
CB
K-D-J
HRQ-2
LBL-1
CKC-1
GRAND CAYMAN
SC
GB2
GB1
WC
LITTLE BAHAMA BANK
N
5 km
Little Bahma Bank
Others

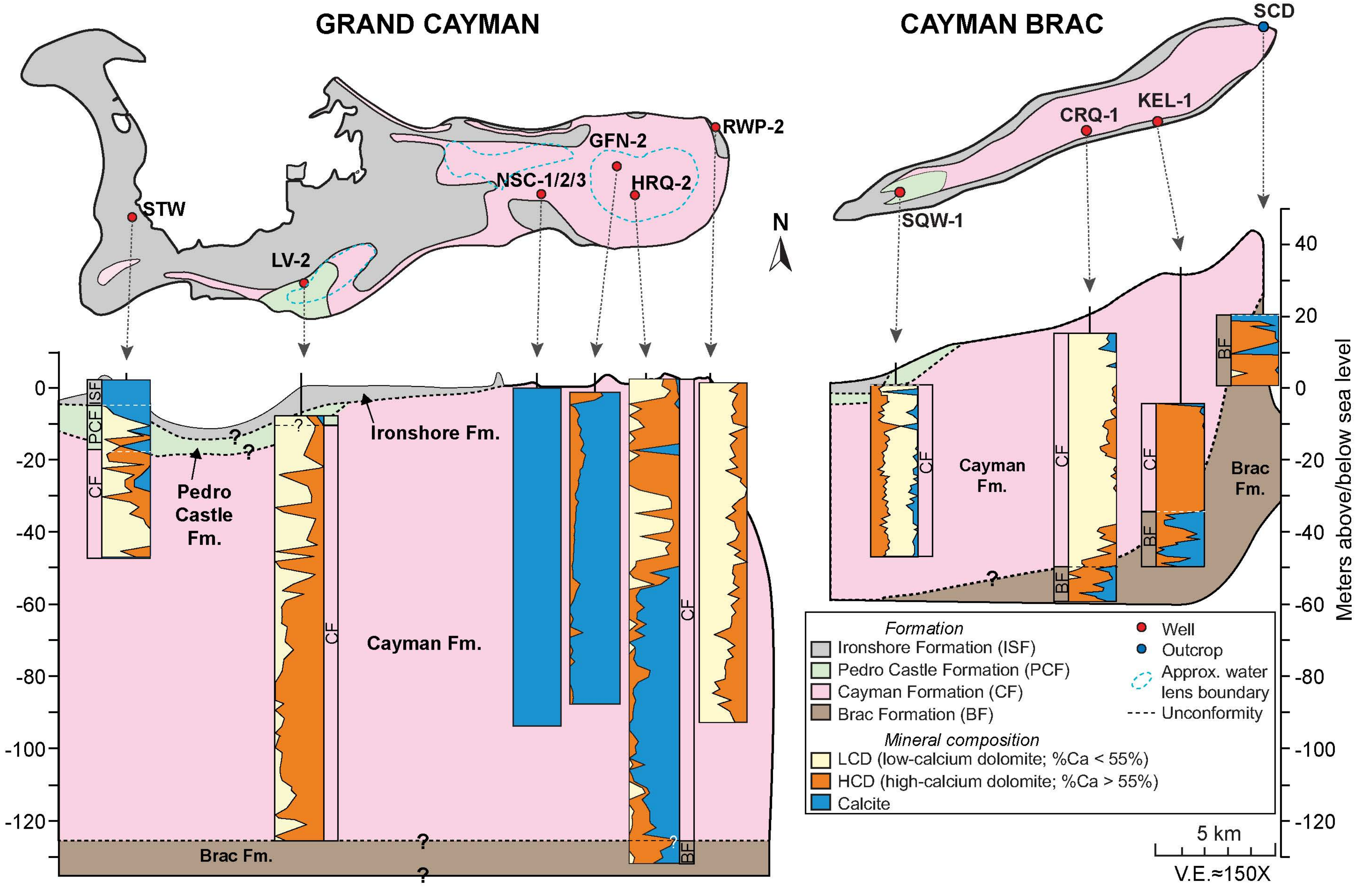


A
B
δ18O (‰) VPDB
δ1CC (‰) VPDB
San Salvador
Aitutaki
Niuea
Niueb Upp.Dol.
Niueb Low. Dol.
Bonaire
Curacao Dol I
Curacao Dol I'
Curacao Dol II
Jamaica Hope Gate Fm.
Yucatan
Enewetak
Barbados
St. Croix
Xisha
Kita-daito-jiama
Unit3
Unit1
Mururoa
Periph.
Interior
Cayman Fm.,Grand Cayman
Periph. Dol.
Transitional Dol.
Interior Dol.
Interior Limestone

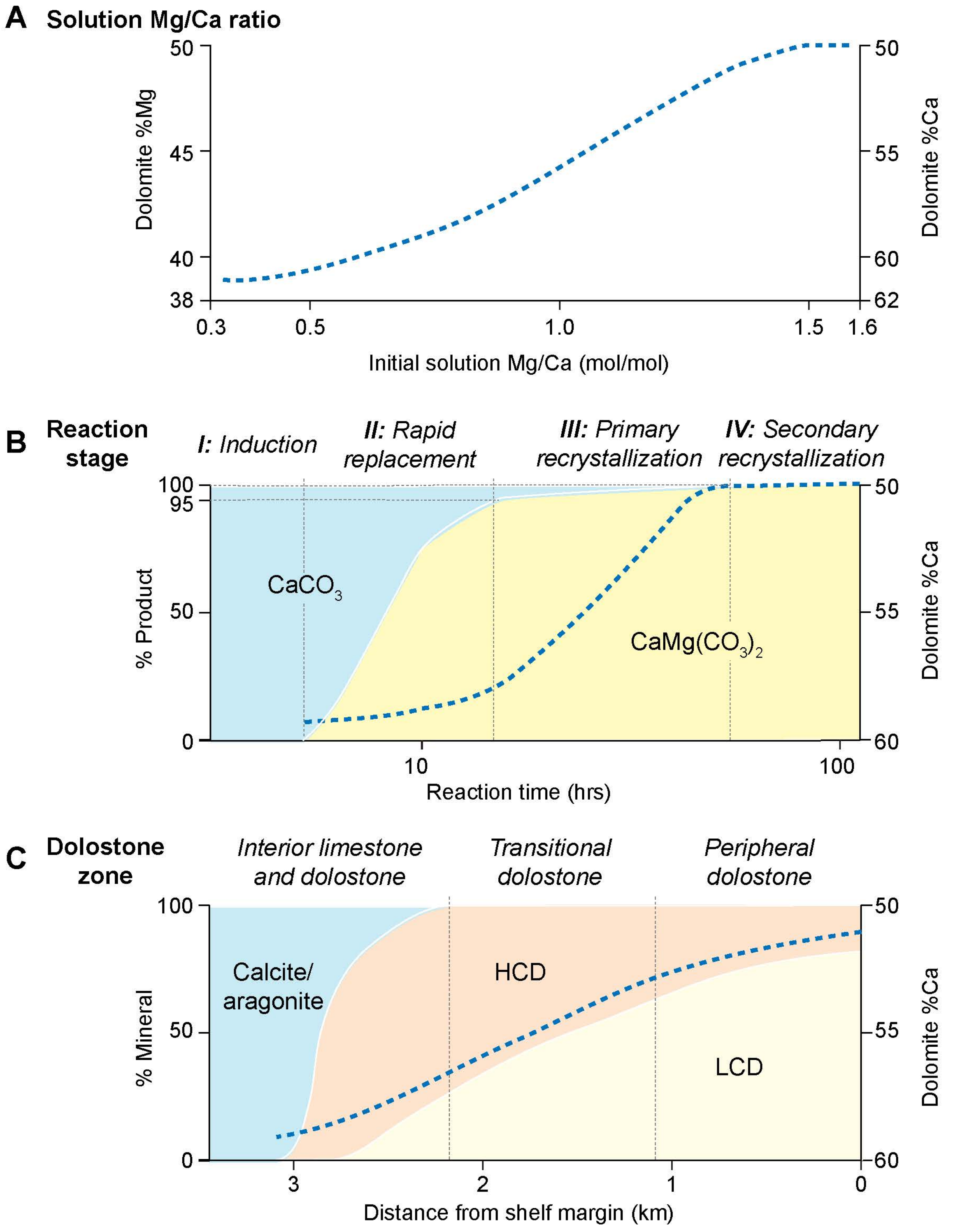
AGE		UNIT	LITHOLOGY	FAUNA
HOL.			Swamp deposits storm deposits	
PLEIST.		*Unconformity* IRONSHORE FORMATION	Limestone	Corals (VC) Bivalves (VC) Gastropods (C)
PLIOCENE	BLUFF GROUP	*Unconformity* PEDRO CASTLE FORMATION	Dolostone (fabric retentive) and limestone	Forams (VC) Corals (C) Bivalves (LC) Gastropods (C) Red algae (C) *Halimeda* (R)
M.MIOCENE	BLUFF GROUP	*Unconformity* CAYMAN FORMATION	Dolostone (fabric retentive) and limestone locally	Corals (VC) Bivalves (LC) Rhodoliths (LC) Gastropods (R) Red algae (LC) Foraminifera (LC) *Halimeda* (R)
L.OLIG.	BLUFF GROUP	*Unconformity* BRAC FORMATION	Limestone or sucrosic dolostone (fabric destructive) with pods of limestone	Bivalves (VC) Gastropods (C) Foraminifera (VC) Red algae (R)

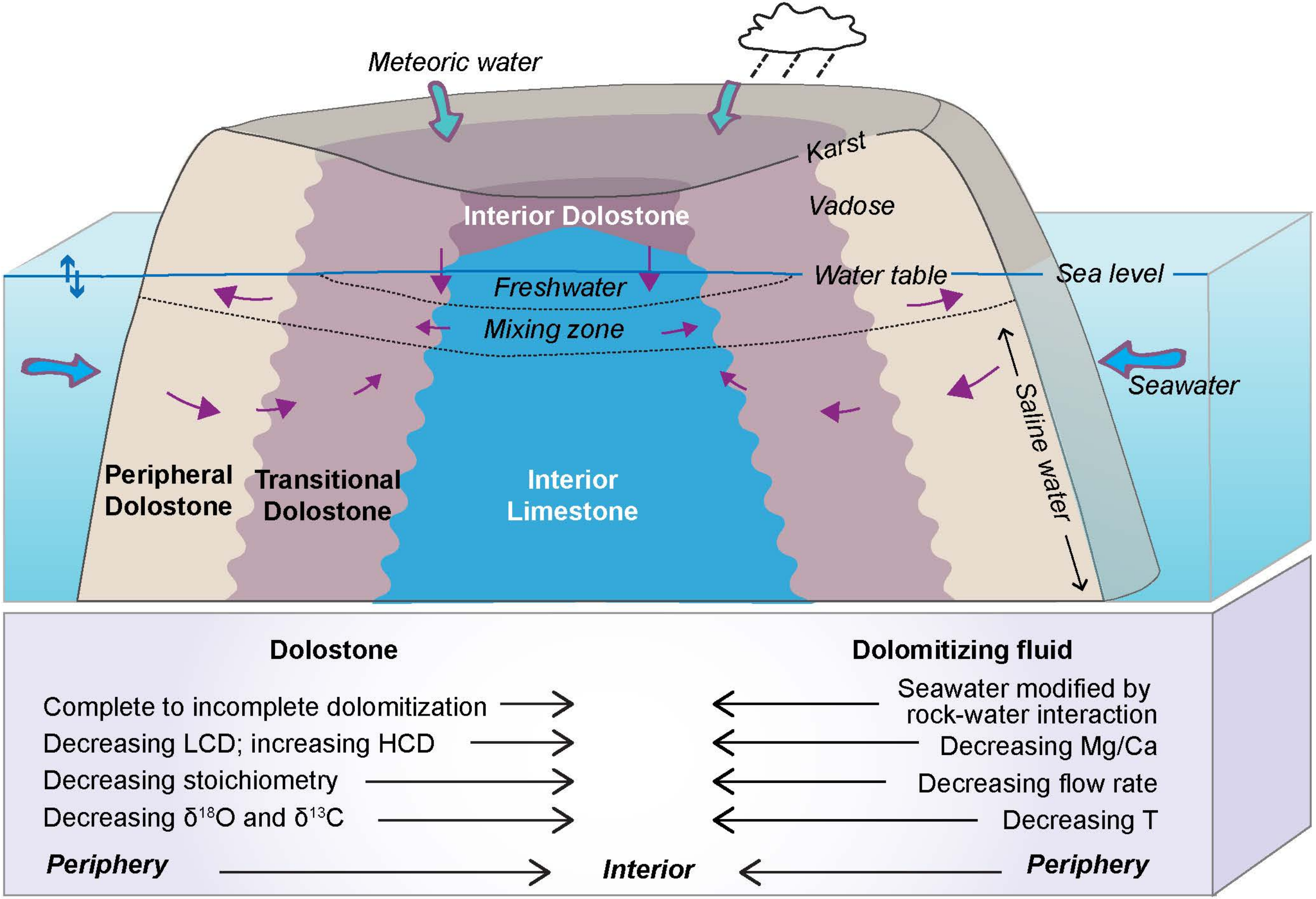
limestone; dolostone; swamp deposits

VC=very common; C=common; LC=locally common; R=rare.

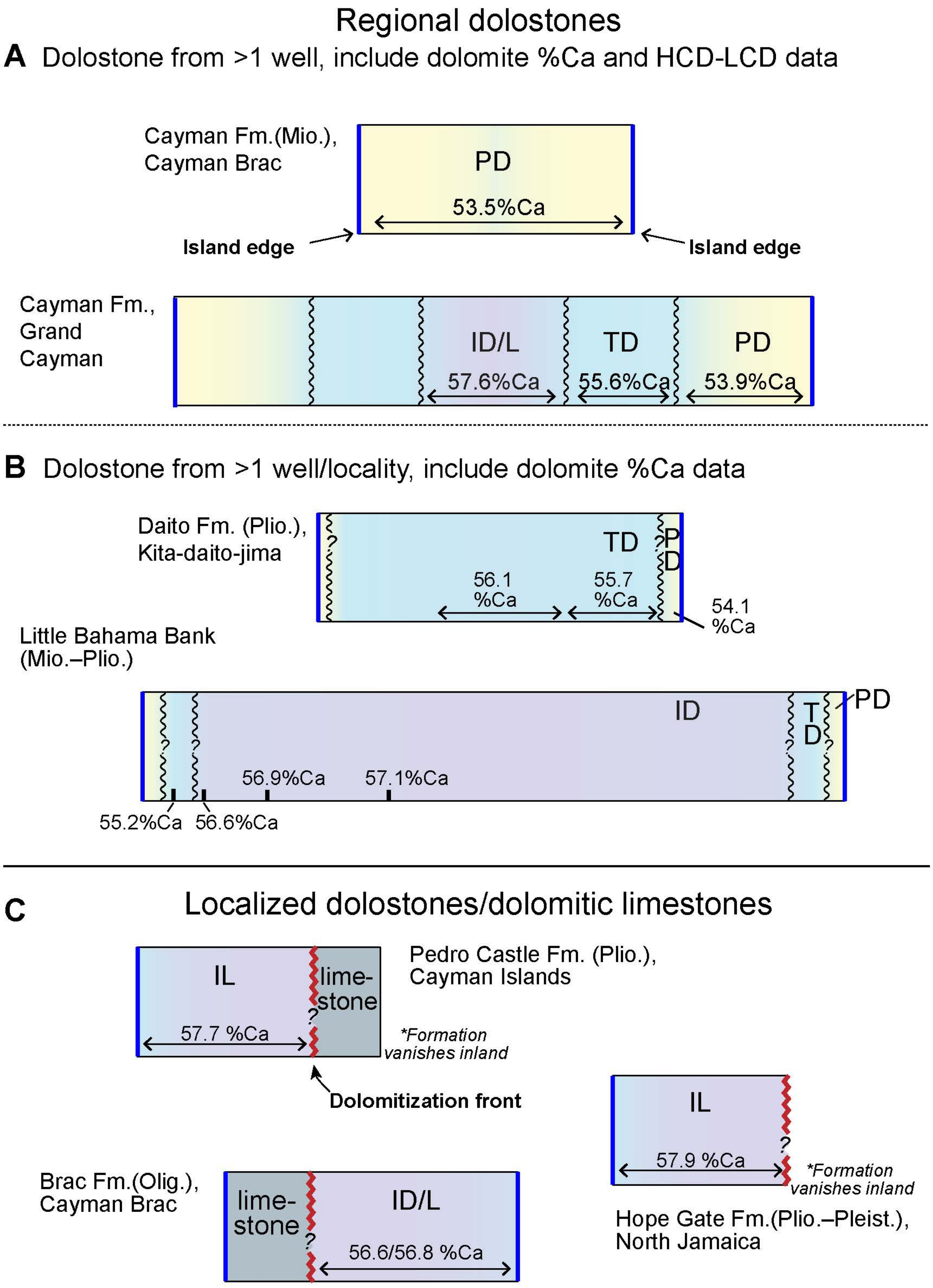


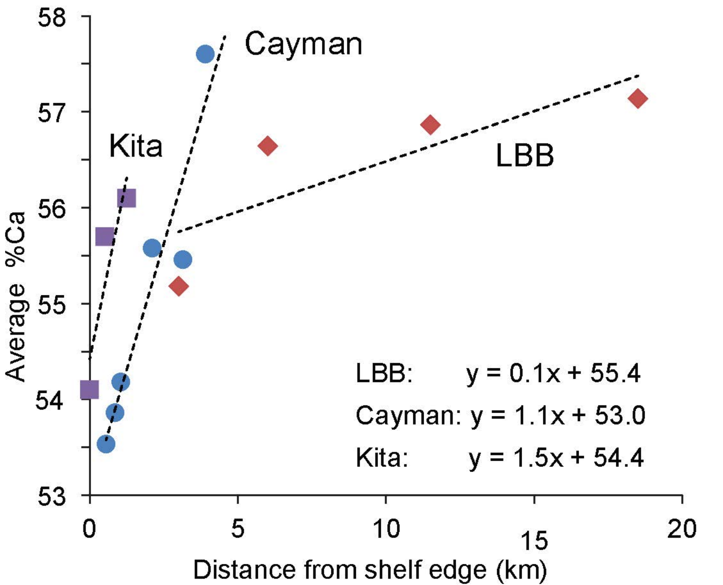
GRAND CAYMAN
CAYMAN BRAC
STW
LV-2
NSC-1/2/3
GFN-2
HRQ-2
RWP-2
SQW-1
CRQ-1
KEL-1
SCD
N
Ironshore Fm.
Pedro Castle Fm.
Cayman Fm.
Brac Fm.
ISF
PCF
CF
BF
Meters above/below sea level
Formation
Ironshore Formation (ISF)
Pedro Castle Formation (PCF)
Cayman Formation (CF)
Brac Formation (BF)
Well
Outcrop
Approx. water lens boundary
Unconformity
Mineral composition
LCD (low-calcium dolomite; %Ca < 55%)
HCD (high-calcium dolomite; %Ca > 55%)
Calcite
5 km
V.E.≈150X


A
Solution Mg/Ca ratio
Dolomite %Mg
Dolomite %Ca
50
45
40
38
50
55
60
62
0.3
0.5
1.0
1.5
1.6
Initial solution Mg/Ca (mol/mol)
B
Reaction stage
I: Induction
II: Rapid replacement
III: Primary recrystallization
IV: Secondary recrystallization
% Product
Dolomite %Ca
100
95
50
0
$CaCO_3$
$CaMg(CO_3)_2$
10
100
Reaction time (hrs)
C
Dolostone zone
Interior limestone and dolostone
Transitional dolostone
Peripheral dolostone
% Mineral
Dolomite %Ca
Calcite/ aragonite
HCD
LCD
3
2
1
0
Distance from shelf margin (km)

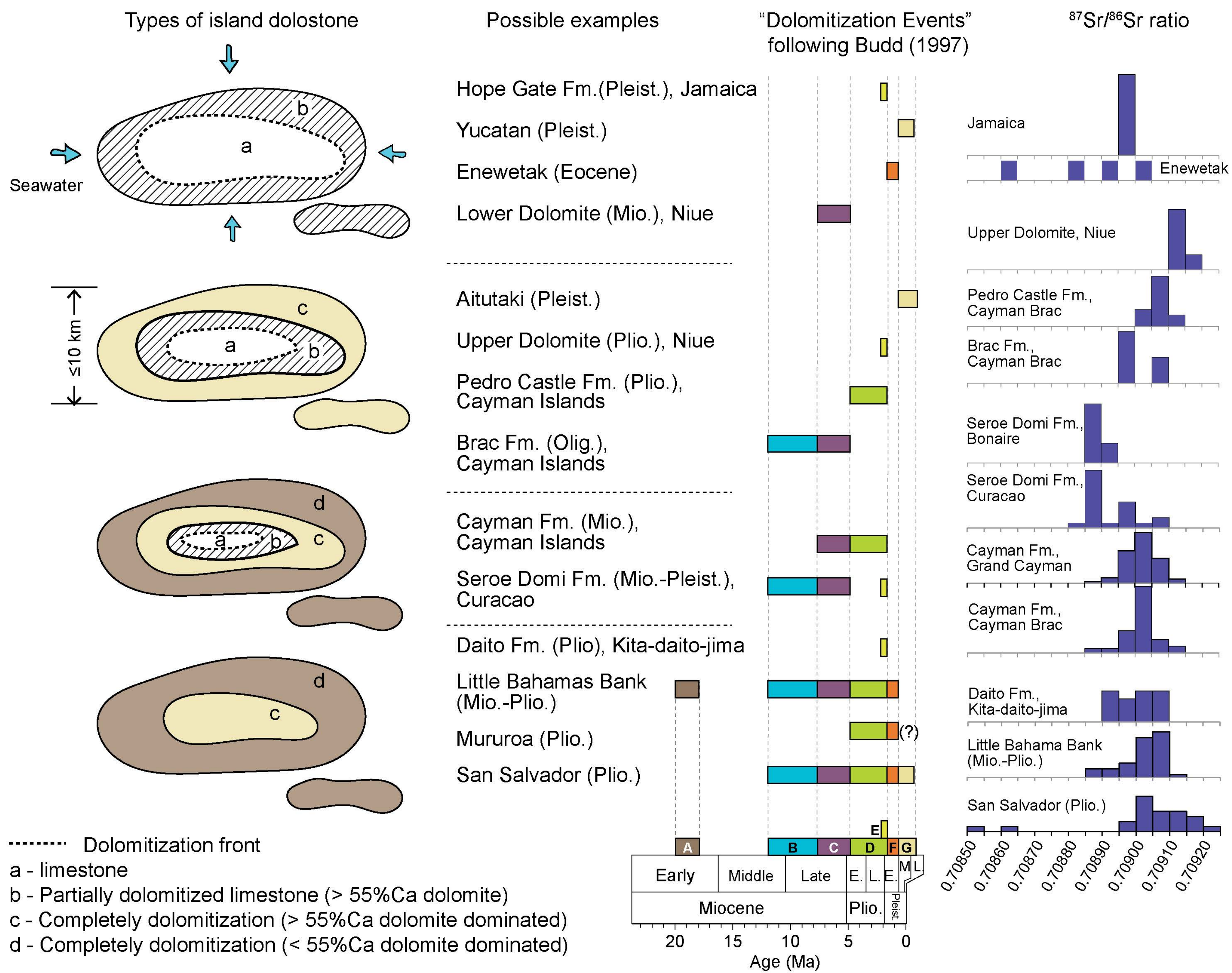


Meteoric water
Karst
Vadose
Interior Dolostone
Water table
Sea level
Freshwater
Mixing zone
Seawater
Saline water
Peripheral Dolostone
Transitional Dolostone
Interior Limestone
Dolostone
Dolomitizing fluid
Complete to incomplete dolomitization
Seawater modified by rock-water interaction
Decreasing LCD; increasing HCD
Decreasing Mg/Ca
Decreasing stoichiometry
Decreasing flow rate
Decreasing δ18O and δ13C
Decreasing T
Periphery
Interior
Periphery


Regional dolostones
A Dolostone from >1 well, include dolomite %Ca and HCD-LCD data
Cayman Fm.(Mio.), Cayman Brac
PD
53.5%Ca
Island edge
Island edge
Cayman Fm., Grand Cayman
ID/L
57.6%Ca
TD
55.6%Ca
PD
53.9%Ca
B Dolostone from >1 well/locality, include dolomite %Ca data
Daito Fm. (Plio.), Kita-daito-jima
TD
PD
56.1 %Ca
55.7 %Ca
54.1 %Ca
Little Bahama Bank (Mio.–Plio.)
ID
TD
PD
56.9%Ca
57.1%Ca
55.2%Ca
56.6%Ca
C Localized dolostones/dolomitic limestones
IL
lime-stone
57.7 %Ca
Pedro Castle Fm. (Plio.), Cayman Islands
*Formation vanishes inland
Dolomitization front
IL
57.9 %Ca
*Formation vanishes inland
Brac Fm.(Olig.), Cayman Brac
lime-stone
ID/L
56.6/56.8 %Ca
Hope Gate Fm.(Plio.–Pleist.), North Jamaica



Cayman
Kita
LBB
LBB: y = 0.1x + 55.4
Cayman: y = 1.1x + 53.0
Kita: y = 1.5x + 54.4
Average %Ca
58
57
56
55
54
53
0
5
10
15
20
Distance from shelf edge (km)



Types of island dolostone
Possible examples
"Dolomitization Events" following Budd (1997)
87Sr/86Sr ratio
Seawater
a
b
c
d
≤10 km
Hope Gate Fm.(Pleist.), Jamaica
Yucatan (Pleist.)
Enewetak (Eocene)
Lower Dolomite (Mio.), Niue
Aitutaki (Pleist.)
Upper Dolomite (Plio.), Niue
Pedro Castle Fm. (Plio.), Cayman Islands
Brac Fm. (Olig.), Cayman Islands
Cayman Fm. (Mio.), Cayman Islands
Seroe Domi Fm. (Mio.-Pleist.), Curacao
Daito Fm. (Plio), Kita-daito-jima
Little Bahamas Bank (Mio.-Plio.)
Mururoa (Plio.)
(?)
San Salvador (Plio.)
A B C D E F G
Early Middle Late E. L. E. M L.
Miocene Plio. Pleist.
20 15 10 5 0
Age (Ma)
Jamaica
Enewetak
Upper Dolomite, Niue
Pedro Castle Fm., Cayman Brac
Brac Fm., Cayman Brac
Seroe Domi Fm., Bonaire
Seroe Domi Fm., Curacao
Cayman Fm., Grand Cayman
Cayman Fm., Cayman Brac
Daito Fm., Kita-daito-jima
Little Bahama Bank (Mio.-Plio.)
San Salvador (Plio.)
0.70850 0.70860 0.70870 0.70880 0.70890 0.70900 0.70910 0.70920
Dolomitization front
a - limestone
b - Partially dolomitized limestone (> 55%Ca dolomite)
c - Completely dolomitization (> 55%Ca dolomite dominated)
d - Completely dolomitization (< 55%Ca dolomite dominated)

Table 1.
Cenozoic island dolostones/dolomites. Pervasively dolomitized examples with laterally widespread throughout an island (A1) are the main foucus of this study.

Island	Formation/ Dolomite strata	#Wells/ outcrops or area	Approx. km from island edge						Age	References
			1	2	3	5	10	20		
A - Extensive dolomite bodies below/on island, pervasive dolomitization										
(A1 Dolomites from >1 well/locations allowing island-wide varations detected)										
Grand Cayman	Cayman Fm.	21	■	■	■	■			E.-M. Mi.	Pleydell and Jones, 1991; Jones and Luth, 2002, 2003a, b; Ren and Jones, 2017
Cayman Brac	Cayman Fm.	4	■	■					E.-M. Mi.	Zhao and Jones, 2012, 2013
Little Bahama Bank	Lower & Upper Dolomite	4	■	■	■	■	■	■	M. Mi.-Pli.	Vahrenkamp and Swart, 1991, 1994
Mururoa	--	5	■	■	■	■			Pli.	Chevalier, 1973; Aissaoui et al., 1986
Kita-daito-jima	Daito Fm.	77	■	■	■				Pli.	Suzuki et al., 2006
(A2 dolomites from 1 well, island-wide variations undetectable)										
San Salvador	--	1	■						L. Mi-Pli.	Supko, 1977; Dawans and Swart, 1988
Kita-daito-jima	--	1		■					L. Mi-Pli.	Schlanger, 1963; Berner, 1965; Suzuki et al., 2006
Great Bahama Bank	--	Unda					■		E.-M. Mi.	Swart and Melim, 2000; Melim and Swart, 2002
Funafuti	--	--	■	■					--	Schlanger, 1963; Berner, 1965;
Xisha Islands	Xuande Fm. / Huangliu Fm.	Xichen-1, Xike-1	■						M.-L. Mi.	Wei et al., 2006, 2008; Wang et al., 2016
B - Localized or restricted distribution of dolostones, pervasive dolomitization										
Bonaire	Seroe Domi Fm.	NW	■	■					Pli.	Bondoian and Murray, 1974; Sibley, 1980, 1982; Lucia and Major, 1994
Caracao	Seroe Domi Fm.	SW	■						M. Mi.-E. Pleist.	Fouke, 1994

C - Localized or restricted distribution of dolomites, partial dolomitization										
Cayman Brac	Brac Fm.	5	■						Olig.	Zhao and Jones, 2012a
Cayman Islands	Pedro Castle Fm.	16	■						Pli.	MacNeil, 2001; Jones and Luth, 2002; MacNeil and Jones, 2003
Niue	Upper Dolomite	Fonakula	■						M.-L. Mi.	Rodgers et al., 1982; Aharon et al., 1987
Niue	Upper Dolomite	DH4			■				Pli.	Wheeler et al., 1999
Jamaica	Hope Gate Fm.	N	■	■	■				E. Pleist.	Land, 1973, 1991
Yucatan	--	NE	■	■					L. Pleist.	Ward and Halley, 1984
Enewetak	--	F-1	■						Eocene	Schlanger, 1963; Bener, 1965; Saller, 1984
Midway	--	Reef Hole	■						--	Ladd et al., 1970
Niue	Lower Dolomite	DH4			■				L. Mi.	Wheeler et al., 1999
Aitutaki	--	Hole 2	■						Pleist.	Hein et al., 1992
Barbados	--	Golden Grove	■	■					Pleist.	Humphrey, 1988, 2000; Machel et al., 1994
St. Croix	--	Krause Lagoon	■						--	Gill et al., 1995

Table 2.
Dolostones and dolomitic limestones from the Brac Formation, Cayman Formation, Pedro Castle Formation and Ironshore Formation on Grand Cayman and Cayman Brac, dolomite stoichiometry, stable isotopes, and interpreted (equivalent) geographic zones.

Formation	Location (Extent of dolomitization)	Geographic Zone (Equivalent)	% LCD> HCD samples	%LCD range (aveg.±1σ)	%Ca range (aveg.±1σ)	δ18O (‰) range (aveg.±1σ)	δ13C (‰) range (aveg.±1σ)	#Well/ XRD	#Well/ Isotopes
Ironshore	Cayman Islands	Rare (<12%) dolomite in Unit A only							
Pedro Castle	Cayman Brac (Partially dolomitized)	= ID/L?	-- --	-- --	55.85–58.95 (57.67±0.61)	-1.82–1.41 (0.23±0.70)	-0.22–2.02 (1.07±0.55)	3/33	3/33
Cayman Formation	Eastern Grand Cayman (>50% formation dolomitized, complete dolomitized in peripheral and partially in the center)	Peripheral Dolostone	79.3	0-100 (71±30)	50.75–57.96 (53.86±1.66)	1.11–5.03 (3.62±0.85)	1.32–3.83 (3.05±0.47)	7/421	4/105
		Transitional Dolostone	74.2	0-100 (39±38)	50.29–59.01 (55.58±2.25)	1.29–4.73 (3.10 ± 0.88)	0.94–3.29 (2.01±0.44)	4/190	2/41
		Interior Dolostone	36.0	0-100 (38±32)	51.29–58.88 (55.46±1.73)	1.36–3.46 (2.37±0.55)	0.52–2.33 (1.46±0.40)	8/341	2/36
		Interior Dolomitic Limestone	2.2	0–100 (2.7±13) (97%)	53.72–59.39 (57.6±0.86)	0.68–3.84 (2.10±1.03)	0.64–2.15 (1.42±0.43)	8/186	2/24
	Western peripheral GC (Completely dolomitized)	=PD-TD?	75.0	0-100 (60±28)	51.20–56.73 (54.18±1.47)	2.00–3.61 (2.68±0.65)	2.03–2.93 (2.44±0.32)	4/84	4/11
	Cayman Brac (Completely dolomitized)	=PD?	92.3	0–100 (73±21)	50.48–57.75 (53.53±1.45)	1.09–3.19 (2.47±0.41)	1.15–3.33 (2.29±0.52)	4/207	4/53
Brac Formation	Cayman Brac (Partially dolomitized)	(Dolomitic limestone) = ID/L?	0	0-36.7 (98% pure HCD)	54.98–57.70 (56.79±0.52)	2.0–3.6 (2.8±0.4)	1.5–2.9 (2.4±0.4)	2/32	1/19
		(Dolostone) =ID?	0	0-32 (88% pure HCD)	55.0–57.7 (56.6±0.5)	0.64–2.35 (1.73±0.48)	0.69–2.74 (1.84±0.69)	5/41[a]	5/41[a]

Information for references and wells. Ironshore Formation: Li and Jones, 2013. Pedro Castle Formation: MacNeil and Jones, 2002; MacNeil, 2003; wells GAM, SQA-2, SQA-4. Cayman Formation (eastern Grand Cayman): Ren and Jones, 2016, 2017; Peripheral dolostone: wells HHD-1, LBL-1, RWP-2, EEZ-1, ESS-1, HMB-1, RTR-1; Transitional dolostone: CKC-1, EEV-2, HRQ-3, FSR-1; Interior dolostone: HRQ-1, HRQ2, HRQ-4, HRQ-5, HRQ-6, HRQ-7, HRQ-8, FFM-1; Interior dolomitic limestone: HRQ-1, HRQ2, HRQ-4, HRQ-5, HRQ-6, HRQ-8, FFM-1, GFN-2. Cayman Formation (western Grand Cayman): Jones and Luth, 2002; wells SHT-2, SHT-3, SHT-5, STW. Cayman Formation (Cayman Brac): Zhao and Jones, 2012a; wells CRQ-1, BW, KEL-1, SQW-1. Brac Formation (Cayman Brac): Zhao and Jones, 2012b; Dolomitic limestone: wells CRQ-1, KEL-1; Dolostone: wells WOJ-3, WOJ-7, CRQ-1, KEL-1, and outcrop section SCD.