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# CHEMISTRY AND MINERAL STABILITY IN SALINE ALKALINE SOIL ENVIRONMENTS

BY

**CONNIE KAREN KOHUT** ©

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY
IN
SOIL CHEMISTRY

DEPARTMENT OF SOIL SCIENCE

EDMONTON, ALBERTA

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# ABSTRACT

Salinization processes can be expected to cause significant changes to the chemical characteristics of a soil but the effects on mineral stability are poorly understood. The primary objectives of this study were to characterize the chemistry and mineralogy of salt-affected soils in Alberta and to investigate clay mineral weathering in solutions of varying salinity and alkalinity in laboratory-controlled dissolution studies. A survey of 50 salt-affected soils in Alberta showed salt efflorescences were usually dominated by sodium and magnesium sulfates. No mean accumulation of trace elements with the exception of Br and Cl were measured, but trace element concentrations between sites were extremely variable, with potentially toxic levels at some sites. Soil solutions extracted from four salt-affected soils ranged in pH from 7.8 to 10.6 and were dominated by Na and $SO_4$. The properties of saturated paste extracts versus immiscibly displaced solutions varied considerably.

A preliminary survey of the clay mineral characteristics indicated that smectites were degraded in many saline soils. Subsequent analysis showed this apparent degradation was a result of interaction with organic matter or from formation of a heat and acid unstable interlayer material. After traditional pretreatments to remove organic matter and carbonates, the clay mineralogy of salt-affected soils was found to be similar to that of non-saline soils. Subsequent layer charge analysis of the smectites showed that the charge distribution was heterogeneous, with the mean layer charge lower than previously observed in Alberta soils. More than half of the clay fraction of one saline soil was composed of well-ordered, authigenic dolomite.

The weathering of clay minerals in laboratory dissolution studies varied considerably with the chemistry of the solution, with minerals generally most stable in saline solutions. Changes in characteristics for most samples were noted after equilibration for a year or more. The direction of change of solution characteristics for most samples was frequently away from equilibrium, with mineral saturation indices becoming increasingly positive with time. Because of the differences in the products of clay mineral dissolution in different chemical environments, a single dissolution reaction that is valid for a mineral in all soils cannot be written. The prediction of clay mineral stability in complex soil environments using simple thermodynamic models may therefore be inappropriate.

# ACKNOWLEDGEMENTS

"Oh how do I thank thee? Let me count the ways". A project this extensive could not have happened without the assistance and occasional interference from a lot of people. I'd like to especially thank my supervisor, Dr. M.J. Dudas for the assistance and guidance he has provided me over the years. He also bears the responsibility of getting me hooked on soils in the first place with inspiring undergraduate soil science courses. The other members of my committee, Dr. D. Smith, Dr. S. Pawluk and Dr. S. Abboud were also there to offer assistance when required and dream up questions to ask in my oral examinations. A warm thanks also to Dr. Karlis Muehlenbachs, my partner in crime in the dolomite investigation, whose enthusiasm and expertise in stable isotopes helped out a lot. Financial support for the adventure was provided primarily by NSERC, with scholarships also received from the Alberta Sugar Company, Province of Alberta and Alberta Research Council.

Accolades must also go to everyone hanging out on the mineralogy/genesis lab, especially Lito Arocena, Mike Abley and Park Yee, who always dropped everything to help me in my occasional crises and to share conversation and birthday cake. To Mike Abley, couldn't have done it without you. Xrayconi, xrayclay, claycon, xraywin - what can I say? Lifesavers, every one.

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# 1. INTRODUCTION

Soil salinity is a serious concern in many areas of the world, with more than 100 countries and all continents affected to some extent (Szabolcs, 1989). Soil salinization is thought to be the number one soil degradation problem in the Northern Great Plains region of North America, with the area of affected land increasing yearly. In Alberta, an estimated 0.65 million ha of dryland and 0.1 million ha of irrigated land are affected by salinity (VanderPluym 1992), with saline seeps most likely to occur where the thickness of the underlying glacial till is less than 50 feet, and where there is significant local relief (Lilley, 1982). Saline soils in Alberta are usually alkaline and dominated by Na and $SO_4$ salts (Szabolcs, 1989) with the source of soluble salts thought to be both the glacial parent material and the underlying bedrock (Miller, 1989). In severely affected soils, evaporite minerals may accumulate on the soil surface in the form of salt efflorescences.

Salinization processes can be expected to alter the chemical composition of a soil. The elements that accumulate in a saline soil will largely reflect the variable chemistry of the groundwater, with the potential for accumulation of mobile trace elements. The halogens Br, I and Cl, as well as B, Mo, Se, U and V have been reported to be highly mobile under neutral to alkaline conditions (Plant and Raiswell, 1983). Little is known about the trace element content of evaporites (Hem, 1985) but some saline soils in the United States have hazardous levels of B and Se (Peryea *et al.*, 1985; Burau, 1985). While background concentrations of some elements in various Canadian soils have been documented (Mills and Zwarich, 1975; Dudas and Pawluk, 1977; McKeague *et al.*, 1979; Dudas and Pawluk, 1980), little attempt has been made to characterize element concentrations in soils infused with soluble salts. Information regarding the accumulation of biologically sensitive trace elements in saline soils will be needed for the eventual management and reclamation of these soils.

The evaporite minerals present in salt efflorescences have been investigated in many parts of the world. Analysis of a large number of efflorescences in North Dakota showed that sodium and magnesium sulfate minerals make up the majority of the mineral assemblage, with the magnesium rich minerals confined to the glaciated part of the state. Konyaite ($Na_2Mg(SO_4)_2 \cdot 5H_2O$) was the most widely occurring mineral identified, with other minerals such as thenardite ($Na_2SO_4$), mirabilite ($Na_2SO_4 \cdot 10H_2O$), epsomite ($MgSO_4 \cdot 7H_2O$), blödite

($Na_2Mg(SO_4)_2 \cdot 4H_2O$) and gypsum ($CaSO_4 \cdot 2H_2O$) also present (Keller *et al.*, 1986). Sodium and magnesium sulfate minerals were also found to dominate efflorescences in other parts of the world such as Spain and Peru (Gumuzzio *et al.*, 1982; Eswaran and Carrera, 1980). In Turkey, salts consist mainly of sulfates and chlorides of Na and Mg, and to a lesser extent also of sodium carbonate minerals, while salt assemblages in Kenya consist mainly of sodium carbonates (Vergouwen, 1981). Halite (NaCl) has been said to be ubiquitous in saline soils (Eswaran *et al.*, 1980) and has been reported to be the most common evaporite mineral in surface horizons of some soils in California (Eghbal *et al.*, 1989). Little work has been done to characterize the salt efflorescence mineralogy in Alberta.

The majority of research regarding the mineralogy of salt-affected soils has focused on the characteristics of the evaporite minerals. Limited information is available on the characteristics of non-evaporite minerals and weathering processes that may occur in soils of high ionic strength and alkalinity, despite the large areas of land affected. Reports of mineral alteration in salt-affected soils have occasionally been documented in the literature. In a study of the fine clay fraction of the A horizon of salt-affected soils in Bulgaria, a large amount of highly interstratified mica-montmorillonite was identified which essentially gave no basal reflections upon X-ray diffraction (Behar *et al.*, 1972). The authors concluded that alkaline conditions increased the solubilities of Al and Si, thus promoting their interlayering in minerals with large expandable layers. This process was thought to be enhanced by alternating wet and dry conditions. Smectite degradation with a concomitant increase in amorphous materials has also been reported in salt-affected soils in Egypt, with soil layers having the highest salt and soda content exhibiting the largest amount of amorphous oxides and broadest X-ray diffraction peaks (Kishk and Hassan, 1972).

Several North American studies have also indicated smectite alteration in soils affected by salts but have primarily focused on Solonetzic soils. Klages and Southard (1968) found that montmorillonite had become so disordered in the surface horizon of a Solonetzic soil that X-ray diffraction of oriented specimens yielded no basal reflections. Whittig (1959) reported the presence of an unusual montmorillonite-like mineral in the coarse clay fraction of surface horizons in Solonetzic soils. The mineral was characterized by extremely diffuse peaks and expansion to 2.0 nm or greater with Mg-saturation and glycerol solvation. For

Solonetzic soils in Montana, Munn and Boehm (1983) concluded that decomposition of inherited smectite occurred in the sola of all sodium-affected soils studied and was most pronounced in the surface horizons. This conclusion was based on the diffuse nature and decreased intensity of smectite X-ray diffraction peaks.

The characteristics of clay minerals in highly saline Alberta soils have not previously been documented. Clay minerals in western Canada are generally inherited from parent material of glacial origin, which is largely derived from underlying Cretaceous sedimentary bedrock. Previous studies have shown that the clay mineralogy of soils throughout Alberta is remarkably similar, and is dominated by smectites, with smaller amounts of mica, kaolinite and occasionally chlorite (Abder-Ruhman, 1980; Kodama, 1979; Dudas and Pawluk, 1982; Warren *et al.*, 1992). Montmorillonite is the common smectite in Canadian prairie soils, with beidellite also frequently identified.

Theoretical considerations suggest that the weathering sequences and stabilities of clay minerals in saline soils will differ from those in well drained soils, since weathering rates depend primarily upon the chemistry of the soil solution. It is generally agreed that pH is an important factor in aluminosilicate mineral dissolution. Both primary and secondary minerals are reported to be thermodynamically more stable in alkaline environments (Rai and Lindsay, 1975). However, laboratory studies investigating the dissolution of silicate minerals indicate that the rate of mineral dissolution increases with increasing pH in basic solutions (Brady and Walther, 1989; Carroll and Walther, 1990; Knauss and Wolery, 1989).

The effect of ionic strength on the stability of clay minerals has never been systematically investigated. It would be expected that mineral stability will increase if solution concentrations of constituent ions are maintained at high levels. For example, montmorillonite is generally considered to be stable in poorly drained environments which maintain high $Si(OH)_4$ and Mg activities (Weaver *et al.*, 1971; Borchardt, 1989). However, increasing salinity may enhance the solubility of weatherable minerals because of the ionic strength dependence of single-ion activity coefficients (Sposito, 1989). Specific components of the soil solution in salt-affected soils may also have a significant effect on mineral weathering. Dilute solutions of $Na_2CO_3$ have been reported to increase Si release from montmorillonite (Nuttig, 1943) and the rate of clay mineral weathering has been reported to be enhanced with increasing exchangeable sodium percentage (Oster and Shainberg, 1979; Frenkel *et al.*, 1983).

The understanding of mineral weathering processes in saline soils is of fundamental importance in predicting and understanding the chemical and physical properties of the system, especially after any potential management and reclamation. Changes that occur in clay mineral characteristics, particularly to soil smectites, will affect the capacity of the soil to exchange and fix cations and retain water and other molecules. It is unclear from the literature what the relative stability of common clay minerals is expected to be in alkaline solutions of high ionic strength. Although fundamental thermodynamic considerations suggest that mineral stability increases with increasing pH, many studies indicate that the dissolution rate also increases under alkaline conditions. In addition, the solubility of Al and Si are expected to increase sharply at high pH values due to ionization of $Al(OH)_3$ and $Si(OH)_4$ respectively. The role of ionic strength in mineral weathering is unclear.

This study was designed to answer some of the questions raised in the preceding discussion regarding the chemical and mineral characteristics of saline soils and the stability of clay minerals in saline, alkaline environments. The following six chapters are written as independent papers, each with specific objectives addressing different aspects of this topic. The body of the thesis can be divided into two parts, the first of which investigates the characteristics of naturally occurring saline soils in Alberta, and the second examining mineral weathering under saline conditions using laboratory analogs of field conditions.

The initial chapter (Chapter 2) was designed as a general survey, and examines the evaporite mineralogy and trace element chemistry of 50 salt-affected soils from various locations in central and southern Alberta. Based on differences in evaporite mineralogy, geography and chemistry, four of these soils were selected for detailed analysis of other chemical and mineralogical characteristics addressed in the next four chapters.

Chapter 3 describes the solution chemistry of these soils, and compares the results obtained from analysis of immiscibly displaced field moist soils and saturated paste extracts. The implications of using saturated paste extracts as a proxy of saline soil solution compositions are also examined. The characteristics of clay minerals in the selected soils were examined using X-ray diffraction analysis and commonly used chemical methods and were compared to the mineral stabilities predicted from analysis of the soil solution data (Chapter 4). Dolomite accumulations and variable smectite layer charge characteristics, unusual features noted in the clay fraction, were subsequently studied more closely. Chapter 5 investigates the hypothesis that the abundance of clay-sized dolomite in one saline soil is due to authigenic formation. The layer charge characteristics of soil smectites are examined in detail in Chapter 6 using the alkylammonium method (Lagaly, 1981).

The second part of this thesis investigates the weathering characteristics of common clay minerals in laboratory controlled dissolution studies and is the subject of the final chapter. It was hoped that the results from controlled dissolution studies would provide insight into weathering characteristics and clay mineral stability in naturally occurring saline soils. The validity of using thermodynamic-based equilibrium models for prediction of mineral stability in soils will also be addressed.

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# 2. EVAPORITE MINERALOGY AND TRACE ELEMENT CONTENT OF SALT-AFFECTED SOILS IN ALBERTA [1]

## 2.1 INTRODUCTION

Salinity is a serious concern in central and southern Alberta, with an estimated 0.65 million ha of dryland and 0.1 million ha of irrigated land affected (VanderPluym, 1992). In many instances, salt efflorescences appear on the the soil surface as a result of the upward capillary movement of groundwater and its subsequent evaporation. The salts in saline soils may originate from glacial drift or bedrock deposits, or both (Miller, 1989).

Evaporite minerals present in salt efflorescences in other parts of the world have been documented in the literature. Investigation of salt lake evaporites in the northern Great Plains region of Canada indicates the crusts are seldom composed of a single mineral but are normally made up a variety of Na and Mg sulfates (Last, 1989). Analysis of a large number of efflorescences in North Dakota showed that sodium and magnesium sulfate minerals make up the majority of the mineral assemblage, with the magnesium rich minerals confined to the glaciated part of the state. Konyaite ($Na_2Mg(SO_4)_2 \cdot 5H_2O$) was the most widely occurring mineral identified, with other minerals such as thenardite ($Na_2SO_4$), mirabilite ($Na_2SO_4 \cdot 10H_2O$), epsomite ($MgSO_4 \cdot 7H_2O$), blödite ($Na_2Mg(SO_4)_2 \cdot 4H_2O$) and gypsum ($CaSO_4 \cdot 2H_2O$) also present (Keller *et al.*, 1986a). Sodium and magnesium sulfate minerals were also found to dominate efflorescences in other parts of the world such as Spain and Peru (Gumuzzio *et al.*, 1982; Eswaran and Carrera, 1980). In Turkey, salts consist mainly of sulfates and chlorides of Na and Mg, and to a lesser extent also of sodium carbonate minerals, while salt assemblages in Kenya are reported to consist mainly of sodium carbonates (Vergouwen, 1981a). Halite (NaCl) has been said to be ubiquitous in saline soils (Eswaran *et al.*, 1980) and has been reported to be the most common evaporite mineral in surface horizons of some soils in California (Eghbal *et al.*, 1989).

The elemental composition of a soil will be inherited from the parent material, and will gradually change due to the influence of the predominating pedogenic processes. Salinization can be expected to alter the chemical

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[1] A version of this chapter has been published in the Canadian Journal of Soil Science 73: 399-409.

composition of a soil by the accumulation of soluble salts. Saline soils in Alberta are also often alkaline. Alkalization processes may lead to accumulation of B, Co, Cr, Cu, Mo, Se, V and Zn in the surface soil (Kabata-Pendias and Pendias, 1984). Many arid saline soils in the United States have hazardous levels of B and Se, and B regeneration following leaching of major soluble salts is a potential problem during soil reclamation (Peryea *et al.*, 1985). Elevated levels of B, Se and V have also been reported in Solonchaks, Solonetzic, saline and meadow soils (Kabata-Pendias and Pendias, 1984).

Little is known about the trace element content of evaporites (Hem, 1985). The chemistry of the salt efflorescences and the underlying soils can generally be expected to reflect the variable chemistry of the groundwater, with the potential for the accumulation of highly mobile trace elements. Geochemical considerations support the hypothesis that oxyanionic trace elements are mobile and accumulate in soils infused with soluble salts. The halogens Br, I and Cl as well as B, Mo, Se, U and V are reported to be highly mobile under neutral to alkaline conditions (Plant and Raiswell, 1983).

While background concentrations of some elements in various Canadian soils have been documented (Mills and Zwarich, 1975; Dudas and Pawluk, 1977; McKeague *et al.*, 1979; Dudas and Pawluk, 1980), little attempt has been made to characterize element concentrations in soils infused with soluble salts. The trace element chemistry of Alberta groundwater is poorly understood and studies have not been conducted on the accumulations and deficiencies of biologically sensitive trace elements in salt crusts and salt affected soils - information that is needed for the eventual management and reclamation of these soils. In addition, little work has been done to characterize salt efflorescence mineralogy in Alberta. The objectives of this study were therefore to characterize the evaporite mineral species and to measure concentrations of selected elements in a general survey of salt affected soils in Alberta.

## 2.2 METHODS AND MATERIALS

A total of 50 salt efflorescences were collected from a variety of locations throughout central and southern Alberta (Fig. 2.1) during the summer and fall seasons. Salt samples were scraped off of the surface of the soil and the underlying surface soil was sampled to a depth of approximately 20 cm. Evaporite minerals in

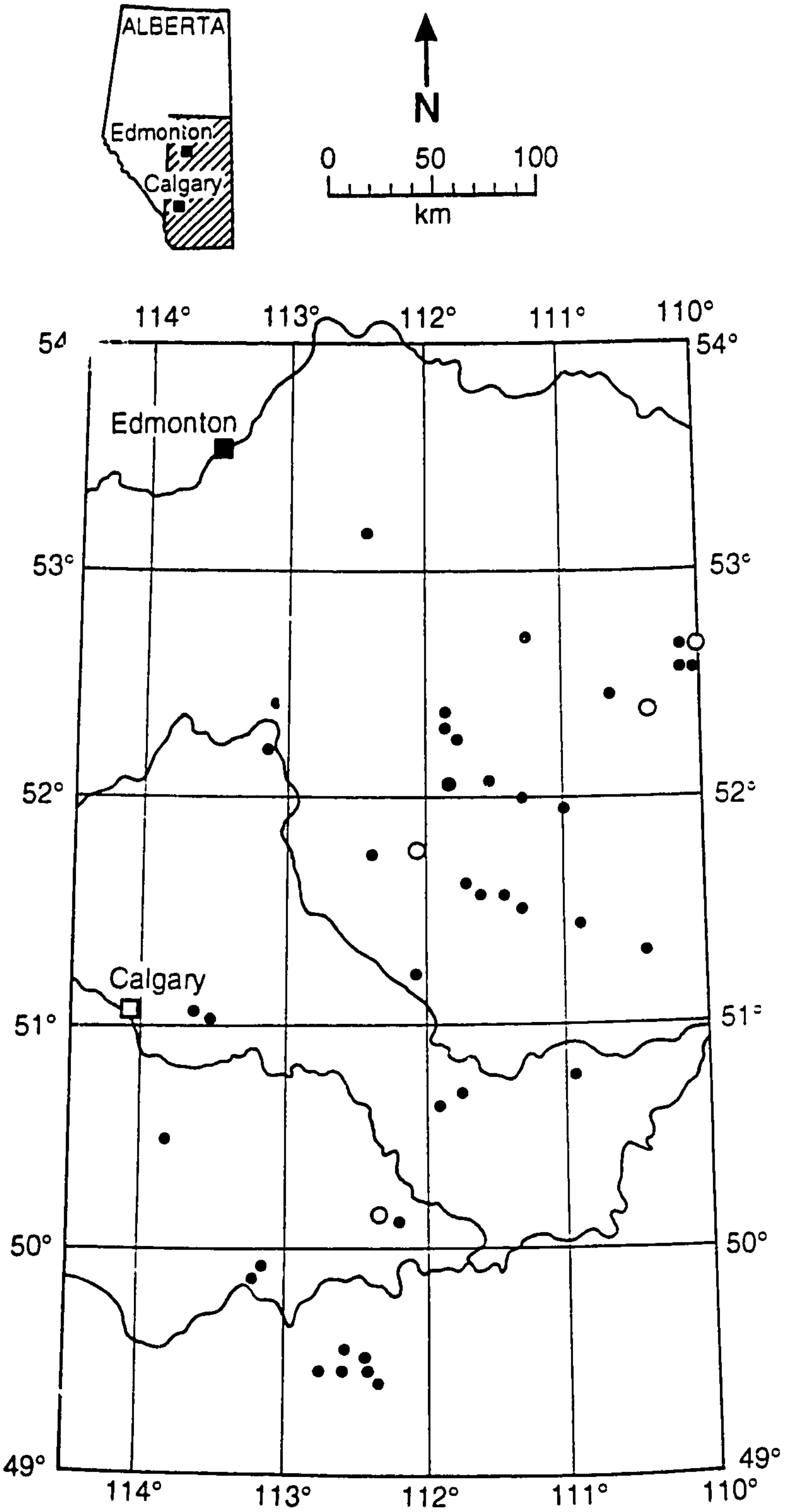

Fig. 2.1. Location of soils analyzed in this study. Hollow circles are the locations of the four sites studied in detail in subsequent chapters.

the salt crusts were identified by X-ray powder diffraction using Co Kα radiation generated at 50 kV and 25 mA.

The salt efflorescences sampled are highly transient in nature, with their characteristics and even existence varying with time. All samples except one were collected from dryland areas, and included playas, evaporitic rings and seeps of various sizes from both cultivated and non-cultivated land. The sampled sites appear to reflect a number of hydrological regimes, including groundwater discharge and seepage from laterally flowing ground water. These hydrological properties were inferred from site characteristics such as topography and features such as springs or soapholes, or from knowledge of the location available from previous studies. For example, several sites were located in the area near Nobleford, Alberta, which has been the subject of many previous studies on groundwater flow and salinity (Sommerfeldt and MacKay, 1982; Stein, 1987; Miller, 1989).

Chemical composition of 42 of the salt samples and 41 of the surface soil samples was determined. Samples were ground, dried and 1 - 3 g encapsulated for analysis of Ag, Al, As, Au, Ba, Br, Cl, Co, Cr, Cs, Fe, Ga, Hf, I, Mn, Mo, Ni, Rb, Sb, Sc, Se, Sr, Ta, Th, Ti, U, V, W, Zn, La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Yb and Lu by instrumental neutron activation analysis. The precision of the method as measured by the coefficient of variation has been found to be less than 5% for most elements (Koons and Helmke, 1978). Boron concentrations were measured by neutron activation prompt-gamma analysis. The analyses were carried out by Nuclear Activation Services Ltd., McMaster Nuclear Reactor, Hamilton, Ontario. The samples were also analyzed for Hg by cold vapor atomic absorption spectrophotometry (Dudas and Pawluk, 1976). Sample pH was determined in a 1:2 sample water ratio. Means, standard deviations and correlation coefficients of the data were calculated using SAS-PC. Differences between selected groups of samples were tested at the 0.05 level of significance using a student's t-test available in Origin technical graphics and data analysis software.

## 2.3 RESULTS AND DISCUSSION

### 2.3.1 Evaporite Mineralogy

Salt crusts on Alberta soils are mineralogically complex, with more than twelve different evaporite mineral species identified in the samples collected (Table

2.1). Thenardite was present in all samples except one, and was usually the most abundant mineral species present (Table 2.1). Sodium magnesium sulfate minerals such as konyaite and blödite were also common and occasionally made up the majority of the evaporite species. Only one sample was dominated by non-sulfate salts; in this instance thermonatrite was the predominant species. Other evaporite minerals identified include gypsum, halite, burkeite, trona, eugsterite, hexahydrite, epsomite and nahcolite. Eugsterite has only recently been described in salt crusts in Kenya and Turkey (Vergouwen, 1981b) and has also been observed in North Dakota in chloridic systems along roadside drainage ditches (Skarie *et al.*, 1987). Similarly, konyaite was not described in the literature until 1982 (van Doesberg *et al.*, 1982) but has been identified in several salt efflorescences since then (Timpson *et al.*, 1986; Keller *et al.*, 1986a; Shayan and Lancucki, 1984). In general, no trends were noted between the occurrence of particular minerals and geographic location. Sites dominated by konyaite or blödite appeared to be slightly more common in southern Alberta, particularly around the Nobleford region, but were scattered throughout the study area, often in close proximity to sites dominated by thenardite. Sites containing sodium carbonate or bicarbonate minerals were also scattered about the study region. Because of the transient nature of salt efflorescences, exactly the same results are unlikely to be obtained upon replication of the study, with the detection and/or relative abundance of various mineral species being dependent upon climatic conditions such as temperature and relative humidity.

The efflorescent crusts were usually comprised of more than one evaporite mineral, although several samples were composed of sodium sulfate alone. A few samples had as many as five evaporite minerals in sufficient quantities to be identified by X-ray diffraction. Regular associations between mineral species did not appear evident, although many samples contained both thenardite and blödite or konyaite because of their common occurrence. Most samples also contained large amounts of quartz and occasionally feldspars. Calcite may have been present in some samples, but its presence could not be confirmed because only one diffraction maximum was observed for the mineral. Calcite was reported to be present in several efflorescence deposits in Colorado (Whittig *et al.*, 1982) but was only found at $>15$ cm depth in the soil of typical saline seeps of North Dakota (Timpson *et al.*, 1986).

Table 2.1. Evaporite minerals in Alberta salt efflorescences.

| Mineral Name | Formula | Occurrence[z] |
|---|---|---|
| thenardite | $Na_2SO_4$ | 49 |
| blödite | $Na_2Mg(SO_4)_2 \cdot 4H_2O$ | 15 |
| konyaite | $Na_2Mg(SO_4)_2 \cdot 5H_2O$ | 12 |
| mirabilite | $Na_2SO_4 \cdot 10H_2O$ | 3 |
| gypsum | $CaSO_4 \cdot 2H_2O$ | 11 |
| halite | $NaCl$ | 3 |
| eugsterite | $Na_4Ca(SO_4)_3 \cdot 2H_2O$ | 5 |
| thermonatrite | $Na_2CO_3 \cdot H_2O$ | 2 |
| trona | $NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$ | 1 |
| nahcolite | $NaHCO_3$ | 1 |
| burkeite | $Na_2CO_3 \cdot 2Na_2SO_4$ | 3 |
| hexahydrite | $MgSO_4 \cdot 6H_2O$ | 2 |
| epsomite | $MgSO_4 \cdot 7H_2O$ | 1 |

[z] Number of samples out of 50 containing the mineral.

Some evaporite minerals are extremely labile, reacting to changes in temperature and humidity that affect their solubility. The occurrence column listed in Table 2.1 indicates the evaporite species that were present at the time of analysis. It is likely that the occurrence of mirabilite and konyaite would be higher, with thenardite and blödite occurrences correspondingly lower, if all salt efflorescences had been analyzed immediately after sampling. It has been well documented that mirabilite rapidly converts to thenardite (Keller *et al.*, 1986a; Gumuzzio *et al.*, 1982). Mirabilite was often seen in the field, dehydrating rapidly to thenardite at room temperature. Under refrigerated conditions however, this transformation was slowed and mirabilite could still be identified in the laboratory using X-ray diffraction. Konyaite, however, dehydrated extremely rapidly to blödite, and could only be identified if samples were X-rayed within several days of sampling, even if stored under refrigerated conditions. Konyaite has previously been reported to be a very unstable mineral, dehydrating at least partly to blödite within a few days (van Doesburg *et al.*, 1982). Timpson *et al.* (1986) found that surface crusts from saline seeps still contained konyaite after 90 days and only transformed completely to blödite after a year. Keller *et al.* (1986a, 1986b) found that konyaite had a large stability range relative to the hydration of blödite and that the two minerals seldom occurred together. This is in contrast to the observations of van Doesburg *et al.* (1982) who found that konyaite occurred with blödite in salt efflorescences. Our study also found the two minerals occurring simultaneously.

With several exceptions, the evaporite mineral species found in this investigation are similar to those reported in the literature for saline areas of the Northern Great Plains. For example, efflorescent crusts in North Dakota are also dominated by Na and Mg sulfates (Keller *et al.*, 1986a; Timpson *et al.*, 1986; Skarie *et al.*, 1987). However, salt crusts in Alberta appear to have a relatively higher proportion of sodium sulfate minerals, while $MgSO_4$-rich minerals such as epsomite and hexahydrite occur only rarely. Our findings also generally concur with the list given by Last (1989) of precipitates occurring in saline lake environments of the northern Great Plains.

The presence of eugsterite in some Alberta samples is notable, because to our knowledge the only previous finding of this mineral in saline soils of North America is by Skarie *et al.* (1987). In addition, the presence of sodium carbonate and bicarbonate minerals is unusual in North American salt efflorescences, which are normally composed of sulfatic minerals. Thermonatrite, present in substantial quantities at two sites, has previously been reported only in salt efflorescences in Kenya (Vergouwen, 1981a) and is not listed by Last (1989) as occurring in the northern Great Plains.

### 2.3.2 Elemental Chemistry

Means and standard deviations for concentrations of major elements in saline surface soils and salt efflorescences are presented in Table 2.2. Previously reported elemental concentrations for soils and crustal rock are included for comparison. Ideally, these comparisons should be conducted with material of the same mineralogical composition, but unfortunately this data is not available; comparison with data commonly found for non-saline soils and crustal material provides some reference point for determining relative changes in elemental content due to salinization processes. Sample numbers of less than 42 for salt efflorescences and less than 41 for soil samples indicate that some samples contained concentrations below detection limits. Sample composition, particularly the extremely high Na concentrations, resulted in interferences and variable detection limits in the determination of some elements. In other cases, the limit of detection possible with neutron activation analysis exceeded the concentration present of a particular element. For the purposes of statistical analysis, those samples with elemental concentrations below detection limits have been omitted.

Sodium is generally the most abundant element in salt efflorescences, comprising up to 30 % of the sample. Amounts of other major elements are near or below the concentrations typically found in soils and crustal rock material. A small amount of soil and/or organic material was unavoidably incorporated into many of the salt samples during the collection procedure, which may account for the fairly high concentrations of relatively immobile elements such as Al and Fe that are not expected to accumulate in evaporite deposits. The amount of non-evaporite material unintentionally sampled was largely a function of salt crust morphology; relatively thick firm crusts were sampled essentially pure, while sampling of powdery thin efflorescences tended to incorporate more soil material.

Concentrations of Fe and Al in the saline soil samples are less than those reported for other soils, while K, Mg and Na values are higher than those expected for non-saline soils. This is likely due to the fact that the salt-affected soils contain

Table 2.2. Concentration (g $kg^{-1}$) of major elements in salt efflorescences and surface saline soils.

| | Salt Efflorescences | | | Surface Soils | | | Other Soils[z] | Crustal Rock[y] |
|---|---|---|---|---|---|---|---|---|
| Element | n | Mean | Standard Deviation | n | Mean | Standard Deviation | | |
| Al | 42 | 24.0 | 8.7 | 41 | 42.6 | 11 | 72 | 82 |
| Ca | 41 | 19.6 | 12 | 40 | 24.0 | 17 | 24 | 41 |
| Fe | 42 | 10.4 | 6.5 | 41 | 18.8 | 7.3 | 26 | 56 |
| K | 22 | 1.48 | 3.9 | 40 | 19.1 | 5.4 | 15 | 21 |
| Mg | 36 | 13.0 | 13 | 35 | 12.5 | 13 | 9 | 23 |
| Na | 42 | 140 | 68 | 41 | 25.9 | 7.3 | 12 | 12 |

[z] Values from Sposito (1989)
[y] Values from Krauskopf (1979)

evaporite minerals as well as the typical aluminosilicate assemblage which would make up the solid portion of most soils.

Concentrations of the trace elements B, Ba, Br, Cl, Co, Cr, Co, Cs, Hf, Mn, Rb, Sb, Sc, Th, U, V and Zn are presented in graphical form showing the range and mean concentration for salt crusts (Fig. 2.2) and soils (Fig. 2.3). Trace element amounts are generally near or below amounts previously reported for till parent material in Alberta. Amounts of Br and Cl appear to be considerably higher than values previously reported for soils (Sposito, 1989); concentrations normally found in till parent material were unavailable for comparison.

The concentration of rare earth elements in saline soils (Fig. 2.4) are close to those reported for till, while concentrations in salt efflorescences (Fig. 2.5) are slightly lower. The rare earth elements are considered essentially immobile under neutral to alkaline conditions (Plant and Raiswell, 1983) and were therefore not expected to accumulate in salt affected soils.

Elemental concentrations were extremely variable from site to site (Table 2.3). Coefficients of variablility (CV) were the highest for the halogens in both types of samples; calculated CV values of 245% (Br) and 275% (Cl) were obtained for salt efflorescences and 134% (Br) and 145% (Cl) for surface soils. As one would expect, the CV appears to be related to the element's relative mobility, with the least mobile elements having the lowest variability between sites. Salt samples generally had a trend towards greater variability between sites; this may be a function of the amount of non-evaporite material gathered accidentally during sampling.

The mean concentrations of other elements expected to accumulate in saline areas, such as Se, Mo, V and U, were generally low and do not indicate that enrichment is occurring. The detection limits for selenium were variable due to to interferences during analysis and ranged from 0.50 to 1.7 mg kg$^{-1}$; only nine salt efflorescence and thirteen soil samples contained selenium in amounts above the detection limits. Of these, Se concentrations in salt efflorescences ranged from 0.60 to 2.6 mg kg$^{-1}$, with a mean of 1.4 mg kg$^{-1}$. The concentration in the underlying soil was essentially the same as that in the salt crust. Selenium concentration in Canadian soils typically ranges from 0.03 to approximately 2 ppm (McKeague *et al.*, 1979).

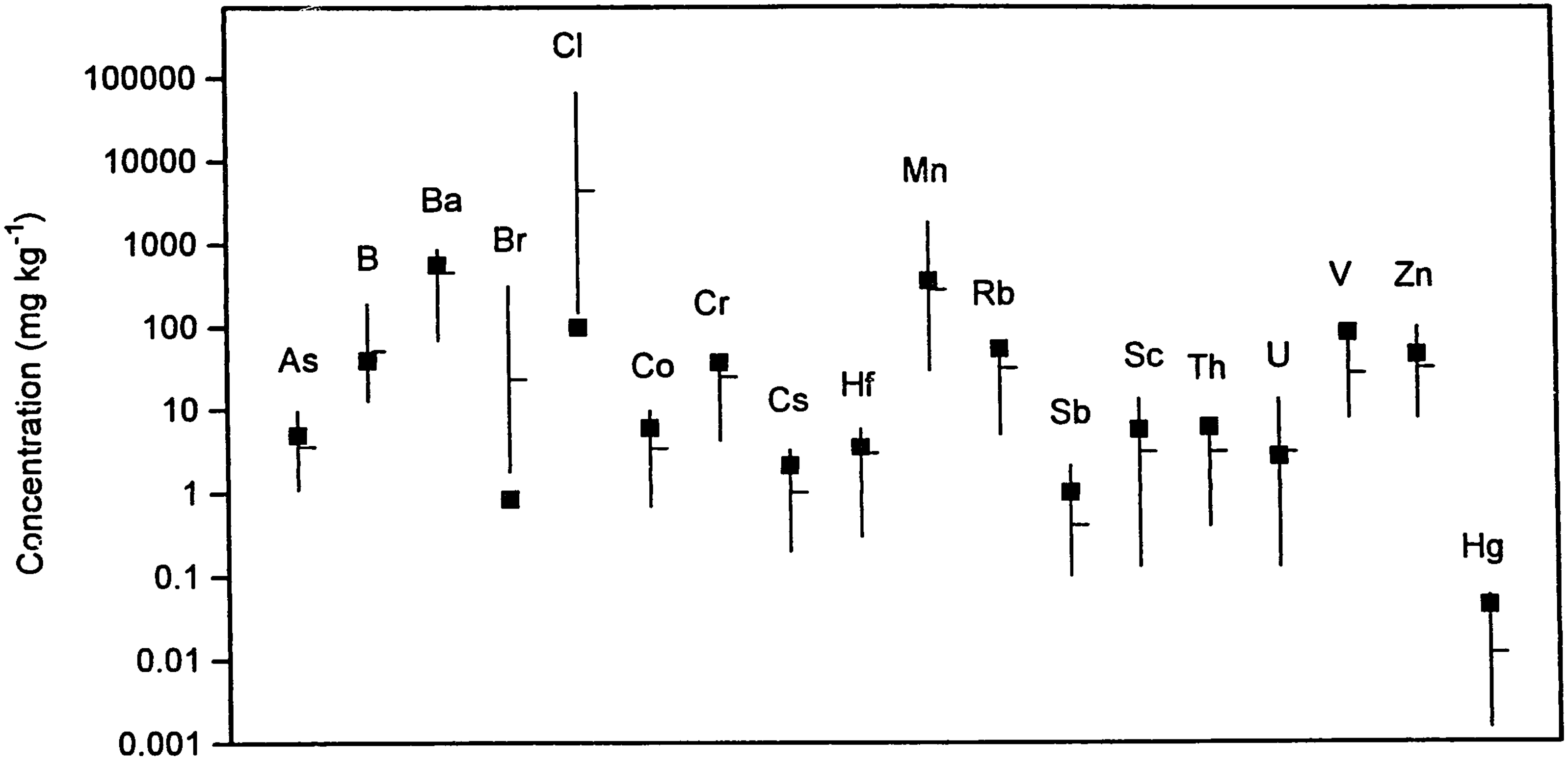

Figure 2.2. Concentration of trace elements (mg kg $^{-1}$) in salt efflorescences. Vertical lines indicate range of values and horizontal lines indicate the means. Squares are reported values for Alberta till (Warren and Dudas, 1992), except for Br and Cl, which are previously reported values for soil (Sposito, 1989).

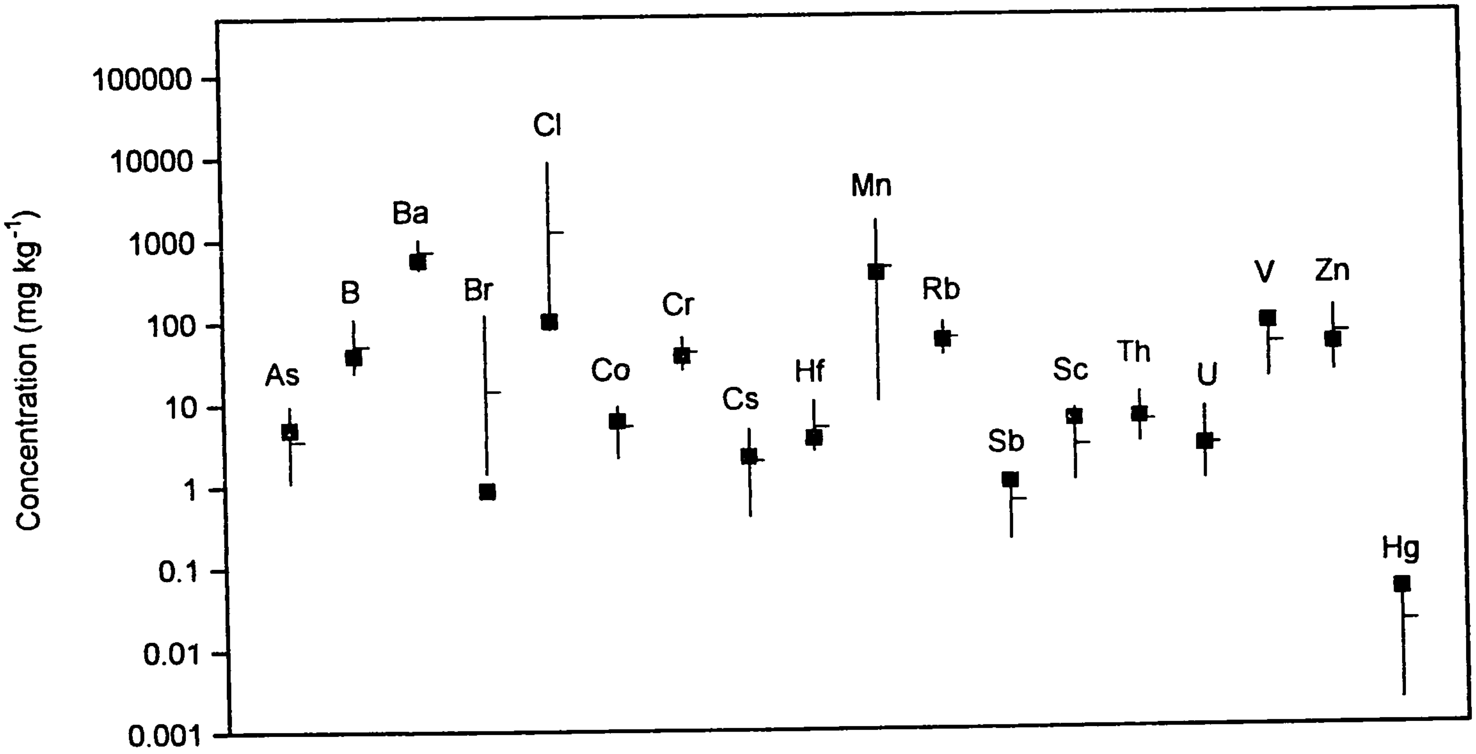

Figure 2.3. Concentrations of trace elements (mg $kg^{-1}$) in saline surface soils. Vertical lines indicate ranges of values and horizontal lines indicate means. Squares are reported values for an Alberta till (Warren and Dudas 1992) except for Br and Cl, which are previously reported values for soil (Sposito 1989).

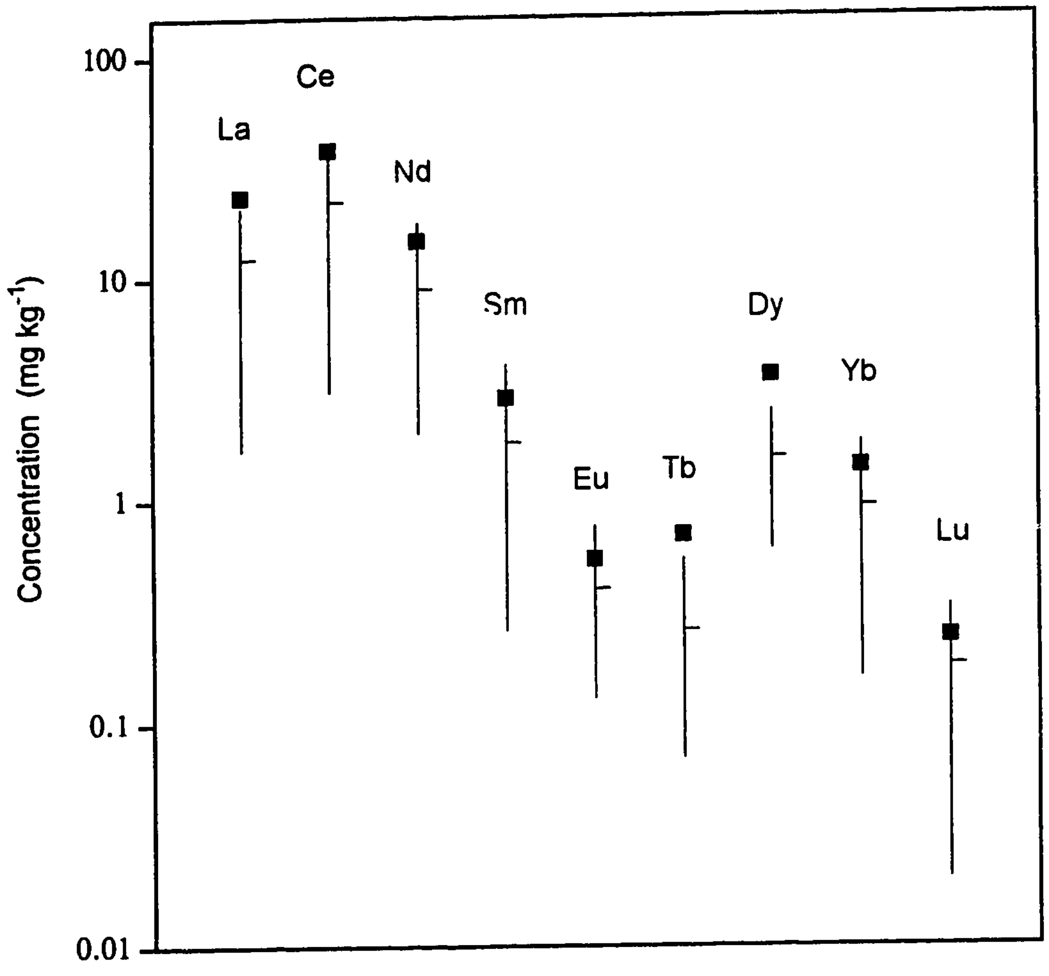

Figure 2.4. Concentration of rare earth elements (mg kg$^{-1}$) in salt efflorescence samples. Vertical lines indicate range of values, horizontal lines indicate means and squares are values for till (Warren and Dudas 1992).

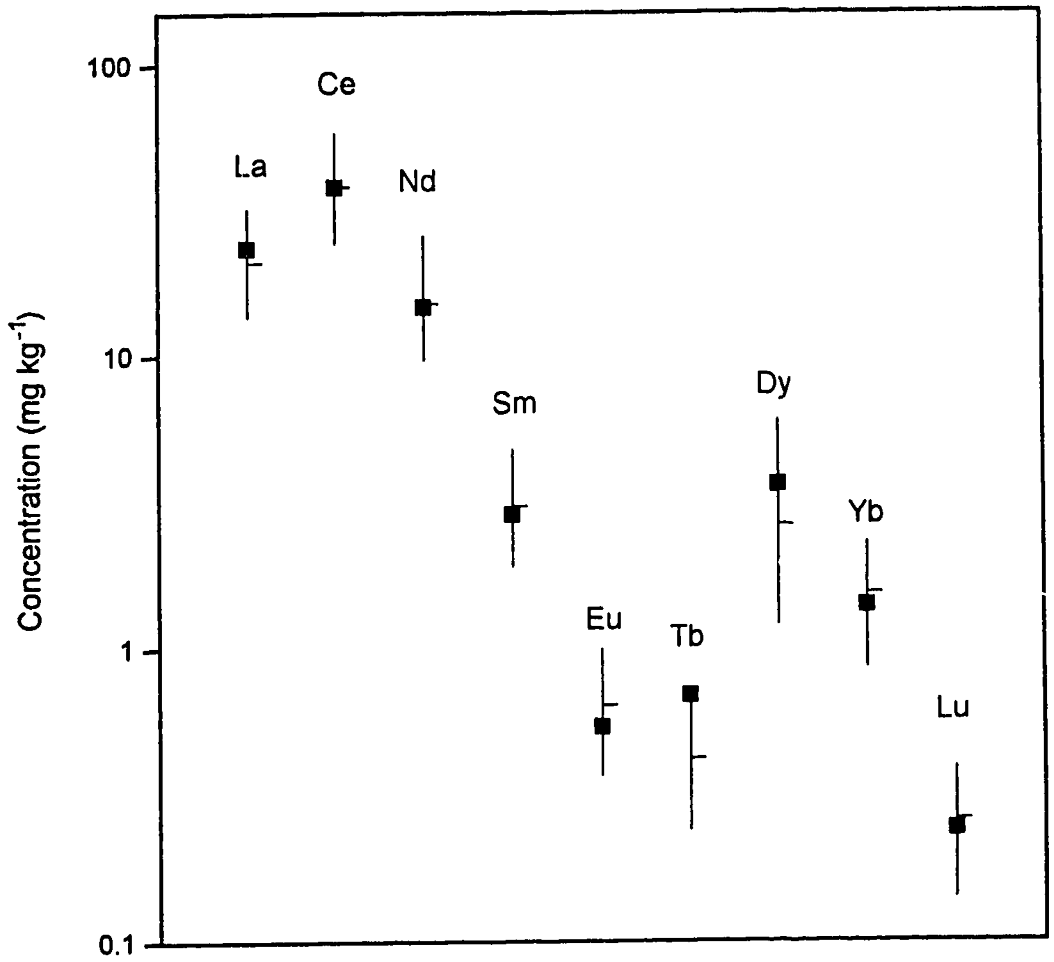

Figure 2.5. Concentration of rare earth elements (mg kg$^{-1}$) in surface soil samples. Vertical lines indicate the range of values, horizontal lines indicate means, and squares are values for till (Warren and Dudas 1992).

Table 2.3. Coefficients of variability (CV) for trace elements in salt efflorescences and surface saline soils.

| | Salt Efflorescences | Surface Soils |
|---|---|---|
| CV (%) | Element(s) | Element(s) |
| > 200% | Br, Cl | none |
| 100 - 200% | Mn | Br, Cl |
| 50 - 100% | As, B, Co, Cs<br>Sb, Sc, U, V, Zn | Cs, Mn, U<br>As, B, Co, Hf |
| 25 - 50% | REE's[z], Ba, Cr<br>Hf, Th | Sb, Sc, Th, V, Zn |
| < 25% | none | REE's, Ba, Cr, Rb |

[z] Rare earth elements

Similarly, many samples contained levels of molybdenum below the detection limits of 0.40 mg $kg^{-1}$. Twenty-nine salt crust samples contained amounts above this level, with a mean concentration of 1.9 mg $kg^{-1}$ and a range of 0.40 to 5.9 mg $kg^{-1}$. Soil samples contained slightly more Mo; the range of 27 samples containing amounts above the detection limit was 0.40 to 11 mg $kg^{-1}$, with a mean value of 2.4 mg $kg^{-1}$. Molybdenum content is reported to be 1 ppm or less in glacial till in Alberta, and averaging 2 ppm in soils (Pawluk and Bayrock, 1969).

Analysis for iodine showed a wide range of detection limits with sample composition hindering consistent results. Available results indicated that iodine concentrations were relatively high and variable. Values ranged from below detection limits to 12 mg $kg^{-1}$, with the higher values being somewhat greater than is typically found in soils. Relatively little I is released by the weathering of soil parent material; I concentration in common igneous rocks, sandstones and carbonate rocks is thought to be consistently $< 1$ ppm (Whitehead, 1984). The high concentrations of Br, Cl and I in many samples are likely due to their very high geochemical mobility. The geochemistry of these elements is typically associated with water chemistry and evaporite deposits (Kabata-Pendias and Pendias, 1984). High Br and I concentrations are associated with relatively deep formation waters (Hitchon *et al.*, 1971) and may indicate a bedrock source of salts (Miller, 1989).

Toxic levels of B are expected to accumulate in arid and semiarid soils infused with salts (Gupta *et al.*, 1985). Surprisingly, mean levels of B in the samples were quite low and fall within the previously reported range for glacial till of 13 - 70 ppm (Pawluk and Bayrock, 1969). This would indicate that B is not accumulating in the majority of soils as a result of salinization processes.

The pH of the samples ranged from 6.6 to 10.7, with a mean value of 9.3 for salt efflorescences and 9.0 for surface soils (data not shown). Since solubility and hence mobility of certain elements is affected by pH, soil alkalinity may be expected to bear a relationship to concentrations of some elements. Among the elements that had a high negative correlation with pH in this study were Cs, Fe, Rb, Sc, V, U and Zn.

The soils in this study are primarily developed from glacial till parent material. The till is largely derived from and can be expected to reflect the characteristics of the underlying bedrock (Pawluk and Bayrock, 1969). Trace element concentrations in soils typically have a fairly close relationship with the material from which they were derived. The relative enrichment or depletion of elements as a result of pedogenic processes can then be easily determined by comparison with geochemical abundance tables. The concentration of constituents in groundwater is often unknown but can be expected to be at least partly controlled by the type of geological material through which it has passed. It was therefore expected that because the bulk of the parent till material is locally derived, those sites located above bedrock of marine origin would contain higher amounts of elements such as B and Se which are present in higher amounts in marine deposits. Twelve of the sample sites were inferred to be located over the marine Bearpaw formation from bedrock geology maps (Pawluk and Bayrock, 1969). Comparison of selected element concentrations obtained from these locations to those from sites underlain by non-marine bedrock indicated that there were no significant differences ($P = 0.05$) between mean concentrations. Since sample numbers were not large, this may be due to coincidence, given the large variablility in elemental content among the sites. It is possible that elemental trends more accurately reflect the type of groundwater flow system, rather than the underlying bedrock.

## 2.4 CONCLUSIONS

The mineralogy of Alberta salt crusts is dominated by sodium and magnesium sulfates, with thenardite being the most widespread mineral in salt efflorescences. Konyaite and blödite are generally of secondary importance. Other evaporite minerals such as gypsum, eugsterite, halite, thermonatrite, trona, nahcolite, burkeite, hexahydrite and epsomite were also identified but were uncommon. No relationships were noted between geographic locations and the types of mineral assemblages observed. Konyaite was found to be unstable with respect to blödite under laboratory conditions, making rapid analysis essential for its identification.

The mean concentrations of most elements analyzed in salt efflorescences and underlying soils fall within the ranges previously reported for soils and till and do not show significant enrichment as a result of salinization processes. The exceptions are Br and Cl, which appear to accumulate in soils infused with soluble salts. Variability in elemental concentrations between sites was extremely high, indicating that specific site data may be necessary for management and reclamation.

Levels of toxic elements in certain locations may be high enough to adversely affect future land use.

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# 3. COMPARISON OF IMMISCIBLY DISPLACED SOIL SOLUTIONS AND SATURATED PASTE EXTRACTS FROM SALINE SOILS [1]

## 3.1 INTRODUCTION

The chemical composition of the soil solution is important to the basic understanding of soil chemical processes. Characterization of the porewater in saline soils can provide insights into the origin of salinity, help predict mineral weathering trends and authigenesis, and aid in the eventual management and reclamation of these soils. Numerous methods have been used in the attempt to obtain a representative solution from soil samples, with no single method of extracting porewater from soil media suitable for all samples. Saturated paste extracts, originally intended for appraising soil salinity in relation to plant growth, are commonly used for other purposes because of the advantages they offer in terms of convenience and large extract volume. For example, extracts from saturated pastes have been used in many studies to characterize the composition and speciation of soil solutions (*eg*. Alzubaidi and Webster, 1983; Heck and Mermut, 1992; Miller *et al.*, 1989) and to predict mineral stabilities (*eg*. Arndt and Richardson, 1989; Curtin and Mermut, 1985; Wilke and Schwertmann, 1977; Heck and Mermut, 1992). Evaporated saturated extracts have also been used to identify the mineralogy of evaporites in soil samples (Eghbal *et al.*, 1989). It is widely felt that although the technique must of necessity alter the composition of soil solutions *in situ*, it still reflects something of the true reactions between the soil solution and solid soil constituents (Sposito, 1989).

The preparation of saturated paste extracts normally involves rewetting a previously dried soil sample to saturation; this process can be expected to alter the characteristics of the soil solution (Qian and Wolt, 1990; Menzies and Bell, 1988; Walworth, 1992). The concentration of ions in a soil extract will also vary with the moisture content of the soil (Reitemeier, 1946; Khasawneh and Adams, 1967; Richards, 1954), but few studies have investigated the variation in chemistry between convenient extracts and solutions directly extracted from field moist soils. Gillman and Bell (1978) compared soil solutions and extracts at various solid:solution ratios and concluded that in highly weathered soils with low ion

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[1] A version of this chapter has been accepted for publication in the Canadian Journal of Soil Science.

concentrations, extracts of various soil:solution ratios provided an accurate estimation of solution composition. A direct comparison of cation concentrations in saturated extracts and soil solutions was conducted on artificially salinized soils in a greenhouse experiment (Janzen and Chang, 1988). This study concluded that saturation extracts provided an accurate measure of the Na, Mg and total salt concentration in the soil solution, and overestimated the Ca concentration. Carter *et al.* (1979) found large differences in cation concentrations between saturated paste extracts and solutions displaced with ethanol over various moisture contents but found that extracts served as a useful indicator of Mg/Ca and Ca/total cation ratios in Solonetzic Bnt horizons.

Despite the common use of saturated paste extracts as an estimate of soil solution composition, no studies have been conducted that compare the chemistry of saturated paste extracts with immiscibly displaced solutions from naturally saline soils. In addition, little information is available regarding the composition of solutions of saline soils in Alberta. The objectives of the study therefore are to characterize the chemistry of soil solutions in salt affected soils in Alberta, to compare the chemical compositions of immiscibly displaced soil solutions and saturated paste extracts, and to determine the subsequent implications of using saturated pastes as proxies of soil solutions in speciation and mineral stability calculations. The feasibility of predicting evaporite mineral formation from the chemistry of the soil solutions will also be investigated.

## 3.2 MATERIALS AND METHODS

Four salt-affected soils from locations near Hanna, Nobleford, Provost and Wainwright, Alberta, Canada were used for this study and included a playa, a saline seep in cultivated land, and evaporitic rings around a pothole slough and a larger saline lake respectively. No plant growth was observed on the soils. The soils were classified as Rego Gleysols because of little or no soil development and saturation during at least parts of the year. Since pedogenesis was very weak or non-existent, samples were taken approximately every 20 cm unless obvious differences in properties, such as the presence of a clay lens, were apparent. The depth to which sampling occurred was determined by the presence of a high water table at the Provost site, reaching the glacial till parent material at the Nobleford site and by the physical difficulty of excavating through the material at the other two sites. Water present on the soil surface was collected at the Wainwright and Nobleford sites. Groundwater was sampled at the Provost site since the water table was reached during sampling and it was physically impossible to collect a surface water sample. No water samples were available at the Hanna location. Water samples were filtered with a 0.2 $\mu$m filter immediately after sampling, and refrigerated for subsequent analysis.

Pore water was extracted from each field moist soil sample using immiscible displacement (Elkhatib *et al.*, 1986), with tetrachloroethylene as the displacing fluid. Saturated pastes of air-dried soil samples ground to $< 2$ mm were also made (Richards, 1954) and solutions extracted under vacuum after 24 hours of equilibration. Extracted solutions from both techniques were immediately filtered through a 0.2 $\mu$m filter and pH and electrical conductivity (EC) measurements taken; samples were then refrigerated prior to further analysis. Calcium, Mg, Na, K, P, Fe, Mn, Al and Si were determined using inductively coupled plasma atomic emission spectrophotometry. Chloride and $SO_4$ were measured using ion chromatography; concentrations of F, $NO_3$ and $PO_4$ were very low compared to the concentration of $SO_4$ in the extracts and could not be determined by this method. Total inorganic carbon (TIC) was measured using a Technicon autoanalyzer. Speciation of the dissolved components was determined using the computer program SOLMINEQ (Kharaka *et al.*, 1988). The gravimetric moisture content of field-moist and saturated samples was determined by oven drying at 105° C for 24 hours.

Practical sodium adsorption ratios ($SAR_p$) were calculated using the equation $SAR_p = [Na^+] / ([Ca^{2+}] + [Mg^{2+}])^{0.5}$, where cation concentrations are in mmol $L^{-1}$. Theoretical SAR's ($SAR_t$) were calculated using the same equation but substituted free ion activities for analytical concentrations. ESP was estimated using the equation $ESP = 100\ ESR/(1 + ESR)$, where $ESR = -0.01 + 0.015\ (SAR)$ (Richards, 1954).

Selected immiscibly displaced soil solutions and saturated paste extracts were allowed to evaporate on the laboratory bench until dry. The residue was subsequently finely ground and analyzed as a random powder mount by X-ray diffraction using Co K$\alpha$ radiation generated at 50 kV and 25 mA.

## 3.3 RESULTS AND DISCUSSION

### 3.3.1 Composition of Immiscibly Displaced Soil Solutions

The characteristics of the soil solutions obtained by immiscible displacement are presented in Table 3.1. The Wainwright site, with an EC of 6 to 24 dS $m^{-1}$, is considerably less saline than the other three locations. Wainwright is the only location where the EC is highest in the surface sample. Solution pH values range from 7.8 to 9.9 and are relatively constant throughout the profiles.

Sodium is the dominant cation present in all soil solution samples. The concentrations of the other major cations are highly variable, with Mg concentrations varying by as much as four orders of magnitude between sites and K concentrations varying by two orders of magnitude. At all sites, Ca is the major cation in lowest abundance. Sulfate dominates the anion chemistry of the soils, with smaller amounts of chloride; chloride concentrations between sites are generally within the same order of magnitude. With the exception of Provost, chloride concentrations are generally highest in the surface layer and decrease with depth. As would be expected, inorganic carbonate species are generally present in the highest amounts in the most alkaline samples.

Concentrations of Al are low or not detectable in all samples, even those with pH > 9, where Al solubility would be expected to increase sharply. Despite the rapid increase of silica solubility expected above pH 9, soluble Si levels in the salt-affected soils are also low and are less than the average concentration of 15 to 20 ppm usually found in soil solutions (Drees *et al.*, 1989).

Phosphorus concentrations are relatively high in all solutions but are extremely high in the Hanna soil, ranging from 100 to 250 mg $L^{-1}$. Soil solution concentrations of phosphate are usually of the order 0.01 to 0.1 mg $L^{-1}$ (Bohn *et al.*, 1985). The high levels of P present in the saline soil solutions are difficult to explain. Phosphorus is normally associated with the solid phase in soils because of rapid adsorption, fixation or precipitation. It is possible that the high percentage of ion-pairing and unidentified kinetic factors may prevent the precipitation or fixation of P onto the solid phase. A portion of the total P may also be in organic form.

### 3.3.2 Composition of Saturated Paste Extracts

The characteristics of saturated paste extracts are presented in Table 3.2. In most cases, saturated paste extracts had a higher water content than the soil under

Table 3.1. Characteristics of immiscibly displaced soil solutions.

| Sample | $H_2O$ content | pH | E.C. | Ca | Mg | K | Na | P | Fe | Si | Al | Cl | $SO_4$ | TIC[z] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| cm | % |  | dS $m^{-1}$ |  |  |  |  | mg $L^{-1}$ |  |  |  |  |  |  |
| **Hanna** |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 0 - 23 | 18 | 9.9 | 45 | 3.6 | 16 | 190 | 3.3E04 | 173 | 0.2 | 13 | n.d.[y] | 6.6E03 | 3.3E04 | 7.4E03 |
| 23 - 50 | 18 | 9.9 | 41 | 1.8 | 2.5 | 130 | 2.3E04 | 250 | 0.3 | 12 | 0.2 | 6.0E03 | 2.2E04 | 6.0E03 |
| 50 - 80 | 22 | 9.6 | 40 | 3.2 | 0.45 | 62 | 2.4E04 | 181 | 0.3 | 12 | 0.1 | 5.6E03 | 2.4E04 | 1.8E03 |
| > 80 | 21 | 9.8 | 42 | 7.4 | 17 | 40 | 2.4E04 | 100 | 0.4 | 12 | n.d. | 4.2E03 | 1.7E04 | 1.4E04 |
| **Wainwright** |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| surface water |  | 9.7 | 9.1 | 6.0 | 11 | 190 | 3.9E03 | 7.1 | 0.4 | 1.4 | 0.5 | 6.6E02 | 1.9E03 | 9.8E02 |
| 0 - 20 | 20 | 9.6 | 24 | 3.4 | 19 | 570 | 1.1E04 | 6.1 | 0.8 | 2.3 | 0.5 | 3.8E03 | 7.3E03 | 2.2E03 |
| 20 - 28 | 30 | 9.6 | 13 | 3.9 | 8.8 | 250 | 4.2E03 | 5.9 | 1.0 | 1.9 | 0.5 | 1.2E03 | 4.2E03 | 9.4E02 |
| 28 - 42 | 18 | 9.3 | 6.4 | 5.4 | 46 | 210 | 5.2E03 | 3.2 | 0.9 | 2.4 | 0.5 | 1.2E03 | 5.2E03 | 8.3E02 |
| 42 - 70 | 25 | 9.1 | 7.4 | 5.7 | 48 | 220 | 4.6E03 | 2.6 | 0.8 | 2.3 | 0.5 | 5.1E02 | 6.4E03 | 5.1E02 |
| > 70 | 27 | 9.0 | 12 | 5.3 | 110 | 250 | 3.7E03 | 1.7 | 0.4 | 2.4 | 0.6 | 8.9E02 | 5.8E03 | 5.0E02 |
| **Nobleford** |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| surface water |  | 8.5 | 32 | 210 | 8.0E03 | 310 | 3.0E04 | 6.7 | 0.3 | 2.8 | 0.4 | 6.7E02 | 9.2E04 | 390 |
| 0 - 20 | 25 | 8.3 | 34 | 210 | 7.1E03 | 230 | 2.7E04 | 9.0 | 0.8 | 3.7 | 1.0 | 2.3E03 | 9.1E04 | 80 |
| 20 - 40 | 27 | 7.8 | 37 | 180 | 1.3E04 | 130 | 2.6E04 | 3.2 | 0.4 | 5.5 | 0.5 | 1.7E03 | 1.0E05 | 17 |
| 40 - 60 | 20 | 8.2 | 35 | 190 | 1.2E04 | 51 | 2.5E04 | 1.6 | 0.3 | 0.8 | 0.4 | 1.4E03 | 1.1E05 | 90 |
| > 60 | 16 | 8.4 | 44 | 320 | 6.5E03 | 30 | 1.9E04 | 2.4 | 0.6 | 1.4 | 0.5 | 1.1E03 | 6.5E04 | 120 |
| **Provost** |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| groundwater |  | 7.5 | 19 | 200 | 5.0E03 | 1760 | 1.5E04 | 1.5 | 0.2 | 5.5 | n.d. | 2.8E03 | 5.9E04 | 170 |
| 0 - 15 | 69 | 8.1 | 37 | 135 | 2.9E03 | 2200 | 3.5E04 | 7.4 | 0.2 | 12 | n.d. | 5.7E02 | 8.9E04 | 49 |
| 15 - 40 | 21 | 8.0 | 44 | 96 | 4.2E03 | 1050 | 4.9E04 | 0.95 | 0.2 | 2.3 | n.d. | 1.1E03 | 1.1E05 | 70 |
| > 40 | 20 | 8.1 | 35 | 100 | 3.9E03 | 1500 | 4.2E04 | 2.4 | 0.2 | 6.0 | n.d. | 1.1E03 | 1.0E05 | 10 |

[z] total inorganic carbon

[y] not detectable

Table 3.2. Characteristics of saturated paste extracts.

| Sample | $H_2O$ content | pH | E.C. | Ca | Mg | K | Na | P | Fe | Si | Al | Cl | $SO_4$ | TIC$^z$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| cm | % | | dS $m^{-1}$ | | | | | mg $L^{-1}$ | | | | | | |
| **Hanna** | | | | | | | | | | | | | | |
| 0 - 23 | 34 | 10.4 | 10 | 4.9 | 0.50 | 120 | 1.9E04 | 160 | 0.2 | 6.8 | 0.02 | 3740 | 1.6E04 | 2990 |
| 23 - 50 | 34 | 10.4 | 25 | 4.1 | 1.7 | 75 | 1.3E04 | 100 | 0.4 | 8.5 | 0.6 | 2520 | 1.2E04 | 2290 |
| 50 - 80 | 83 | 10.5 | 16 | 2.9 | 4.8 | 46 | 8.6E03 | 58 | 0.4 | 7.8 | 0.6 | 1320 | 6.2E03 | 1340 |
| > 80 | 129 | 10.6 | 11 | 2.5 | 0.56 | 38 | 2.8E03 | 22 | 0.3 | 7.2 | 0.6 | 810 | 3.4E03 | 630 |
| **Wainwright** | | | | | | | | | | | | | | |
| 0 - 20 | 39 | 10.2 | 12 | 3.5 | 1.5 | 220 | 3.9E03 | 3.2 | 0.5 | 4.3 | 0.6 | 1400 | 3.3E03 | 740 |
| 20 - 28 | 67 | 10.1 | 5.8 | 3.4 | 2.7 | 83 | 1.1E03 | 2.7 | 0.5 | 4.7 | 0.5 | 1050 | 1.6E03 | 240 |
| 28 - 42 | 29 | 10.0 | 8.9 | 6.2 | 2.3 | 120 | 2.4E03 | 1.3 | 0.4 | 3.5 | 0.5 | 645 | 3.7E03 | 310 |
| 42 - 70 | 42 | 9.4 | 7.2 | 5.4 | 13 | 180 | 1.7E03 | 1.1 | 0.4 | 2.8 | 0.5 | 630 | 3.9E03 | 130 |
| > 70 | 36 | 9.0 | 7.3 | 4.4 | 12 | 140 | 1.6E03 | 1.1 | 0.4 | 3.3 | 0.5 | 250 | 3.4E03 | 110 |
| **Nobleford** | | | | | | | | | | | | | | |
| 0 - 20 | 48 | 8.3 | 23 | 410 | 4060 | 91 | 1.5E04 | 5.8 | 0.4 | 4.8 | 0.5 | 830 | 5.5E04 | 35 |
| 20 - 40 | 42 | 8.0 | 32 | 190 | 9140 | 64 | 1.5E04 | 3.9 | 0.3 | 6.0 | 0.5 | 1250 | 8.7E04 | 180 |
| 40 - 60 | 39 | 8.2 | 26 | 205 | 5870 | 32 | 1.3E04 | 1.7 | 0.3 | 1.1 | 0.5 | 1300 | 5.5E04 | 74 |
| > 60 | 39 | 8.4 | 23 | 200 | 3240 | 25 | 7.6E03 | 1.4 | 0.3 | 0.91 | 0.5 | 420 | 3.2E04 | 110 |
| **Provost** | | | | | | | | | | | | | | |
| 0 - 15 | 38 | 8.3 | 27 | 140 | 2120 | 1300 | 2.6E04 | 4.1 | 0.2 | 8.3 | n.d.$^y$ | 480 | 6.8E04 | 24 |
| 15 - 40 | 26 | 8.5 | 32 | 100 | 2920 | 1410 | 3.2E04 | 0.3 | 0.2 | 1.2 | n.d. | 950 | 8.3E04 | 75 |
| > 40 | 29 | 8.5 | 37 | 130 | 3770 | 1900 | 4.8E04 | 0.8 | 0.2 | 2.2 | n.d. | 920 | 1.1E05 | n.a.$^x$ |

[z] total inorganic carbon
[y] not detectable
[x] not available

field conditions. The pH values of saturated paste extracts were generally higher than those recorded for immiscibly displaced solutions and was particularly marked in the Hanna and Wainwright soils. This is likely primarily due to the lower ionic strength of the saturated paste extracts. Drying and subsequent rewetting of soils to saturation may have also brought about changes in pH (Bartlett and James, 1980; Walworth, 1992; Warren, 1991). Electrical conductivities of the saturated paste extracts were consistently lower than those of the immiscibly displaced solutions, primarily due to a greater dilution effect, although drying and rewetting may also play a role. Conductivity of saturation extracts has previously been found to provide an accurate representation of the total ions in solution (Janzen and Chang, 1988), and should be inversely proportional to the moisture contents of the soil at extraction (Richards, 1954).

Dilution may increase total amounts of soluble salts in solution because of increased dissolution of sparingly soluble salts (*eg.* gypsum), or hydrolysis of exchangeable cations. Alternatively, dilution may decrease solution concentrations simply due to increased water volume. Divalent cations in solution may also decrease when lower valence cations go into solution in exchange for cations of higher valence. For example, dilution has been found to increase the total amount of solution K with a corresponding decrease in exchangeable K (Khasawneh and Adams, 1967). Some differences in composition may also be due to the pressure at which solution extraction occurred, with immiscibly displaced samples expected to contain porewater from smaller pores than vacuum extracted saturated pastes. The variation in composition of soil solution with pore size or extraction pressure has never been systematically investigated, except for the study by Fernandez-Marcos *et al.* (1979) which found a small increase in pH and a decrease in Si concentration as the soil solution extraction pressure increased.

With few exceptions, levels of Na, Mg and K in all samples were higher in immiscibly displaced solutions than in saturated paste extracts. Calcium and P levels were higher in saturated paste extracts than immiscibly displaced solutions in most samples. Higher concentrations of Ca may be due to gypsum dissolution in saturated paste extracts, since the widest differences were noted in Nobleford soil samples where gypsum was previously detected in the solid phase (unpublished data). Higher P levels may be a consequence of drying and rewetting of soil samples to saturation; soluble P has previously been seen to increase sharply when air dried soils were rewetted and may be due to a resurgence in biological activity (Bartlett and James, 1980; Warren, 1991). There were no observable trends between silicon concentrations and the method of solution extraction. In the Wainwright soil and top three layers of the Nobleford soil, Si levels in the saturated paste extracts were consistently higher than those measured in immiscibly displaced solutions. The trend was reversed in the Provost and Hanna soils.

The fundamental premise of using saturation extracts as a method of measuring salinity lies in the fact that the soluble salt concentration in saturation extracts is directly related to that at field-moisture ranges (Richards, 1954). Linear regression analysis between ion concentrations in saturated paste extracts and immiscibly displaced solutions in this study showed variable correlations and linear relationships for each chemical property analyzed (Table 3.3). Chemical compositions of saturated paste extracts were corrected to field moisture content by multiplying by the ratio of water content at saturation to the water content in the field (data not shown). This correction improved the relationship between the composition of solutions from the two extraction techniques in the case of EC, Mg, P, and Cl and worsened it for the other chemical properties. This indicates, therefore, that the relationship between the composition of saturated paste extracts and *in situ* soil solutions is not linear in the study soils and likely involves significant interactions with the solid phase.

### 3.3.3 Speciation of Extracted Soil Solutions

Speciation calculations using SOLMINEQ showed that the majority of the divalent cations in the extracted solutions occur as ion pairs, while monovalent cations occur primarily as the free ion (Table 3.4). The percentage of Ca occurring as $Ca^{2+}$ in immiscibly displaced solutions ranged from 9 to 21 %, with the lowest values occurring in soils with the highest EC and vice versa. Mg speciation showed a similar trend, with the proportion of $Mg^{2+}$ ranging between 3 to 18 %. Potassium present as $K^+$ in immiscibly displaced solutions ranged from 67 to 90% while $Na^+$ concentrations were between 63 and 81% of the total ion species. The amount of free $K+$ was found to be always higher than free $Na+$ in a given sample because of the slightly higher stability of the Na ion pairs relative to those of K. Again, the highest concentration of the free ion was in the least saline Wainwright soil.

Table 3.3. Linear relationship between properties in saturated paste extracts (y) and immiscibly displaced soil solutions (x). Electrical conductivity (EC) is expressed in dS $m^{-1}$ while concentrations are in mg $L^{-1}$.

| Variable | Regression Equation | $r^z$ |
|---|---|---|
| EC | $y = 4.61 + 0.46x$ | 0.62 |
| Ca | $y = 14.1 + 0.74x$ | 0.87 |
| Mg | $y = 92.4 + 0.59x$ | 0.97 |
| K | $y = - 18.6 + 0.86x$ | 0.89 |
| Na | $y = 10210 + 0.91x$ | 0.87 |
| P | $y = 0.25 + 0.49x$ | 0.86 |
| Si | $y = 1.8 + 0.48x$ | 0.86 |
| Cl | $y = 334 + 0.33x$ | 0.80 |
| $SO_4$ | $y = - 4851 + 0.78x$ | 0.94 |
| $SAR_p$ | $y = 110 + 0.41x$ | 0.72 |
| $SAR_t$ | $y = 215 + 0.38x$ | 0.75 |

$^z$ correlation coefficient

Table 3.4. Calculated species distribution of selected constituents in immiscibly displaced soil solutions and saturated paste extracts of surface horizons.

| | | Species (% of total) | |
|---|---|---|---|
| Sample | Constituent | Immiscibly Displaced Solutions | Saturated Paste Extracts |
| Hanna | P | $HPO_4^{2-}$ (32), $NaHPO_4^-$ (54), $MgPO_4^-$ (11) | $HPO_4^{2-}$ (46), $NaHPO_4^-$ (46), $CaPO_4^-$ (6) |
| | Ca | $Ca^{2+}$ (9), $CaSO_4^\circ$ (9), $CaCO_3^\circ$ (68), $CaPO_4^-$ (12) | $Ca^{2+}$ (10), $CaSO_4^\circ$ (8), $CaCO_3^\circ$ (44), $CaPO_4^-$ (38) |
| | Mg | $Mg^{2+}$ (4), $MgSO_4^\circ$ (16), $MgCO_3^\circ$ (57), $MgPO_4^-$ (18) | $Mg^{2+}$ (4), $MgSO_4^\circ$ (13), $MgCO_3^\circ$ (32), $MgPO_4^-$ (48) |
| | K | $K^+$ (75), $KSO_4^-$ (10), $KCO_3^-$ (14) | $K^+$ (82), $KSO_4^-$ (9), $KCO_3^-$ (8) |
| | Na | $Na^+$ (63), $NaSO_4^-$ (17), $NaCO_3^-$ (18) | $Na^+$ (72), $NaSO_4^-$ (15), $NaCO_3^-$ (12) |
| Wainwright | P | $HPO_4^{2-}$ (45), $NaHPO_4^-$ (29), $MgPO_4^-$ (20), $MgHPO_4^\circ$ (5) | $HPO_4^{2-}$ (63), $NaHPO_4^-$ (15), $MgPO_4^-$ (10), $CaPO_4^-$ (10) |
| | Ca | $Ca^{2+}$ (16), $CaSO_4^\circ$ (11), $CaCO_3^\circ$ (70) | $Ca^{2+}$ (19), $CaSO_4^\circ$ (10), $CaCO_3^\circ$ (68) |
| | Mg | $Mg^{2+}$ (9), $MgSO_4^\circ$ (22), $MgCO_3^\circ$ (64) | $Mg^{2+}$ (11), $MgSO_4^\circ$ (20), $MgCO_3^\circ$ (64) |
| | K | $K^+$ (85), $KSO_4^-$ (7), $KCO_3^-$ (8) | $K^+$ (88), $KSO_4^-$ (5), $KCO_3^-$ (7) |
| | Na | $Na^+$ (75), $NaSO_4^-$ (12), $NaCO_3^-$ (11) | $Na^+$ (80), $NaSO_4^-$ (9), $NaCO_3^-$ (9) |
| Nobleford | P | $HPO_4^{2-}$ (3), $MgHPO_4^\circ$ (76), $MgPO_4^-$ (16), $NaHPO_4^-$ (4) | $HPO_4^{2-}$ (4), $MgHPO_4^\circ$ (76), $MgPO_4^-$ (16), $NaHPO_4^-$ (3) |
| | Ca | $Ca^{2+}$ (13), $CaSO_4^\circ$ (86) | $Ca^{2+}$ (14), $CaSO_4^\circ$ (86) |
| | Mg | $Mg^{2+}$ (11), $MgSO_4^\circ$ (88) | $Mg^{2+}$ (11), $MgSO_4^\circ$ (89) |
| | K | $K^+$ (79), $KSO_4^-$ (21) | $K^+$ (80), $KSO_4^-$ (20) |
| | Na | $Na^+$ (63), $NaSO_4^-$ (37) | $Na^+$ (67), $NaSO_4^-$ (33) |
| Provost | P | $HPO_4^{2-}$ (7), $MgHPO_4^\circ$ (71), $MgPO_4^-$ (9), $NaHPO_4^-$ (12) | $HPO_4^{2-}$ (8), $MgHPO_4^\circ$ (66), $MgPO_4^-$ (14), $NaHPO_4^-$ (10) |
| | Ca | $Ca^{2+}$ (13), $CaSO_4^\circ$ (86) | $Ca^{2+}$ (14), $CaSO_4^\circ$ (86) |
| | Mg | $Mg^{2+}$ (11), $MgSO_4^\circ$ (89) | $Mg^{2+}$ (11), $MgSO_4^\circ$ (89) |
| | K | $K^+$ (79), $KSO_4^-$ (20) | $K^+$ (80), $KSO_4^-$ (20) |
| | Na | $Na^+$ (66), $NaSO_4^-$ (34) | $Na^+$ (66), $NaSO_4^-$ (34) |

In general, calculations showed that the majority of Ca and Mg ion pairs in the lower pH Provost and Nobleford sites were in the form of sulfates, while Hanna and Wainwright soils were generally dominated by carbonate ion pairs . Ion-pairing with phosphate was also important at the Hanna site. Sulfate was the major ion-pair with K and Na in Nobleford, Provost and Wainwright soils; the ion-pairs $KCO_3^-$ and $NaCO_3^-$ were also present in considerable concentrations at Hanna, particularly in the upper horizons.

The speciation of P varied considerably between sites, with Mg, Na or Ca complexes becoming more significant than $HPO4^-$ in the more saline soils. For example, at Provost and Nobleford, $MgHPO_4^\circ$ and $MgPO_4^-$ were the dominant P species. Smaller amounts of $NaHPO_4^-$ and $HPO_4^{2-}$ were also present. In the Hanna soil, $NaHPO_4^-$ was the dominant P species, followed by $HPO_4^{2-}$. At Wainwright, due to its lower salinity, $HPO_4^{2-}$ was the major P species and ion pairs with the cations of lesser abundance.

The degree of ion-pair formation would be expected to vary between the chemically different saturated paste extracts and immiscibly displaced solutions. Speciation of the major cations in saturated paste extracts showed similar trends to those calculated for immiscibly displaced solutions (Table 3.4), with the concentrations of free ions in saturated paste extracts being consistently higher because of the lower ionic strength of these solutions. Phosphorus speciation between the two extraction techniques however varied substantially in the highly alkaline Hanna and Wainwright soils. Since the pH values of the saturated paste extracts in these soils were consistently over half a pH unit higher than in immiscibly displaced solutions , the difference in P speciation is likely primarily due to differences in the activity of the hydrogen ion.

### 3.3.4 Relationship between Electrical Conductivity and Ionic Strength

Electrical conductivities have often been used to estimate the ionic strength of a soil solution, and the relationship has been studied by many (*eg.* Griffin and Jurinak, 1973; Alva *et al.*, 1991; Walworth, 1992). Most previous investigations have found a similar and very strong statistical correlation between the two properties, but in general have not studied solutions with high salinities. The often-cited work by Griffin and Jurinak (1973) does include several samples with EC's > 20, but the scatter of points appears to increase at these high values.

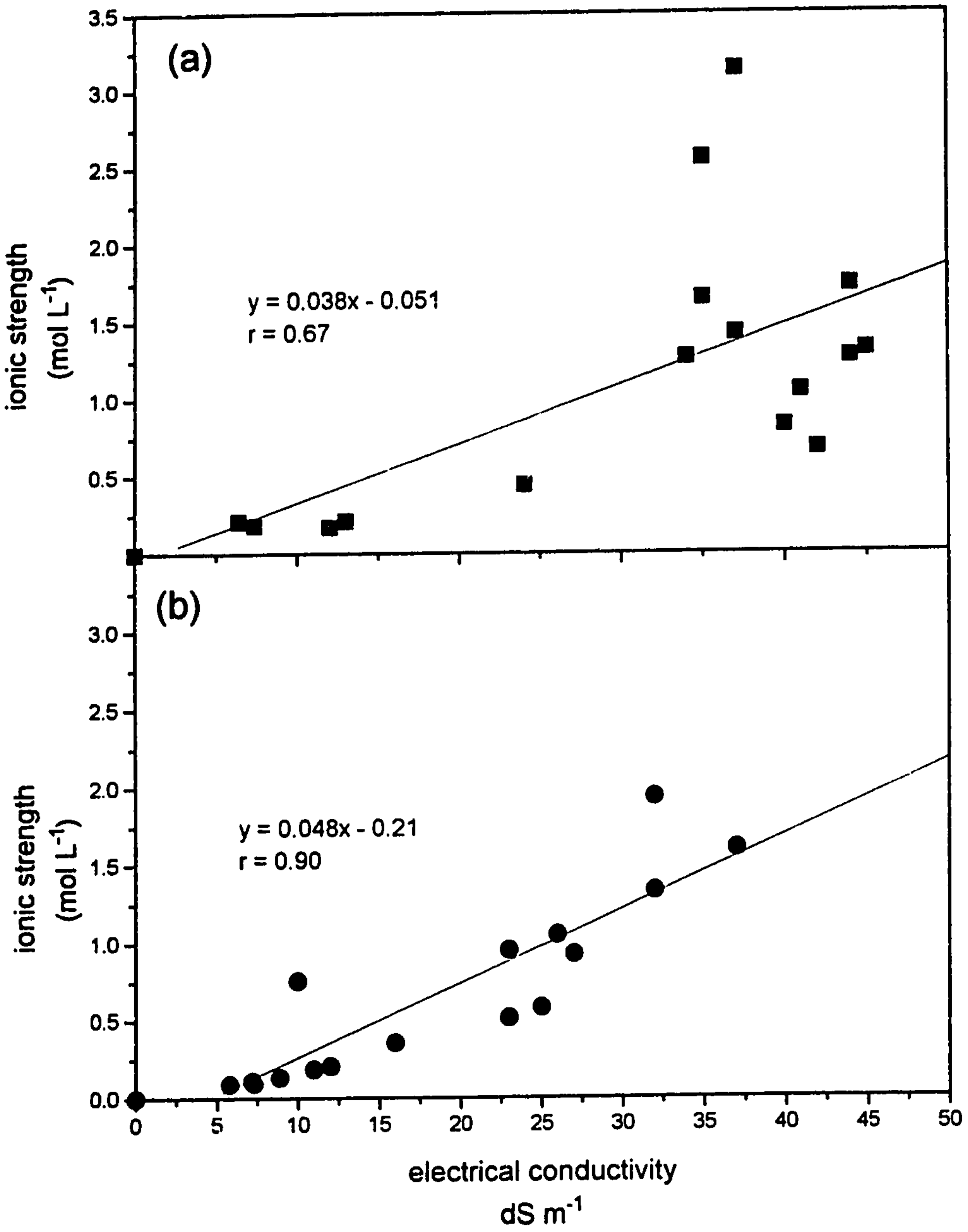

Fig. 3.1 Relationship between ionic strength and electrical conductivity of (a) immiscibly displaced soil solutions and (b) saturated paste extracts. The dotted line represents the relationship documented by Griffin and Jurinak (1973) for soil extracts and river waters.

The relationship between EC and true ionic strength, as calculated by SOLMINEQ (corrected for ion-pair formation), in this study is not well correlated (Fig. 3.1), particularly in the more concentrated immiscibly displaced solutions ($r = 0.62$). The correlation improves considerably ($r = 0.89$) for the lower conductivity saturated paste extracts. The statistical relationship of $I = 0.0127\ EC - 0.0003$, as developed by Griffin and Jurinak (1973) and used by many researchers, fits the data in this study only at EC's of less than 15. This is likely due to the large correction for ion interactions in concentrated brines. This would lead to the conclusion that for solutions of very high salinity, ionic strength cannot be estimated accurately by an EC measurement.

### 3.3.5 Sodium Adsorption Ratio and Exchangeable Sodium Percentage

The potential sodium hazard of a soil is usually estimated by calculating SAR and ESP values from the composition of saturated paste extracts, and is almost universally determined by using total analytical concentrations of Na, Ca and Mg instead of their free cationic concentrations (Sposito and Mattigod, 1977). SAR and ESP values from saturated paste extracts and immiscibly displaced solutions of the soils in this study are compared in Table 3.5. $SAR_p$ values in immiscibly displaced soil solutions range from 48 to 3257, and $ESP_p$ values range from 41 to 98, reflecting the high concentration of Na relative to that of divalent cations. With few exceptions, these values are lower than those calculated for the lower ionic strength saturated paste extracts. The correlation between $SAR_p$ from the two extraction techniques is not particularly good (Table 3.3), with the widest discrepancies between the highest SAR values. If the SAR values from the Hanna soil are not considered in the analysis, the correlation between the saturated paste extracts and immiscibly displaced solution improves considerably, with $r^2 = 0.85$.

$SAR_t$ values (calculated from free ion activities) are considerably higher than $SAR_p$ values because of the greater correction for ion-pairs, complexes and activity coefficients of the divalent cations relative to Na (Bresler *et al.*, 1982). The two values were observed to diverge more widely as the EC of the soil solution increased, but were highly correlated ($r^2 = 0.99$) for both saturated paste extracts and immiscibly displaced solutions (Fig. 3.2). Sposito and Mattigod (1977) have previously stated that the relationship between the two parameters will decrease significantly above SAR values of 10 due to random variation in anionic

Table 3.5. Sodium adsorption ratios and exchangeable sodium percentages calculated from analytical concentrations and free ion activities of extracted soil solutions.

| Sample cm | saturated paste extracts | | | | immiscibly displaced solutions | | | |
|---|---|---|---|---|---|---|---|---|
| | $SAR_t$ | $SAR_p$ | $ESP_t$ | $ESP_p$ | $SAR_t$ | $SAR_p$ | $ESP_t$ | $ESP_p$ |
| Hanna | | | | | | | | |
| 0 - 23 | 4506 | 2150 | 99 | 97 | 4166 | 1669 | 98 | 96 |
| 23 - 50 | 2884 | 1324 | 98 | 95 | 6200 | 2670 | 99 | 98 |
| 50 - 80 | 1777 | 725 | 96 | 92 | 8248 | 3258 | 99 | 98 |
| > 80 | 708 | 416 | 92 | 86 | 2084 | 1103 | 97 | 94 |
| Wainwright | | | | | | | | |
| 0 - 20 | 735 | 445 | 92 | 87 | 1038 | 539 | 94 | 89 |
| 20 - 28 | 160 | 106 | 71 | 61 | 481 | 272 | 88 | 80 |
| 28 - 42 | 311 | 208 | 82 | 76 | 261 | 158 | 80 | 70 |
| 42- 70 | 126 | 88 | 65 | 57 | 214 | 139 | 76 | 67 |
| > 70 | 121 | 91 | 64 | 58 | 114 | 75 | 63 | 53 |
| Nobleford | | | | | | | | |
| 0 - 20 | 105 | 50 | 61 | 43 | 157 | 69 | 70 | 50 |
| 20 - 40 | 75 | 33 | 53 | 33 | 120 | 49 | 64 | 42 |
| 40 - 60 | 78 | 37 | 54 | 35 | 118 | 48 | 64 | 41 |
| > 60 | 53 | 28 | 44 | 29 | 106 | 49 | 61 | 42 |
| Provost | | | | | | | | |
| 0 - 15 | 253 | 120 | 79 | 64 | 305 | 138 | 82 | 67 |
| 15 - 40 | 274 | 126 | 80 | 65 | 305 | 162 | 85 | 71 |
| > 40 | 392 | 166 | 85 | 71 | 321 | 142 | 83 | 68 |

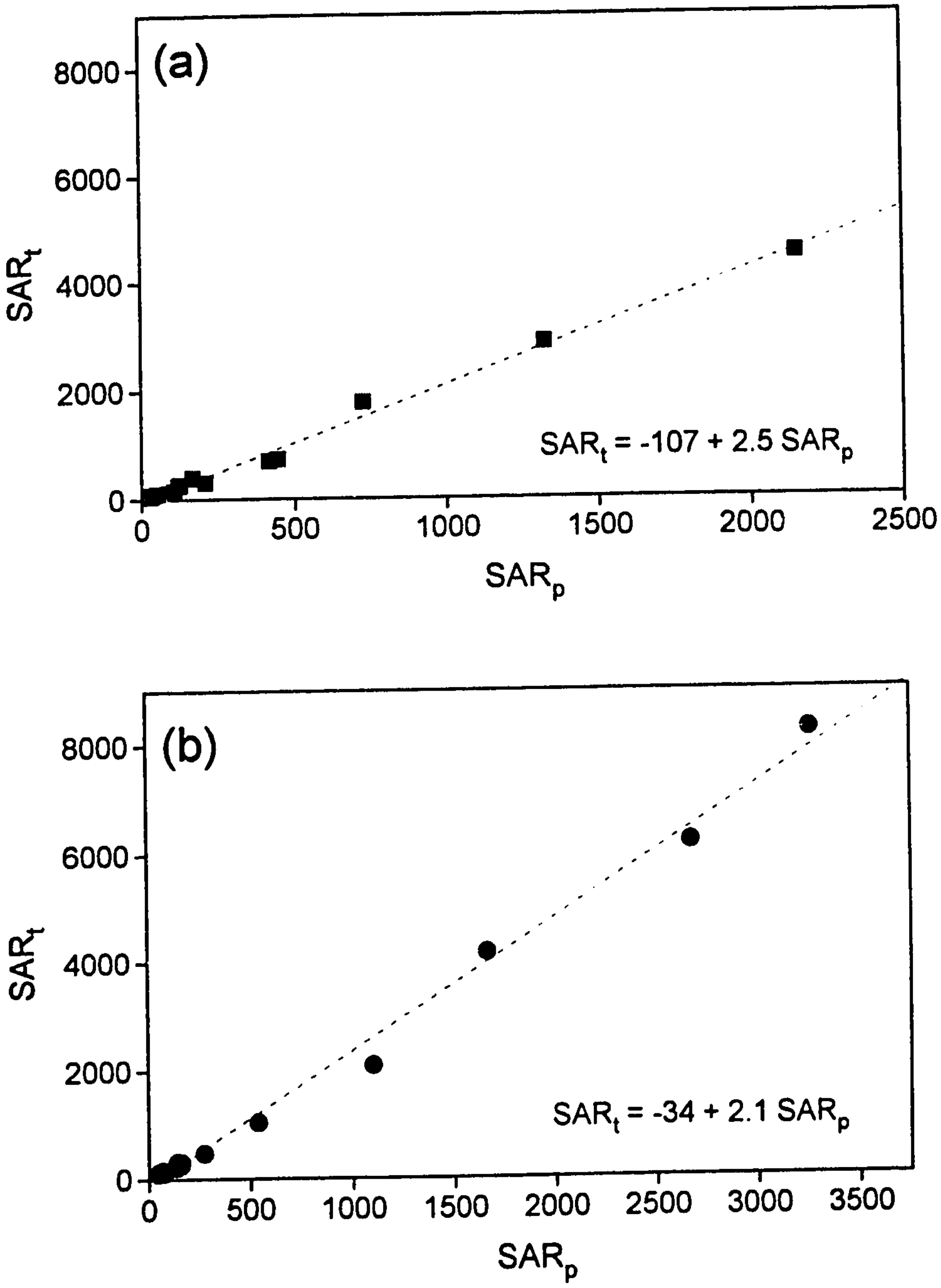

Fig. 3.2 Relationship between theoretical SAR values and practical SAR values for (a) immiscibly displaced soil solutions and (b) saturated paste extracts.

composition and increasing amounts of complexing anions and Na. Given that the solutions in this study are dominated by complexing anions and all SAR values are above 10 and range up to 8000 or more, the strong positive statistical correlation between $SAR_p$ and $SAR_t$ is surprising. This may indicate that even under extremely saline conditions, an empirical equation may be of value in estimating the true SAR of the soil solution from analytical concentrations.

### 3.3.6 Mineral Stability

Saturation indices (SI) were calculated with SOLMINEQ (Kharaka *et al.*, 1988) using the relationship $SI = \log (IAP/K_{sp})$ where IAP is the ion activity product for the mineral and $K_{sp}$ is the equilibrium solubility product. $K_{sp}$ values from Lindsay (1979) for Mg-montmorillonite and beidellite were added to the SOLMINEQ database. Negative SI values indicate undersaturation of the soil solution with respect to the mineral, suggesting that the mineral would be unstable under these conditions. Positive SI values indicate supersaturation of the soil solution with respect to the mineral, suggesting that the mineral is stable or is thermodynamically favored to precipitate. Values close to zero generally indicate that the mineral is at or close to equilibrium with the soil solution.

As would be expected from the previous discussion on variation in ion concentrations and speciation, saturation indices (SI) showed some variability between samples and method of soil solution extraction. The SI of minerals commonly found in soils are presented in Fig. 3.3 for the Hanna, Nobleford and Wainwright surface horizons and are predominantly positive, indicating mineral stability. The lack of detectable Al at Provost precluded any prediction of aluminosilicate stability. Quartz was usually at or near equilibrium in all samples, while negative SI values were frequently only seen for anorthite and amorphous silica. Saturation indices for phyllosilicate minerals were the generally furthest from equilibrium (most positive) in the Nobleford soil with chlorite the most stable of the clay minerals. Similar SI trends were generally seen with depth in a given soil because of similar chemical compositions.

Since the composition of the saturated paste extract differed from immiscibly displaced solutions, different SI values resulted. However, similar trends in relative mineral stability or instability were often seen despite the numerical disparities. The differences between SI values of the two different solution extracts

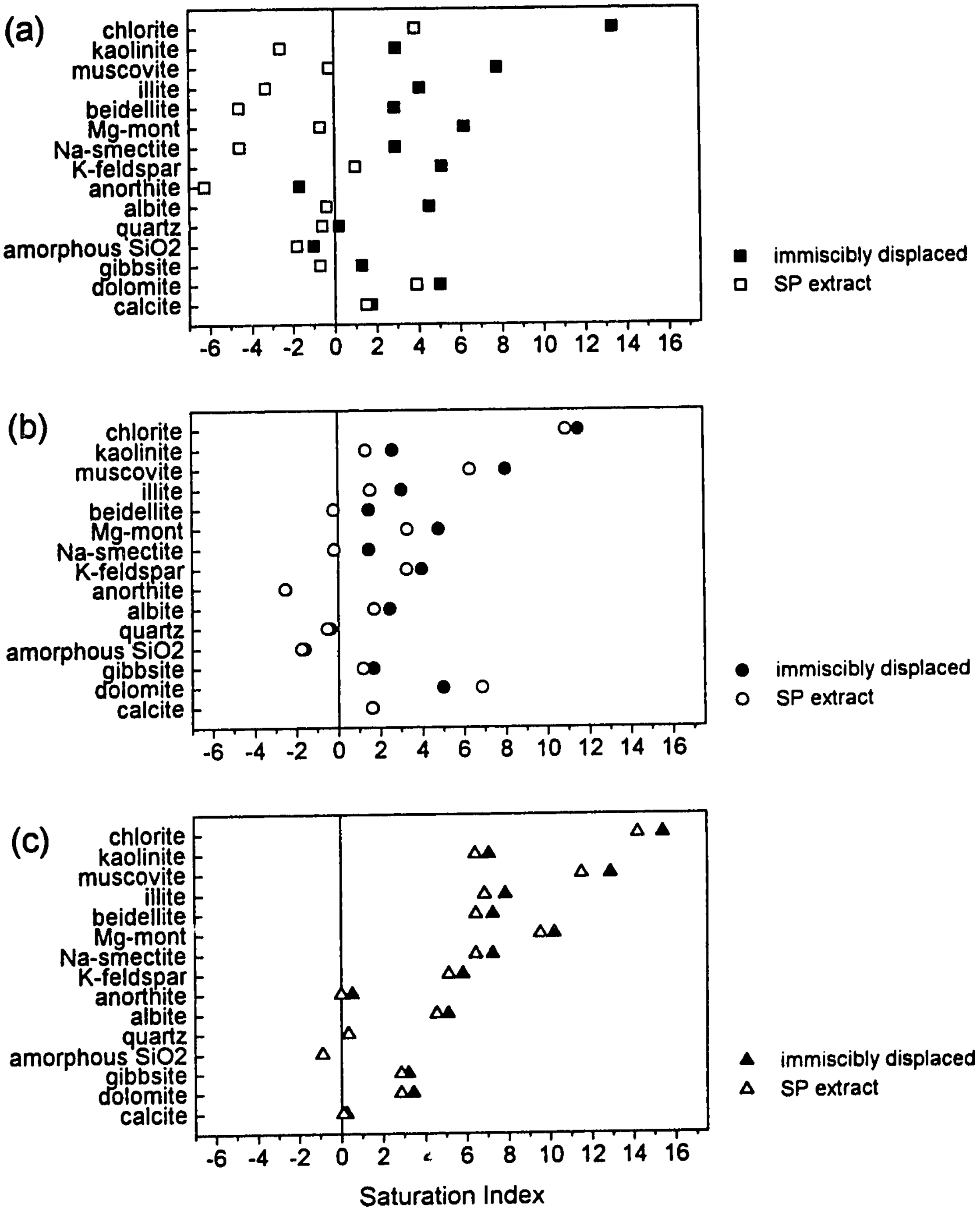

Fig 3.3 Saturation indices for selected minerals in the surface soil samples (a) Hanna, (b) Wainwright and (c) Nobleford.

were smallest in the Nobleford samples and greatest in the Hanna samples (Fig. 3.3).

This is likely due to the differences in pH values between the two methods of solution extraction. The differences in the calculated SI values from the Hanna soil are such that different conclusions would be drawn regarding clay mineral stability depending upon which extraction method was used, *i.e.*, montmorillonite, beidellite, kaolinite and illite would be predicted unstable based on saturated paste extract data whereas these minerals would be considered stable in solutions reflecting the composition of immiscibly displaced solutions.

### 3.3.7 Evaporite Mineral Formation

The chemical formula and log $K_{sp}$ values of evaporite minerals referred to in this paper are outlined in Table 3.6. The minerals formed after the evaporation of selected soil solutions were distinctly different between the chemically similar Provost and Nobleford sites and the higher pH Hanna and Wainwright locations (Table 3.7). Evaporated solutions from the Provost and Nobleford sites were dominated by Na and Mg sulfate minerals but specific minerals varied considerably between samples, despite similar initial solution chemistries. In the evaporated Nobleford samples, the saturated paste extracts and surface water contained little or no thenardite, whereas thenardite was a significant component in immiscibly displaced porewaters. The predominance of konyaite in saturated paste extracts was not noted in the Provost samples but may be due to lower Mg concentrations than in the Nobleford soil. Both of these soils also had other hydrated Mg sulfates in some samples. The lability of hydrated Na and Mg sulfate minerals is well known with respect to small changes in temperature and moisture status (Whittig *et al.*, 1982; Keller *et al.*, 1986). It is likely that differences in the time and rate of drying in the laboratory influenced the formation of specific evaporite minerals. It should also be noted that despite variable amounts of halite in all of the artificially evaporated solutions, no halite was detected in either salt efflorescence present on the soil surface at the time of sampling. This is likely due to the high solubility of halite relative to the other evaporites and may account for the scarcity of halite previously reported for salt efflorescences in Alberta (Chapter 2).

In the Hanna samples, clear differences were seen between the mineralogy of evaporated saturated paste extracts and immiscibly displaced solutions (Table

Table 3.6. Properties of evaporite minerals referred to in the study.

| Mineral | Chemical Formula | log $K_{sp}$ @ 25°C[z] | Mineral | Chemical Formula | log $K_{sp}$ @ 25°C |
|---|---|---|---|---|---|
| blödite | $Na_2Mg(SO_4)_2\cdot 4H_2O$ | -2.347 | leonite | $K_2Mg(SO_4)_2\cdot 4H_2O$ | -3.979 |
| burkeite | $Na_6CO_3(SO_4)_2$ | -0.772 | loewite | $Na_{12}Mg_7(SO_4)_{13}\cdot 15H_2O$ | n.a. |
| epsomite | $MgSO_4\cdot 7H_2O$ | -1.881 | magnesite | $MgCO_3$ | -8.05 |
| eugsterite | $Na_4Ca(SO_4)_3\cdot 2H_2O$ | n.a.[y] | mirabilite | $Na_2SO_4\cdot 10H_2O$ | -1.214 |
| gaylussite | $CaNa_2(CO_3)_2\cdot 5H_2O$ | -9.421 | nahcolite | $NaHCO_3$ | -0.541 |
| glaserite | $NaK_3(SO_4)_2$ | -3.803 | natron | $Na_2CO_3\cdot 10H_2O$ | -0.825 |
| glauberite | $Na_2Ca(SO_4)_2$ | -5.425 | pentahydrite | $MgSO_4\cdot 5H_2O$ | -1.285 |
| gypsum | $CaSO4\cdot 2H_2O$ | -4.581 | pirssonite | $Na_2Ca(CO_3)_2\cdot 2H_2O$ | -9.234 |
| hexahydrite | $MgSO_4\cdot 6H_2O$ | -1.635 | schoenite | $K_2Mg(SO_4)_2\cdot 6H_2O$ | -4.328 |
| huntite | $CaMg_3(CO_3)_4$ | -30.62 | starkeyite | $MgSO_4\cdot 4H_2O$ | -0.887 |
| hydromagnesite | $Mg_5(CO_3)_4(OH)_2\cdot 3H2O$ | -38.53 | thenardite | $Na_2SO_4$ | -0.29 |
| kieserite | $MgSO_4\cdot 4H_2O$ | -0.123 | thermonatrite | $Na_2CO_3\cdot H_2O$ | -0.01 |
| konyaite | $Na_2Mg(SO_4)_2\cdot 5H_2O$ | n.a. | trona | $Na_3H(CO_3)_2\cdot 2H_2O$ | -0.455 |

[z] Values taken from the thermodynamic database in the geochemical model PHRQPITZ (Plummer and Parkhurst 1990) except for $K_{sp}$ of huntite, hydromagnesite, thenardite, trona, nahcolite and thermonatrite which are taken from the SOLMINEQ database.

[y] not available

Table 3.7. Minerals present in evaporated soil solutions, associated waters and salt efflorescences.

| Sample (cm) | Evaporite Minerals | |
|---|---|---|
| **Hanna** | immiscibly displaced porewater | saturated paste extract |
| 0 - 20 | $Na_2SO_4 > NaCl > Na_2CO_3 \cdot H_2O = Na_6CO_3(SO_4)_2$ | $NaCl > Na_6CO_3(SO_4)_2$ |
| 23 - 50 | $Na_2SO_4 > NaCl > Na_2CO_3 \cdot H_2O = NaHCO_3$ | $NaCl > Na_6CO_3(SO_4)_2$ |
| 50 - 80 | $NaCl >> Na_2SO_4 = Na_2CO_3 \cdot H_2O$ | $NaCl > Na_6CO_3(SO_4)_2$ |
| > 80 | $Na_2SO_4 > NaCl > Na_2CO_3 \cdot H_2O$ | |
| **Nobleford** | | |
| surface water | $Na_2Mg(SO_4)_2 \cdot 5H_2O >> Na_2SO_4 > NaCl > CaSO_4 \cdot 2H_2O$ | |
| 5 - $0^z$ | $Na_2SO_4 > Na_2Mg(SO_4)_2 \cdot 5H_2O > Na_2Mg(SO_4)_2 \cdot 4H_2O > Na_4Ca(SO_4)_3 \cdot 2H_2O > CaSO_4 \cdot 2H_2O$ | |
| | immiscibly displaced porewater | saturated paste extract |
| 0 - 23 | $Na_2SO_4 > MgSO_4 \cdot 6H_2O > NaCl > CaSO_4 \cdot 2H_2O$ | $Na_2Mg(SO_4)_2 \cdot 5H_2O > NaCl > Na_2SO_4 > CaSO_4 \cdot 2H_2O$ |
| 23 - 40 | $Na_2Mg(SO_4)_2 \cdot 5H_2O > Na_2SO_4 > MgSO_4 \cdot 6H_2O > NaCl$ | $Na_2Mg(SO_4)_2 \cdot 5H_2O > NaCl > CaSO_4 \cdot 2H_2O$ |
| 40 - 60 | $Na_2Mg(SO_4)_2 \cdot 5H_2O > NaCl > = Na_2SO_4 > CaSO_4 \cdot 2H_2O$ | $Na_2Mg(SO_4)_2 \cdot 4H_2O >> Na_2Mg(SO_4)_2 \cdot 5H_2O > NaCl > Na_2SO_4 > CaSO_4 \cdot 2H_2O$ |
| > 60 | $Na_2SO_4 > Na_{12}Mg_7(SO_4)_{13} \cdot 15H_2O > NaCl > CaSO_4 \cdot 2H_2O$ | $Na_2Mg(SO_4)_2 \cdot 5H_2O >> NaCl > Na_2SO_4 > CaSO_4 \cdot 2H_2O$ |
| **Provost** | | |
| 5 - $0^z$ | $Na_2SO_4 >> Na_2Mg(SO_4)_2 \cdot 5H_2O > Na_2Mg(SO_4)_2 \cdot 4H_2O$ | |
| groundwater | $Na_2Mg(SO_4)_2 \cdot 5H_2O >> Na_2SO_4 > NaCl > CaSO_4 \cdot 2H_2O$ | |
| | immiscibly displaced porewater | saturated paste extract |
| 0 - 15 | $Na_2SO_4 >> Na_2Mg(SO_4)_2 \cdot 5H_2O > NaCl$ | $Na_2SO_4 > MgSO_4 \cdot 6H_2O > NaCl$ |
| 15 - 40 | $Na_2SO_4 >> Na_{12}Mg_7(SO_4)_{13} \cdot 15H_2O >> NaCl = CaSO_4 \cdot 2H_2O$ | $Na_2SO_4 > Na_2Mg(SO_4)_2 \cdot 5H_2O > MgSO_4 \cdot 6H_2O > NaCl$ |
| > 40 | $Na_2SO_4 >> Na_2Mg(SO_4)_2 \cdot 5H_2O >> NaCl$ | $Na_2SO_4 >> Na_2Mg(SO_4)_2 \cdot 5H_2O = MgSO_4 \cdot 6H_2O$ |

[z] Present as salt efflorescence on soil surface at time of sampling.

3.7). While halite was common in both types of evaporated solutions, burkeite was the only other mineral present in saturated paste extracts. Immiscibly displaced solutions however generally contained no burkeite but had thenardite, thermonatrite and occasionally nahcolite in the mineral assemblage. A similar trend was seen at the Wainwright location (data not shown). This would indicate that the amount or activity of water in the evaporating solution influences the crystallization process, with $SO_4$ and $CO_3$ being segregated into burkeite in the more dilute saturated paste extracts.

Calculated SI of evaporite minerals showed that the majority of evaporites were unstable in the soil solutions except for huntite, hydromagnesite and magnesite which frequently had positive SI. The relative stability of candidate evaporites in selected samples are presented in Fig 3.4. Variability between sample depth and method of extraction for a given site was normally minor. As expected, the SI of evaporite minerals varied with solution composition; generally minerals containing Na and $SO_4$ had the least negative SI values while K-containing evaporites had the most negative SI values, and Mg-containing evaporites were most stable in solutions of higher Mg concentrations.

There are a number of limitations in attempting to predict evaporite mineral formation from solution composition data. For example, thermodynamic data for many evaporites is not available, kinetics and mineral quantities are not addressed by an equilibrium model such as SOLMINEQ and the extreme lability of some evaporite minerals is not taken into account. Also, in reality, as minerals precipitate, the solution composition will also change, but since many minerals thermodynamically favored to form do not actually precipitate, predicting these changes is difficult. Despite all of the potential flaws in this technique, modelling should still theoretically provide a first approach in assessing the relative stability of minerals in the soil solution.

For purposes of prediction, it was assumed that minerals in thermodynamic equilibrium or supersaturated with respect to the input concentrations would precipitate first, and as water evaporated and ion concentrations increased, evaporites with less negative SI values would precipitate before minerals with more negative SI. The relationship between minerals formed in an evaporated solution with those predicted to form was poor. Minerals such as huntite, hydromagnesite, and magnesite which were frequently favored to precipitate were not detected in any

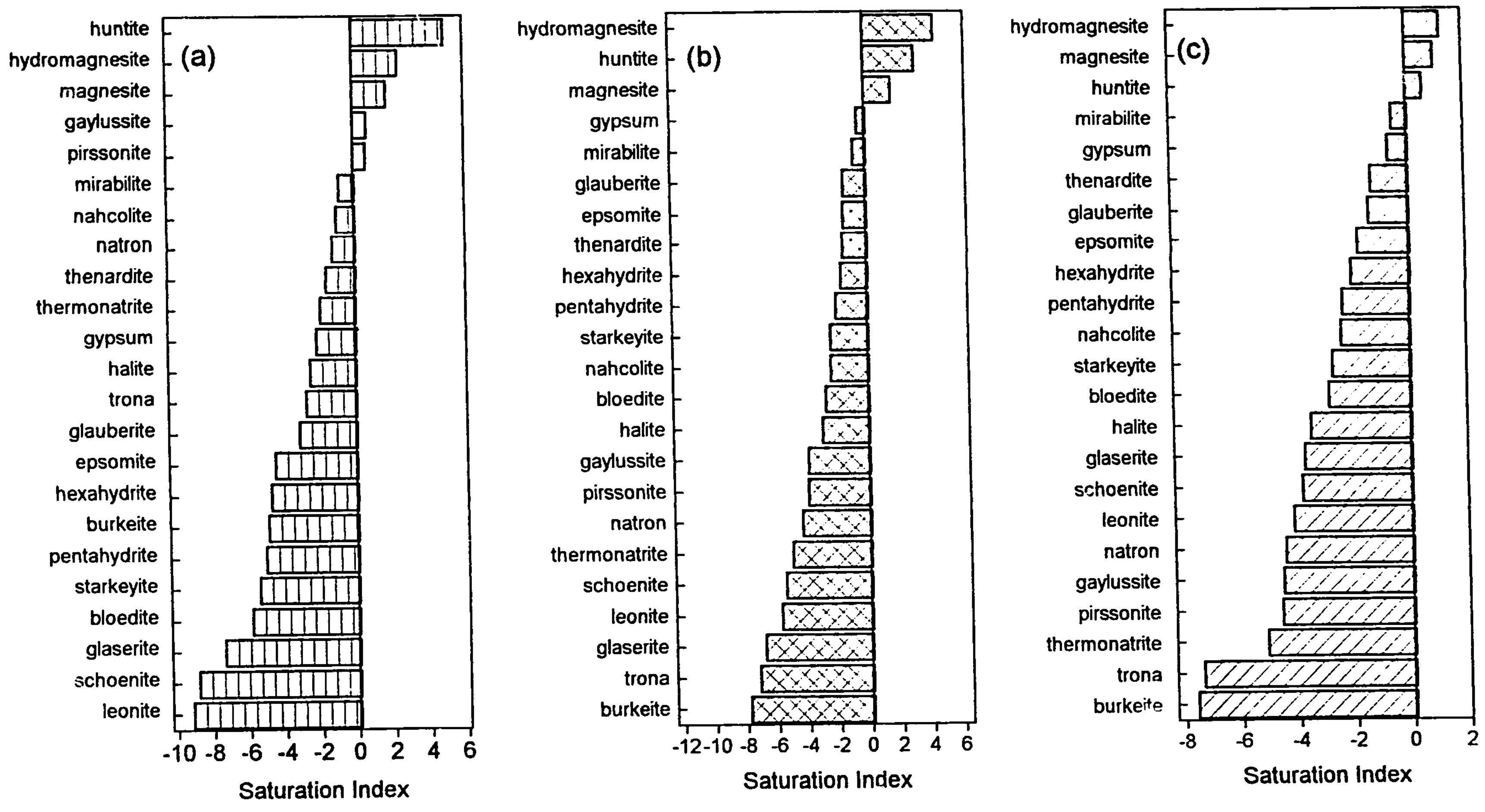

Fig 3.4 Saturation indices for selected evaporite minerals in immiscibly displaced soil solutions from (a) Hanna, (b) Nobleford and (c) Provost.

of the samples. Minerals with more negative SI were often predominant over minerals with similar chemical constituents and less negative SI. For example, the SI of burkeite is considerably more negative than those of thenardite and thermonatrite but was still the dominant sulfate mineral in evaporated saturated paste extracts of the Hanna soil. It has previously been stated that despite the large number of evaporites that can theoretically form, only a very small number have been detected in soils (Stoops *et al.*, 1978). This would appear to be true in artificially evaporated soil solutions as well.

## 3.4 CONCLUSIONS

Soil solutions extracted from four saline soils in Alberta are dominated by Na and $SO_4$. Concentrations of other major cations varied by several orders of magnitude between sites but generally Ca is present in the lowest concentrations. Phosphorus concentrations also vary by several orders of magnitude, and are considerably higher than typical soil solutions. This is probably due to the high amount of ion-pairing occurring in the solutions.

Comparison of characteristics of immiscibly displaced solutions and saturated paste extracts from a given soil show that considerable variation exists between all chemical properties investigated and that a simple relationship between them does not exist. Discrepancies appear to increase as the solution concentration of a given ion increases and may be the result of many interrelated reactions such as exchange, precipitation, dissolution and hydrolysis occurring upon dilution. Other factors, such as drying and rewetting of the soil sample and different extraction pressures, may also result in different solution characteristics. Sodium, Mg and K and anion concentrations were generally higher in immiscibly displaced solutions, while Ca and P levels were higher in saturated paste extracts. Silicon concentrations did not vary consistently with the method of extraction and despite alkaline pH values were within or below levels typically found in soils. The relationship between EC and ionic strength in soil extracts was not highly correlated and differed with the extraction method, indicating that for solutions of very high salinity, ionic strength cannot be correctly estimated by measuring the EC of the solution.

Differences in composition between immiscibly displaced soil solutions and saturated paste extracts resulted in considerable differences in properties normally inferred from the soil solution characteristics such as speciation, SAR and ESP values and mineral stabilities. While in many cases trends were similar, the use of saturated paste extracts as a proxy of soil solution can lead to very different numerical values and can occasionally lead to drastically different conclusions, particularly in regard to mineral stability. Although the relationship between SAR values in saturated paste extracts and immiscibly displaced solutions was poor, a strong positive statistical correlation was discovered between theoretical and practical SAR's for both types of extracts. This may be of practical use in quickly determining SAR's (and consequently ESP values) corrected for ion-pairs, complexes and activity coefficients from analytical concentrations for solutions with extremely high SAR values.

Evaporite mineral formation in saline soils cannot be accurately predicted from the chemistry of soil solutions or from the minerals formed from the evaporation of soil solutions. Distinct differences were seen between the mineralogy of evaporated immiscibly displaced solutions and saturated paste extracts for highly alkaline solutions. This study showed that even in chemically similar solutions, different minerals formed, likely as a result of differences in evaporation conditions.

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# 4. CHARACTERISTICS OF CLAY MINERALS IN SALINE ALKALINE SOILS OF ALBERTA [1]

## 4.1 INTRODUCTION

Theoretical considerations and laboratory studies suggest that mineral weathering and formation in poorly drained saline soils can be expected to differ from well drained non-saline soils. Poor drainage affects redox potential and the movement of soluble constituents, while soil alkalinity will affect mineral stabilities. Using thermodynamic stability diagrams, Rai and Lindsay (1975) reported that the stability of both primary and secondary minerals increases with increasing pH. However, laboratory studies investigating the dissolution of common silicate minerals such as kaolinite (Carroll and Walther, 1990), muscovite (Knauss and Wolery, 1989), quartz (Brady and Walther, 1989) and feldspars (Knauss and Wolery, 1986) indicate that the rate of mineral dissolution increases with increasing pH in basic solutions. Mineral characteristics will also be affected by the composition of the soil solution. By definition, saline soils have high ionic strengths. Laboratory studies have indicated that the rate of quartz dissolution increases with increasing electrolyte content (Dove and Crerar, 1990), but the effect of ionic strength on the dissolution of other minerals is unclear. Specific components of the soil solution in salt-affected soils may also have a significant effect on mineral weathering. For example, several investigators have reported that the rate of clay mineral weathering is enhanced with increasing exchangeable sodium percentage (Oster and Shainberg, 1979; Frenkel *et al.*, 1983).

Reports of mineral alteration in salt-affected soils have occasionally been documented in the literature. In a study of the fine clay fraction of the A horizon of salt-affected soils in Bulgaria, a large amount of highly interstratified mica-montmorillonite was identified which essentially gave no basal reflections upon X-ray diffraction (Behar *et al.*, 1972). The authors concluded that alkaline conditions increased the solubilities of Al and Si, thus promoting their interlayering in minerals with large expandable layers. This process was thought to be enhanced by

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[1] A version of this chapter has been accepted for publication in the Soil Science Society of America Journal.

alternating wet and dry conditions. Smectite degradation with a concomitant increase in amorphous materials has also been reported in salt-affected soils in Egypt, with soil layers having the highest salt and soda content exhibiting the largest amount of amorphous oxides and broadest X-ray diffraction peaks (Kishk and Hassan, 1972).

Studies in North America have also indicated smectite alteration in soils affected by salts. Klages and Southard (1968) found that montmorillonite had become so disordered in the surface horizon of a Solonetzic soil that X-ray diffraction of oriented specimens yielded no basal reflections. Whittig (1959) reported the presence of an unusual montmorillonite-like mineral in the coarse clay fraction of surface horizons in Solonetzic soils. The mineral was characterized by extremely diffuse peaks and expansion to 2.0 nm or greater with Mg-saturation and glycerol solvation. For Solonetzic soils in Montana, Munn and Boehm (1983) concluded that decomposition of inherited smectite occurred in the sola of all sodium-affected soils studied and was most pronounced in the surface horizons. This conclusion was based on the diffuse nature and decreased intensity of smectite X-ray diffraction peaks. Lewis and Drew (1973) found poorer crystallinity of montmorillonite in the A horizons of slick spots in Nebraska compared to adjacent soils.

Based on the foregoing, it is unclear whether silicate minerals will be stable or unstable under saline alkaline conditions. While some previous studies indicate that smectite degradation may be occurring in salt-affected surface soils, basic thermodynamic principles suggest that the stability of silicate minerals increases with increasing pH. Laboratory studies, however, show that the rate of dissolution of silicate minerals increases with increasing pH above pH 8. The effect of salinity on the weathering of minerals is unclear.

Limited information is available on the characteristics of non-evaporite minerals in saline alkaline soils despite the large areas of land affected. Reports from North America deal with Solonetzic soils, which have undergone significantly more pedogenesis than the soils in this study. Clay minerals in western Canada are generally inherited from parent material of glacial origin, and show little or no evidence of alteration, primarily because of the youthfulness of the soils (Kodama, 1979). Previous studies have shown that the clay mineralogy of soils throughout Alberta is remarkably similar, and is dominated by smectites, with smaller amounts of mica, kaolinite and occasionally chlorite (Abder-Ruhman, 1980; Kodama, 1979; Dudas and Pawluk, 1982).

Soil investigations in saline seeps and groundwater discharge areas have generally focused on reclamation and management techniques, rather than on the mineralogical transformations and weathering characteristics occurring under these chemical conditions. The characteristics of clay minerals in severely saline soils in Alberta have not previously been investigated but would be expected to differ from other soils because of differences in the weathering environment. Therefore, the objectives of this study were to characterize the clay mineral components of selected saline alkaline soils in Alberta and to determine their stability relative to the soil solution chemistry.

## 4.2 MATERIALS AND METHODS

For an initial survey of clay mineral characteristics, thirty-nine soils possessing a distinct salt crust were sampled throughout semi-arid central and southern Alberta. Salt efflorescences were scraped from the surface and the underlying soil sampled to a depth of approximately 20 cm. All samples except one were collected from dryland areas, and included playas, evaporitic rings and saline seeps of various sizes from both cultivated and non-cultivated land. The clay fraction of these samples was separated using gravity sedimentation techniques after soluble salts, primarily sodium sulfates, were removed by repeated deionized water washing and decantation (Jackson, 1979). Sub-samples were Ca and K-saturated by repeated treatments with 1 M solutions of the respective chloride salts, washed free of excess electrolyte and made into oriented specimens for X-ray diffraction (XRD) analysis on glass slides using the paste method (Thiesen and Harward, 1962). Diffractograms of the oriented clay slides were obtained with a Philips diffractometer (Model 1710, Philips Electronics Ltd., Scarborough, Ontario, Canada) equipped with a LiF curved crystal monochromator using CoK$\alpha$ radiation generated at 50 kV and 25 mA, a step size of 0.05° 2$\Theta$ and an accumulation time of 2 seconds step$^{-1}$. Calcium-saturated clays were analyzed after equilibration at 54% relative humidity (RH) and solvation with ethylene glycol and glycerol. Diffractograms of K-saturated specimens were obtained after heating at 105°, 300° and 550°C and analyzed at 0% RH and after equilibration at 54% RH.

Four of the sites from the initial survey were subsequently selected for detailed analysis and sampled in May, 1991. They were located near Hanna, Nobleford, Wainwright, and Provost, Alberta and included a playa, a saline seep in cultivated land, and evaporitic rings around a pothole slough and a larger saline lake respectively. No plant growth was observed on the soils. The soils were classified as Typic Cryaquents (Rego Gleysols) because of little or no soil development and saturation during at least parts of the year; the horizon designation for these soils would consistently be Cgz (Soil Survey Staff, 1988). Since pedogenesis was very weak or non-existent, samples were taken approximately every 20 cm unless obvious differences in properties such as the presence of a clay lens were apparent. The depth to which sampling occurred was limited by the presence of a high water table at the Provost site, reaching the glacial till parent material at the Nobleford site and by the physical difficulty of excavating through the material at the other two sites.

Pore water was extracted from each sample using immiscible displacement (Elkhatib *et al.*, 1986), with tetrachloroethylene as the displacing fluid. Extracted solutions were immediately filtered through a 0.22 $\mu$m filter and pH and electrical conductivity (EC) measurements taken; samples were then refrigerated prior to further analysis. Calcium, Mg, Na, K, P, Fe, Mn, Al and Si were determined using inductively coupled plasma atomic emission spectrophotometry. Chloride and $SO_4$ were measured using ion chromatography. Speciation of the dissolved components was determined with the computer program SOLMINEQ using Pitzer equations to calculate activity coefficients in solutions of high salinity (Kharaka *et al.*, 1988).

The bulk soils were air-dried and ground to pass a 2-mm sieve. Total carbonate values were evaluated using a titrimetric technique modified from Bundy and Bremner (1972). The soils were ultrasonified for 3 minutes at 400 W and soluble salts removed from the samples as previously described. Since the dominant soluble salt in the soils was $Na_2SO_4$, clays were essentially Na-saturated: once excess $Na_2SO_4$ was removed by deionized water washings, stable suspensions persisted for the particle size separations. The clay fraction ($< 2.0$ $\mu$m) of the soils was separated using sedimentation techniques and then further subdivided by centrifugation into 2 - 0.2 $\mu$m, 0.2 - 0.08 $\mu$m and $<$ 0.08 $\mu$m size fractions

(Jackson, 1979). Samples were analyzed by XRD as previously described to obtain information on the mineralogical characteristics of the untreated soil.

Sub-samples were treated with sodium hypochlorite to remove organic matter (OM) (Anderson, 1963). Carbonates were removed using 10% HCl dropwise for a few minutes until effervescence had stopped. This technique was used rather than buffered sodium acetate because of large quantities of dolomite in some samples. Soluble salt removal and dispersion were conducted as described above. The samples were fractionated into sand (0.05 to 2 mm), silt (50 to 2.0 $\mu$m) and clay ($< 2.0$ $\mu$m) fractions using a combination of wet sieving and sedimentation techniques. The clay fraction was subdivided into 3 size fractions in the same way as the untreated samples. The quantities of each particle size were determined from the relative mass of the oven dry separates.

X-ray diffraction patterns for each treated clay fraction were obtained as previously described. Selected samples were examined after Li-saturation and heating, using techniques similar to those of Jaynes and Bigham (1987), to determine if tetrahedrally substituted smectites were present. The calcium exchange capacity (CaEC) and potassium exchange capacity (KEC) were determined using the techniques of Jackson *et al.* (1986) and were used to estimate quantities of smectite and vermiculite. Portions of the Ca-saturated clays were dissolved in HF and $HNO_3$ using microwave dissolution (Warren *et al.*, 1990) and the K in the resulting solution analyzed by atomic absorption spectroscopy (AAS). Mica content was estimated by assuming all K was associated with micas and that $K_2O$ content in soil mica was equal to 100 g $kg^{-1}$ (Jackson, 1979). Subsamples of the clay separates were sequentially extracted using acid ammonium oxalate (AOX) and citrate-bicarbonate-dithionite (CBD) (McKeague, 1978) to provide information on amorphous Al, Si and Fe materials and crystalline Fe oxides respectively. Aluminum and Fe were measured using AAS, while Si was determined using a reduced molybdate colorimetric procedure (Weaver *et al.*, 1968). In all cases, matrix solutions were carefully matched between the standards and samples.

## 4.3 RESULTS AND DISCUSSION

### 4.3.1 General Soil Characteristics

Selected characteristics of the four soils analyzed in detail are described in Table 4.1. Examination of the particle size distribution indicates that Wainwright,

Table 4.1. Particle size distribution$^z$, $CaCO_3$ equivalents and selected chemical properties of the study soils.

| Sampling Depth (cm) | Sand | Silt | Clay | Fine Clay | fine/total clay | $CaCO_3$ g kg$^{-1}$ | pH | EC dS/m |
|---|---|---|---|---|---|---|---|---|
| | % | | | | | | | |
| | | | | **Wainwright** | | | | |
| 0 - 20 | 68 | 17 | 15 | 6 | 0.40 | 76 | 9.6 | 24 |
| 20 - 28 | 34 | 35 | 31 | 8 | 0.36 | 106 | 9.6 | 13 |
| 28 - 42 | 92 | 4 | 4 | 1 | 0.25 | 56 | 9.3 | 6 |
| 42 - 70 | 71 | 15 | 14 | 4 | 0.29 | 101 | 9.1 | 7 |
| > 70 | 79 | 11 | 10 | 1 | 0.10 | 74 | 9.0 | 12 |
| | | | | **Hanna** | | | | |
| 0 - 23 | 72 | 13 | 15 | 5 | 0.33 | 47 | 9.9 | 45 |
| 23 - 50 | 66 | 17 | 17 | 4 | 0.24 | 45 | 9.9 | 41 |
| 50 - 80 | 26 | 27 | 47 | 18 | 0.38 | 63 | 9.6 | 40 |
| > 80 | 22 | 30 | 48 | 22 | 0.46 | 55 | 9.8 | 42 |
| | | | | **Nobleford** | | | | |
| 0 - 20 | 39 | 40 | 21 | 6 | 0.29 | 10 | 8.3 | 34 |
| 20 - 40 | 46 | 30 | 23 | 11 | 0.48 | 0.7 | 7.8 | 37 |
| 40 - 60 | 47 | 32 | 21 | 9 | 0.43 | 7.1 | 8.2 | 35 |
| > 60 | 34 | 39 | 27 | 0.4 | 0.02 | 234 | 8.4 | 44 |
| | | | | **Provost** | | | | |
| 0 - 15 | 54 | 16 | 31 | 2 | 0.07 | 167 | 8.1 | 37 |
| 15 - 40 | 71 | 8 | 21 | 3 | 0.14 | 84 | 8.0 | 44 |
| > 40 | 64 | 10 | 26 | 3 | 0.12 | 115 | 8.1 | 35 |

$^z$ sand (2.0 - 0.05 mm), silt (50 - 2.0 $\mu$m), clay ($<$ 2.0 $\mu$m), fine clay ($<$ 0.2 $\mu$m)

Provost and the upper layers of the Hanna soil are dominated by sand-sized particles. Below a depth of 50 cm, the Hanna pedon becomes clayey in texture. The Nobleford soil is loamy throughout the profile. The proportion of fine clay (< 0.2 μm) to the total clay fraction ranges from 0.07 to 0.48, whereas ratios previously reported for Alberta soils are usually 0.50 or higher, with the exception of eluviated horizons which have ratios ranging from 0.20 to 0.47 (Abder-Ruhman, 1980; Spiers *et al.*, 1984). Although not specifically quantified, particles < 0.08 μm in many of the samples were essentially non-existent. Particles in the 2 - 0.2 μm range dominate the clay fraction.

The low proportion of fine clay in many of the samples may be an indication of intense weathering processes, particularly of the smectite minerals which tend to dominate the smallest size fractions. It may also indicate the lack of significant mineral neoformation, even though the soil solution chemistry appears to favor the precipitation of common phyllosilicates. Alternatively, the low proportion of fine clay may be due to physical factors such as removal by overland flow or the action of fluctuating groundwater.

### 4.3.2 Soil Solution Chemistry

The study soils were highly saline and sodic, and soil solutions were dominated by Na and $SO_4$ ions. The negative logarithms of selected ion activities in the immiscibly displaced solutions are presented in Table 4.2. The amounts of Mg, Ca and K varied substantially between the four sites, with Provost and Nobleford having the highest concentrations of Mg and Ca. The EC of the immiscibly displaced soil solutions ranged from 6 to 45 dS $m^{-1}$ while pH values ranged from 7.8 to 9.9 (Table 4.1), with little variation with depth at each site. Silicon concentrations ranged from 0.80 to 13 mg $L^{-1}$ and did not appear to be correlated with pH. Aluminum values were low, with the highest concentration reaching only 1 mg $L^{-1}$. No aluminum was detectable in the soil solution at the Provost site, precluding the calculation of aluminosilicate stability in this location. Again, Al concentration did not appear to be correlated with pH despite the expected increased solubility of Al at pH > 9.

A stability diagram (Fig. 4.1) was developed from structural formulae available in Lindsay (1979) and average solution compositions for constituent

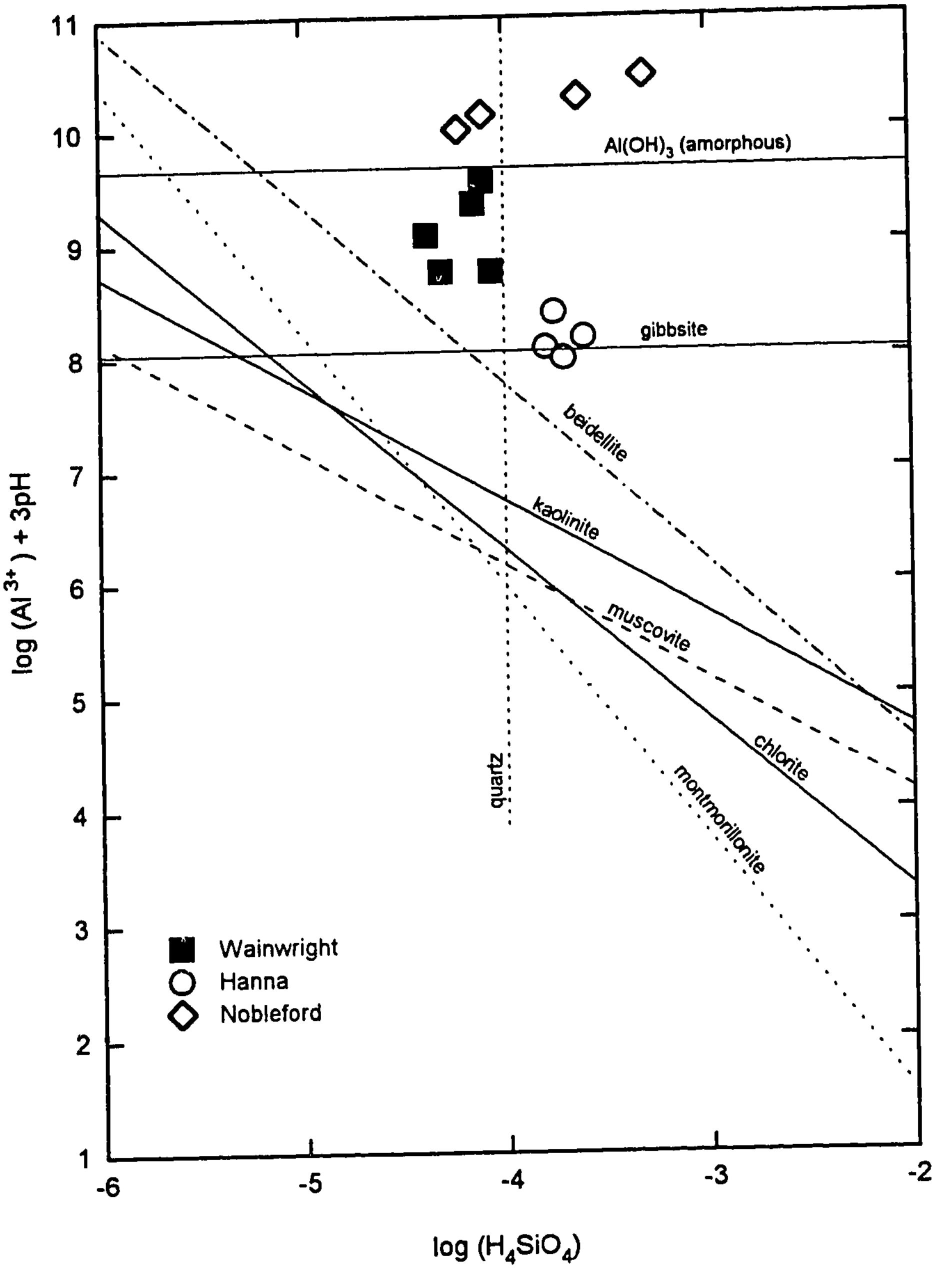

Fig. 4.1 Stability diagram for common minerals in the < 2 μm fraction showing the composition of three saline soil solutions in terms of pH$_4$SiO$_4$ and pAl$^{3+}$ + 3pH.

Table 4.2. Negative logarithms of selected ion activities in soil solutions.

| Sample Depth (cm) | $pH_4SiO_4$ | $pAl^{3+}$ | $pCa^{2+}$ | $pMg^{2+}$ | $pK^+$ | $pNa^+$ |
|---|---|---|---|---|---|---|
| | | | Wainwright | | | |
| 0 - 20 | 4.30 | 20.1 | 4.74 | 4.09 | 2.03 | 0.487 |
| 20 - 28 | 4.38 | 19.7 | 4.57 | 4.32 | 2.34 | 0.881 |
| 28 - 42 | 4.15 | 18.6 | 4.46 | 3.49 | 2.43 | 0.803 |
| 42 - 70 | 4.10 | 17.8 | 4.46 | 3.39 | 2.40 | 0.847 |
| > 70 | 4.06 | 17.6 | 4.45 | 3.00 | 2.38 | 0.936 |
| | | | Hanna | | | |
| 0 - 23 | 3.30 | 21.3 | 4.93 | 4.48 | 2.52 | 0.0537 |
| 23 - 50 | 3.79 | 21.6 | 5.18 | 5.41 | 2.69 | 0.196 |
| 50 - 80 | 3.60 | 20.6 | 5.03 | 5.73 | 3.03 | 0.163 |
| > 80 | 3.70 | 21.4 | 4.50 | 4.44 | 3.20 | 0.189 |
| | | | Nobleford | | | |
| 0 - 20 | 3.63 | 14.6 | 3.56 | 1.72 | 2.50 | 0.159 |
| 20 - 40 | 3.30 | 12.9 | 3.71 | 1.50 | 2.77 | 0.168 |
| 40 - 60 | 4.22 | 14.6 | 3.68 | 1.55 | 3.19 | 0.203 |
| > 60 | 4.10 | 15.1 | 3.33 | 1.73 | 3.37 | 0.331 |
| | | | Provost | | | |
| 0 - 15 | 3.14 | n.d.[z] | 3.74 | 2.08 | 1.51 | 0.0527 |
| 15 - 40 | 3.80 | n.d. | 3.97 | 1.99 | 1.84 | -0.0889 |
| > 40 | 3.41 | n.d. | 3.92 | 2.00 | 1.68 | -0.0104 |

[z] not detectable

elements (Table 4.2). This shows that montmorillonite is the most stable phyllosilicate except under conditions of very low silica activity. The state of equilibrium assumed between the extracted soil solution and clay minerals for these calculations was justified by the expectation that the contacting soil solution would have a long residence time because of very poor drainage. High activities of constituent ions and alkaline pH values cause a relative shift downward of the stability lines (Fig. 4.1) for many clay minerals as compared to stability diagrams constructed for typical soil solutions. Seasonal fluctuations in the solution chemistry may be expected in the soils as the moisture content changes and may alter the relative position of the stability lines as well as the position of points plotted in terms of $pH_4SiO_4$ and $pAl^{3+} + 3pH$. At the time of sampling (May), the stability diagrams indicate that the soil solutions were supersaturated with respect to common phyllosilicates and plotted closer to the stability lines for quartz and amorphous $Al(OH)_3$ or gibbsite. This would suggest that the clay minerals are stable in the saline environment and actually should be precipitating.

### 4.3.3 Clay Mineralogy

The initial survey of the clay mineralogy of salt affected soils indicated that the minerals present in 20 of the 39 samples were similar to those found in non-saline soils, consisting of an admixture of smectite, kaolinite, mica, chlorite and quartz. The other samples from the initial survey showed partial or complete degradation of smectites. Of this group, diffraction maxima for the smectites ranged from appearing very broad and ragged to being essentially absent, and were particularly noticeable after solvation with ethylene glycol or glycerol (Fig. 4.2a). This unusual diffraction behavior is similar to that previously reported for salt-affected surface soils (Behar *et al.*, 1972; Klages and Southard, 1968; Whittig, 1959) and has previously led to the conclusion that smectite degradation or intensive interstratification is occurring under these conditions. Klages and Southard (1968), however, noted these characteristics after pretreatments to remove OM and carbonates. Two soils displaying smectite alteration on XRD patterns (Nobleford and Provost) were subsequently analyzed further.

In the Nobleford soil, this behavior was observed only in the coarse clay fraction and only in the 0 - 20 cm layer. In the Provost samples the phenomenon appeared to occur at all sampling depths, although slightly more pronounced in the

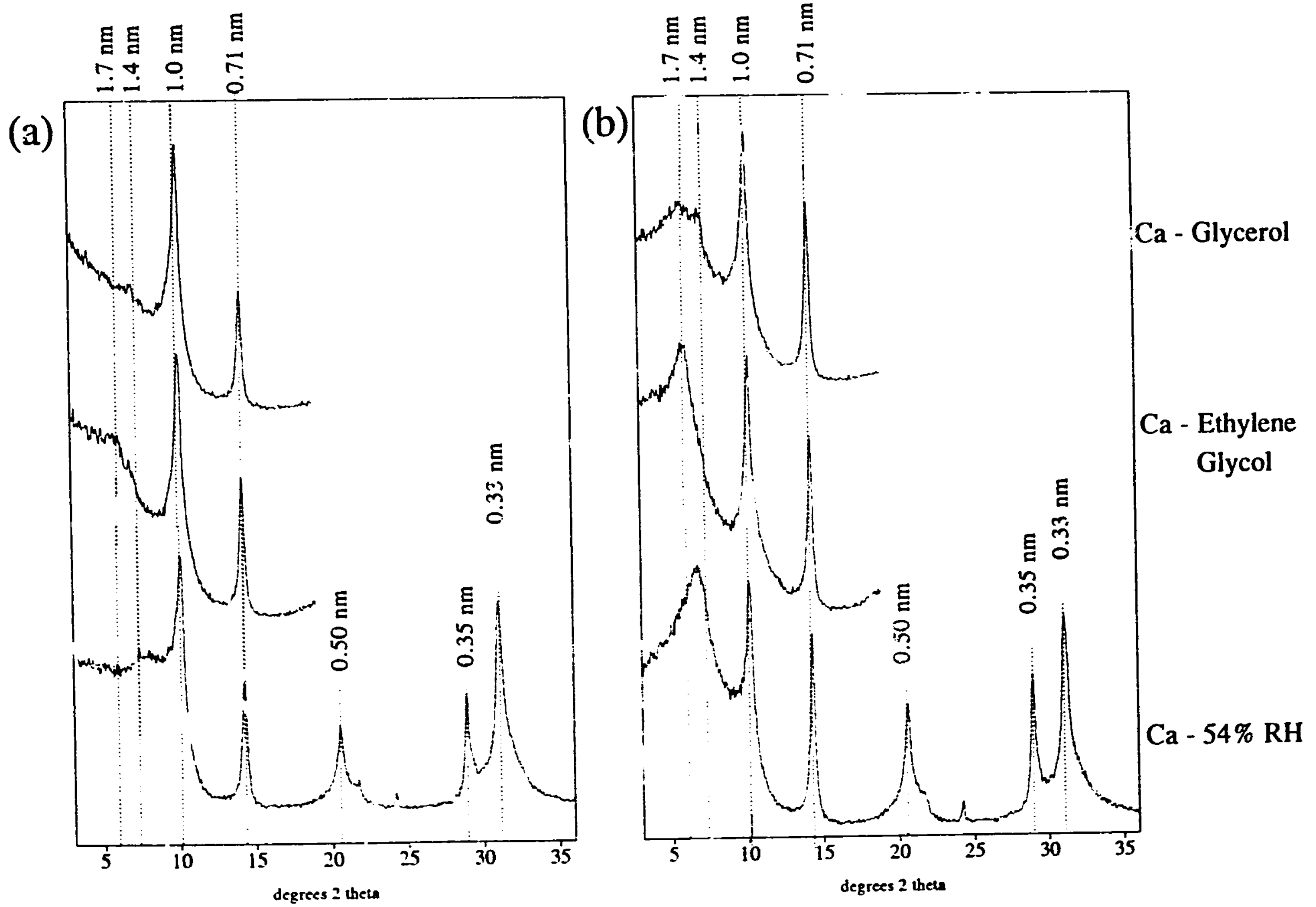

Fig. 4.2. X-ray diffractograms of the 2 to 0.2 μm fraction of the 0 to 20 cm layer at Nobleford: (a) before pretreatment, (b) after removal of organic matter.

surface layer. After removal of organic matter, fairly typical smectite peaks were observed on the Ca-saturated treatments (Fig. 4.2b). This would indicate that organic matter has a significant interaction with the smectite minerals, essentially resulting in the disappearance of the d(001) spacings. Some organic compounds may have penetrated between the layers without regular expansion of the lattice or were anchored at frayed edges, reducing the intensity and sharpness of the basal reflections (Lagaly, 1981). The exact mechanism causing this phenomenon and why it only occurs in some salt-affected soils is unclear. The addition of alkylammonium cations to the samples for determination of layer charge produced extremely broad smectite peaks similar to those described above before removal of organic matter ((Chapter 6), suggesting that this phenomenon is related to alterations in the smectite structure rather than to the type and amount of organic matter present.

Unusual diffraction characteristics were also noted for several other samples in the survey. For example, examination of x-ray diffractograms from the Wainwright site after K-saturation but before carbonate removal shows the presence of an intergrade-type mineral which displays peaks at 1.0 nm, 1.4 nm and intermediate between the two end members (Fig. 4.3a). This was noted at all depths in the profile for the coarse clay fractions only and was most pronounced in the surface layers. This behavior disappeared after heating to 300° C or treatment with 10% HCl (Fig. 4.3b), indicating that the interlayer material is unstable in the presence of heat and acid. We speculate that it may be composed of hydroxy-Mg material, since alkaline conditions are reported to favor the formation of such interlayers in phyllosilicates (Carstea *et al.*, 1970).

The remaining clay fractions showed no noticeable differences in phyllosilicate diffraction characteristics before and after pretreatments to remove OM and carbonates, suggesting that the differences in XRD patterns discussed above were not the result of the chemical treatment. Comparison of clay mineralogy from all four sites after pretreatments showed only slight variation in mineralogy between locations and with depth. Selected characteristics are presented in Table 4.3. The clay fractions generally contained a mixture of mica, kaolinite, smectite, vermiculite and chlorite, with smectite being the most abundant mineral in most samples. Quartz was ubiquitous in the coarse clay fraction. Diffraction peaks for coarse clay fractions were generally sharp and symmetrical for non-expanding

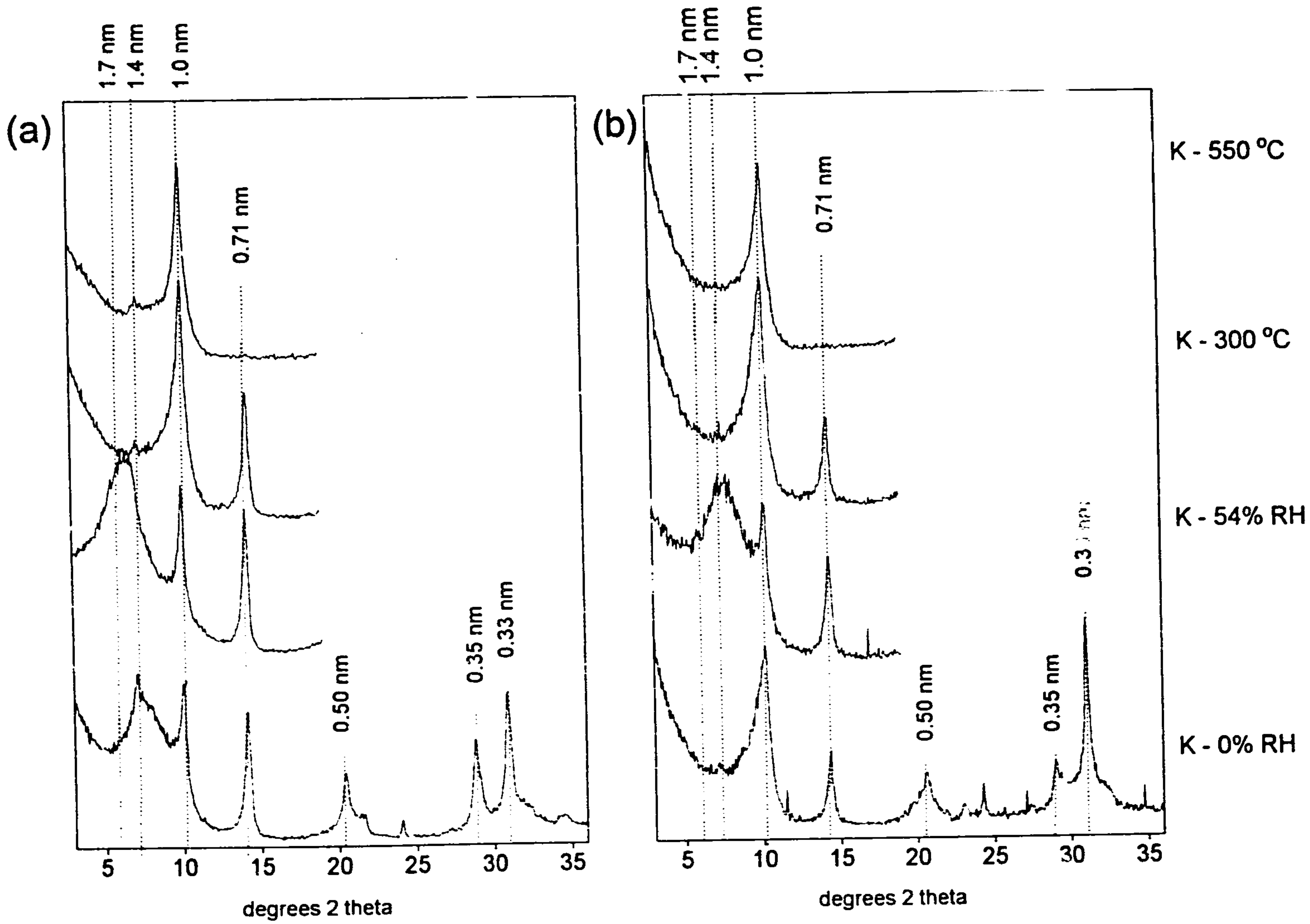

Fig. 4.3. X-ray diffraction patterns of the < 2μm fraction of the layer > 70 cm at Wainwright: (a) before pretreatment, (b) after removal of carbonates.

Table 4.3. Selected characteristics of clay fractions in the study.

| Depth (cm) | Size Fraction ($\mu$m) | CaEC | KEC | % vermiculite | % smectite | % mica$^z$ |
|---|---|---|---|---|---|---|
| | | (cmol$_c$ kg$^{-1}$) | | | | |
| | | | **Wainwright** | | | |
| 0 - 20 | 2 - 0.2 | 54 | 45 | 6 | 43 | 22 |
| | < 0.2 | 66 | 57 | 6 | 54 | 15 |
| 20 - 28 | 2 - 0.2 | 50 | 40 | 6 | 38 | 20 |
| | < 0.2 | 70 | 55 | 10 | 52 | 15 |
| 28 - 42 | 2 - 0.2 | 65 | 42 | 15 | 40 | 20 |
| | < 0.2 | 60 | 60 | - | 57 | 12 |
| 42 - 70 | 2 - 0.2 | 71 | 28 | 30 | 27 | 16 |
| | < 0.2 | 64 | 57 | 5 | 54 | 16 |
| > 70 | < 2 | 63 | 44 | 12 | 42 | 18 |
| | | | **Hanna** | | | |
| 0 - 23 | 2 - 0.2 | 32 | 26 | 4 | 25 | 24 |
| | 0.2 - 0.08 | 52 | 47 | 3 | 45 | 25 |
| | < 0.08 | 70 | 61 | 6 | 58 | 18 |
| 23 - 50 | 2 - 0.2 | 53 | 36 | 11 | 34 | 23 |
| | < 0.2 | 73 | 68 | 3 | 65 | 18 |
| 50 - 80 | 2 - 0.2 | 17 | 17 | - | 16 | 25 |
| | 0.2 - 0.08 | 57 | 49 | 5 | 47 | 20 |
| | < 0.08 | 80 | 66 | [illegible] | 63 | 17 |
| > 80 | 2 - 0.2 | 23 | 18 | 3 | 17 | 23 |
| | 0.2 - 0.08 | 62 | 54 | 5 | 50 | 17 |
| | < 0.08 | 71 | 9 | 8 | 56 | 15 |
| | | | **Nobleford** | | | |
| 0 - 20 | 2 - 0.2 | 37 | 31 | 4 | 30 | 25 |
| | < 0.2 | 54 | 45 | 6 | 43 | 25 |
| 20 - 40 | 2 - 0.2 | 32 | 23 | 6 | 22 | 23 |
| | 0.2 - 0.08 | 59 | 46 | 8 | 44 | 23 |
| | < 0.08 | 74 | 51 | 15 | 49 | 19 |
| 40 - 60 | 2 - 0.2 | 32 | 22 | 6 | 21 | 22 |
| | <0.2 | 62 | 44 | 12 | 42 | 23 |
| > 60 | <2.0 | 47 | 35 | 8 | 33 | 18 |
| | | | **Provost** | | | |
| 0 - 15 | < 2 | 34 | 34 | - | 32 | 20 |
| 15 - 40 | < 2 | 34 | 28 | 4 | 27 | 25 |
| > 40 | < 2 | 32 | 30 | 1 | 29 | 22 |

$^z$ Remaining clay mineral components were not specifically quantified but consisted primarily of kaolinite and quartz as determined from XRD patterns.

phyllosilicates and markedly broader and more diffuse in the fine clay fractions. Peak broadening is primarily attributed to particle size effects, but crystal disorder and mixed layering may also play a role.

Incomplete collapse of expanding minerals after K-saturation and heating, as evidenced by broad asymmetrical peaks in the K 0% RH., K 300°C and K 550°C treatments, was noted for many samples, particularly for particles $< 0.2\ \mu m$. The lack of complete collapse upon heating is likely due to the presence of interlayer components which serve to prop open the silicate sheets (MacEwan and Wilson, 1984) and which may be composed of Mg, Al or Fe oxides (Rich, 1968). Although Al and Fe interlayer materials are normally associated with acid conditions, these elements display amphoteric characteristics and may also be important in alkaline soils, particularly those with $pH > 9$. Alternating redox conditions may play a role in the precipitation of Fe oxides in the interlayer. Low redox potentials would result in the formation of $Fe^{2+}$, which may enter the interlayer of expanding minerals and precipitate as oxidizing conditions return.

Slight differences were noted in the XRD characteristics of the expanding phyllosilicates between sites and as compared to those in previous studies of non-saline soils in Alberta. Hanna, the site with the highest pH, displayed smectite peaks most similar to those found in non-saline Alberta soils. Smectites in the Wainwright soil showed rehydration to 1.4 to 1.5 nm after K-saturation and equilibration at 54 % RH (Fig. 4.3b), indicating a very low charge species at this site. The broadness of smectite peaks was notable in the soils from Nobleford and Provost and may indicate minerals of lower crystallinity. Smectite diffraction maxima in the Provost site were the most unusual (Fig. 4.4). Although the smectite peaks sharpened somewhat after removal of organic matter and carbonates, they were still fairly broad and jagged, indicating possible deterioriation of the smectite structure. The intensities of the diffraction maxima were extremely low and often only 2 to 3 times higher than the background intensity. The high background of the diffractograms also indicates a considerable amount of poorly crystalline or amorphous material.

Beidellite is commonly reported for Canadian prairie soils (Dudas and Pawluk, 1982; Lim and Jackson, 1984; Spiers *et al.*, 1984; Warren and Dudas, 1992) but was not detected in this study. A 1.7 to 1.8 nm diffraction maximum after Ca-saturation and glycerol solvation indicates that the charge of the smectite

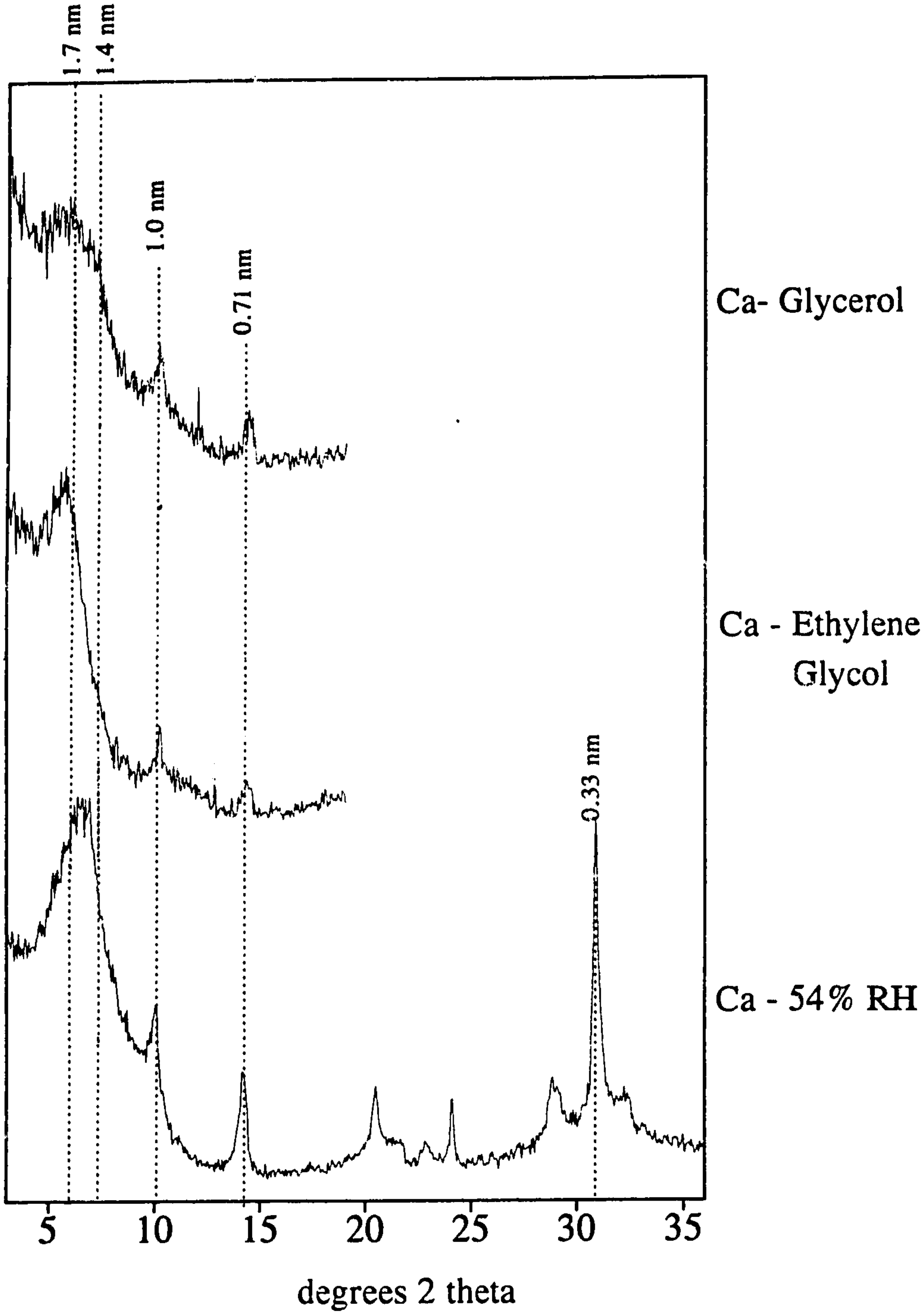

Fig. 4.4. X-ray diffraction patterns of the < 2 μm fraction of the surface layer at Provost.

components is predominantly in the octahedral sheet, characteristic of montmorillonite. This was confirmed by the lack of re-expansion of Li-saturated samples following heating and glycerol solvation (Jaynes and Bigham, 1987).

Vermiculite is not normally reported for prairie soils. In this study, because all expanding phyllosilicates gave a diffraction maximum at about 1.7 or 1.8 nm after Ca-saturation and glycerol solvation, their vermiculitic character was identified by analyzing the behavior of the expanding component after K-saturation and rehydration. The loss of the expandable nature of the mineral was determined by comparing the relative intensities of the 1.0 nm peak to the 0.72 nm kaolinite peak between the K 54% RH and Ca saturated treatments. A component showing this behavior was noted in many clay samples and was most noticeable in the fine clay fractions. Other workers have identified soil minerals that show characteristics of both vermiculite and smectite by expanding to 1.8 nm upon Ca-saturation and ethylene glycol and glycerol solvation, but then collapse to 1.0 nm after K-saturation (Egashira *et al.*, 1982; Senkayi *et al.*, 1983).

In some samples, no obvious rehydration or collapse of the K-saturated specimens was observed despite the fact that diffraction peaks in Ca-saturated treatments indicated the presence of considerable amounts of expandable phyllosilicates. Rehydration of the mineral was therefore extremely diffuse and marked only by a slight rise in the background of the diffractogram; this may indicate an extremely heterogeneous charge distribution.

K-fixation in the study soils may be attributed to fixation by both weathered micaceous material and high charge smectitic layers. Some mica may also be present as an interstratified phase in the expanding clays. Estimation of K fixation by X-ray diffraction analysis was generally higher than that measured by the determination of KEC. This would indicate that $NH4^+$ is effective at replacing some of the "fixed" K during measure of exchange capacity. This was previously reported to occur with $K^+$ fixed in edge-interlayer sites in illite and weathered mica (Sawhney, 1972). The heterogeneous distribution of charge in the smectite minerals may also play a role; although $K^+$ may not be fixed in the traditional sense, it is likely held tightly enough in some areas of the mineral structure to prevent significant rehydration from occurring.

Ammonium oxalate dissolution showed relatively low but variable amounts of amorphous Al, Si and Fe in each sample (Table 4.4), with no readily apparent

Table 4.4. Aluminum, silicon and iron extracted by acid ammonium oxalate and iron extracted by subsequent citrate-bicarbonate-dithionite treatment of the individual clay separates.

| Depth (cm)<br>d | Size Fraction ($\mu$m) | Oxalate Extraction |  |  |  | CBD Extraction |  |
|---|---|---|---|---|---|---|---|
|  |  | $Fe_o$ | Al | Si | Al/Si | $Fe_d$ | $Fe_o$/Fe |
|  |  |  | g $kg^{-1}$ |  |  | g $kg^{-1}$ |  |
|  |  |  | Wainwright |  |  |  |  |
| 0 - 20 | 2 - 0.2 | 9.1 | 1.1 | 0.63 | 1.7 | 7.3 | 1.2 |
|  | < 0.2 | 9.3 | 1.0 | 0.82 | 1.2 | 15 | 0.62 |
| 20 - 28 | 2 - 0.2 | 10 | 0.95 | 0.59 | 1.6 | 8.9 | 1.1 |
|  | < 0.2 | 12 | 1.3 | 0.68 | 1.9 | 13 | 0.98 |
| 28 - 42 | 2 - 0.2 | 18 | 1.4 | 1.2 | 1.2 | 8.8 | 2.0 |
|  | < 0.2 | 9.3 | 0.96 | 0.74 | 1.3 | 11 | 0.85 |
| 42 - 70 | 2 - 0.2 | 13 | 1.1 | 1.3 | 0.84 | 7.0 | 1.9 |
|  | < 0.2 | 7.3 | 1.1 | 0.93 | 1.2 | 9.5 | 0.77 |
| > 70 | < 2 | 10 | 1.3 | 1.1 | 1.2 | 6.3 | 1.6 |
|  |  |  | Hanna |  |  |  |  |
| 0 - 23 | 2 - 0.2 | 5.4 | 2.1 | 0.50 | 4.2 | 8.6 | 0.63 |
|  | 0.2 - 0.08 | 4.3 | 1.1 | 0.63 | 1.7 | 11 | 0.41 |
|  | <0.08 | 6.6 | 1.3 | 0.71 | 1.9 | 11 | 0.62 |
| 23 - 50 | 2 - 0.2 | 6.2 | 1.7 | 0.68 | 2.5 | 12 | 0.53 |
|  | < 0.2 | 7.6 | 1.7 | 0.76 | 2.2 | 14 | 0.54 |
| 50 - 80 | 2 - 0.2 | 2.7 | 0.56 | 0.26 | 2.2 | 8.8 | 0.31 |
|  | 0.2 - 0.08 | 5.2 | 1.4 | 0.59 | 2.4 | 15 | 0.35 |
|  | < 0.08 | 5.7 | 1.9 | 0.75 | 2.5 | 15 | 0.39 |
| > 80 | 2 - 0.2 | 3.7 | 0.71 | 0.33 | 2.2 | 13 | 0.29 |
|  | 0.2 - 0.08 | 4.7 | 1.4 | 0.51 | 2.7 | 15 | 0.32 |
|  | < 0.08 | 4.6 | 1.4 | 0.67 | 2.1 | 14 | 0.33 |
|  |  |  | Nobleford |  |  |  |  |
| 0 - 20 | 2 - 0.2 | 7.6 | 1.5 | 0.28 | 5.4 | 10 | 0.73 |
|  | < 0.2 | 5.2 | 2.0 | 0.68 | 2.9 | 9.4 | 0.55 |
| 20 - 40 | 2 - 0.2 | 2.4 | 2.1 | 0.30 | 7.0 | 6.9 | 0.35 |
|  | 0.2 - 0.08 | 3.7 | 1.5 | 0.58 | 2.6 | 11 | 0.33 |
|  | < 0.08 | 4.2 | 1.4 | 0.65 | 2.1 | 14 | 0.33 |
| 40 - 60 | 2 - 0.2 | 3.7 | 2.1 | 0.34 | 6.3 | 7.4 | 0.50 |
|  | < 0.2 | 4.6 | 1.5 | 0.69 | 2.2 | 11 | 0.41 |
| > 60 | < 2 | 2.9 | 1.6 | 0.29 | 5.5 | 7.9 | 0.37 |
|  |  |  | Provost |  |  |  |  |
| 0 - 15 | < 2 | 8.5 | 1.5 | 1.3 | 1.1 | 6.8 | 1.3 |
| 15 - 40 | < 2 | 9.0 | 1.4 | 0.48 | 3.0 | 11.5 | 0.78 |
| > 40 | < 2 | 3.5 | 0.76 | 0.22 | 3.4 | 7.9 | 0.44 |

trends between depths or size fractions. The calculation of Al/Si ratios has been commonly used to infer the presence of allophane and imogolite, with ratios of 1.6 to 3.2 reported for allophane from various soils (Parfitt and Childs, 1988). Neither allophane nor imogolite is reported to form under alkaline conditions (Wada, 1989), but there are components in these soils, particularly at the Hanna and Wainwright sites which may have similar compositions based on the AOX-extractable Al/Si ratio.

The amorphous fraction of the Nobleford soil is relatively Al-rich as indicated by high Al/Si ratios, particularly in the 2 - 0.2 μm size fraction. The proportion of amorphous Si increases with decreasing particle size. The Provost soil indicates a relative increase in the proportion of Al with increasing depth, although the absolute amounts of both elements decrease with depth.

Extraction of iron with citrate-bicarbonate-dithionite ($Fe_d$) after AOX extraction showed that crystalline Fe oxides such as goethite and hematite were present in variable amounts between the samples. No apparent accumulation trends at various depths or particle size fractions were evident at the Nobleford and Provost locations. The soils at Wainwright and Hanna showed higher amounts of $Fe_d$ in the finer clay fractions at each depth. The ratio of $Fe_o$ to $Fe_d$ indicates that 3 of the 4 sites have lower ratios with increasing sample depth. This may indicate alternating oxidation and reduction of iron close to the soil surface, resulting in the build-up of fine grained poorly crystalline or amorphous Fe oxides. This trend is particularly noticeable in the Provost site which has a water table within 40 cm of the surface. Alternating redox conditions would be expected to occur at or near the soil surface as the water table fluctuates seasonally.

## 4.4 CONCLUSIONS

Despite high ionic strength and alkalinity, X-ray diffraction and selected chemical analysis indicate that clay minerals in salt-affected soils in Alberta are generally similar to those in non-saline soils. Slight alteration of the expanding phyllosilicates may be occurring; tetrahedrally substituted smectites such as beidellite were not detected in saline soils, while a high charge smectite or vermiculite capable of K fixation was evident in many clay fractions. Some interlayering may also be occurring in these minerals. The weathering environment in which these clays are found may result in structural changes and/or alteration of the layer charge of the expanding minerals. Future research will investigate the charge characteristics of these minerals.

The XRD characteristics of clays in saline soils may be significantly affected by traditional pretreatments for removal of non-clay material prior to particle size separation. Removal of carbonates using HCl appears to alter the diffraction characteristics of some K-saturated clays, while the lack of organic matter removal may affect the diffraction characteristics of smectite minerals to such an extent that their occurrence would not be noted. This may account for some of the previous reports of highly interstratified smectites in surface layers of salt-affected soils.

The soil solution chemistry of the four sites studied in detail shows moderate to low levels of Al and Si despite alkaline pH's and poor drainage. Comparison of the solution chemistry to stability regions calculated for clay minerals shows that solutions are supersaturated with respect to common phyllosilicates, indicating that they are stable and should be precipitating. Despite the favorable conditions for clay formation, the low proportion of fine clay in the samples suggests that neoformation of phyllosilicates is not occurring, probably as the result of factors such as unfavorable kinetics. The lack of fine clay may also be a function of physical processes and therefore not related to pedogenesis. If the system can be assumed to be at or near to equilibrium because of the long residence time of the soil solution, the levels of Si and Al may be controlled by quartz and amorphous $Al(OH)_3$ or gibbsite respectively.

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# 5. AUTHIGENIC DOLOMITE IN A SALINE SOIL IN ALBERTA [1]

## 5.1 INTRODUCTION

The origin of dolomite is of intense interest to many earth scientists and is commonly referred to as the "dolomite problem". Despite being common in ancient sediments and thermodynamically favored to precipitate from seawater and many saline soil solutions, modern dolomite is rare. Well-ordered dolomite has never been synthesized under earth surface conditions. Extensive research has been conducted on the conditions necessary for dolomite formation; it is generally accepted that dolomite formation should be favored in solutions with elevated Mg/Ca ratios, high carbonate ion concentrations, low ionic strength relative ' seawater and low or absent sulfate concentrations (Burton *et al.*, 1992). Modern dolomite deposition has only been reported from several restricted sedimentary environments (*eg*. Persian Gulf sabkhas (Wells, 1962), Coorong region lakes in South Australia (Alderman and Skinner, 1957), supratidal sediments in the Bahamas (Shinn *et al.*, 1965), Deep Springs Lake in California (Peterson *et al.*, 1963)). Although a possible secondary origin for dolomite has been suggested in soils (Sherman *et al.*, 1962; St. Arnaud and Herbillon, 1973), pedogenic formation has never been proven to occur.

Although dolomite and calcite are common constituents of most soil parent materials in Alberta, pedogenic processes normally result in the movement and/or removal of carbonates from the solum. Inherited carbonate minerals persist in the larger size sand and silt fractions, whereas the more reactive clay sized material ($<$ 2 $\mu$m) weathers more quickly. Secondary carbonate accumulations are possible under appropriate conditions, but it is generally accepted that only calcite will precipitate in soil (Doner and Lynn, 1989). The possibility of pedogenic dolomite formation has important implications in soil genesis and in determining the physical and chemical properties of a soil, as well as contributing information to help solve the "dolomite problem". During the course of an investigation of the clay mineral characteristics of saline soils in Alberta (Chapter 4), more than half of the $< 2$ $\mu$m fraction of one site was found to be composed of dolomite. Accumulation of

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[1] A version of this chapter has been submitted for publication to the Soil Science Society of America Journal.

carbonates in the finest size fraction has been used previously to indicate a secondary or authigenic origin (Rostad and St. Arnaud, 1970). The objectives of this study were therefore to determine the origin and characteristics of the soil dolomite accumulations.

## 5.2 MATERIALS AND METHODS

The soil sampled was located in a shallow saline depression (approximately 100 $m^2$) near the town of Provost in east-central Alberta, Canada and was classified as a Typic Cryaquent (Rego Gleysol) because of little or no soil development and saturation during at least parts of the year. Salt efflorescences, consisting primarily of thenardite ($Na_2SO_4$), were present on the soil surface as a result of upward capillary movement of groundwater and its subsequent evaporation. No vegetation was present on the sampling site because of the extremely high salinity and poor drainage, but was established nearby on the margins of the depression. The soils in this area were developed from surficial deposits of glacial origin and largely reflect the composition of underlying or nearby Cretaceous bedrock (Pawluk and Bayrock, 1969); the area was glaciated approximately 10,500 years ago (Pettapiece, 1969). Any detrital soil dolomite will be inherited from marine bedrock of Devonian age. The sample site had a small amount of standing water at the time of sampling but does dry out completely during periods of the year.

Soil samples were collected at 3 depths, with the water table reached at 40 cm. Porewater was extracted from each field-moist sample using immiscible displacement (Elkahatib *et al.*, 1986) with tetrachloroethylene as the displacing fluid. Solutions were filtered immediately after extraction through a 0.22 $\mu$m filter and pH and electrical conductivity measurements taken; samples were then refrigerated prior to further analysis. Major cations were determined using inductively coupled plasma atomic emission spectrophotometry, while Cl and $SO_4$ were measured using ion chromatography. Total inorganic carbon was determined using a Technicon autoanalyzer. The chemical composition of the soil porewater (Table 5.2) was used as input for the geochemical model SOLMINEQ (Kharaka *et al.*, 1988) to determine dolomite stability. The saturation index for well-ordered dolomite ($K_{sp} = 10^{-18.060}$) was positive at all depths, indicating precipitation is thermodynamically favored.

Sand (2 - 0.5 mm), silt (50 - 2 $\mu$m) and clay ($< 2$ $\mu$m) fractions of the soil were separated using a combination of wet sieving and sedimentation techniques, after removal of soluble salts by repeated washing with deionized water until a stable dispersed suspension was achieved (Jackson, 1979). Total carbonate analysis was conducted on each size fraction using a titrimetric procedure (Bundy and Bremner, 1972) and the amount of dolomite determined using a selective dissolution technique (Petersen *et al.*, 1966). Diffractograms of the $< 2$ $\mu$m fraction were obtained with a Philips diffractometer (Model 1710, Philips Electronics Ltd., Scarborough, Ontario, Canada) equipped with a LiF curved crystal monochromator using CoK$\alpha$ radiation generated at 50 kV and 25 mA, a step size of 0.05° 2$\Theta$ and an accumulation time of 2 seconds step$^{-1}$. Quartz was used as an internal standard. Average dolomite unit cell parameters were calculated from X-ray diffraction (XRD) patterns using an indexing and least squares powder diffraction program, written by D.E. Appleman and H.T. Evans (1973), and revised for microcomputer use by P.H. Benoit (1986). Calculated dolomite cell parameters were compared to values published for standard dolomite by the Joint Committee on Powder Diffraction Standards, powder diffraction file #36-426. Dolomite stoichiometry was calculated using the equation $N_{CaCO3} = M\,d + B$, where $N_{CaCO3}$ is the mole percent $CaCO_3$ in the lattice, $d$ is the observed $d_{(104)}$ spacing in Angstroms, M is 333.33 and B is -911.99 (Lumsden and Chimahusky, 1980).

Stable isotope analysis of soil carbonates was conducted by reacting size-fractionated samples from which soluble salts had been removed with 100% phosphoric acid at 25° C using the technique of Epstein *et al.* (1964). The O isotopic composition of water was determined by the method of $CO_2$-$H_2O$ equilibration at 25 °C (Epstein and Mayeda, 1953). The duration of the equilibration was extended to one week because of the high salinity of the solutions. Oxygen isotope fractionation factors between dolomite and the soil solution were calculated using the relationship $\alpha = 1000 + \delta^{18}O_{\text{dolomite(SMOW)}} / 1000 + \delta^{18}O_{\text{H2O(SMOW)}}$ (Faure, 1991). Dolomite formation temperatures were calculated using the equation $1000 \ln \alpha_{\text{dol-H2O}} = 3.20\,(10^6 T^{-2}) - 1.50$ (Northrop and Clayton, 1966). Radiocarbon dating of the inorganic carbon was conducted by the Environmental Isotopes Laboratory, Alberta Environmental Centre, Vegreville, Alberta.

## 5.3 RESULTS AND DISCUSSION

Dolomite is concentrated in the $< 2\ \mu m$ fraction of the soil, with progressively smaller amounts with increasing particle size (Table 5.1). Scanning electron microscopy (Plate 5.1) shows that this dolomite is extremely fine grained and may partially exist as a coating on the non-carbonate minerals present in this fraction, primarily quartz, kaolinite and illite. Some rhombohedral crystals are evident, but most of the dolomite does not have this characteristic form. Many of the crystals also appear to be conglomerates of smaller crystals. Small amounts of calcite are also present in most sub-samples, despite the lack of detection of this mineral during chemical analysis. This anomaly is likely due to the assumption in the chemical dissolution technique that all Mg is from dolomite. The presence of small amounts of XRD undetectable Mg carbonates or Mg enriched dolomite would therefore result in underestimation of calcite quantities.

The radiocarbon age of the clay-sized carbonates ranges from 1270 to 5270 years B.P., proving that the dolomite is of recent origin, since relict dolomite in the soil contains no $^{14}C$. Small amounts of pedogenic calcite may influence the age only slightly. The radiometric age need not reflect the age of dolomite formation, but may be a mixing age between dolomite formed at different times or may reflect mixing of 'new' and 'old' carbon, respectively derived from atmospheric $CO_2$ and groundwater.

The clay-sized dolomite is well ordered based on the presence of ordering reflections of the proper relative intensity (Goldsmith and Graf, 1959) (Fig. 5.1), and stoichiometric, with Ca-content ranging from 0.50 to 0.53. Slight broadening of diffraction maxima is attributed to small particle size. Average unit cell parameters calculated from XRD patterns indicate that the dolomite has crystal lattices slightly expanded in the z direction ($c=1.603$ nm) relative to standard dolomite ($c=1.602$ nm). Dolomite from the lowest depth has lattices that are slightly expanded in the x direction ($a=0.4811$ nm) relative to standard dolomite ($a=0.4809$ nm), whereas dolomite in the top 2 samples show a slight contraction in the x direction ($a=0.4806$ nm). The differences in the unit cell parameters of the soil dolomite are minimal, particularly when the effects of errors associated with X-ray diffraction such as preferred orientation are taken into account. The crystal properties of the dolomite suggest that precipitation occurred at a very slow rate. The formation of well-ordered dolomite is not favored by highly saline

Table 5.1. Isotopic composition and concentration of carbonate minerals in different soil size fractions

| Sample | size distribution(%)[z] | dolomite[y] (%) | calcite (%) | $C_{14}$ age[x] | dolomite $\delta^{18}O$ | dolomite $\delta^{13}C$ | calcite $\delta^{18}O$ | calcite $\delta^{13}C$ |
|---|---|---|---|---|---|---|---|---|
| | | | | | (PDB)[w] | | (PDB) | |
| 0 - 15 cm | | | | | | | | |
| sand | 54 | 3.9 | n.d.[v] | - | -7.1 | -1.1 | - | - |
| silt | 16 | 6.0 | n.d. | - | -8.9 | -0.13 | -6.0 | -1.9 |
| clay | 30 | 54 | 5.6 | 1270±60 | -1.6 | -2.0 | -6.4 | -3.5 |
| 15 - 40 cm | | | | | | | | |
| sand | 71 | 1.3 | n.d. | - | -8.4 | -0.06 | -4.2 | -2.4 |
| silt | 8 | 3.8 | n.d. | - | -8.4 | -0.13 | -0.30 | -1.0 |
| clay | 21 | 52 | 0.97 | 5270±70 | -4.2 | -3.8 | -3.6 | -3.7 |
| > 40 cm | | | | | | | | |
| sand | 64 | 1.4 | n.d. | - | -7.7 | -0.11 | - | - |
| silt | 10 | 26 | n.d. | - | -5.4 | -2.0 | -2.1 | -1.4 |
| clay | 26 | 55 | 4.1 | 3160±80 | -4.0 | -3.4 | -6.1 | -4.3 |

[z] Sand (2.0 to 0.5 mm), silt (50 to 2 μm), clay (< 2 μm)

[y] Percentage of carbonate minerals expressed as g dolomite or calcite per 100 g of soil.

[x] Radiocarbon age of the inorganic carbon expressed as years before present

[w] isotopic values reported in the standard delta (δ) notation as per mil deviation from PDB

[v] not detectable using x-ray diffraction or selective dissolution techniques

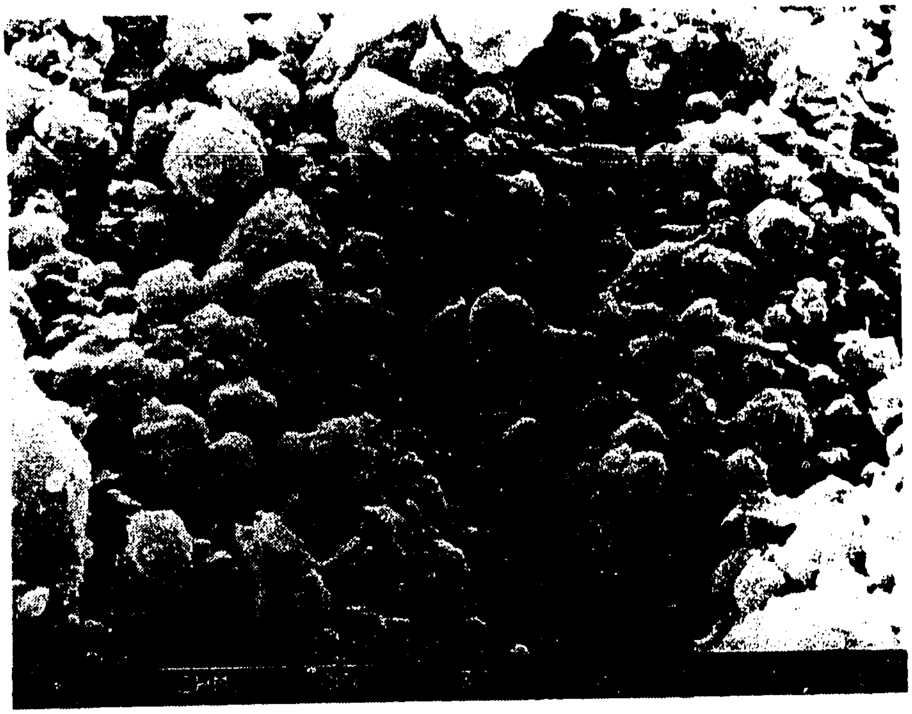

Plate 5.1 Scanning electron micrograph of clay-sized dolomite.

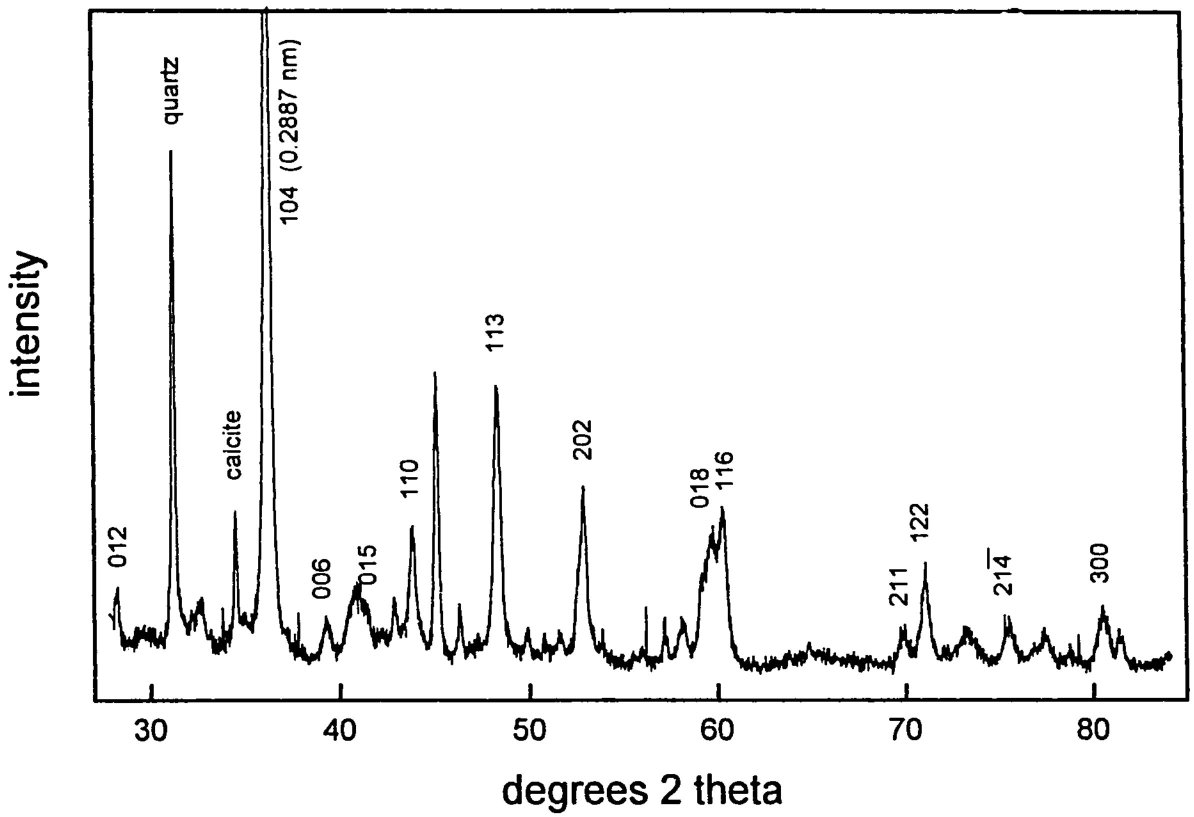

Fig. 5.1. X-ray diffraction pattern of the clay fraction from the 15 - 40 cm depth of the soil. Values above diffraction peaks are selected hkl indices for dolomite, showing that the mineral is well-ordered and stoichiometric.

environments because precipitation is commonly rapid and the concentration of foreign ions is high (Folk and Land, 1975). Most previously reported modern dolomites are Ca-rich and poorly ordered (Last, 1990).

Stable isotope ratios have been used previously to distinguish between new and inherited carbonate in soils (Rabenhorst *et al.*, 1984; Margaritz and Amiel, 1980). Pedogenic carbonates form under different conditions than detrital material and consequently should have a different isotopic composition. Isotopic analysis of the carbonates in this study shows that the dolomite in the clay-sized fraction is enriched in $^{18}O$ and depleted in $^{13}C$ relative to dolomite present as larger particles (Table 5.1), indicating different origins. The $\delta^{13}C$ values for dolomite in the sand and silt samples in the study soil are similar to values previously reported for detrital dolomite in Alberta soils (Miller *et al.*, 1987), suggesting that the mineral in these size fractions is detrital in nature. The more negative $\delta^{13}C$ values in fine-grained samples with higher dolomite content indicate authigenesis and reflect a significant contribution from soil $CO_2$. The proportion of dolomite in each sample is highly correlated with decreasing $\delta^{13}C$ values ($r = -0.91$) and increasing $\delta^{18}0$ values ($r = 0.93$) (Fig. 5.2). Extrapolation to 100% dolomite gives a $\delta^{13}C$ value of -5.7 and a $\delta^{18}O$ value of -1.3, suggesting that these values characterize completely authigenic soil dolomite.

In soil, the $\delta^{13}C$ compositions of pedogenic carbonate depends on the isotopic composition of the soil $CO_2$, which is related to the type of biomass and rate of respiration; the $\delta^{13}C$ of authigenic calcite is generally accepted as enriched by +10.2 per mil relative to soil $CO_2$ (Margaritz and Amiel, 1980). Although the $\delta^{13}C$ values for atmospheric $CO_2$ usually average around -7 per mil (Keeling, 1958), values for soil $CO_2$ are normally much lower and range from -24 to -16 per mil depending on the type of vegetation which dominates in the region (Margaritz and Amiel, 1980). At high rates of respiration, the $\delta^{13}C$ value of $CO_2$ gas in soil normally reflects the $\delta^{13}C$ composition of the organic matter (Cerling, 1984). At low respiration rates, such as those assumed for the study soil because of the lack of vegetation and extreme salinity, diffusion from the atmosphere can be largely expected to control the isotopic composition of the soil $CO_2$. The $\delta^{13}C$ of the soil $CO_2$ in this case will therefore likely reflect the average $\delta^{13}C$ of the atmosphere, particularly at the soil surface. The $\delta^{13}C$ of the $< 2\ \mu m$ dolomite at depths below 15 cm is lower than that in the surface sample. Carbon isotope values might be

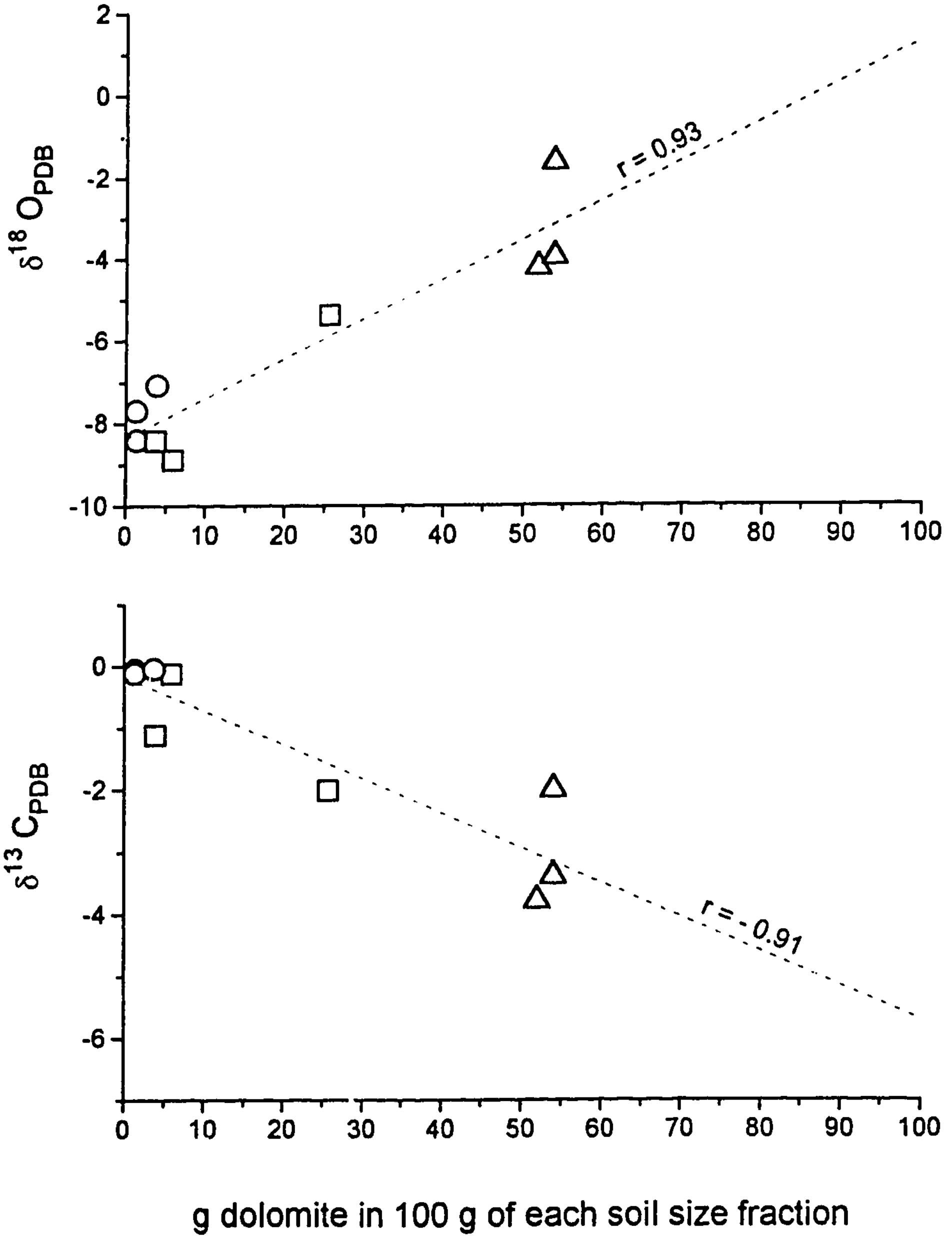

Fig. 5.2. Isotopic composition versus the dolomite content in a given size fraction. Triangles represent clay (< 2 μm), squares represent silt (50 to 2 μm) and circles represent sand (2 to 0.5 mm) size fractions.

expected to decrease with depth because of an increasing respiration component relative to the diffusive flux.

The $\delta^{18}O$ of soil carbonate should be related to the oxygen isotopic composition of local meteoric water (Cerling, 1984). In the highly evaporitic environment of the study soil however, the $\delta^{18}O$ of the soil water has been greatly enriched, with greater evaporative enrichment of near surface soil solution (Table 5.2). The enrichment of $\delta^{18}O$ in the porewater at the soil surface is reflected in the more positive $\delta^{18}O$ value of the associated clay-sized dolomite.

The relationship between $\delta^{18}O$ dolomite , $\delta^{18}O$ water and temperature is not well understood under earth surface conditions because of the absence of low temperature experimental results and doubtful extrapolation from high temperature environments (Land, 1980). Oxygen isotope fractionation factors $\alpha^{18}O$ observed between dolomite and water in the clay size fraction range between 1.038 to 1.041. This results in the calculation of dolomite formation temperatures ranging from 4 to 14 °C, which are not unreasonable given that the mean annual temperature in the area is approximately 4 °C (Naeth *et al.*, 1993). This would suggest that dolomite precipitates directly from soil porewater.

The most commonly accepted dolomitization model is the replacement of a precursor carbonate (Last, 1990). This is clearly not happening in this instance because of the lack of isotopic equilibrium between calcite and dolomite; the different C-isotopic compositions of the carbonate phases suggest that they were formed at different times. It is therefore unlikely that dolomite formed simply by the solid state diffusion of Mg into calcite. It has been suggested that at 25 °C, dolomite should be enriched in $^{18}O$ by 4 to 7 per mil relative to calcite coexisting at equilibrium (Northrop and Clayton, 1966; Sheppard and Schwarcz, 1970). Using this approach, only the carbonate minerals in the surface sample could by considered to be at equilibrium, with a difference in $\delta^{18}O$ values of 5.6 per mil. At lower depths, dolomite is more enriched in $\delta^{18}O$ than the coexisting calcite. I feel that the dolomite formed as a direct precipitate, with the $\delta^{13}C$ content of the dolomite largely reflecting that of atmospheric and/or groundwater C and the $\delta^{18}O$ content dependent upon the isotopic characteristics of both meteoric water and groundwater and extensively modified by evaporation. Precipitation would be largely induced by evaporation processes, with freezing of soil solutions perhaps an additional formation mechanism.

Table 5.2. Selected characteristics of soil porewater and associated groundwater.

| Sample | pH | $I^z$ | Mg | Ca | K | Na | $SO_4$ | Cl | $HCO_3$ | Mg/Ca | $\delta^{18}O^y$ (SMOW) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | mol kg $^{-1}$ | | | | | | | | |
| 0 - 15 cm | 8.1 | 1.4 | 0.14 | 0.0038 | 0.065 | 1.8 | 1.1 | 0.019 | 0.0046 | 37 | -10.9 |
| 15 - 40 cm | 8.0 | 1.7 | 0.21 | 0.0029 | 0.032 | 2.6 | 1.4 | 0.038 | 0.0068 | 72 | -11.5 |
| > 40 cm | 8.1 | 1.6 | 0.19 | 0.0029 | 0.045 | 2.1 | 1.2 | 0.038 | 0.001 | 66 | -12.5 |
| ground-water | 7.5 | 1.1 | 0.23 | 0.0056 | 0.049 | 0.7 | 0.67 | 0.085 | 0.014 | 41 | -12.9 |

[z] Ionic strength

[y] Isotopic values reported in the standard delta (δ) notation as per mil deviation from SMOW.

Although the mechanism is unknown, sulfate concentrations > 0.021 M are reported to severely inhibit dolomite formation (Gunatilaka, 1986). The soil porewaters in this study are extremely saline and have sulfate concentrations greater than 1 molal (Table 5.2). The molal ratios of Mg to Ca range from 37 to 72 and favor dolomite formation (Folk and Land, 1975). It has been suggested that extremely elevated Mg/Ca ratios and disruption of hydration spheres around Mg as a result of high salinity may more than compensate for the possible inhibitory effects of sulfate (Burton *et al.*, 1992). Dolomite formed by direct crystallization may also not be subject to the same kinetic inhibitory effects of $SO_4$ reported for the dolomitization of $CaCO_3$.

## 5.4 CONCLUSIONS

Dolomite accumulations in the clay-sized fraction of a saline soil in Alberta were proved to be of recent origin using radiocarbon analysis. The dolomite is well-ordered and stoichiometric, indicating that crystallization occurred at a slow rate. The stable isotopic composition of the clay-sized dolomite is substantially different from the detrital dolomite in the sand and silt fractions, confirming a pedogenic origin. The evidence also suggests that the dolomite formed by direct precipitation from the soil solution rather than from the dolomitization of a precursor carbonate.

It should be noted that this study was a part of a large survey of salt-affected soils in Alberta (Chapter 4) but the site described in this paper is the only one where large amounts of dolomite were detected in the surface clay fraction. This would imply that very specific chemical and physical conditions are required for dolomite precipitation.

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# 6. LAYER CHARGE CHARACTERISTICS OF SMECTITES IN SALT-AFFECTED SOILS IN ALBERTA [1]

## 6.1 INTRODUCTION

The layer charge characteristics of expanding phyllosilicates are likely the most important property determining the physical and chemical characteristics of soil. Both the mean layer charge density and distribution of charge are fundamental in controlling processes such as cation exchange and fixation and adsorption of water and other molecules. X-ray diffraction characteristics after various pretreatments have been used to provide general information about the nature of the layer charge. For example, lack of rehydration of an expanding phyllosilicate after K-saturation has been used to identify high charge minerals, while rehydration has been indicative of lower charged smectites (Harward *et al.*, 1969). Chemical composition and exchange capacity measurements have also been used to estimate charge density, but provide only a mean value and do not address the heterogeneity that is thought to be characteristic of 2:1 minerals. The multi-mineralic nature of soils also introduces considerable error into this technique. The alkylammonium method, in which the basal spacings of expanding clay minerals are measured after intercalation with a series of different chain length alkylammonium cations, is being increasingly used for determining the layer charge characteristics of soil clays (*eg.* Ross and Kodama, 1986; Senkayi *et al.*, 1985; Laird *et al.*, 1988). This method depends only on the interlayer charge density of the mineral and the length of the alkyl chain (Lagaly and Weiss, 1969) and has the distinct advantage of portraying the charge distribution in addition to determining the mean layer charge (Stul and Mortier, 1974; Lagaly and Weiss, 1976).

Clay minerals in western Canada are generally inherited from parent material of glacial origin, which is largely derived from underlying Cretaceous sedimentary bedrock. Previous studies have shown that the clay mineralogy of soils throughout Alberta is remarkably similar, showing no or little evidence of alteration, and is dominated by smectites, with smaller amounts of mica, kaolinite and occasionally chlorite (Abder-Ruhman, 1980; Kodama, 1979; Dudas and Pawluk, 1982; Warren *et al.*, 1992). Montmorillonite is the common smectite in prairie soils, with beidellite also frequently identified. Detailed information on the

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[1] A version of this chapter has been submitted for publication to Clays and Clay Minerals.

layer charge of smectites in the province is lacking except for work done by Warren *et al.* (1992) which reported the mean layer charge of Alberta smectites to be 0.399 mol (-)/$O_{10}(OH)_2$ in calcareous till and 0.372 mol (-)/$O_{10}(OH)_2$ in anthropogenically acidified soil.

It is unclear whether expanding phyllosilicates that occur in very saline, alkaline environments have similar characteristics to those that occur in non-saline soils. While marked degradation of smectites has been reported in some salt-affected soils (Whittig, 1959; Klages and Southard, 1968; Lewis and Drew, 1973), detailed analysis of clay mineralogy in Alberta saline soils showed only slight alterations (Chapter 4). Differences were noted primarily for smectite layer charge characteristics as deduced from X-ray diffraction analysis, which showed expansion behavior characteristic of both high-charge and low-charge smectites, with variations between sites and size fractions. It has been suggested by Reid (1992) that increasing salinity results in decreasing smectite layer charge in saline soils in California. Previous investigations of the porewater chemistry in Alberta saline soils (Chapter 3) indicates that conditions conducive to smectite neoformation may exist in the poorly drained, high ionic strength environment of the study sites. If smectites are forming in these environments, or alternatively if intense weathering is occurring, changes would be expected to be seen in the finest size fractions. The variability in weathering environments between different saline soils and within a given soil profile may also manifest itself as different layer charge characteristics between samples. The objectives of the study, therefore, were to determine the layer charge characteristics of smectites found in salt-affected soils in Alberta and investigate the variation in layer charge between locations and size fractions.

## 6.2 MATERIALS AND METHODS

Four salt-affected soils, detailed characteristics of which have been reported earlier in the thesis, were used for this study. The soils were located near Hanna, Nobleford, Wainwright and Provost, Alberta and included a playa, a saline seep in cultivated land and evaporitic rings around a pothole slough and a larger saline lake, respectively. The soils were classified as Typic Cryaquents (Rego Gleysols) because of little or no soil development and saturation during at least parts of the year. Since pedogenesis was very weak or non-existent, samples were taken approximately every 20 cm unless obvious differences in texture or color were noted.

Samples were treated with sodium hypochlorite to remove organic matter (OM) (Anderson, 1963) and carbonates were removed using 10% HCl dropwise for a few minutes until effervescence had stopped. This technique was used rather than buffered sodium acetate because of large quantities of dolomite in some samples. The soils were ultrasonified for 3 minutes at 400 W, and the clay fraction (< 2.0 μm) of the soils was separated using sedimentation techniques after soluble salts had been removed by repeated deionized water washings and decantations. The < 2.0 μm fraction was then further subdivided by centrifugation into coarse (2 - 0.2 μm), fine (0.2 - 0.08 μm) and very fine (< 0.08 μm) size fractions (Jackson, 1979). The amount of fine or very fine clay was low in many samples (Chapter 3) and therefore layer charge analysis was only conducted for samples where adequate quantities of the solids could be separated.

Sub-samples were Ca and K-saturated by repeated treatments with 1 M solutions of the respective chloride salts, washed free of excess electrolyte and made into oriented specimens for X-ray diffraction analysis on glass slides using the paste method (Thiesen and Harward, 1962). Diffractograms of the oriented clay slides were obtained after 7 pretreatments. Calcium-saturated clays were analyzed after equilibration at 54% RH and solvation with ethylene glycol and glycerol. Diffractograms of K-saturated specimens were obtained after heating at 105°, 300° and 550°C and analyzed at 0% RH and after equilibration at 54% RH. Selected samples were examined after Li-saturation and heating, using techniques similar to those of Jaynes and Bigham (1987), to determine if tetrahedrally substituted smectites were present. The $d_{060}$ values of randomly oriented specimens showed that the soil smectites were dioctahedral.

The layer charge characteristics of expanding phyllosilicates were determined by treating portions of each clay sample with various alkylammonium hydrochloride solutions and analyzing by X-ray diffraction (XRD) (Lagaly and Weiss, 1969; 1976). The n-alkylammonium hydrochloride compounds with chain lengths of 6 to 18 C atoms were prepared from their respective amines as described by Ruhlicke and Kohler (1981), except HCl gas was generated by bubbling air through concentrated HCl rather than using compressed HCl gas. Clay samples were Na-saturated, washed free of excess electrolyte, and equilibrated with aqueous solutions of n-alkylammonium hydrochlorides ranging in length from 6 to 18 carbon atoms for 24 to 48 hours using the method of Laird (1987). Samples were washed free of excess alkylammonium salts with 95% ethanol and mounted as oriented samples using the paste technique (Theissen and Harward, 1962; Laird, 1987). Slides were dried under vacuum at 65 °C for 24 hours. Diffractograms of the clay slides were obtained with a Philips diffractometer equipped with a LiF curved crystal monochromator using CoK$\alpha$ radiation generated at 50 kV and 25 mA, a step size of 0.05° 2$\Theta$ and an accumulation time of 2 seconds step$^{-1}$. The relative humidity in the sample chamber was maintained at 0% relative humidity (RH) during analysis.

The mean layer charge density and charge distribution of the soil smectites was calculated by analyzing the increase in basal spacings with alkylammonium chain length within the monolayer/bilayer transition range as described by Lagaly (1981). Monolayer arrangements were recognized by $d_{001}$ values of 1.36 nm and bilayer arrangements indicated by $d_{001}$ values of > 1.77 nm. The area available for a monolayer alkylammonium cation in the interlayer space is referred to as the equivalent area ($A_e$) (Lagaly and Weiss, 1975):

$$A_e = (d_{100})\cdot(d_{010}) / 2\sigma$$

where $d_{100}$ and $d_{010}$ are the unit cell dimensions for the phyllosilicate and $\sigma$ is the layer charge density. Values for the product $(d_{100})$ $(d_{010})$ are usually taken as 0.465 nm$^2$ for dioctahedral smectites (Lagaly and Weiss, 1969). The monolayer rearranges into a bilayer if the area of the flat-lying alkylammonium ion becomes larger than the equivalent area. At the monolayer/bilayer transition the area occupied by the alkylammonium cation ($A_c$) becomes equal to the equivalent area $A_e$, where:

$$A_c\ (\mathrm{nm}^2) = 0.567\ C_n + 1.4$$

and $C_n$ is the number of carbon atoms in the alkylammonium chain (Lagaly and Weiss, 1969). The layer charge of the smectite may then be calculated from the critical chain length at the transition by the equation:

$$\sigma = (d_{100})\ (d_{010}) / 2\ A_c$$

where $\sigma$ is expressed in units of moles of charge per half unit cell (mol(-)/$O_{10}(OH)_2$). The largest value of $C_n$ on the monolayer plateau represents the maximum layer charge and the smallest value of $C_n$ on the bilayer plateau represents the lowest layer charge (Stul and Mortier, 1974; Lagaly and Weiss, 1975).

Analysis of the monolayer/bilayer transition in detail allows the construction of charge distribution histograms showing the fraction of the total smectite with layer charge within different ranges. To determine the frequency of interlayer spaces with a given charge, the percentage of bilayers of alkylammonium ions was determined from the d(001) values at various alkylammonium chain lengths using peak migration curves (Lagaly, 1981). The weighted mean values for the smectite layer charge were then calculated based on the resulting frequency distributions. Since alkylammonium ions near crystal edges may not occupy an entire equivalent surface ($A_e$) of the layer (Stul and Mortier, 1974), corrections for particle size effects were made as described by Lagaly (1992).

## 6.3 RESULTS

Detailed characteristics of the solution chemistry and clay mineralogy have previously been reported (Chapter 3 and Chapter 4). Briefly, the study soils were highly saline and sodic, with the electrical conductivity of immiscibly displaced soil solutions ranging from 6 to 45 dS $m^{-1}$ and pH values ranging from 7.8 to 9.9. The chemistry of the soil solutions was dominated by Na and $SO_4$ ions. The coarse clay fraction of the soils generally contained a mixture of mica, kaolinite, smectite, and chlorite, with smectite being the most abundant mineral in most samples. Quartz was ubiquitous in this size fraction, with chlorite present only in small amounts. The finer clay fractions were dominated by smectite, with small amounts of hydrous mica and kaolinite often noted in the 0.2 to 0.08 $\mu$m clay fraction. Clay samples from the Wainwright soil showed XRD characteristics typical of low charge smectite with rehydration to 1.4 to 1.5 nm after K-saturation and equilibration at 54% RH, while lack of noticeable rehydration after K-saturation, indicative of high charge smectite or soil vermiculite, was seen primarily in samples from the Nobleford soil.

Most X-ray patterns for the n-alkylammonium saturated specimens showed similar characteristics, with broad low angle reflections indicative of smectites containing monolayer or bilayer alkylammonium complexes in the interlayer region. Sharper peaks at 1.0 nm and 0.72 nm seen in the coarser clay fractions were characteristic of discrete mica and kaolinite respectively. Some broadening and reduction in the intensity of the 1.0 nm mica peak was usually noted after alkylammonium treatments, indicating partial replacement of interlayer K by alkylammonium cations.

The transition from a monolayer to bilayer took place over a number of different alkylammonium chain lengths for all samples, indicating a heterogeneous charge distribution. A typical series of X-ray patterns showing the gradual increase in d-spacings with increasing alkylammonium chain length is shown in Fig. 6.1. The calculated mean layer charge densities of the expanding clay minerals ranged from 0.261 to 0.339 mol(-) per half unit cell and are summarized in Table 6.1. The charge was assumed to be predominantly in the octahedral layer because of the lack of expansion of Li-saturated samples after heating and glycerol solvation (Chapter 4). Some variation in layer charge was seen between sites, and between depths and size fractions for a given soil, but all calculated layer charges were considerably lower than previously reported for soil material in Alberta (Warren *et al.*, 1992). The highest layer charges were noted for samples from Nobleford, with Wainwright samples consistently having the lowest layer charges because of a much higher proportion of low charge layers than other soils (Fig. 6.2). Layer charge in samples from Hanna was quite evenly distributed over a wide range of charge densities (Fig. 6.3). In general, charge heterogeneity appears to be more pronounced in the finer size fractions in most Nobleford samples and similar between size fractions in the other soils.

The lower mean layer charge seen in the finer fractions of some samples is primarily due to variations in the charge distribution. For example, the layer charge distribution in the coarse clay fraction at 40 to 60 cm at Wainwright is fairly evenly distributed over a wide range of charges, while the vast majority of the charge in the $< 0.2$ $\mu$m fraction is concentrated at the lower end (Fig. 6.4). In Nobleford, where the layer charge density was found to decrease with decreasing particle size, analysis of the charge distribution shows that this is largely because the finer fractions had a lower proportion of high charge layers (Fig. 6.5).

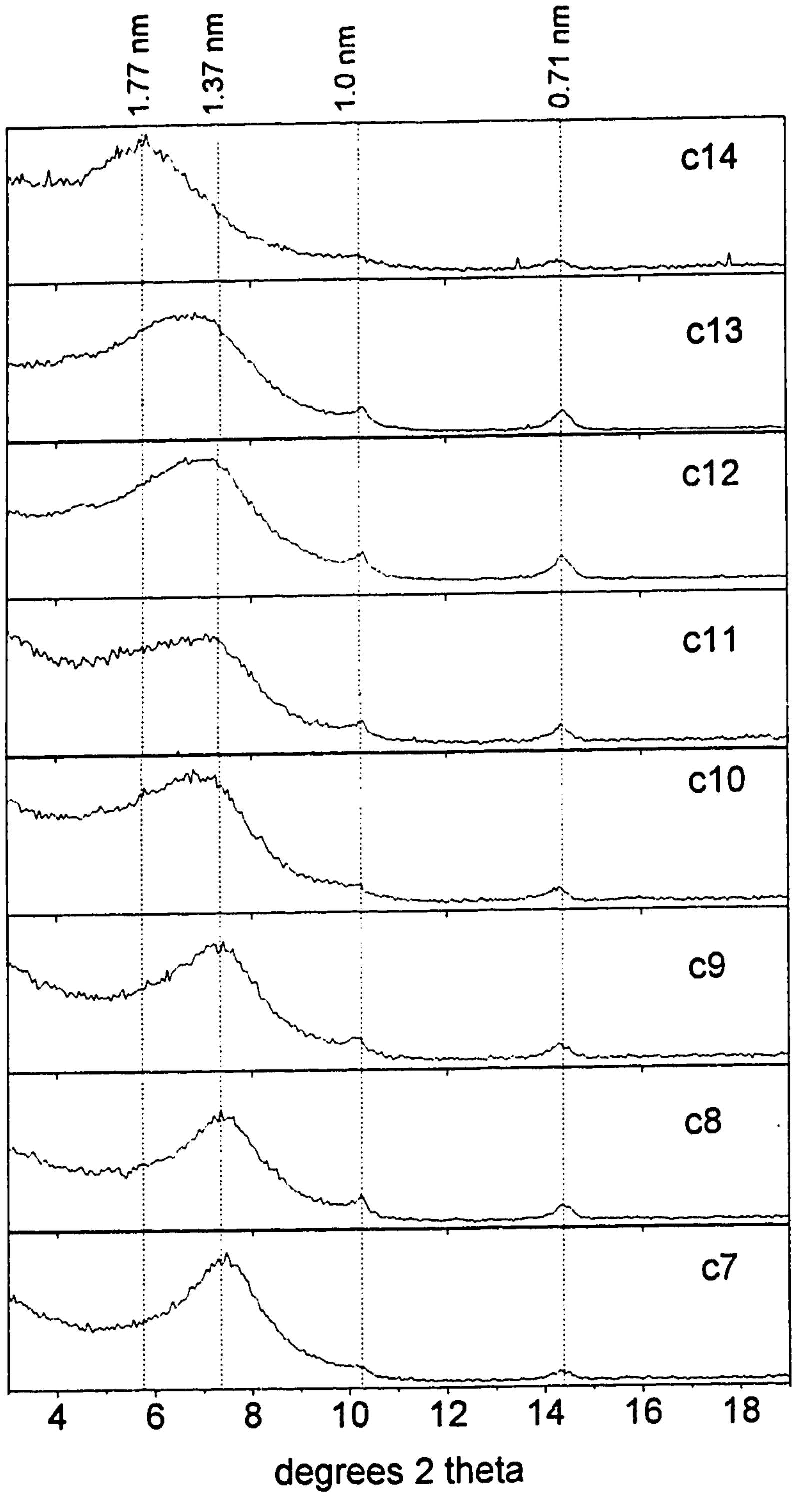

Fig 6.1. X-ray diffraction patterns for the alkylammonium saturated < 2.0 μm fraction of the < 70 cm layer in the Wainwright soil. $C_n$ refers to the number of carbons in the alkylammonium chain.

Table 6.1. Mean layer charge of smectites from salt-affected soils.

| | Mean Layer Charge[z] | | |
|---|---|---|---|
| Sample (cm) | size fraction (µm) | | |
| Hanna | 2 to 0.2 | 0.2 to 0.08 | < 0.08 |
| 0 - 23 | 0.317 | 0.312 | 0.301 |
| 23 - 50 | 0.282 | 0.309 | nd[y] |
| 50 - 80 | 0.276 | 0.299 | 0.309 |
| > 80 | 0.280 | 0.292 | 0.299 |
| Wainwright | | | |
| 0 - 20 | 0.278 | 0.281 | nd |
| 20 - 28 | 0.292 | 0.290 | 0.291 |
| 28 - 42 | 0.279 | 0.261 | nd |
| 42 - 70 | 0.289 | 0.265 | nd |
| > 70 | 0.296 | nd | nd |
| Nobleford | | | |
| 0 - 20 | 0.324 | nc[x] | nc |
| 20 - 40 | 0.323 | 0.309 | 0.312 |
| 40 - 60 | 0.339 | 0.308 | nd |
| > 60 | 0.338 | nd | nd |

[z] expressed as mol(-) per mol $O_{10}(OH)_2$
[y] not determined because of insufficient amounts of samples
[x] not calculated (see text)

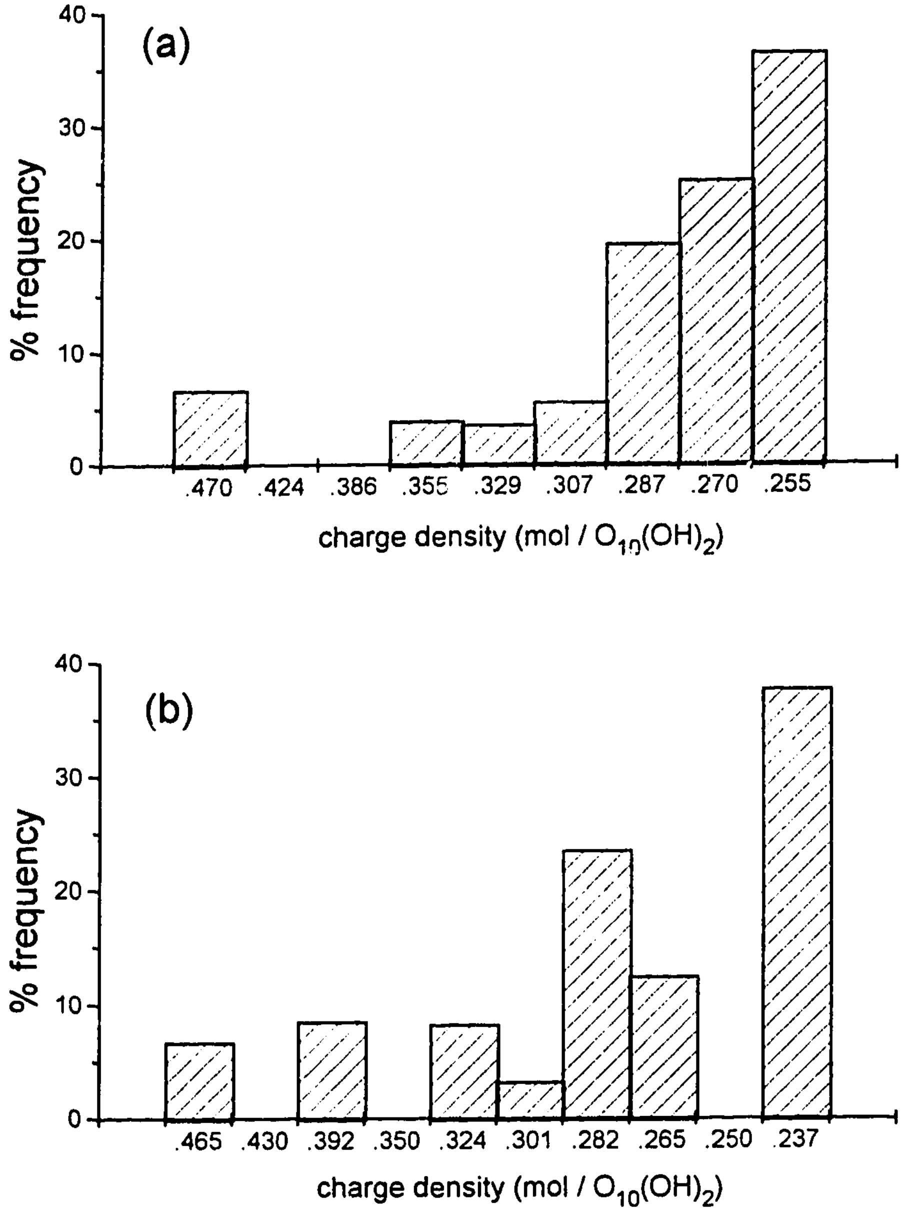

Fig 6.2. Distribution of layer charge in (a) < 0.2 μm size fraction and (b) 2.0 to 0.2 μm size fraction of the 0 to 20 cm layer of the Wainwright soil.

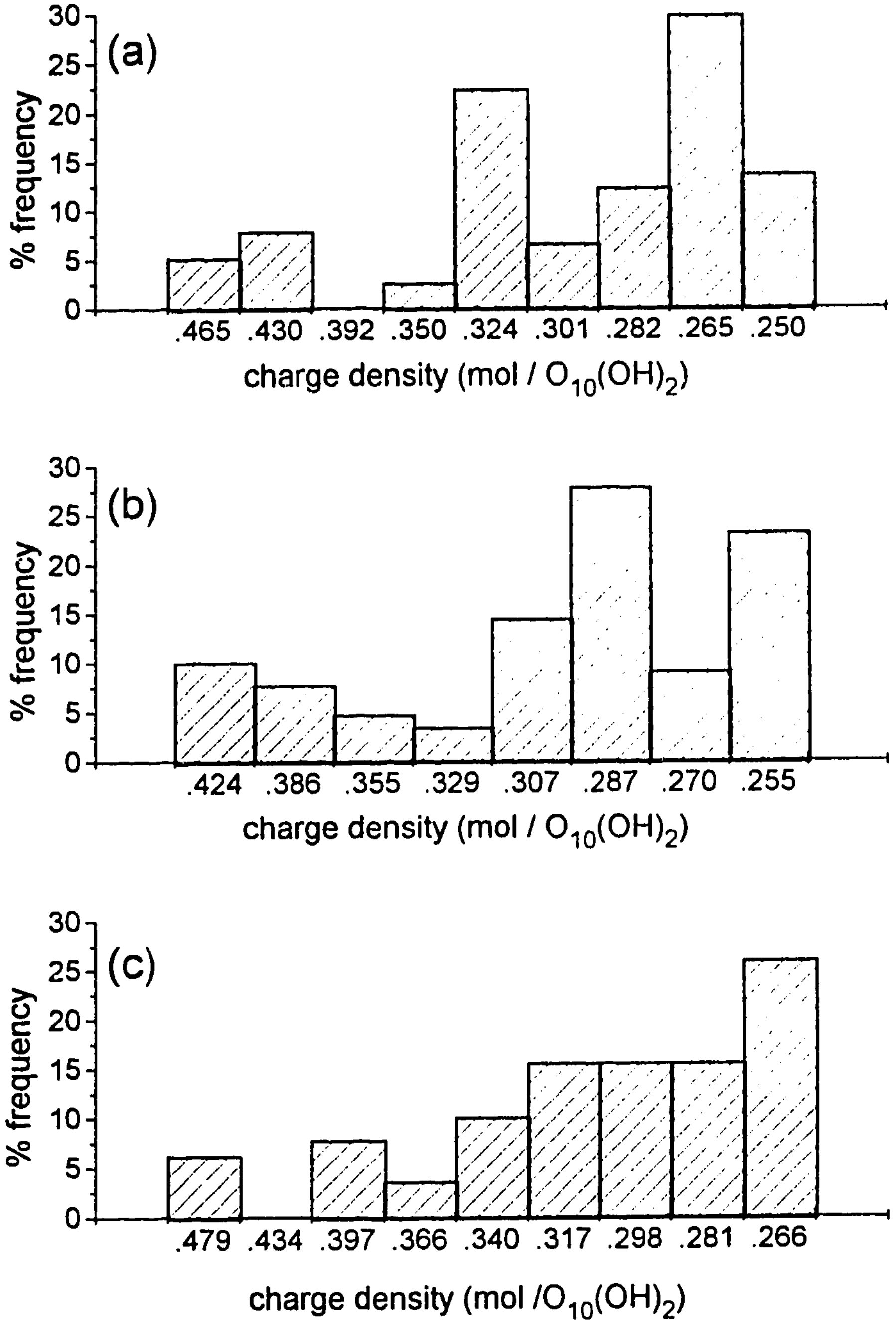

Fig. 6.3. Distribution of layer charge in (a) 2 to 0.2 μm fraction, (b) 0.2 to 0.08 μm fraction and (c) < 0.08 μm fraction of the 50 to 80 cm layer of the Hanna soil.

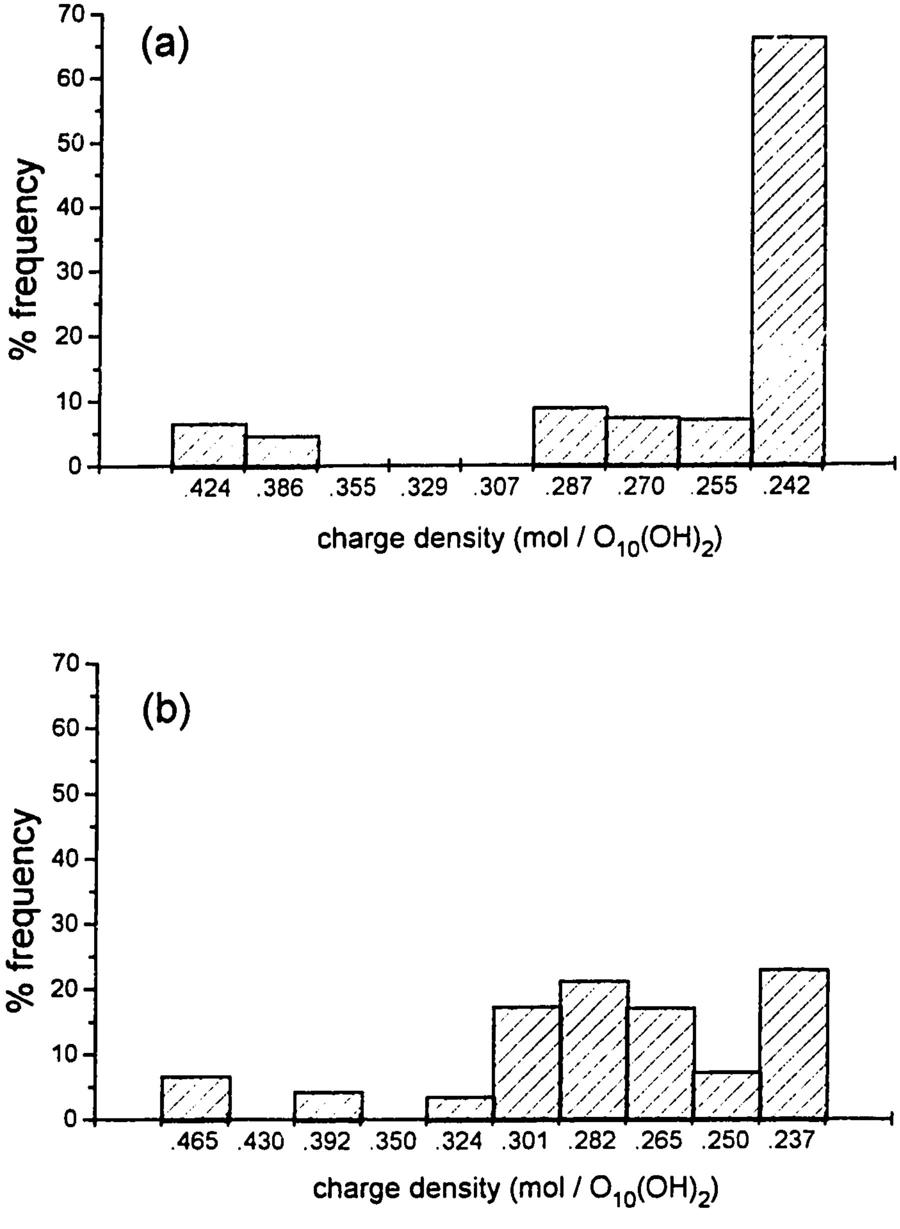

Fig 6.4. Distribution of layer charge in (a) < 0.2 μm size fraction and (b) 2.0 to 0.2 μm size fraction of the 28 to 42 cm layer of the Wainwright soil.

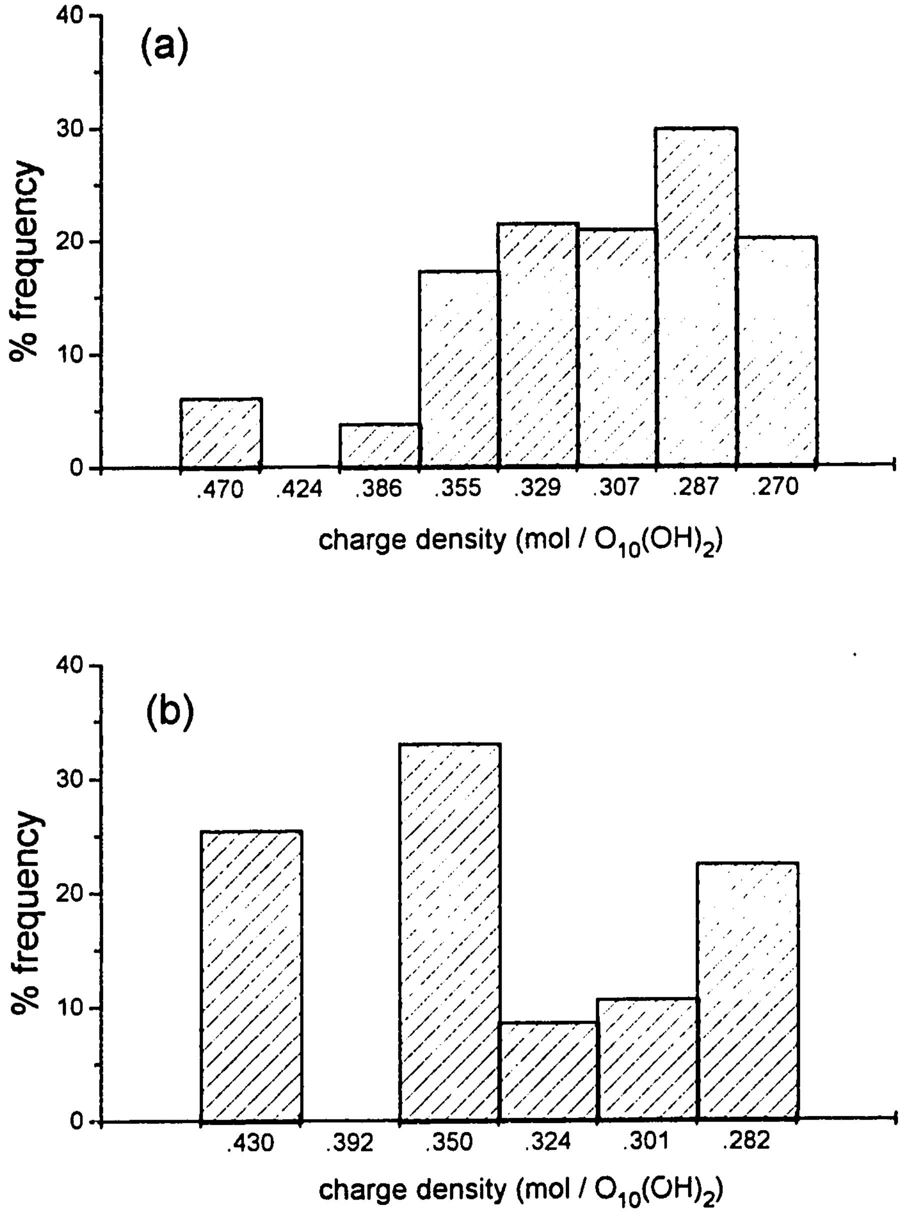

Fig 6.5. Distribution of layer charge in (a) < 0.2 μm size fraction and (b) 2.0 to 0.2 μm size fraction of the 40 to 60 cm layer of the Nobleford soil.

No consistent patterns were seen when looking at the variation of mean layer charge with depth and particle size for each soil. A relationship between layer charge and sample depth was seen in the Hanna and Nobleford soils, but with the opposite trend in each soil; layer charge decreased with depth in the Hanna soil, while Nobleford samples showed an increasing layer charge with increasing depth. No clear trends between layer charge and sample depth were noted in the Wainwright soil.

Smectites from the Nobleford soil and the surface layer of the Hanna soil showed a decrease in layer charge with decreasing particle size. Below a depth of 23 cm in the Hanna soil, the reverse trend was seen, in which layer charge increased with decreasing particle size. Samples from the top 28 cm of the Wainwright soil showed essentially no variation with particle size, while samples below this depth showed a slight decrease in layer charge density with decreasing particle size.

Unusual X-ray diffraction characteristics were seen for several samples after treatment with alkylammonium ions in which diffraction traces gently sloped downward from 3° $2\Theta$ with no smectite peaks readily apparent. Mica diffraction peaks were also greatly reduced or non-existent. This behavior was seen in the fine and very fine clay fractions of the surface layer of the Nobleford soil and to some extent from all samples from the Provost soil. No layer charge density values could be calculated for these samples because of the difficulty of identifying smectite diffraction peaks. Although the 0.2 to 0.08 $\mu$m fraction from the Nobleford surface sample is predominantly composed of smectite (Fig. 6.6), only a very slight increase in the baseline intensity where smectite diffraction maxima would be expected to occur is noted after equilibration with alkylammonium cations (Fig. 6.7). Similar behavior was seen after analysis of the $< 0.08$ $\mu$m fraction of this soil sample (Fig. 6.8a). Previous X-ray diffraction analysis of these samples after traditional pretreatments (Fig. 6.6 and Fig. 6.8b) shows smectite diffraction peaks that although broad, are fairly typical of finely crystalline montmorillonite in Western Canada. Rehydration after K-saturation results in a very broad elevation of the baseline rather than an expected distinct diffraction maximum between 1.2 and 1.4 nm, and would imply that the layer charge density is heterogeneous. However, this diffraction behavior on K-54% RH treatment is not restricted to these

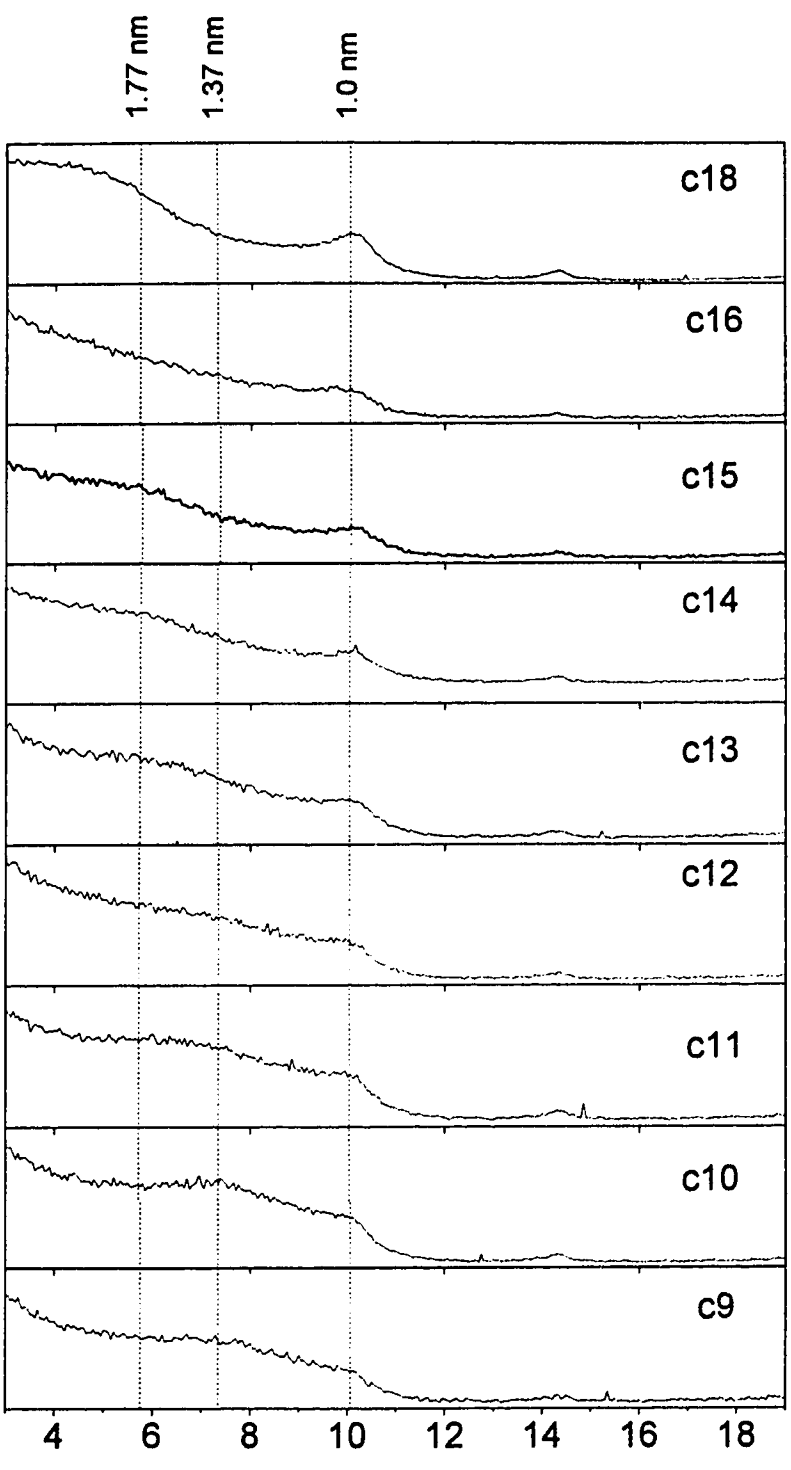

Fig 6.6. X-ray diffraction patterns for the alkylammonium saturated 0.2 to 0.08 μm fraction of the 0 - 20 cm layer in the Nobleford soil. $C_n$ refers to the number of carbons in the alkylammonium chain.

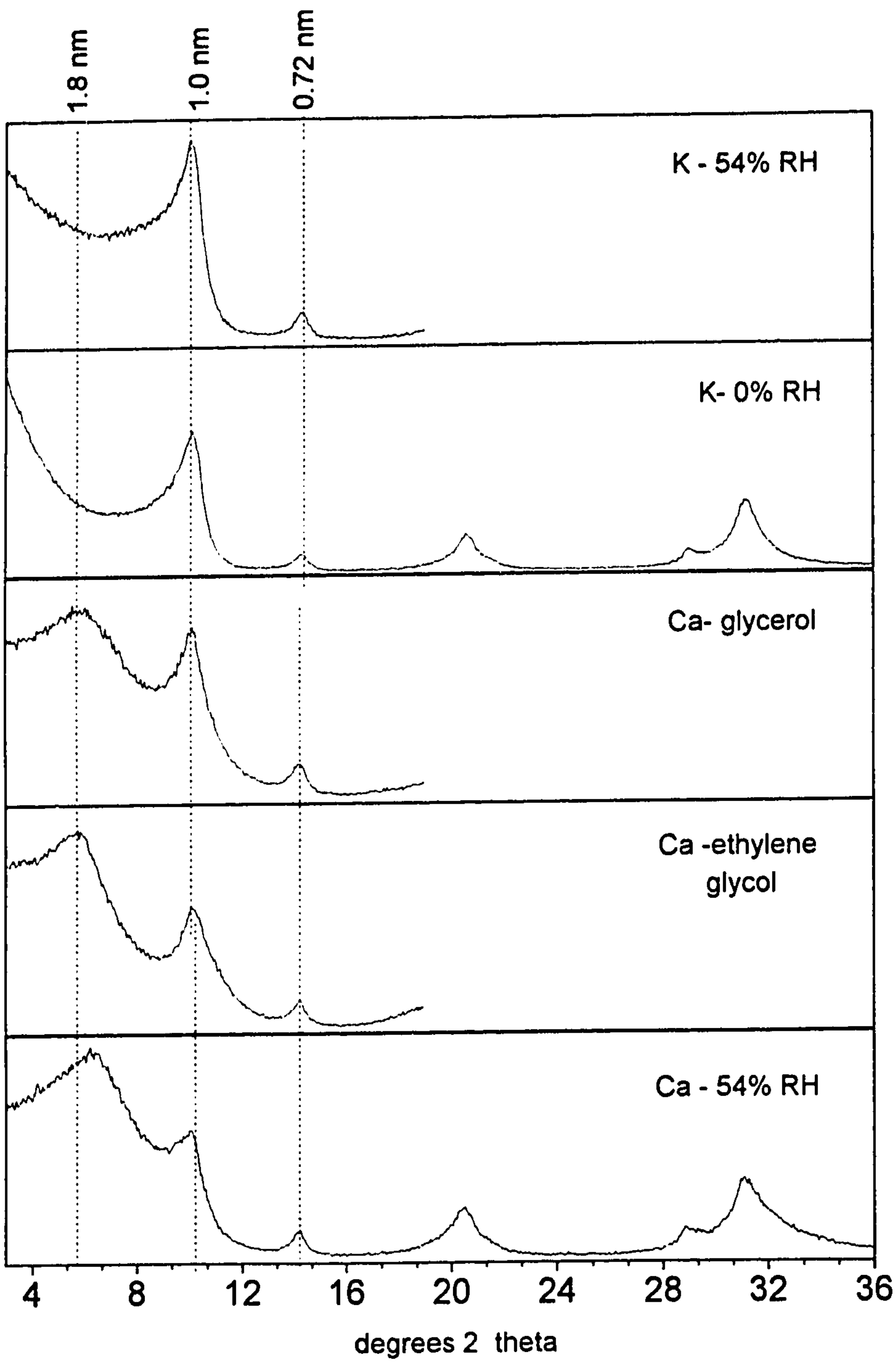

Fig 6.7. X-ray diffraction patterns of the 0.2 to 0.08 μm fraction of the 0 to 20 cm layer in the Nobleford soil after traditional pretreatments.

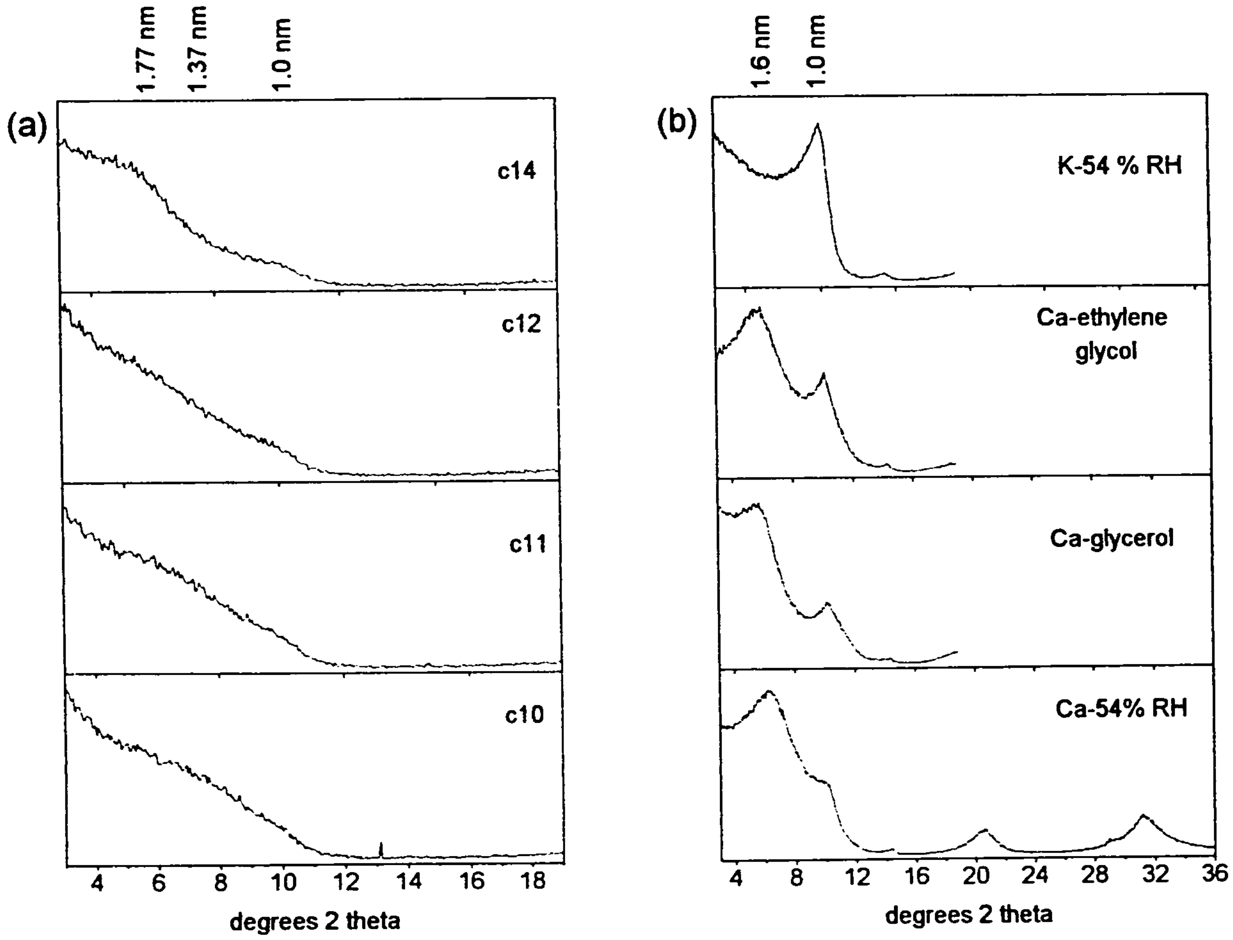

Fig 6.8. X-ray diffractograms of (a). alkylammonium saturated and (b) traditional pretreatments of the < 0.08 μm fraction of the 0 to 20 cm layer at Nobleford.

samples alone and is seen for most other samples from the Nobleford and Hanna soils.

## 6.3 DISCUSSION

All samples showed considerable charge heterogeneity as evidenced by a large transition range from the monolayer to the bilayer. This appears to be a characteristic feature of soil smectites (Stul and Mortier, 1974; Lagaly and Weiss, 1976; Lagaly, 1981). Charge heterogeneity may be attributed to different charges along a given silicate layer or different charges between layers. Since charge distribution in most of the samples remains approximately the same with decreasing particle size, this implies that the latter conditions exist. If only a small region at crystal edges contributes most to charge heterogeneity, charge heterogeneity would be expected to increase as particle size decreases, as seen in samples from the Nobleford soil.

While it is not altogether surprising to see differences in layer charge characteristics between soils from different geographic locations, the variability between samples in a single pedon is unexpected. The latter may be the result of different smectite origins or different weathering processes and rates occurring within the profile. Explanations are complicated by the fact that consistent changes with depth or particle size do not occur between sites. Since these soils are in low topographic positions, the possibility of transport of differently charged smectite from topographic highs through wind or water cannot be discarded. There may also be variations in the mineralogical composition of the parent materials from which the soils in this study are derived. While smectite is expected to be largely inherited in Alberta soils, it can also be formed in soils by transformation of micas or chlorite, both of which are commonly found in Alberta soils, or may be precipitated from solution. Smectites derived from the weathering of mica are likely to be tetrahedrally substituted, approaching beidellite in chemical composition (Borchardt, 1989). No beidellite was detected in these soils (Chapter 4). Mica-derived smectites would also be expected to have a relatively high layer charge unless significant charge reduction had occurred. Since mica occurs primarily in the coarse clay fraction, alteration products would be expected to accumulate in this size fraction as well. The presence of high charge layers in the coarse clay fractions of the Nobleford soil and a decrease with particle size suggests that a portion of the smectite may be micaceous in origin. A charge reduction with decreasing particle size in soil clays has been previously interpreted as indicating transformation of illite into smectite (Lagaly, 1981).

Transformation from chlorite is highly unlikely in these environments because of the expected stability of chlorite under the conditions found in the study soils (Chapter 3). Reid (1992) has suggested that decreasing smectite layer charge in saline soils may be due to neoformation of low-charged smectites under conditions of high salinity since montmorillonite might be expected to form pedogenically from solutions high in Si, Al and Mg (Borchardt, 1989). Since minerals precipitated from solution would be expected to accumulate in the finest size fractions, the low proportion of fine clay to total clay found in the majority of the samples (Chapter 4) suggests that this is not a major factor. The Al concentration in the soil solutions is also very low in all sites, and may limit possible smectite neoformation.

Variation in layer charge characteristics between samples may also be due to differences in weathering processes at different soil depths and locations. Generally, mineral weathering would be expected to be most pronounced in the finest size fractions because of their greater surface area, and would also be expected to be most intense at or near the soil surface. There are several potential mechanisms for alteration of smectite layer charge. One suggested process for reduction of layer charge is the dealumination of the smectite tetrahedral sheet and subsequent silication (Komarneni *et al.*, 1985). However, laboratory dissolution studies (Chapter 6) indicate that under the chemical conditions that would exist in the soil solution, Si is released from montmorillonite in preference to Al.

Another possible mechanism for changes in smectite layer charge is the oxidation or reduction of structural Fe (Stucki *et al.*, 1984). It has been suggested that in a strongly reducing environment, Fe leaves the montmorillonite structure to form a sulfide, and Mg enters the same sites from the surrounding solution so that the gross clay mineralogy is unchanged (Drever, 1971). This would have the net result of increasing the smectite layer charge. All of the soils in this study showed characteristics of alternating oxidation-reduction conditions, with distinct mottling at at least some depths. Sustained reducing conditions, as indicated by soil color, were seen at the lower depths of the Hanna and Wainwright soils. Changes in the oxidation state of Fe in the smectite structure due to periodic or prolonged reducing conditions are therefore likely.

Reduction of the intensity of the 1.0 nm peak in many samples after equilibration with alkylammonium compounds (*eg.* Fig. 6.8) suggests that alteration of the micaceous component may introduce some error into the determination of layer charge. It has been previously established that alkylammonium cations will result in displacement of K in micas, with the degree of K depletion dependent upon the characteristics of the mineral and the experimental techniques (Laird *et al.*, 1987). This displacement has been reported to result in the false identification of vermiculite in soil samples (Ross and Kodama, 1986; Laird *et al.*, 1987). Although no vermiculite was noted in this study, differences in the characteristics of the micaceous component between samples may result in different degrees of K depletion and hence slightly different layer charge characteristics, and may account for the presence of higher charge layers.

The extreme broadening and essential disappearance of smectite diffraction maxima in some samples after intercalation with alkylammonium compounds of all chain lengths has not been previously documented, and may be a result of the alkylammonium ions penetrating between the layers without regular expansion of the lattice, reducing the intensity and sharpness of the basal reflections (Lagaly 1981). The possibility that this phenomenon was the result of incorrect sample treatment and handling was rejected because all samples were treated in exactly the same way. Basal reflections are normally weakened and broadened only in the transition range; this may suggest that charge characteristics of some samples may always cause the smectites to appear to be in transition from a monolayer to bilayer of alkylammonium molecules. Disappearance of smectite diffraction maxima previously seen in some of these samples after traditional XRD analysis was suggested to be the result of interaction with soil organic matter (Chapter 4). It is unclear why the phenomenon is only seen in some clays from saline soils, but must be due to fundamental alterations in the mineral structure.

## 6.4 CONCLUSIONS

The mean layer charge of clays from salt-affected soils was found to range between 0.261 to 0.339 mol(-)$O_{10}(OH)_2$ per half unit cell, considerably lower than values previously reported for non-saline Alberta soils. Analysis of the charge characteristics shows that the layer charge distribution is heterogeneous and varies inconsistently with location, depth and particle size. The lowest mean layer charge densities were found in the Wainwright soil, which also had the lowest salinity of those soils studied; the Hanna and Nobleford soils had similar salinities but different layer charge characteristics. The layer charge of smectites in some samples could not be determined because of the essential disappearance of their diffraction maxima after intercalation with alkylammonium compounds.

Differences in layer charge between samples may be due to differences in origin or weathering processes. The lack of any consistent relationships between samples and the likely addition of clay particles from other locations through physical processes complicates potential explanations. Differences in origin due to smectite neoformation or weathering of other minerals is unlikely. It is probable that the alternating redox conditions or strongly reducing environments present in the study soils influenced the oxidation state of structural Fe, and hence played a major role in determining smectite layer charge. It is also possible that differences in layer charge between samples is largely due to variable K depletion of the micaceous component by alkylammonium cations.

It is clear that no generalizations can be made about smectite layer charge characteristics in salt-affected soils in Alberta, except that the mean layer charge appears to be lower and more heterogeneous than that of non-saline soils based on the limited data available. Future research that investigates variation in charge characteristics between soils derived from the same parent material and differing only in drainage and electrical conductivity may elucidate the role of salinity and redox potential on smectite layer charge more clearly.

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# 7. STABILITY OF STANDARD CLAY MINERALS IN LABORATORY CONTROLLED DISSOLUTION EXPERIMENTS

## 7.1 INTRODUCTION

The understanding of mineral weathering processes has important implications in predicting the chemical and physical properties of a soil. Relative dissolution rates of soil minerals have never been systematically investigated, but mineral stabilities can be expected to vary between different soil environments since weathering reactions partly depend upon the chemistry of the aqueous phase. Mineral weathering and relative stabilities are often deduced from qualitative weathering sequences such as that derived by Jackson and Sherman (1953) or by comparing thermodynamic stability constants with soil solution characteristics.

The dissolution behavior of aluminosilicates in general is not well understood, primarily because of the wide range of mineral compositions that exist in nature and the influence of kinetic factors. It is generally agreed that pH is an important factor in aluminosilicate dissolution, with the stability of both primary and secondary minerals reported to increase with increasing pH (Rai and Lindsay, 1975). However, laboratory studies investigating the dissolution of common silicate minerals such as kaolinite (Carroll and Walther, 1990), muscovite (Knauss and Wolery, 1989), quartz (Brady and Walther, 1989) and feldspars (Knauss and Wolery, 1986) indicate that the rate of mineral dissolution increases with increasing pH in basic solutions. The increased dissolution rate at alkaline pH has been attributed to the interaction of OH with surface Si groups and the formation of charged activated complexes on the mineral surface (Brady and Walther, 1989).

The effect of ionic strength on mineral dissolution has been systematically investigated only for quartz, which has been reported to have an increased dissolution rate with increased electrolyte concentration (Dove and Crerar, 1990). Dove and Crerar suggest that electrolytes accelerate the dissolution rate by adsorbing to the quartz surface and increasing the accessibility of water molecules to the Si-O-Si bonds. Fundamental chemical principles suggest that since dissolution is an equilibrium reaction, it would not be favored in soil solutions with high activities of component ions. For example, montmorillonite is generally considered to be stable in poorly drained environments which maintain high $Si(OH)_4$ and Mg activities (Weaver *et al.*, 1971; Borchardt, 1989). However, increasing salinity may enhance the solubility of weatherable minerals because of the ionic strength dependence of single-ion activity coefficients (Sposito, 1989). Specific components of the weathering solution may also affect mineral dissolution rates. For example, dilute solutions of $Na_2CO_3$ have been reported to increase Si release from montmorillonite (Nuttig, 1943). The type of cation on the exchange complex of expanding clay minerals will also likely effect the rate of dissolution (Frenkel *et al.*, 1983; Lahann and Roberson, 1980), with Na-saturated minerals likely to weather at the fastest rate (Bar-on and Shainberg, 1970).

Investigations of clay mineral dissolution have previously been conducted for chlorite (Kittrick, 1982), muscovite (Mattigod and Kittrick, 1979; Lin and Clemency, 1981), illite (Reesman, 1974; Routson and Kittrick, 1971), kaolinite (Kittrick, 1966; May *et al.*, 1982), and montmorillonite (Kittrick, 1971; May *et al.*, 1982; Churchman and Jackson, 1976) among others. Typically, the purpose of these studies was to obtain accurate standard free energy of formation ( $\Delta G°_f$) values. Experimental parameters were thus established to facilitate the pursuit of this objective, and normally have not reflected conditions present in soils. Experimental techniques have varied widely and have often been selected primarily to facilitate analyses. For example, montmorillonite stability and weathering studies have typically been carried out in artificially acid environments, primarily to ensure that aluminum is present as $Al^{3+}$ (Kittrick, 1971; Weaver, 1971). Many studies have also added minerals of known solubility to minimize the degrees of freedom and number of required analyses (*eg*. Mattigod and Kittrick, 1979; Kittrick, 1971; Kittrick, 1982).

Comparison of clay mineral dissolution studies in seawater may more closely resemble the behavior expected in saline soil solutions because of closer similarities in pH and ionic strength. MacKenzie and Garrels (1965) found that Si was rapidly released from clay minerals placed in seawater, with concentrations highest in solutions containing montmorillonite. Carroll and Starkey (1960) also found that clays released appreciable amounts of constituent ions when placed in seawater, with montmorillonite again being the most reactive of the minerals tested.

The thermodynamic constants derived from solubility experiments and through other techniques can theoretically be used to predict mineral stability, since the direction of change in mineral assemblages will be towards equilibrium. However, the validity of standard free energies of formation derived for variable-composition phyllosilicates by the solubility method has been seriously questioned, with results thought to be invalid due to experimental deficiencies and conceptual flaws (May *et al.*, 1986; Churchman and Jackson, 1976; Bassett *et al.*, 1979). Prediction of mineral weathering and stability in soil solutions using equilibrium-based models which incorporate these thermodynamic constants may therefore be unjustified.

It is unclear from the literature what the relative stability of common clay minerals is expected to be in alkaline solutions of high ionic strength, but dissolution studies in seawater suggest that constituents are rapidly released, with montmorillonite being the most reactive. Although fundamental thermodynamic considerations suggest that the stability of most minerals increases with increasing pH, many studies indicate that dissolution rates also increases under alkaline conditions. In addition, the solubility of Al and Si are expected to increase sharply at high pH values due to ionization of $Al(OH)_3$ and $Si(OH)_4$ respectively. The role of ionic strength in mineral weathering is unclear. Many previous investigations have shown that clay minerals will react measurably with aqueous solutions in the laboratory, and that dissolution and precipitation can be determined by monitoring solution species. The specific dissolution characteristics of a mineral can be expected to vary widely depending upon the characteristics of the surrounding solution. The objective of this study therefore was to determine the stability of common clay minerals (montmorillonite, kaolinite, muscovite and chlorite) in solutions of varying salinity and alkalinity by assessing constituent release and changes in solid phase characteristics during laboratory controlled dissolution studies. The results of the dissolution experiments will be compared to results predicted by an equilibrium-based model in order to establish the validity of the model.

## 7.2 MATERIALS AND METHODS

### 7.2.1 Clay Minerals

The montmorillonite and kaolinite used in this study were obtained from the Clay Minerals Society Source Clay Minerals Repository, University of Missouri, Columbia, MO. The montmorillonite used was source clay SAz-1 (Ca-montmorillonite (Cheto), Arizona), while the kaolinite was source clay KGa-1 (well-crystallized, Georgia). X-ray diffraction analysis of both minerals as random powder mounts and oriented specimens did not indicate the presence of any crystalline contaminants. The 0.2 to 5.0 μm size fraction was separated using gravity sedimentation and centrifugation techniques (Jackson, 1979), with the fine clay fraction discarded to reduce the amount of poorly crystalline or amorphous material. The chlorite (clinochlore, Yancey County, NC, USA) and muscovite (Madras, India) were obtained as massive specimens from Ward's Natural Science Establishment, Inc., Rochester, NY. The muscovite was separated into thin sheets by hand and cut into small pieces using scissors, while the chlorite was reduced in size with a hammer and chisel. Both were then dry ground in a swing mill grinder for several minutes. The 0.2 to 53 μm size fraction of the chlorite and muscovite were separated as described above after wet sieving to remove the coarsest particles. X-ray diffraction analysis of the muscovite did not reveal any crystalline contaminants but the chlorite was found to contain small amounts of hydroxylapatite, present as fine crystals within the larger clinochlore sample.

All samples were Na-saturated by washing 3 times with 1 M NaCl, and washed free of excess electrolyte as determined by the $AgNO_3$ test. Sodium was selected as the exchangeable cation to standardize all samples since Na was the dominant cation in most of the equilibrating solutions. The samples were then freeze-dried, finely ground in an agate mortar and pestle and weighed into bottles for the equilibration experiments. A mixture of the above clays was also prepared and was composed of 50% montmorillonite, 20% kaolinite, 20% muscovite and 10% chlorite by weight. This was designed to investigate potential differences in mineral dissolution characteristics in a multi-component system and approximates the clay mineral assemblage common in Alberta soils.

The chemical composition of the Na-saturated minerals was determined after microwave dissolution (Warren and Dudas, 1990), with the extracts being analyzed for Ca, K, Fe, Mg, Si and Al by atomic absorption spectrophotometry (AAS). Inductively coupled plasma emission spectroscopy was used to confirm results from selected samples. Mineral structural formulae were calculated using the method of Jackson (1979).

Sub-samples of each mineral were Ca and K-saturated by repeated treatments with 1 M solutions of the respective chloride salts, washed free of excess electrolyte and made into oriented specimens for X-ray diffraction analysis on glass slides using the paste method (Thiesen and Harward, 1962). Diffractograms of the oriented clay slides were obtained with a Philips diffractometer (Model 1710, Philips Electronics Ltd., Scarborough, Ontario, Canada) equipped with a LiF curved crystal monochromator using CoK$\alpha$ radiation generated at 50 kV and 25 mA, a step size of 0.05° 2$\Theta$ and an accumulation time of 2 seconds step$^{-1}$. Calcium-saturated clays were analyzed after equilibration at 54% relative humidity (RH) and solvation with ethylene glycol and glycerol. Diffractograms of K-saturated specimens were obtained after heating at 105°, 300° and 550°C and analyzed at 0% RH and after equilibration at 54% RH. Cation exchange capacities of Ca-saturated clays were determined by replacing Ca with Mg (Jackson *et al.*, 1986), and surface areas determined using the EGME method (Carter *et al.*, 1965). Layer charge density of the montmorillonite was determined using the alkylammonium method (Ruehlicke and Kohler, 1981), with the methodology described in detail in Chapter 6. The quantity of amorphous material was estimated by extraction with acid ammonium oxalate (AOX) (McKeague, 1978), and subsequent analysis of Fe, Al and Si in the extracts by AAS. In samples with low Si concentrations, Si was determined colorimetrically (Weaver *et al.*, 1968). Selected characteristics of the clay mineral fractions used in the experiment are summarized in Table 7.1. Analyses were generally conducted in triplicate.

At the end of the batch equilibration experiments, sub-samples of the total solids remaining in the sample bottles for each treatment were analyzed by the methods described above. The remainder of each solid sample was dispersed in distilled water and centrifugation methods (Jackson, 1979) used to separate any particles < 0.2 $\mu$m that may have appeared during the course of the experiment. Generally, samples from solutions A and B required several distilled water washings to remove soluble salts before a stable dispersed suspension was achieved. Any fine clay that was collected was analyzed by X-ray diffraction, and if present in sufficient quantity, was also analyzed by the same methods as the total clay fraction for determination of CEC and chemical composition.

### 7.2.2 Equilibration Methods and Solution Analyses

Five types of solutions were used in this experiment for equilibration with the mineral samples and are designated as solutions A through E (Table 7.2). Future identification of samples by these letters refers to the placement of a specific mineral sample in one of these solutions. Solutions A and B were alkaline brines,

Table 7.1. Characteristics of standard clay samples before equilibration.

| Mineral | CEC cmol $kg^{-1}$ | Surface Area $m^2$ $g^{-1}$ | AOX extractable | | | Chemical Composition | | | | | Structural Formulae |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Al | Si | Fe | Si | Al | Mg | Fe | K | |
| | | | g $kg^{-1}$ | | | g $kg^{-1}$ | | | | | |
| chlorite | 2.5 | 43 | 7.1 | 4.8 | 5.8 | 145 | 99 | 215 | 82 | - | $(Mg_{4.75}Fe_{0.78}Al_{0.73})(Si_{2.76}Al_{1.24})O_{10}(OH)_8$ |
| kaolinite | 1.6 | 27 | 1.5 | 0.25 | n.d.[z] | 224 | 204 | - | - | - | $(Si_{4\cdot02}Al_{3.98})O_{10}(OH)_8$ |
| muscovite | 3.9 | 42 | 20 | 7.9 | 4.3 | 216 | 162 | 8.2 | 44 | 81 | $K_{0.84}(Si_{3.14}Al_{0.86})(Al_{1.6}Fe_{0.32}Mg_{0.14})O_{10}(OH)_2$ |
| montmorillonite | 110 | 720 | 2.4 | 0.71 | 0.25 | 292 | 93 | 48 | 12 | 0.99 | $(Si_{3.94}Al_{0.06})(Al_{1.11}Mg_{0.76}Fe_{0.08})O_{10}(OH)_2$ |

[z] not detectable

Table 7.2. Initial characteristics of the equilibrating solutions.

| Solution | pH | EC dS m$^{-1}$ | Ca | Mg | K | Na | Si mg kg$^{-1}$ | Al | CO3 | HCO3 | SO4 | Cl |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A | 10.0 | 45 | 22 | 16 | 200 | 30000 | 0.41 | 0.17 | 17000 | 2700 | 35000 | 14000 |
| B | 8.1 | 33 | 200 | 5300 | 1400 | 20000 | 0.40 | 0.07 | nd$^{z}$ | 214 | 63000 | 1700 |
| C | 9.9 | 0.36 | nd | nd | nd | 88 | nd | 0.03 | 14 | 103 | nd | 100 |
| D | 8.1 | 0.032 | nd | nd | nd | 48 | nd | nd | nd | 15 | nd | 4 |
| E | 5.8 | 0.006 | nd | nd | nd | 0.10 | nd | nd | nd | 6.7 | nd | nd |

$^{z}$ not detectable

prepared from laboratory chemicals to approximate the composition of porewater in two different Alberta saline soils (Chapter 3). Solutions C and D were distilled water adjusted with $Na_2CO_3$ to the approximate pH of solutions A and B, respectively. Solution E was distilled water. Silica and aluminum present in solutions A and B and cations other than Na in solutions C and D are likely the result of contaminants present in the laboratory chemicals. Some changes in soluble carbonate species undoubtedly occurred in all solutions due to exposure with atmospheric $CO_2$.

Sets of triplicate 20% suspensions (22 g/440 ml for montmorillonite, chlorite and kaolinite and 18.5 g/370 ml for muscovite and the clay mixture) of each mineral/solution combination were placed in 500 ml polyethylene bottles, resulting in a total of 75 equilibrating samples. Minerals placed in solutions A and B were washed with portions of the respective brine just before the start of the equilibration period to minimize the effect of any initial cation exchange reactions on the solution composition. Samples were placed on a laboratory bench (temperature approximately 22°C) and were shaken gently by hand at regular intervals. Caps were placed loosely on the sample bottles to prevent excessive evaporation of solution. Redox potentials of the solutions were checked periodically using a Pt combination electrode, and showed that relatively constant electrode potentials of approximately 150 mV were maintained in the sample bottles during the experiment. Aliquots were taken periodically from each suspension to determine if equilibrium was being approached. Final samplings at the end of the experiment were staggered for the various minerals and occurred at 365 days for the clay mixture, 425 days for muscovite, and 453 days for kaolinite and 454 days for montmorillonite and chlorite. During sampling, mineral suspensions were well-stirred, making sure all solids were suspended and aliquots immediately removed with a wide-mouthed pipet. This method was used to minimize any changes to the solid:solution ratio as a result of repeated sampling. Samples were centrifuged at 13,000 rpm for 40 minutes to provide clear supernatant solutions for analysis. Muscovite samples from solutions C, D, and E required filtration through a 0.22 $\mu$m filter for solution clarification.

Electrical conductivity (EC), pH and soluble carbonate species were measured immediately after centrifugation, with the latter being determined by HCl titration. Dissolved silica, as mononuclear $Si(OH)_4$, was analyzed by the colorimetric method of Weaver *et al.* (1968). Polymeric Si is not expected at the relatively low concentrations found in this study (Churchman and Jackson, 1976). Aluminum was determined using the pyrocatechol violet method (Dougan and Wilson, 1974). Other cationic constituents were measured using AAS. Selected properties of the solutions as a function of time are displayed in the appendix. Sulfate and Cl were measured periodically in selected solutions by turbidimetric (Rhoades, 1982) and colorimetric methods (Adriano and Doner, 1982) respectively. Analytical results were used as input for the geochemical model SOLMINEQ (Kharaka *et al.*, 1988) for speciation calculations. Activity coefficients were calculated using the Pitzer equation.

## 7.3 RESULTS

### 7.3.1 Montmorillonite

Selected characteristics of montmorillonite-containing solutions at the beginning and end of the experiment are displayed in Table 7.3. The concentrations of constituent ions in solution A, a pH 10 brine, showed a net decrease from the beginning to the end of the equilibration period. Solution B, a brine with lower pH, showed a decrease in Si and Al concentrations and increase in soluble Mg levels. Iron concentrations were below detection limits in both brines. It was suspected that this was in part due to analytical interferences in AAS analysis caused by the high Na content of these solutions but the colorimetric determination of Fe using the method of Olson and Ellis, Jr. (1982), a method not unduly affected by interferences, also indicated undetectable Fe concentrations in solutions A and B. The lower ionic strength solutions C, D and E generally showed an increase in the soluble levels of all constituent ions, with the highest concentrations attained in solution E, distilled water.

As noted earlier, only montmorillonite particles between 2 and 0.2 μm were used in the experiment, but < 0.2 μm particles were detected at the end of the equilibration in every solution. Although not specifically quantified, the amount of fine clay was observed to be considerably less in solution B. The XRD characteristics of both size fractions equilibrated in solutions B through E were very similar to those of the untreated montmorillonite sample. Diffraction maxima of equilibrated montmorillonite samples after K-saturation and heating to 105° or 300° C appeared slightly broader and more asymmetrical than those of untreated

Table 7.3. Mean concentrations of selected elements in solutions equilibrating with montmorillonite at the beginning and end of the experiment.

Values in brackets are standard deviations of replicated analyses.

| Solution | Sampling Date | pH | Si | Al | Mg | Fe |
|---|---|---|---|---|---|---|
| | | | mg $L^{-1}$ | | | |
| A | Day 1 | 10 | 4.7 (±0.3) | 0.53 (±0.13) | 20 (±0.3) | nd$^{z}$ |
| | Day 454 | 10 | 3.7 (±0.3) | nd | 8.2 (±0.2) | nd |
| B | Day 1 | 7.6 | 7.5 (±0.1) | 0.11 (±0.07) | 4710 (±84) | nd |
| | Day 454 | 8.7 | 5.3 (±0.1) | nd | 9050 (±655) | nd |
| C | Day 1 | 9.2 | 9.1 (±0.1) | 0.74 (±0.08) | 11.1 (±2.6) | 1.5 (±0.1) |
| | Day 454 | 8.8 | 13.5 (±0.7) | 0.49 (±0.06) | 163 (±12) | 23.5 (±1.5) |
| D | Day 1 | 9.4 | 10.0 (±1.3) | 0.92 (±0.04) | 18.1 (±1.1) | 1.93 (±0.08) |
| | Day 454 | 8.6 | 22.3 (±1.1) | 1.14 (±0.09) | 331 (±38) | 51.7 (±2.7) |
| E | Day 1 | 9.5 | 12.1 (±1.0) | 0.91 (±0.05) | 20.2 (±1.0) | 1.89 (±0.09) |
| | Day 454 | 8.6 | 24.7 (±3.9) | 1.27 (±0.26) | 348 (±35) | 64.6 (±5.0) |

$^{z}$ not detectable

montmorillonite, and suggest that incomplete collapse of the structure occurred due to the formation of hydroxy-interlayer material. Complete collapse to 1.0 nm occurred for all samples after heating to 550° C.

X-ray diffraction analysis of the $< 0.2$ μm fraction that had equilibrated in solution A showed very different characteristics (Fig. 7.1a). Diffractograms of K-saturated specimens at 0% RH showed the presence of an intergrade-type mineral displaying a broad peak at 1.4 nm with an extended shoulder down to approximately 1.0 nm. This behavior was not evident after heating to 300 °C or after treatment with dilute HCl (Fig. 7.1b), indicating that the interlayer material was unstable with regard to heat and acid. The montmorillonite was also seen to rehydrate to 1.6 nm after being equilibrated at 54% RH. Since the d-spacing measured in the untreated montmorillonite after the K-54% RH treatment was 1.2 nm, this indicates that the interaction of the interlayer material with the montmorillonite from solution A is such that water molecules can still expand the montmorillonite structure. These unusual XRD characteristics are similar to those previously reported in the clay fraction of some naturally occurring saline soils (Chapter 4).

The coarser fraction of montmorillonite equilibrated in solution A showed these intergrade mineral characteristics to a much lesser degree (Fig. 7.2a). Analysis of the clay after the K-0% RH treatment showed an asymmetrical diffraction maximum at 1.1 nm, with equilibration at 54% RH expanding the montmorillonite to 1.3 nm, only slightly higher than expected. After treatment with dilute HCl, diffraction characteristics resembled other montmorillonite samples (Fig. 7.2b).

In an attempt to identify this intergrade material, samples were treated with 5 ml of 2% HCl for approximately 30 seconds; the aqueous phase was then separated by low-speed centrifugation and analysed by AAS. Marked effervescence was noted upon addition of acid to the solid, and was particularly strong for the $< 0.2$ μm fraction, indicating some accumulation of carbonates. No crystalline phase other than montmorillonite was noted by X-ray diffraction. Acid extracts were dominated by Ca, and contained smaller quantities of Mg, Al, and Si (Table 7.4). The fine clay fraction had slightly higher amounts of Mg, Al and Si, some of which may have been released from the montmorillonite itself. The obvious difference between the acid extracts of the two size fractions is the Ca

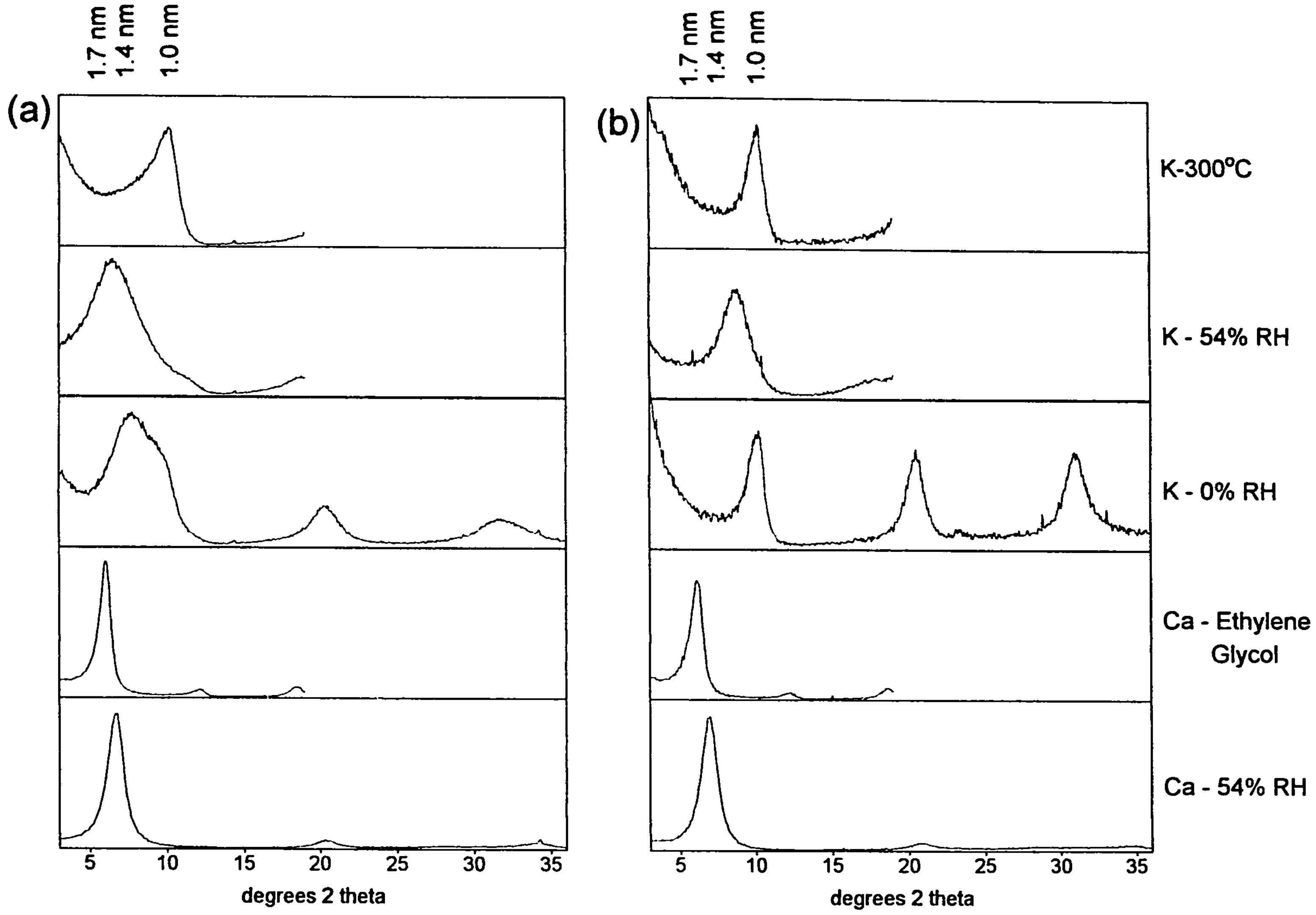

Fig. 7.1. Diffractograms of < 0.2 μm fraction of montmorillonite after equilibration in solution A; (a) before HCl treatment, (b) after HCl treatment.

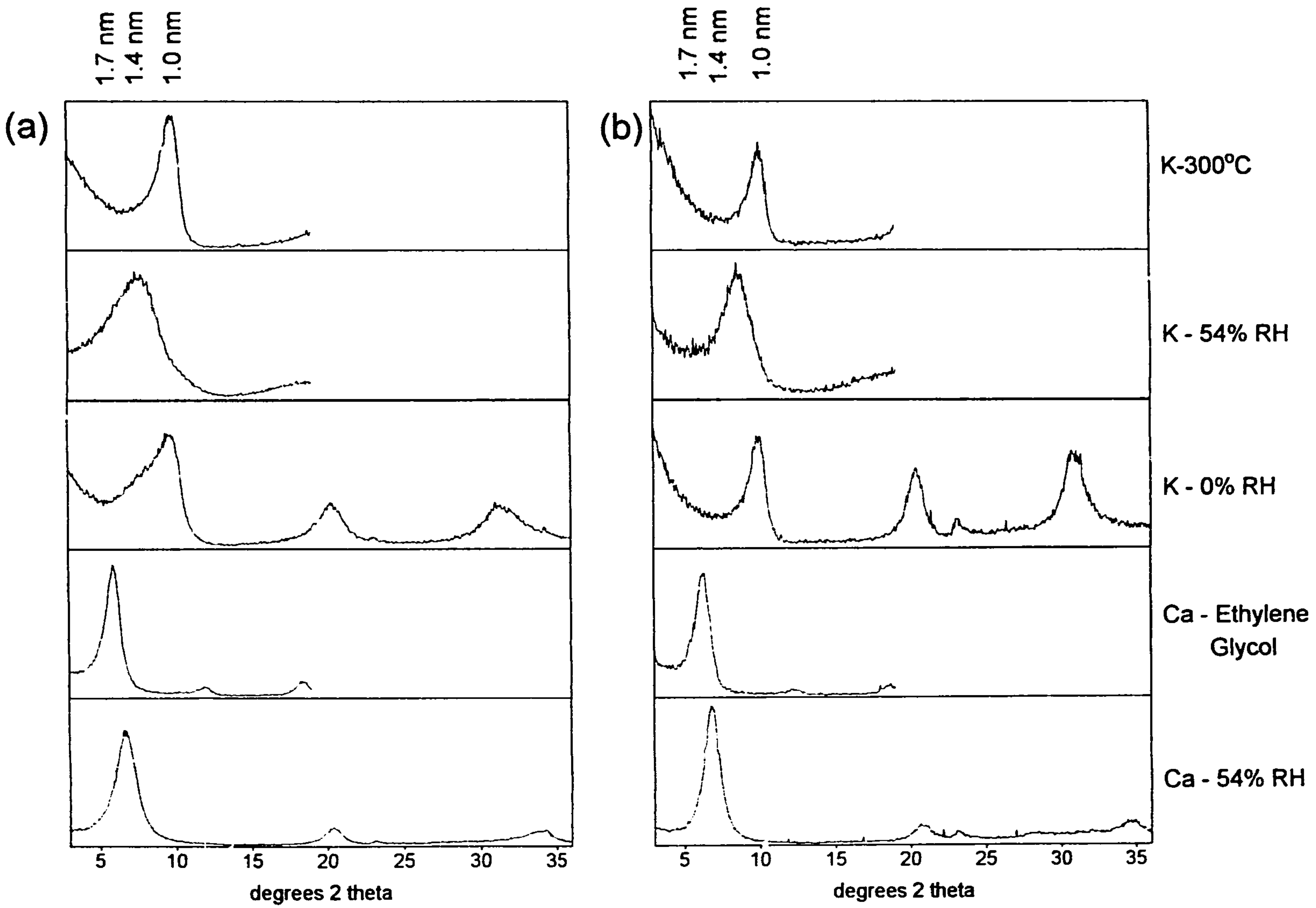

Fig. 7.2. X-ray diffractograms of the 0.2 to 5 μm fraction of montmorillonite equilibrated in solution A; (a) before HCl treatment, (b) after treatment with HCl.

concentration. Even though no carbonate minerals were detectable by X-ray diffraction, the dominance of Ca and the effervescence noted upon acid addition suggests that a carbonate mineral is present and is potentially causing the intergrade characteristics.

Table 7.4. Elements present in HCl extracts of montmorillonite equilibrated in pH 10 brine (solution A) for 454 days.

| Size Fraction | Mg | Ca | Al | Fe | Si |
|---|---|---|---|---|---|
| | | | $g\ kg^{-1}$ | | |
| 2 - 0.2 $\mu$m | 0.36 | 3.9 | 0.43 | 0.05 | 0.51 |
| < 0.2 $\mu$m | 0.48 | 12.3 | 0.69 | 0.07 | 0.56 |

The CEC of all montmorillonite samples before and after equilibration were very similar (Table 7.5), indicating that the dissolution occurring over the course of 454 days did not affect the total layer charge of the mineral. Analysis of layer charge characteristics (data not shown) using the alkylammonium method also showed virtually identical results for each sample before and after equilibration, confirming that the total layer charge was unchanged in the experiment.

Concentrations of Fe, Si and Al extractable by ammonium oxalate showed similar trends (Table 7.5), with montmorillonite equilibrated in solution A containing higher amounts of each element than in the original material and other samples having lower amounts. Comparison of Al/Si ratios of the amorphous material shows a net enrichment of Al in solution A samples, and depletion in samples C, D and E. Poorly ordered material from solution B had the same proportions of Al and Si as the starting montmorillonite.

The chemical composition and calculated structural formulae of the equilibrated montmorillonite samples were virtually identical to that of the starting material (data not shown). However, one interesting feature noted after total montmorillonite dissolution is the distribution of K between the size fractions. The

Table 7.5. Mean cation exchange capacities and concentrations of Fe, Al and Si extracted by acid ammonium oxalate for montmorillonite equilibrated for 454 days in different solutions. Values in brackets are the standard deviations of replicated analyses.

| Solution | CEC cmol $kg^{-1}$ | AOX extractable Al | AOX extractable Si | AOX extractable Fe |
|---|---|---|---|---|
| | | g $kg^{-1}$ | g $kg^{-1}$ | g $kg^{-1}$ |
| A | 112 (±1.3) | 2.7 (±0.20) | 0.90 (±0.10) | 0.31 (±0.02) |
| B | 109 (±3.0) | 1.4 (±0.10) | 0.41 (±0.06) | 0.16 (±0.004) |
| C | 113 (±5.2) | 1.7 (±0.10) | 0.45 (±0.02) | 0.16 (±0.007) |
| D | 110 (±1.0) | 1.7 (±0.01) | 0.56 (±0.10) | 0.17 (±0.003) |
| E | 110 (±2.5) | 1.7 (±0.08) | 0.57 (±0.003) | 0.17 (±0.004) |

original montmorillonite sample contained approximately 1 g $kg^{-1}$ K within its structure. A small amount of structural K has often been previously reported for pure montmorillonite samples (van Olphen and Fripiat, 1979). After 454 days of equilibration, the K content of the coarse clay ($> 0.2$ $\mu$m) fraction was an order of magnitude higher than the fine particles ($< 0.2$ $\mu$m), except for samples equilibrated in solution B which showed essentially no differences between size fractions. This would suggest that K is selectively removed from the finest montmorillonite particles during weathering in solutions of low K activity. The differences in K content between the equilibrated size fractions may also indicate differences in the crystal structure. Potassium fixation is normally associated with high layer charge or with charge that originates in the tetrahedral sheet (Malla and Douglas, 1987). The greater K fixation in the larger particle sizes therefore suggests that these minerals have a higher proportion of tetrahedral charge, randomly located high charge layers within the structure, or both. However, any changes in charge distribution would have to be such that the total layer charge of the sample was essentially unchanged because little variation for the total solids was recorded after CEC mesurements and layer charge density analysis.

### 7.3.2 Kaolinite

Silicon was released from kaolinite equilibrated in all solutions, with the lowest concentrations measured in the alkaline brine solutions A and B, and the highest concentrations attained in solution E, distilled water (Table 7.6). Soluble aluminum levels remained approximately constant in solution A from the beginning to the end of the equilibration period, and were consistently below detection limits in the other solutions. Previous kaolinite dissolution experiments between pH 5 to 8 have also not detected any soluble Al (Siever and Woodford, 1973). The greater solution concentrations of Si relative to Al in most samples suggest incongruent dissolution and conservation of Al in the solid phase. Carroll-Webb and Walther (1988) previously found that Si was preferentially dissolved over Al in the pH range 4.0 to 9.3, with stoichiometric dissolution above this pH. It has been suggested that tetrahedral Si units hydrolyze to $H_4SiO_4$ as they detach from the solid, leaving an Al-oxide-hydroxide surface on the kaolinite (Siever and Woodford, 1973).

A trace amount of mineral material with a diameter $< 0.2$ $\mu$m was separated at the end of the experiment for solutions C, D and E. No fine clay was

Table 7.6. Mean concentrations of selected elements in solutions equilibrating with kaolinite at the beginning and end of the experiment. Values in brackets are standard deviations of replicate analyses.

| Solution | Sampling Date | pH | Si | Al |
|---|---|---|---|---|
| | | | mg L$^{-1}$ | |
| A | Day 1 | 10 | 0.39 (±0.08) | 0.36 (±0.02) |
| | Day 453 | 10 | 0.66 (±0.02) | 0.33 (±0.03) |
| B | Day 1 | 7.6 | 0.55 (±0.10) | nd$^{z}$ |
| | Day 453 | 7.8 | 0.60 (±0.06) | nd |
| C | Day 1 | 9.4 | 0.53 (±0.08) | nd |
| | Day 453 | 8.8 | 1.5 (±0.10) | nd |
| D | Day 1 | 7.7 | 0.82 (±0.04) | nd |
| | Day 453 | 7.7 | 3.0 (±0.62) | nd |
| E | Day 1 | 7.4 | 0.98 (±0.10) | nd |
| | Day 453 | 7.4 | 3.9 (±0.23) | nd |

$^{z}$ not detectable

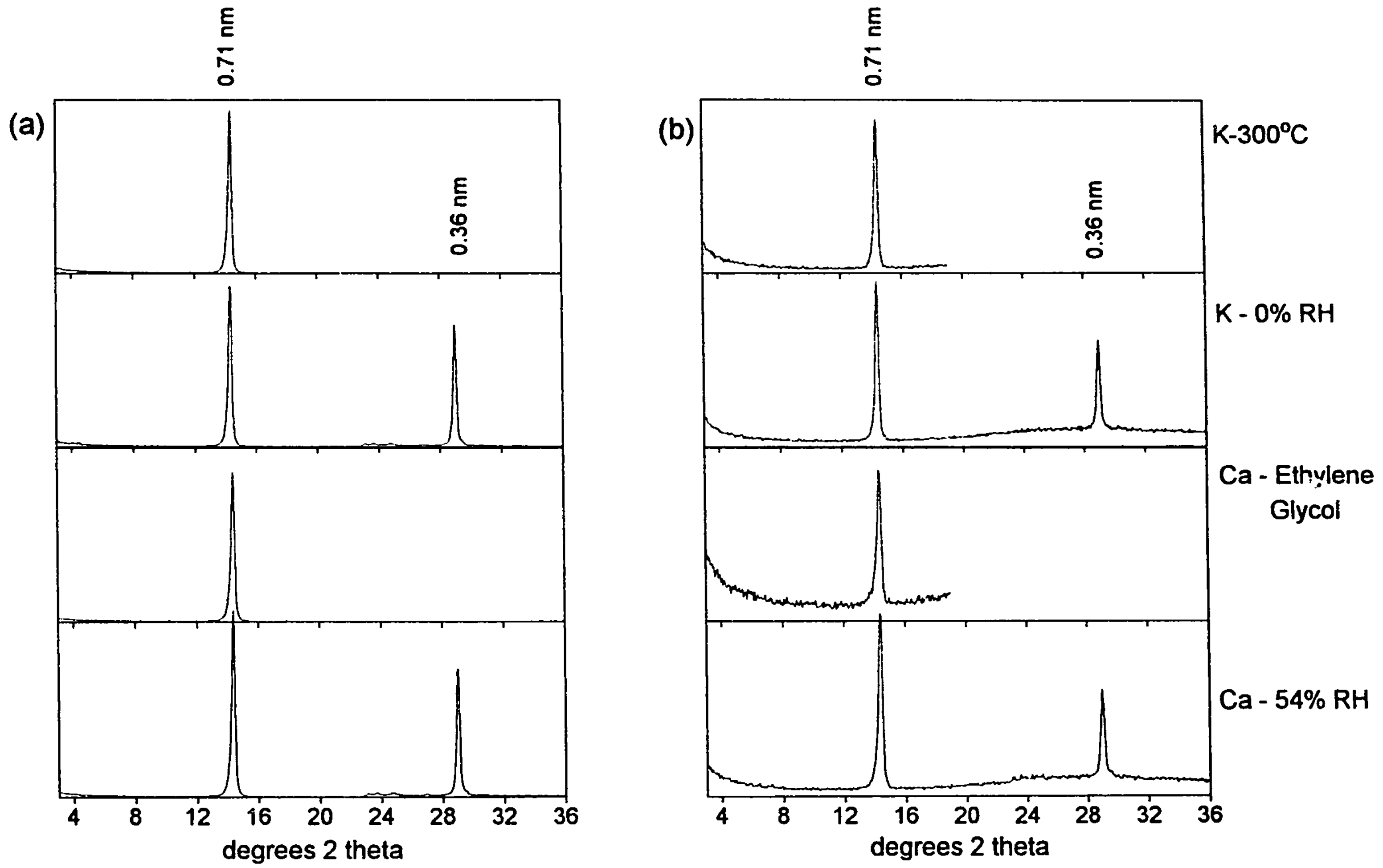

Fig 7.3. X-ray diffractograms of the (a) 0.2 to 5 μm fraction and (b) < 0.2 μm fraction of kaolinite equilibrated in solution C for 453 days.

Table 7.7. Mean cation exchange capacities and concentrations of Fe, Al and Si extracted by acid ammonium oxalate for kaolinite equilibrated for 444 days in different solutions. Values in brackets are the standard deviations of replicated analyses.

| Solution | CEC cmol kg$^{-1}$ | AOX extractable | | |
|---|---|---|---|---|
| | | Al | Si | Fe |
| | | g kg$^{-1}$ | | |
| A | 7.4 (±0.90) | 0.58 (±0.08) | 0.17 (±0.01) | nd[z] |
| B | 2.4 (±0.07) | 0.54 (±0.06) | 0.12 (±0.02) | nd |
| C | 1.8 (±0.04) | 0.49 (±0.09) | 0.10 (±0.01) | nd |
| D | 1.7 (±0.03) | 0.36 (±0.06) | 0.08 (±0.01) | nd |
| E | 1.5 (±0.03) | 0.47 (±0.07) | 0.10 (±0.01) | nd |

[z] not detectable

detected in samples equilibrated in solutions A and B, suggesting that kaolinite weathering processes are more intense in the lower ionic [illegible] solutions.

X-ray diffraction characteristics of all samples were similar to that of the starting material. The baseline of the diffractograms of the fine clay appeared slightly higher than those of the associated larger particles (Fig. 7.3), suggesting a greater amount of poorly crystalline or amorphous material. This was most noticeable in solution C samples, which also showed kaolinite peak intensities to be only about one fifth of that measured in the coarser size fraction, suggesting lower mineral crystallinity. Peak intensities of the two size fractions from solutions D and E were similar.

Cation exchange capacity measurements showed distinct differences between different samples with the CEC of kaolinite equilibrated in solution A being over four times higher than that of the original sample (Table 7.7). The CEC of kaolinite equilibrated in solution B also increased slightly. The exchange capacities of kaolinite equilibrated in the other solutions were similar to the starting material and within the range previously reported for this sample (van Olphen and Fripiat, 1979). Analysis of kaolinite chemical composition indicated that minor differences existed between the amounts of Si and Al for each sample and were likely the result of analytical variability.

The amount of AOX-extractable material in all samples was low (Table 7.7), with amounts of Fe consistently below detection limits. Amounts of amorphous Si in equilibrated samples were slightly lower than that of the starting material, with the lowest amounts in solutions D and E. Amounts of AOX-extractable Al were similar between samples and were less than half the amount present in the original kaolinite sample.

### 7.3.3 Muscovite

The concentrations of constituent ions in solutions equilibrating with muscovite on the first and last day of the experiment are presented in Table 7.8. Some Si was released in all solutions, with the lowest concentrations in the brine solutions A and B and the highest in distilled water. Aluminum concentrations were generally higher on day 1 than at the end of the equilibration period for all treatments. Soluble K levels increased over time in all solutions, with the greatest changes in K concentrations noted for the brine solutions A and B. Relatively

Table 7.8. Mean concentrations of selected elements in solutions equilibrating with muscovite at the beginning and end of the experiment. Values in brackets are standard deviations for replicated analyses.

| Solution | Sampling Date | pH | Si | Al | K |
|---|---|---|---|---|---|
| | | | mg L$^{-1}$ | | |
| A | Day 1 | 10 | 0.92 (±0.14) | 0.97 (±0.06) | 271 (±2) |
| | Day 425 | 10 | 0.67 (±0.03) | 0.84 (±0.02) | 535 (±29) |
| B | Day 1 | 7.7 | 0.75 (±0.08) | 0.05 (±0.03) | 1767 (±22) |
| | Day 425 | 7.7 | 2.8 (±0.2) | nd$^{z}$ | 2550 (±40) |
| C | Day 1 | 9.3 | 0.92 (±0.01) | 0.82 (±0.04) | 7.3 (±0.03) |
| | Day 425 | 8.9 | 4.7 (±0.2) | 0.83 (±0.02) | 16 (±1.0) |
| D | Day 1 | 8.8 | 1.3 (±0.1) | 1.2 (±0.1) | 1.8 (±0.2) |
| | Day 425 | 8.4 | 6.8 (±0.2) | 0.8 (±0.2) | 9.4 (±0.7) |
| E | Day 1 | 8.9 | 1.3 (±0.1) | 1.6 (±0.2) | 1.7 (±0.01) |
| | Day 425 | 8.5 | 7.0 (±0.3) | 1.1 (±0.2) | 10 (±1.6) |

[z] not detectable

higher proportions of K than Si or Al were dissolved from the muscovite, suggesting that the dissolution of interlayer K was favored over dissolution of tetrahedral or octahedral cations.

Fine clay (< 0.2 μm) was separated from all samples, but amounts and characteristics varied considerably between treatments. A small amount of fine particles separated from solution A samples was identified as calcite and contained no muscovite; this mineral may be a relict of the separation procedure in which $CaCl_2$ was added to the bulk solution to flocculate any clay present. Only a trace amount of fine material, barely adequate to prepare a slide for XRD, was separated from solution B samples. X-ray diffraction analysis of this material showed characteristics typical of highly amorphous substances, with only a small amount of muscovite (Fig. 7.4). The largest quantities of < 0.2 μm particles were separated from solutions C, D and E. Diffraction analysis showed that although composed only of muscovite, peaks were broader and of lower intensity than those of the larger size fractions (Fig. 7.5). Diffractograms of the 0.2 to 53 μm fraction of each treatment were indistinguishable from each other and that of the starting muscovite.

An increase in cation exchange capacity was noted for all muscovite samples, with the largest increases noted for muscovite equilibrated in brine solutions A and B (Table 7.9). The chemical composition of the muscovite at the end of the experiment was very similar between treatments (data not shown), with minor differences likely accounted for by analytical variability. All samples contained less K than the amount present in the starting material but were similar in the concentrations of other constituent elements. In previous muscovite solubility studies which lasted for 2 years, muscovite composition was found to change very little except for an apparent decrease in K content (Mattigod and Kittrick, 1979; Rosenberg *et al.*, 1984).

The amount of oxalate-extractable material was lower in all equilibrated muscovites relative to the original sample. The greatest reduction in AOX-extractable Si was seen for samples equilibrated in solutions C, D and E, while Al showed the greatest reduction in solution D samples. The ratio of Al to Si in the extracted material was lower in solution A samples and higher in other treatments relative to the ratio in the original sample, with the greatest change noted for

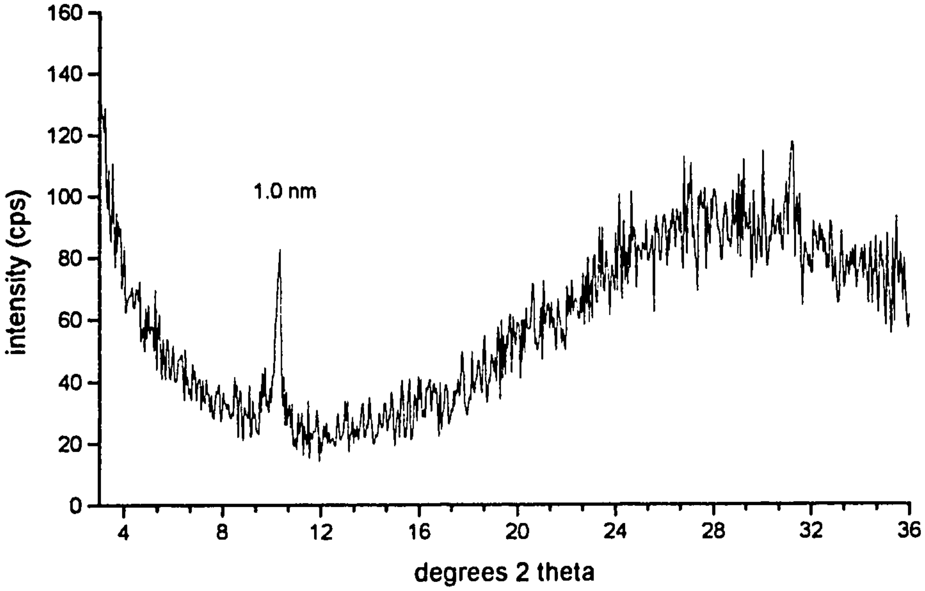

Fig 7.4. X-ray diffractogram of the < 0.2 μm fraction of muscovite equilibrated in solution B for 425 days.

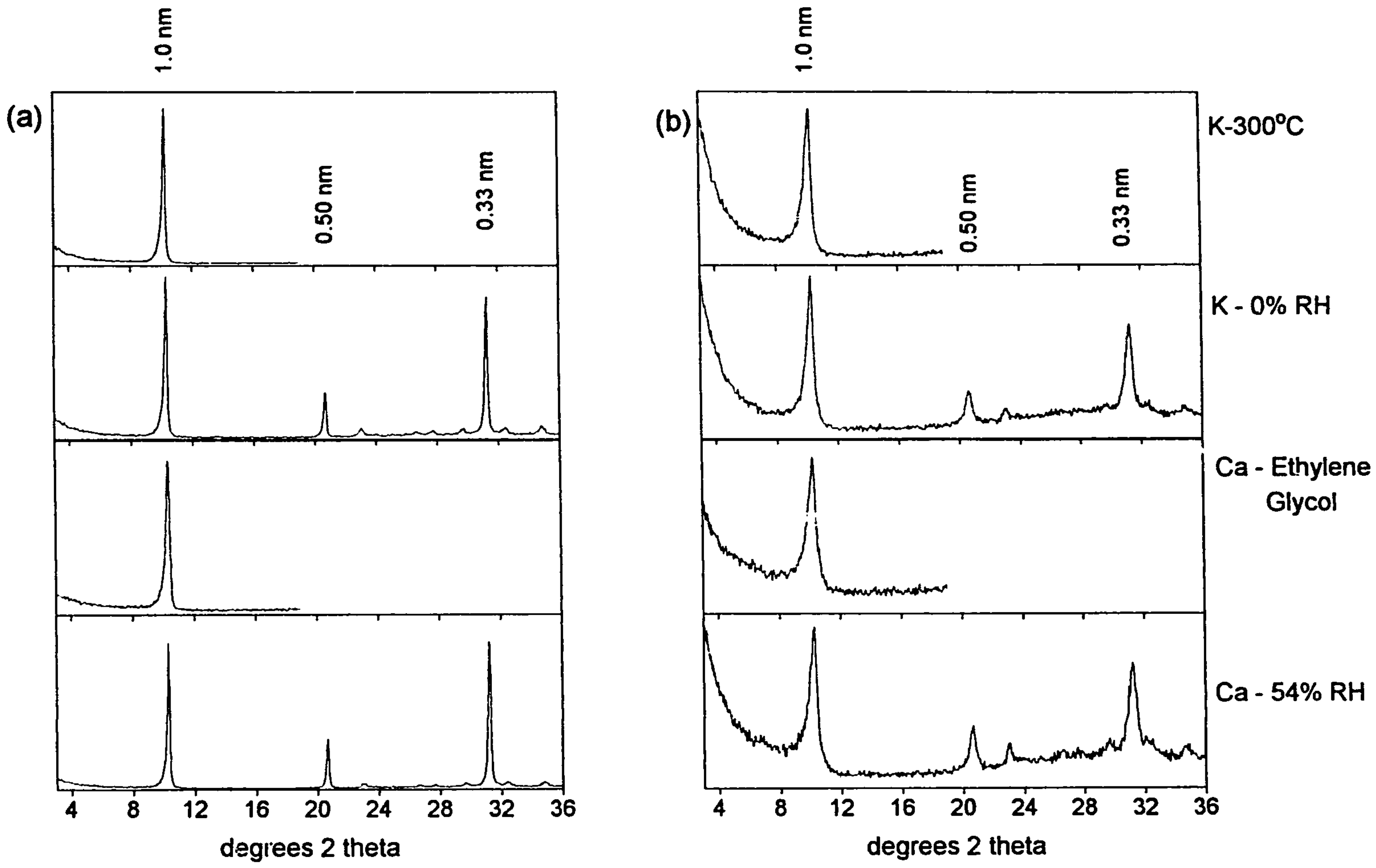

Fig 7.5. X-ray diffractograms of the (a) 0.2 to 53 μm fraction and (b) < 0.2 μm fraction of muscovite equilibrated in solution C for 425 days.

Table 7.9. Mean cation exchange capacities and concentrations of Fe, Al and Si extracted by acid ammonium oxalate for muscovite equilibrated for 425 days in different solutions. Values in brackets are the standard deviations of replicated analyses.

| Solution | CEC cmol kg$^{-1}$ | AOX extractable | | |
|---|---|---|---|---|
| | | Al | Si | Fe |
| | | g kg$^{-1}$ | | |
| A | 10.9 (±0.5) | 9.5 (±0.5) | 4.7 (±0.2) | 2.2 (±0.2) |
| B | 9.4 (±0.3) | 10.3 (±0.2) | 3.7 (±0.6) | 2.4 (±0.1) |
| C | 4.4 (±0.06) | 10.4 (±0.4) | 2.7 (±0.1) | 2.5 (±0.2) |
| D | 4.2 (±0.01) | 7.3 (±0.6) | 2.1 (±0.1) | 1.7 (±0.2) |
| E | 4.0 (±0.1) | 8.7 (±0.1) | 1.9 (±0.02) | 2.0 (±0.1) |

solution E. Iron concentrations extracted by AOX were similar between samples and were approximately half of the amount in the original sample.

### 7.3.4 Chlorite

The concentrations of Mg and Si in solutions equilibrated with chlorite on day 1 and day 454 are presented in Table 7.10. Of the various treatments, the greatest amounts of Si were released into the brine solutions A and B. Silicon concentrations in these solutions showed little change from the beginning to the end of the experiment. The lower ionic strength solutions had lower initial Si concentrations, which showed only a slight increase after 454 days. Soluble Mg levels were consistently higher at the end of the experiment for all solutions except for brine A, in which levels decreased slightly. Aluminum and Fe concentrations were checked periodically for the various solutions, and were always below detection levels.

In contrast to the other [illegible]lorite samples did not contain any particles < 0.2 $\mu$m at the end [illegible]eriment. X-ray diffraction analysis of the solids showed no noticeable differences from that of the starting material, with typical diffractograms shown in Fig. 7.6. The chemical characteristics of chlorite after equilibration are presented in Table 7.11. Cation exchange capacity measurements showed that chlorite equilibrated in solution A had a CEC almost three times higher than that of the original sample. No differences were noted in the CEC of the other equilibrated chlorite samples.

Analysis of dissolved samples for constituent elements showed very similar results, with minor differences between samples likely the result of analytical variability (data not shown). Amounts of amorphous material as measured by AOX extraction were similar between the different treatments and in contrast to the other minerals discussed, consistently slightly higher than that in the original sample.

### 7.3.5 Clay Mixture

The concentrations of selected constituents in solutions equilibrating with the clay mixture at the beginning and end of the experiment are shown in Table 7.12. Generally, the concentrations of Si, Al, Mg, and Fe reflect the proportion of each mineral present in the mixture. For example, Fe concentrations in the 50% montmorillonite mixture on both day 1 and day 365 are about half as much as

Table 7.10. Mean concentrations of selected elements in solutions equilibrating with chlorite at the beginning and end of the experiment. Values in brackets are standard deviations for replicated analyses.

| Solution | Sampling Date | pH | Si | Mg |
|---|---|---|---|---|
| | | | mg L$^{-1}$ | |
| A | Day 1 | 10 | 1.4 (±0.30) | 15.7 (±0.4) |
| | Day 454 | 10 | 1.4 (±0.03) | 12.6 (±0.7) |
| B | Day 1 | 8.3 | 1.6 (±0.06) | 5172 (±70) |
| | Day 454 | 8.2 | 1.6 (±0.04) | 9763 (±38) |
| C | Day 1 | 9.6 | 0.93 (±0.04) | 1.5 (±0.2) |
| | Day 454 | 8.9 | 1.1 (±0.02) | 8.0 (±0.8) |
| D | Day 1 | 9.1 | 0.56 (±0.02) | 2.3 (±0.2) |
| | Day 454 | 8.7 | 1.1 (±0.01) | 19.2 (±0.7) |
| E | Day 1 | 9.0 | 0.64 (±0.05) | 2.3 (±0.1) |
| | Day 454 | 8.6 | 1.0 (±0.03) | 22.0 (±0.3) |

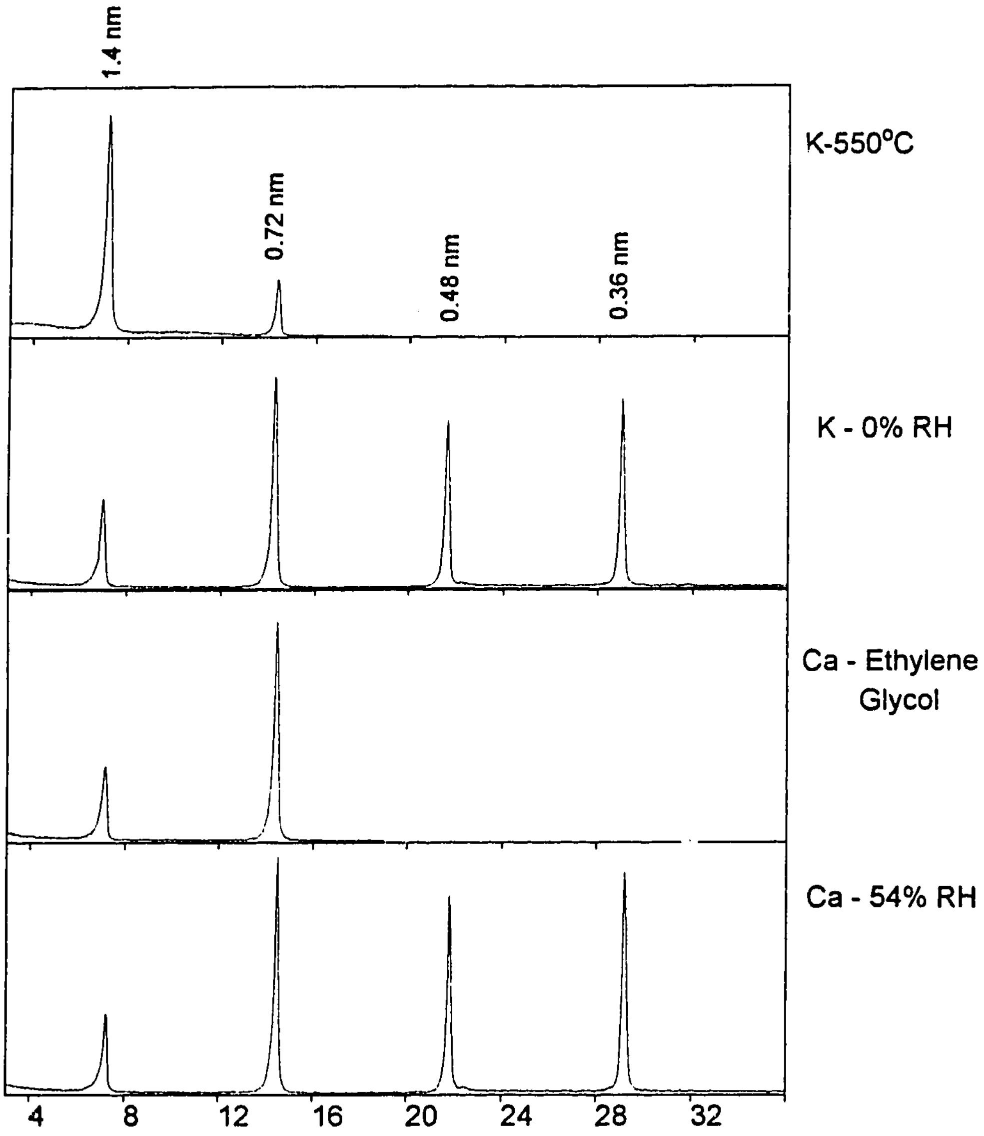

Fig 7.6. X-ray diffractograms of chlorite equilibrated in solution A for 454 days.

Table 7.11. Mean cation exchange capacities and concentrations of Fe, Al and Si extracted by acid ammonium oxalate for chlorite equilibrated for 454 days in different solutions. Values in brackets are the standard deviations of replicated analyses.

| Solution | CEC cmol kg$^{-1}$ | AOX extractable | | |
|---|---|---|---|---|
| | | Al | Si | Fe |
| | | g kg$^{-1}$ | | |
| A | 7.0 (±0.3) | 7.8 (±0.4) | 5.3 (±0.6) | 6.6 (±0.5) |
| B | 2.5 (±0.1) | 8.2 (±0.1) | 5.5 (±0.2) | 6.6 (±0.1) |
| C | 2.9 (±0.1) | 8.3 (±0.5) | 5.4 (±0.1) | 7.0 (±0.1) |
| D | 2.4 (±0.1) | 7.6 (±0.0) | 5.3 (±0.2) | 6.9 (±0.2) |
| E | 2.7 (±0.1) | 8.7 (±0.1) | 5.6 (±0.2) | 7.7 (±0.1) |

Table 7.12. Mean concentrations of selected elements in solutions equilibrating with the clay mixture at the beginning and end of the equilibration experiment. Values in brackets are standard deviations of replicate analyses.

| Solution | Sampling Date | pH | Si | Al | Mg | Fe | K |
|---|---|---|---|---|---|---|---|
| | | | | | mg $L^{-1}$ | | |
| A | Day 1 | 10 | 3.0 (±0.2) | 0.45 (±0.03) | 15.7 (±1.6) | nd$^z$ | 228 (±6) |
| | Day 365 | 10 | 2.8 (±0.2) | 0.38 (±0.02) | 6.6 (±0.2) | nd | 419 (±20) |
| B | Day 1 | 7.8 | 4.2 (±0.2) | 0.02 (±0.02) | 5190 (±126) | nd | 1626 (±14) |
| | Day 365 | 7.5 | 2.2 (±0.2) | nd | 12860 (±2790) | nd | 2640 (±333) |
| C | Day 1 | 9.2 | 4.3 (±0.4) | 0.37 (±0.01) | 8.5 (±1.2) | 0.86 (±0.08) | 1.8 (±0.3) |
| | Day 365 | 8.9 | 7.4 (±0.2) | 0.97 | 58 | 11 | 7.9 |
| D | Day 1 | 9.4 | 6.7 (±0.3) | 0.66 (±0.04) | 14 (±0.6) | 1.3 (±0.04) | 0.88 (±0.24) |
| | Day 365 | 8.8 | 9.4 (±0.1) | 2.5 (±0.2) | 171 (±0.3) | 24 (±3.0) | 112.8 (±1.0) |
| E | Day 1 | 9.4 | 7.6 (±0.4) | 1.2 (±0.2) | 14 (±0.1) | 1.5 (±0.03) | 1.0 (±0.3) |
| | Day 365 | 8.8 | 10.2 (±0.2) | 2.4 (±0.2) | 114 (±19) | 33 (±1.1) | 10.7 (±1.2) |

$^z$ not detectable

solutions containing 100% montmorillonite. It was assumed that the muscovite component would be the only source of soluble K. Although initial K release is lower than that seen in muscovite-containing solutions, comparison of concentrations at the end of the experiment shows amounts of K in solutions D and E are actually higher than those seen for pure muscovite, even though the mixture contained one fifth the amount. Final potassium concentrations in solution C containing the clay mixture were about half of that seen for pure muscovite, while K concentrations in solution A mixtures were only slightly lower.

After 365 days of equlibration, a small amount of < 0.2 $\mu$m particles were present in all samples. The fine clay was composed primarily of montmorillonite, with trace amounts of kaolinite and muscovite in some samples. No chlorite was detected in this size fraction. X-ray diffraction analysis of the > 0.2 $\mu$m particles showed characteristics similar to the original sample but with slightly less montmorillonite. Fine montmorillonite from mixtures equilibrating with solution A again showed unusual intergrade characteristics virtually identical to those reported previously for pure montmorillonite, except that this time calcite was clearly identified as a diffraction peak at 0.303 nm. No changes were noticed in the characteristics of the > 0.2 $\mu$m fraction equilibrated in solution A (Fig. 7.7).

Cation exchange capacity measurements of the < 0.2 $\mu$m particles confirmed that this size fraction was composed primarily of montmorillonite, with a CEC of approximately 115 cmol kg$^{-1}$. Cation exchange capacities of the > 0.2 $\mu$m particles ranged from 49 to 57 cmol kg$^{-1}$, confirming the predominance of non-expanding phyllosilicates in this size fraction.

## 7.4 DISCUSSION

Mineral weathering characteristics observed during the experiment were seen to vary both with the mineral species and the characteristics of the equilibrating solution. In terms of constituent release to solution, montmorillonite was the most reactive of the clay minerals investigated, likely because of its very high surface area in relation to the other minerals. Of the non-expanding phyllosilicates, muscovite was the most reactive, with steady dissolution of interlayer K (see appendix) and higher amounts of Si dissolved than chlorite. Soluble concentrations of some constituents, such as K in muscovite-containing solutions and Fe and Mg in montmorillonite-containing solutions, were still steadily

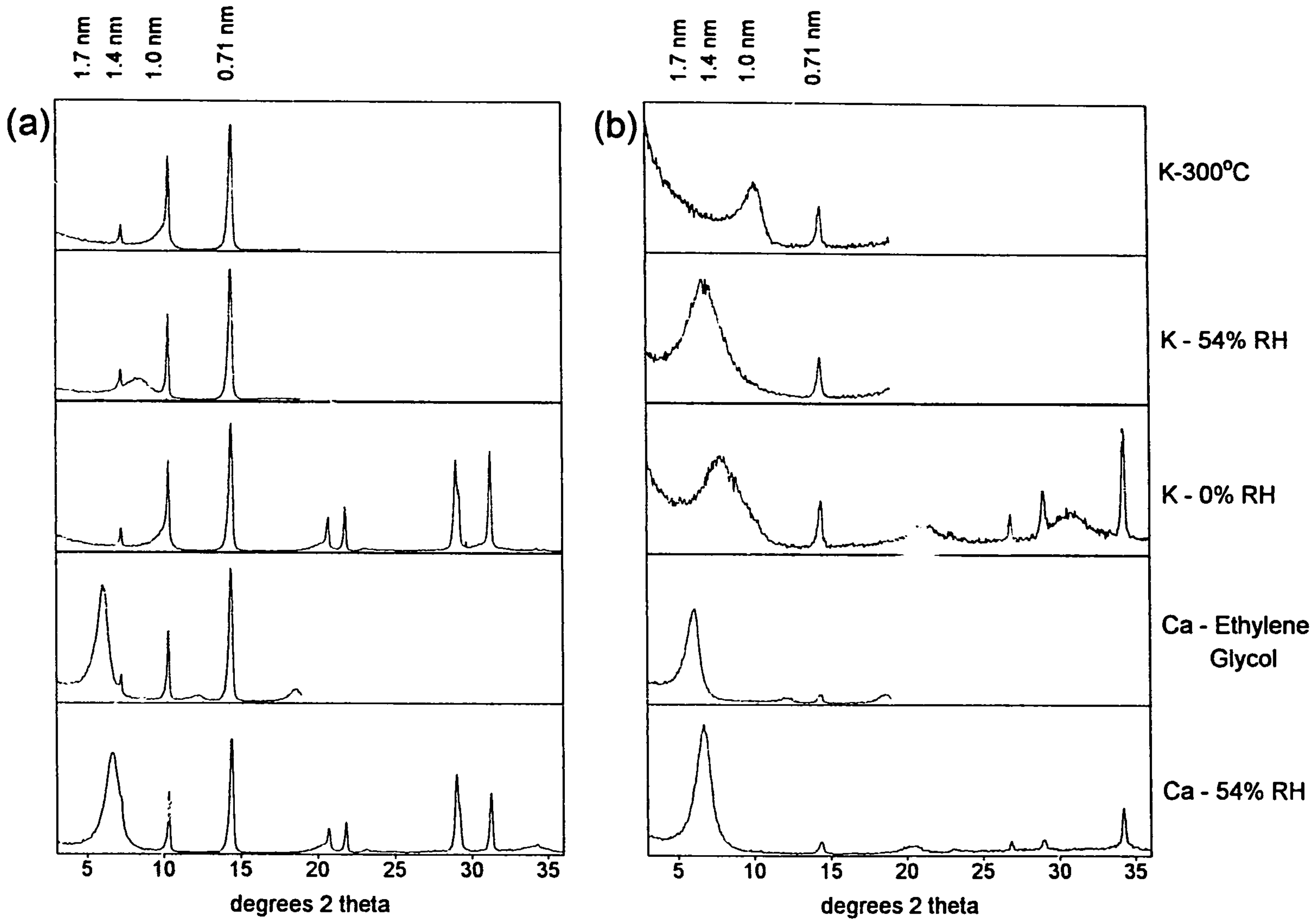

Fig. 7.7. X-ray diffractograms of the (a) > 0.2 μ fraction and (b) < 0.2 μm fraction of the clay mixture equilibrated for 365 days in solution A.

increasing at the end of the experiment (see appendix), indicating that steady-state conditions had not yet been attained.

The low or undetectable Al concentrations observed in many equilibrating solutions were not unexpected because Al solubility is expected to be low at near neutral pH values, largely because of formation of $Al(OH)_3$. For example, within hours of starting muscovite dissolution experiments, Lin and Clemency (1981) noted that solutions were saturated with gibbsite and that Al concentrations were controlled by pH and gibbsite solubility. Higher soluble Al concentrations were expected in pH 10 solution A samples because of the formation of $Al(OH)_4^-$; this behavior was in fact only noted for kaolinite and muscovite samples. In addition to appearing in solution, Al which is released from the clay mineral may also precipitate on the mineral surface or in a newly formed solid phase. In the case of montmorillonite, dissolved Al may precipitate in the interlayer region.

There were often striking differences in cation release when the same mineral was equilibrated in different solutions. Montmorillonite appeared to be the most stable in solutions of high ionic strength and dissolved to a much greater degree when placed in solutions with few dissolved constituents. Dissolution was also greatest at lower pH in solutions of comparable ionic strength. For example, cation release was generally lowest in solutions A and B, intermediate in solution C and highest in solutions D and E. Distilled water leaching of Na-saturated montmorillonite has previously been reported to dissolve considerable amounts of the mineral, lower cation exchange capacity and charge density and release high amounts of Mg and Si (Bar-on and Shainberg, 1970). In this experiment, Na-hydrolysis evidently occurred in solutions D and E as marked by a rapid increase in pH for all minerals except kaolinite (see appendix), but because of the poor buffering capacity of these solutions the effect appeared to be only short term.

Based on soluble Si levels, kaolinite also showed the greatest stability in solutions with the highest ionic strength and pH, with Si concentrations consistently lowest in solution A and highest in solution E. Generalizations regarding the stability of muscovite and chlorite in high ionic strength solutions are difficult to make since the release of different constituents showed opposite trends in the same solution. In muscovite samples, the highest soluble Si concentrations and lowest K concentrations were measured in solutions with the lowest ionic strength and pH. Chlorite also showed inconsistent patterns of cation release with solution type with distilled water samples having the lowest Si concentrations but relatively high amounts of Mg. This would imply that for chlorite, tetrahedral Si was released in preference to components of the interlayer hydroxide sheet under conditions of high ionic strength and moderately alkaline pH values.

Different concentrations of different mineral constituents were often noted in the same solutions. For example, soluble Si concentrations were normally lower than those of the other constituents measured, despite generally being the predominant element in the mineral. Comparison of the relative molar proportions of constituents released to solution with the proportions in the mineral suggest that either non-stoichiometric dissolution was occurring in many samples or that some elements dissolved from the mineral such as Si and Al subsequently reprecipitated. This is most noticeable in montmorillonite samples, which had much higher soluble concentrations of Mg and Fe than Si or Al, with the greatest differences at the end of the experiment. This may indicate a preferential dissolution of the octahedral sheet or greater precipitation of released Si and Al in solutions of low ionic strength. Initial incongruent dissolution of silicates is widely recognized, but is expected to become congruent as dissolution reactions proceed (Xie and Walther, 1992). The differences in solute activity ratios in equilibrating solutions from that of the chemical composition of the bulk sample may also be due to different compositional subgroups, such as those along crystal edges or faces, or to the dissolution of another non-detectable solid phase (Rosenberg *et al.*, 1984).

It is generally accepted that K will be released from muscovite when solution concentrations are below a critical value (Fanning *et al.*, 1989). Alternatively, in solutions of high soluble K content, release of structural K from micas is not expected. In this experiment, K is released to all solutions, even solutions A and B which initially contained 200 and 1400 mg $L^{-1}$ respectively. While ion-pairing in the brines will reduce the activity of $K^+$ to some extent, K release is still surprising under these conditions. The observation of K release in all solutions is confirmed by increases in CEC and by the analysis of dissolved muscovite, in which K content is similar in each equilibrated sample and lower than that of the starting material.

To some extent, changes in physical or chemical characteristics were detected for every mineral sample and largely depended upon the type of equilibrating solution. The observation of particles $< 0.2$ $\mu$m in many samples implies that either precipitation of solids from solution or a reduction in particle size occurred over a year or more. Fine muscovite particles were previously noted to occur after two year solubility experiments, and were attributed to physical breakdown of larger crystals (Mattigod and Kittrick, 1979). This fine clay fraction generally appeared to be less crystalline and enriched in amorphous materials as compared to the starting sample and the coarser size fractions.

Changes in CEC as a function of the type of equilibrating solution were noted for all minerals except montmorillonite, which had similar CEC's in all samples. Since CEC is considered a material constant for smectite clays as a result of isomorphous substitution, it would not be expected to change with decreasing particle size but only with a fundamental change in the mineral structure.

Increases in CEC were generally noted for non-expanding phyllosilicates which had been equilibrated in solutions of high ionic strength. The source of the CEC of kaolinite is somewhat controversial, and has been suggested to be the result of ionic substitution (Bollard *et al.*, 1976), to arise from exposed SiOH- and -AlOH sites (Ferris and Jepson, 1975), or to be the result of expandable mineral impurities (Lim *et al.*, 1980). None of these reasons appear likely for the increased CEC noted for kaolinite equilibrated in solution A, which may instead be due to the deprotonation of hydroxyl sites along crystal edges. Enhanced negative charge of kaolinite surfaces due to deprotonation at pH values above 9 has previously been noted (Xie and Walther, 1992).

An increase in the CEC of chlorite was noted only for samples equilibrated in solution A, and is again speculated to be the result of deprotonation of hydroxyl groups. Chlorite has previously been shown to develop a small pH-dependent negative charge after acid treatment which is thought to result from broken particle edges and exposed hydroxyl groups (Jones, 1981). Cation exchange capacities for chlorite have been reported to be largely dependent upon the completeness of the hydroxide interlayer sheet (Barnhisel and Bertsch, 1989), but solution analyses do not indicate that the interlayer sheet weathered to any extent. The CEC of micas is expected to increase as unhydrated interlayer cations are replaced with exchangeable cations (Fanning *et al.*, 1989). A higher CEC was measured for all equilibrated muscovite samples, with increasing soluble K levels over time supporting the hypothesis that replacement of interlayer K was the major mechanism for the increase in exchange capacity.

The amount of amorphous material in the samples at the end of the experiment varied considerably with the mineral species. The amount of amorphous material in montmorillonite increased slightly only in those samples equilibrated in solution A. Given that the solubility of Al, Si and Fe are expected to increase sharply at pH 10, this is the opposite behavior than what was expected. Higher amounts of AOX-extractable material in equilibrated chlorite samples suggests that at least a portion of Si, Al and Fe released from the mineral was precipitated as poorly ordered solids. Lower amounts of amorphous material were noted for muscovite and kaolinite samples after equilibration. It is likely that some of the Al and Si detected in the equilibrating solutions over time originated from the amorphous material rather than from the crystalline clay. It also indicates that the Al, Fe and Si that did dissolve likely did not reprecipitate as non-crystalline phases. The different trends in relative loss or gain of amorphous material seen between different minerals in similar solutions are unexpected and may be due to dissimilarities in the character of the AOX-extractable material, minor differences in solution conditions or may a function of the dissolution process specific to each mineral.

Saturation indices (SI) for the clay minerals in the study were calculated from solution compositions at the beginning (day 1) and end of the experiment (Fig. 7.8):

$$SI = \log (IAP/K_{sp})$$

where IAP is the ion activity product and $K_{sp}$ is the equilibrium solubility product; values were calculated using SOLMINEQ (Kharaka *et al.*, 1988). The activity of $Fe^{3+}$ in solutions with concentrations below detection limits were assumed to be controlled by amorphous $Fe(OH)_3$ (Lindsay, 1979). Because of the great variability in thermodynamic constants, particularly for variable-composition phyllosilicates, a range of $K_{sp}$ values from the literature were added to the SOLMINEQ database. Stability constants for illite and beidellite were also added for comparison. Since the composition of minerals in this study were not precisely the same as those for which stability constants were determined, comparison of experimental ion activity products to cited $K_{sp}$ values allowed only a rough estimation of mineral stability in the weathering environments.

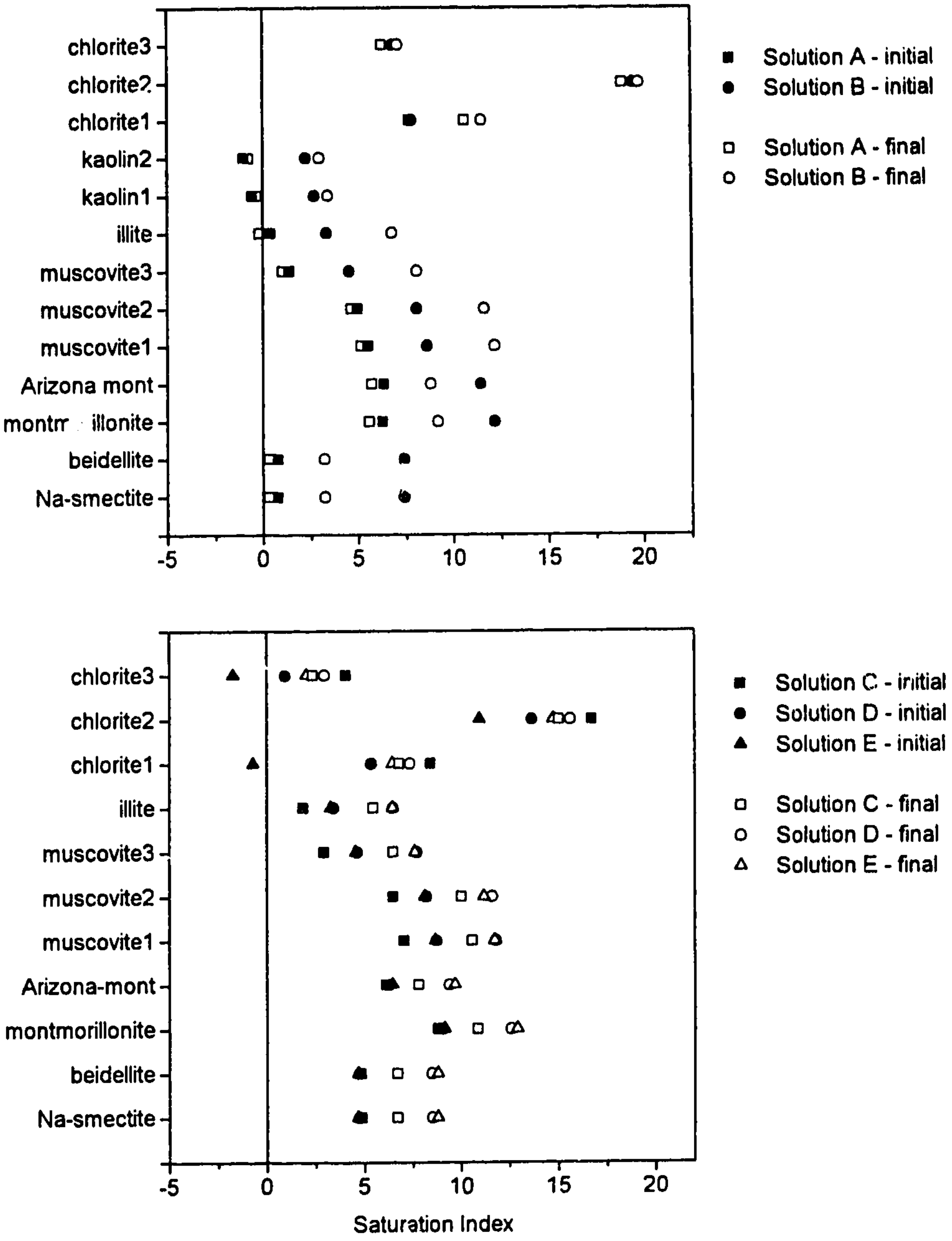

Fig 7.8. Saturation indices of mineral species calculated from inital and final solution compositions. Log $K_{sp}$ values used for Na-smectite, muscovite 1, kaolinite 1 and chlorite 1 are from Kharaka et al. (1988), for beidellite, mg-montmorillonite, and muscovite 3 are from Lindsay (1979), values for muscovite 3, kaolinite 2 and chlorite 3 are from Rai and Lindsay (1975) and values for Arizona montmorillonite from Tardy and Fritz (1981).

Figure 7.8 shows that in the high ionic strength solutions A and B, the trend in solution characteristics was generally towards equilibrium (mineral SI became less positive). In the low ionic strength solutions C, D and E, systems generally moved away from equilibrium, with mineral SI becoming increasingly positive over time, the result of the steady increase in soluble concentrations of constituent ions. The numerical values vary considerably depending upon the $K_{sp}$ value used but show similar trends. Except for kaolinite in solution A and chlorite in solution E, solutions were supersaturated with respect to the relevant mineral species after 1 day. After 454 days, montmorillonite SI became less positive in solutions A and B, while solutions C, D and E became increasingly supersaturated. Saturation indices for muscovite increased over time in all solutions except for solution A in which a slight decrease was noted. Chlorite containing solutions moved away from equilibrium except for solution C in which SI values decreased after 454 days. Kaolinite was slightly less unstable in solution A after time, and became increasingly supersaturated in solution B. Kaolinite stability was not modelled in the low ionic strength solutions because the Al concentrations were below detection limits during the experiment.

It was expected that over the period of the experiment, the direction of change in solution characteristics would be towards equilibrium with a given mineral. The trend away from equilibrium for many minerals as indicated by increasingly positive SI values may imply that mineral dissolution is not controlled solely by equilibrium processes. Although the log $K_{sp}$ values used in the calculation of SI values are likely inaccurate to some degree because of the differences in chemical composition of the minerals used, this should not result in the major discrepancies seen in solution evolution.

Essential features of calculating the standard free energy of formation of minerals by the solubility method are that: equilibrium solution conditions are attained or at least approached during the experiment, the mineral has not altered its composition from that of the original material and that a valid equation can be written for the dissolution reaction. It is unlikely that any of these conditions were attained in this experiment. Solution concentrations at the end of the experiment were still steadily increasing for many mineral/solution treatments (see appendix), indicating that equilibrium had not been reached. Different solution concentrations of mineral constituents implies that the composition of the mineral was altered over the course of the experiment, introducing further error into the attempt to derive the standard free energy of formation for the starting sample. Generally, equations that are written for aluminosilicate dissolution (*eg*. Kittrick, 1971) show that Al released from the mineral is present in solution as $Al^{3+}$. In this experiment, and under conditions found in most soils, it is unlikely that any or all of the dissolved Al is present as $Al^{3+}$ because of the changes in Al speciation with pH. Under alkaline conditions, tetrahedral $Al(OH)_4^-$ is expected to be the dominant Al species in solution. An appropriate dissolution reaction for montmorillonite under highly alkaline conditions, simplified by assuming that released Al and Si do not precipitate, may be:

$$[(Si_{3.94}Al_{0.06})(Al_{1.11}Mg_{0.76}Fe_{0.08})O_{10}(OH)_2]^{0.31-} + 8.68\ H_2O + 1.32\ H^+ =$$
$$3.94\ H_4SiO_4 + 1.17\ Al(OH)_4^- + 0.76\ Mg^{2+} + 0.08\ Fe(OH)_3$$

Realistically however, particularly under conditions found in most soils, at least partial precipitation of dissolved constituents can be expected. For example, the products of montmorillonite dissolution will potentially include gibbsite or amorphous $Al(OH)_3$, amorphous silica and amorphous or poorly ordered aluminosilicates, as well as iron oxides or hydroxides and soluble components, with soluble Al likely present primarily as $Al(OH)_4^-$ and $Al(OH)_2^+$ species. It is therefore difficult to write a single valid reaction for the dissolution of clay minerals in a variety of soil systems because of the effects of pH and other solution constituents on speciation and precipitation of the reaction products. In this experiment for example, a brief analysis of the results of montmorillonite equilibration show that at the end of 454 days, different log $K_{sp}$ values could be calculated for each of the five equilibrating solutions because of different concentrations of soluble constituents. This may be at least in part due to different dissolution reactions occurring in chemically different solutions. The dependence of calculated equilibrium constants on the type of equilibrating solution has been previously noted for beidellite equilibrated in dissimilar solutions (Misra and Upchurch, 1976).

It is doubtful that accurate standard free energies of formation could be calculated from solubility experiments conducted under conditions similar to those found in soils because of the problems outlined above in attaining equilibrium, possible changes to the composition of the starting mineral over time and in writing accurate dissolution equations. A single dissolution reaction is not likely to be appropriate for different soil systems. The prediction of mineral stability in soils using thermodynamic geochemical models may therefore be invalid, since they generally utilize simple dissolution reactions with aqueous products and standard free energies of formation derived from solubility experiments conducted under extreme chemical conditions. A simple improvement could be obtained if the fate of dissolved Al and Si (precipitated vs soluble) at various pH values could be incorporated into model dissolution reactions.

## 7.5 CONCLUSIONS

Dissolution of clay minerals was found to vary considerably depending upon the chemistry of the equilibrating solution. Montmorillonite was the most stable in solutions of high ionic strength and pH, with the greatest release of constituent ions to distilled water. Muscovite released the largest amounts of Si in distilled water but considerable amounts of K were dissolved in all solutions, even those of high initial K concentration. In solutions equilibrating with chlorite, the highest Si and lowest Mg levels were measured in pH 10 brines. Dissolution of many samples was observed to be non-stoichiometric, with greater amounts of interlayer or octahedrally coordinated cations released relative to Si. Comparison of soluble constituent concentrations at the end of the experiment indicates that montmorillonite was generally the most reactive of the minerals studied, followed by muscovite, chlorite and kaolinite. Kaolinite samples were relatively unreactive, with Si concentrations in distilled water and pH 10 brines consistently less than 5 and 1 mg $L^{-1}$, respectively, over the duration of the experiment, and Al levels usually below detection limits. A physical mixture of these minerals showed dissolution characteristics which reflected the proportion of each individual mineral in the sample except for slightly higher K release rates.

Some changes in mineral characteristics after a year or more were noted for all samples. Although the experiments were conducted on mineral samples > 0.2 $\mu$m in diameter, finer particles were noted at the end of the experiment for at least some treatments for all minerals except chlorite. The fine fraction from muscovite and kaolinite samples was generally similar in XRD characteristics to the coarser particles except for a slight decrease in crystallinity. The greatest quantity of fine material was found in montmorillite samples, with montmorillonite equilibrated in pH 10 brine for 454 days showing marked alteration of XRD characteristics due to the formation of a heat and acid unstable interlayer material. Increases in CEC were detected for non-expanding phyllosilicates equilibrated in pH 10 brine, and was likely the result of deprotonation of surface or edge hydroxyl groups. No consistent trend was seen in the amount of amorphous material for each mineral after equilibration, with greater quantities of AOX-extractable material in chlorite samples, and lower amounts in muscovite and kaolinite samples.

Solution concentrations for many mineral/solution treatments were still increasing at the end of the experiment, indicating that equilibrium conditions had not been attained. Comparison of mineral SI values calculated on day 1 and at the end of the experiment showed that in many cases, SI values became increasingly positive, moving away from the expected equilibrium solution conditions. Changes in solution characteristics interpreted to be towards equilibrium (SI became less positive) were seen only for montmorillonite equilibrated in saline brines and for chlorite in a low ionic strength solution of pH 8.9. It is unlikely that accurate $\Delta G_f$ values can be derived from solubility experiments conducted under condition similar to those found in soils because of the difficulty of writing a valid dissolution equation which accounts for the uncertainty of the reaction products in different chemical environments. The prediction of clay mineral stability in complex soil environments using simple thermodynamic models may therefore be inappropriate.

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# 8. GENERAL DISCUSSIONS AND CONCLUSIONS

The results of the investigations described in detail in the previous six chapters provide fundamental information regarding the chemistry of saline soils in Alberta, and provide some insight into the mineral weathering processes occurring under conditions of high ionic strength and alkalinity. Each individual chapter was intimately related by the characteristics of the soil solution. For example, the evaporite minerals present in salt efflorescences investigated in Chapter 2 primarily reflect the composition of the evaporating soil water and the relative stability and alterations of clay minerals (Chapters 4 and 6) can be expected to largely be controlled by the characteristics of the aqueous phase. The chemical and stable isotopic properties of the soil solution also play a role in elucidating the formation of authigenic minerals such as dolomite (Chapter 5). The solutions used in the equilibration of standard clay minerals in Chapter 7 were designed to mimic the chemistry of porewater from two saline soils investigated in Chapter 3 and clarify the effects of salinity and alkalinity under a controlled environment.

The results from the general survey of trace element chemistry and evaporite mineralogy of salt-affected soils in Alberta show that marked variability in characteristics are present. While the mean concentrations of elements other than Br and Cl in salt efflorescences and underlying soils fall within the ranges previously reported for soil material, levels of potentially toxic elements in some locations may be high enough to adversely affect future land use. The mineralogy of Alberta salt crusts is dominated by sodium and magnesium sulfates but also contains many other evaporite minerals. The highly transient nature of salt efflorescences makes analysis difficult, and the results can be expected to vary seasonally and even perhaps diurnally as climatic conditions change.

Four salt-affected soils from the above survey that varied geographically, chemically and mineralogically were selected for detailed analysis. Solutions extracted from these soils by immiscible displacement and saturated paste extracts had electrical conductivities ranging from 6 to 45 dS $m^{-1}$. The cation suite was dominated by Na, with Mg and K concentrations varying by several orders of magnitude between sites. Calcium was the major cation in lowest abundance in all locations. Sulfate was the predominant anion, with chloride often second in abundance. Amounts of Al and Si were lower than typically found in soil solutions, despite pH values up to 10.6. Considerable variation was seen between the properties of saturated paste extracts and immiscibly displaced solutions, often leading to very different results for sodium adsorption ratios, speciation and prediction of mineral stability.

A preliminary survey of the clay mineralogy of the 50 surface soils studied in Chapter 2 showed marked smectite degradation in many locations. Subsequent analysis showed that this apparent degradation was the result of interactions with organic matter or the result a heat unstable smectite interlayer material. After treatment to remove carbonates with dilute acid, typical smectite diffraction maxima were seen. After traditional pretreatments, the clay mineralogy of salt-affected soils was found to be similar to that of non-saline soils. Slight changes were sometimes noted in X-ray diffraction maxima of the smectite minerals, indicating lower crystallinity and both low charge and high charge characteristics.

Subsequent detailed analysis of smectite layer charge density showed that the mean layer charge of clays from saline soils was lower than that previously reported for non-saline soils. The layer charge was found to vary inconsistently with location, depth and particle size. The charge distribution was also heterogeneous, with a considerable proportion of high charge layers in some samples, and a high proportion of low charge layers in other. The addition of alkylammonium compounds to some clay fractions resulted in the disappearance of smectite diffraction maxima. This phenomenon is similar to that noted in Chapter 4 which occurs as the result of interaction with naturally occurring organic matter and implies unusual charge characteristics which prevent diffraction from occurring.

More than half of the clay fraction at one saline soil was composed of well-ordered, stoichiometric dolomite. Stable isotope and radiocarbon analysis showed that the dolomite was authigenic, or secondary, in origin, with an average age of approximately 3260 years. The mineral likely formed as a direct precipitate from the soil solution. It has previously been accepted that dolomite does not form in soils.

One of the primary conclusions reached after the investigation of saline soils in Alberta was that no sweeping generalizations about their nature can be made. Although united by the bond of high salinity, poor drainage and minimal pedogenesis, the specific chemical and mineralogical characteristics of each location varied greatly.

The results from the laboratory controlled dissolution studies provide many insights into weathering processes and relative stability of minerals under specific conditions. The dissolution of clay minerals was found to vary considerably depending on both the characteristics of the mineral and the equilibrating solution. Montmorillonite was the most reactive of the minerals studied, followed by muscovite, chlorite and kaolinite. This would imply that in soils, the greatest changes should be noted for the smectite fraction.

Montmorillonite was the most stable in solutions of high ionic strength and pH in terms of constituent release but formed an acid and heat unstable intergrade-mineral, similar to that seen in a saline soil investigated in Chapter 4. Curiously, the soil from which the highly saline and alkaline equilibrating solution was duplicated did not show this characteristic.

Muscovite showed release of interlayer K in all solutions, even brines containing considerably quantities of soluble K. These results were confirmed by increasing CEC and decreasing K content of all muscovite samples and suggest that weathering to hydrous mica, especially in fine particles, may occur in all saline soils regardless of solution characteristics. Broadened mica peaks were, in fact, detected in soil clay fractions, with fine clay fractions showing the lowest [illegible]y. Chlorite and kaolinite showed only minor release of constituent ions [illegible] equilibration experiments and essentially no change in mineral characteristics. [illegible] observations are confirmed by the investigation of saline soil samples in Chapter 4, in which weathering of kaolinite and chlorite minerals was not observed.

The equilibration experiments did not reach steady-state conditions after a period of a year or more, with soluble concentrations in many mineral/solution treatments still increasing at the end of the experiment. While it was expected that solutions should evolve towards equilibrium conditions, the opposite was frequently observed, with mineral saturation indices increasing at every sampling due to continued cation release. The magnitude and trend of solution changes suggests that mineral dissolution may not be controlled solely by equilibrium processes. It is difficult to say if this occurs in soils as well because of the differences between the systems, primarily in the solid to solution ratios. The presence of dissolved organic species in "real" soils likely also plays a role in mineral weathering.

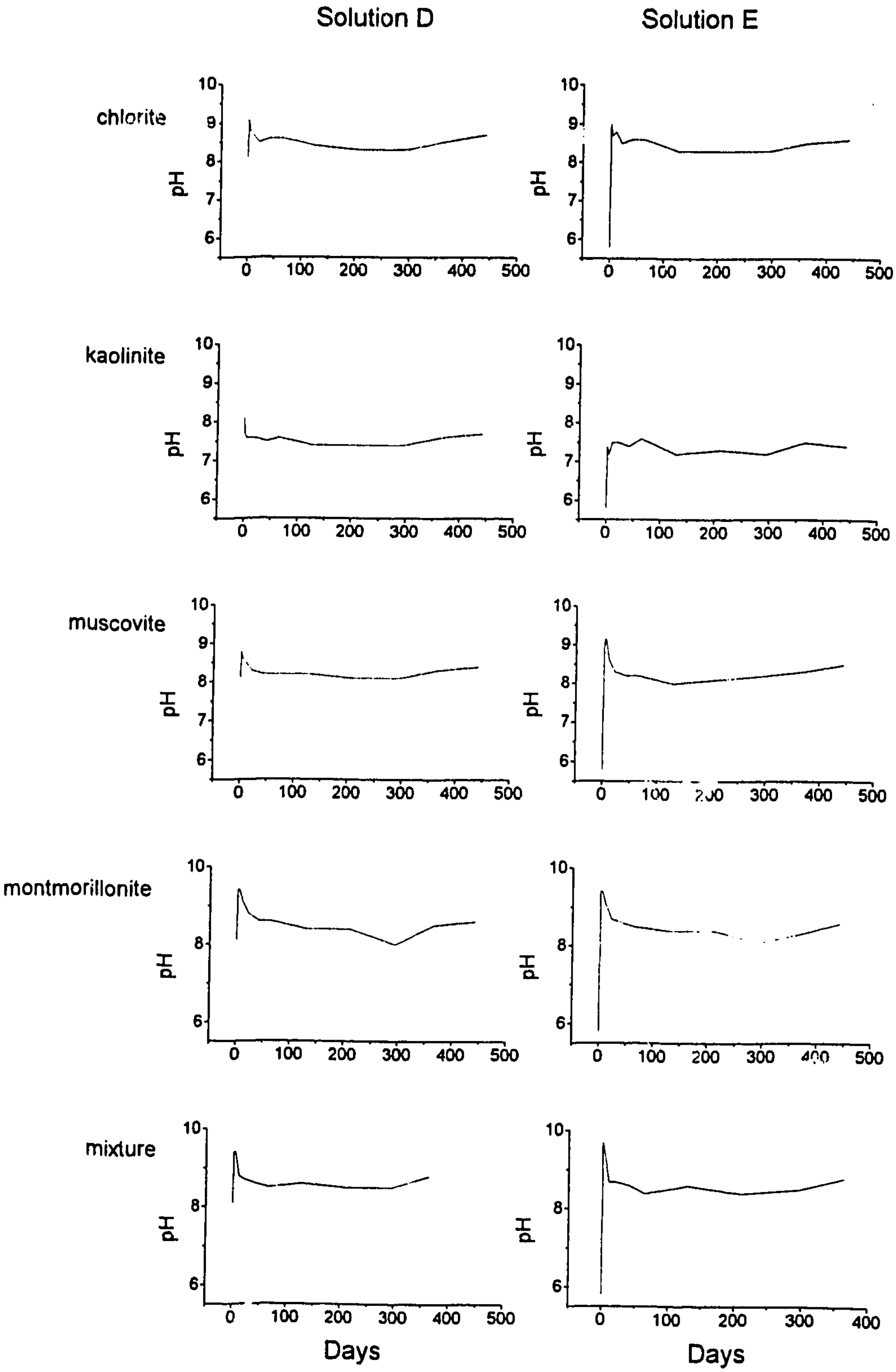
Several observations made from the results of the equilibration experiments raise doubts regarding the use of geochemical models for accurate prediction of mineral stability in soils. For clay minerals, these models frequently use standard free energy of formation values derived from solubility experiments and simple dissolution reactions appropriate only for specific conditions. Previous solubility experiments, particularly for smectites, have been conducted under highly acidic conditions or have added minerals of known solubility. While this simplifies the experimental procedure, it may not reflect the actual dissolution reactions occurring in soil environments. This experiment shows that different thermodynamic constants can potentially be derived from solubility experiments conducted in solutions of different composition and that cation release in mixtures may be different from that found in a pure system. It is difficult to write a single valid reaction for the dissolution of clay minerals in different soil systems because of the expected differences in precipitation and speciation of reaction products. The variable composition and crystallinity of soil minerals also makes prediction of their stability from thermodynamic constants for a single mineral of known composition questionable. For these reasons, the calculated mineral stabilities reported in Chapters 2 and 3 based solely on soil solution composition may be invalid.

Much of the research component of this thesis has been directed at elucidating the effect of salinity and alkalinity on mineral characteristics. While some progress has been made, the research also raises several unanswered questions that could be addressed by future research and may have importance in understanding the behavior of clay minerals both in soils and in industrial applications such as clay liners. One of the recurring questions throughout much of this thesis is "why only in this soil"? A most intriguing and unusual problem seen only in some samples was the interaction of organics with smectite minerals that resulted in the essential disappearance of diffraction maxima. Future research that addresses the specific mineralogical characteristics and properties of the soil solution and organic matter that lead to this phenomenon would be invaluable in understanding the interaction between organics and expanding phyllosilicates. The development and properties of acid and heat unstable smectite interlayer material under some conditions should also be addressed. Again, why does it occur only in some soils? Of the four soils studied in detail, this phenomenon was seen only in the Wainwright soil of relatively low salinity and high pH. In the laboratory dissolution experiments it developed in the high pH brine. Although pH > 9 appears to be a common factor, the pH 10 soil from which the dissolution brine was approximated did not show these characteristics.

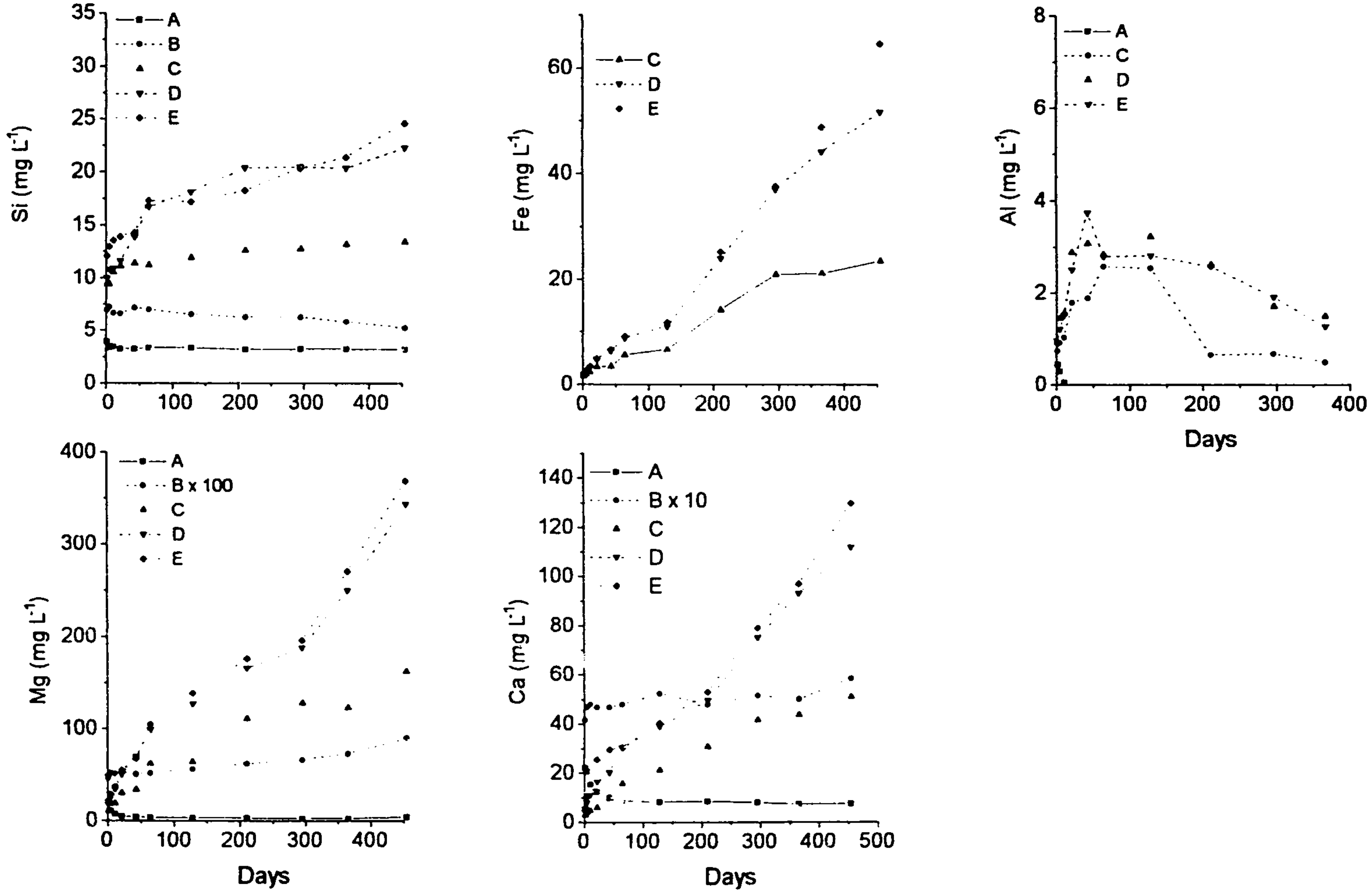
Another area of research interest may be the alteration of smectite layer charge characteristics in systems with alternating or permanently reducing conditions. Results from this thesis suggest that the oxidation state of structural iron may play a major role in determining layer charge characteristics in poorly drained evironments. Investigations of the layer charge characteristics of expanding phyllosilicates of variable iron content, perhaps through analysis after magnetic separation would provide more information. This area may also be clarified by studies that investigate the variation in charge characteristics between soils derived from the same parent material and differing only in drainage, or in laboratory experiments where redox is controlled at various levels.

The authigenic formation of dolomite is another area of special interest to many earth scientists. Studies which address the associations of the dolomite with the mineral matrix (perhaps through the use of thin sections and electron microprobe analsysis, as well as high resolution scanning electron microscopy) will provide valuable information regarding the formation conditions of this mineral. It would also be educational to do studies in adjacent areas to determine if this is an isolated occurrence or is common to this drainage basin.

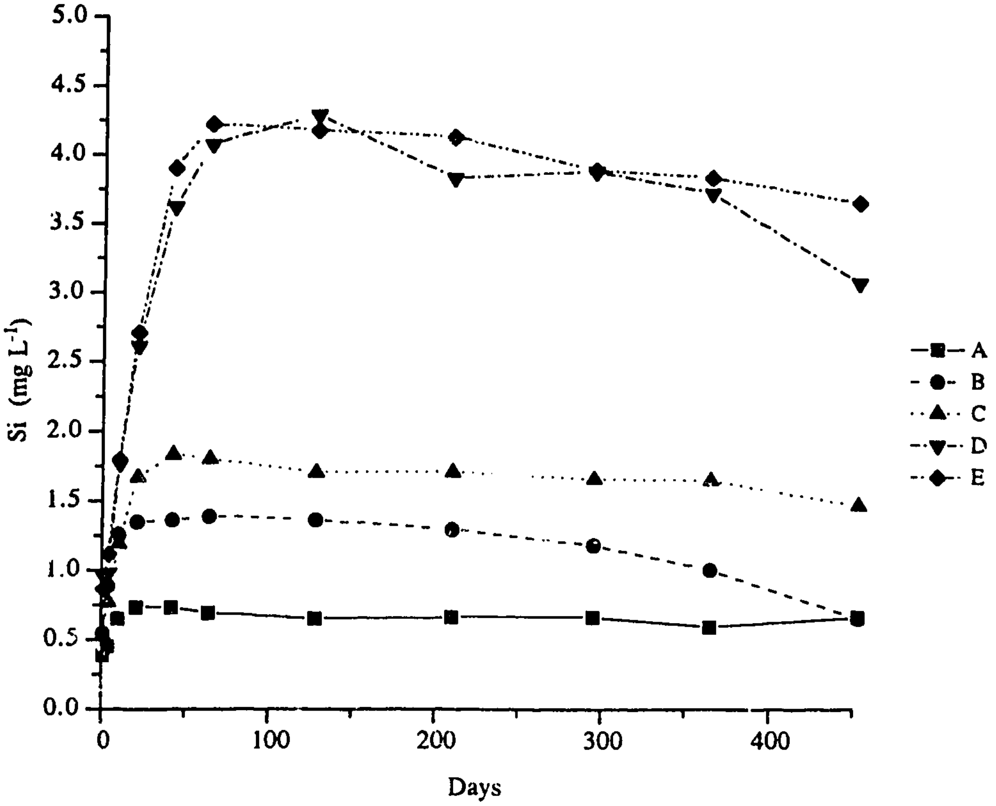
# 9. APPENDIX



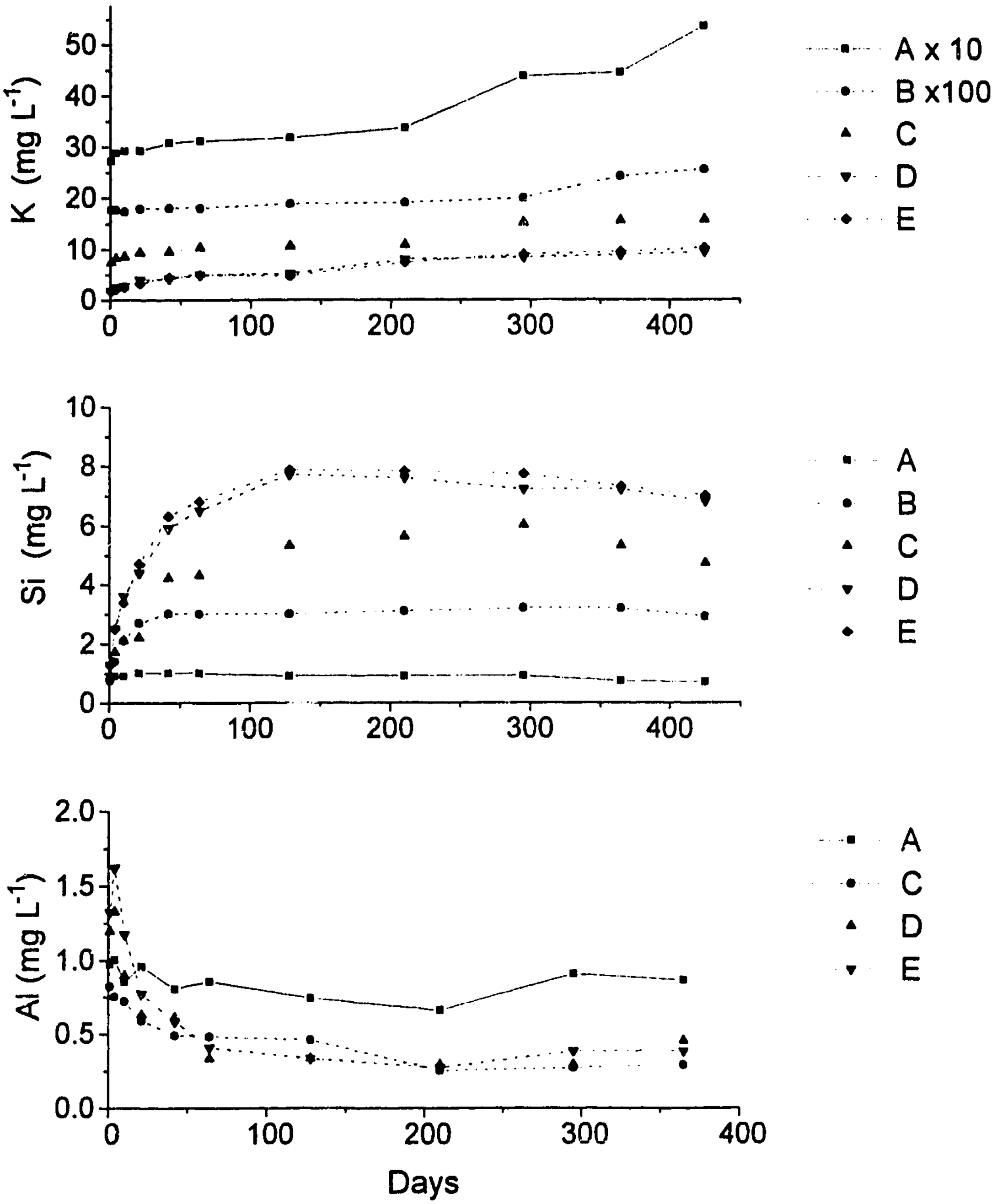
Variation in pH values over time for minerals equilibrated in solution D (distilled water adjusted to an initial pH of 8.1 with $Na_2CO_3$) and solution E (distilled water).



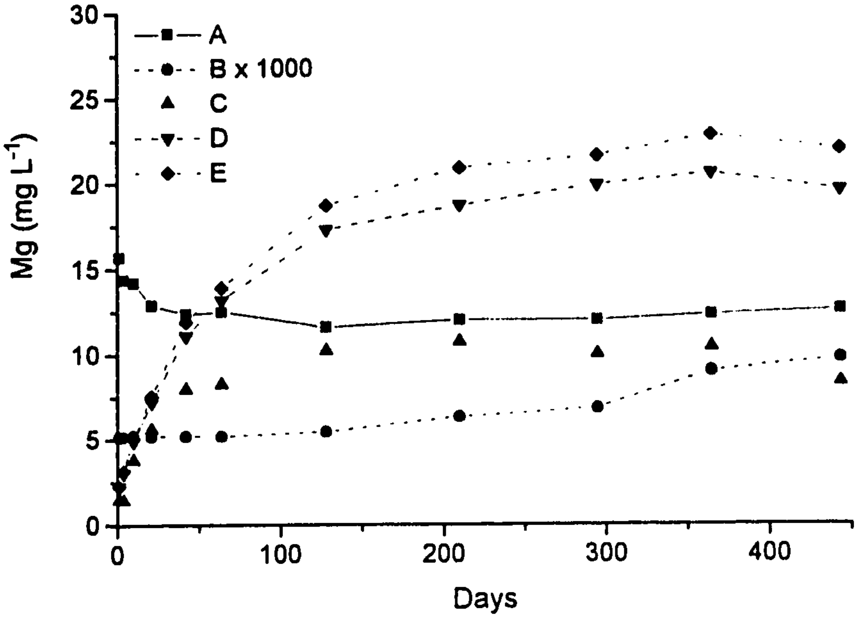
Concentrations of selected constituents in solutions equilibrating with montmorillonite.

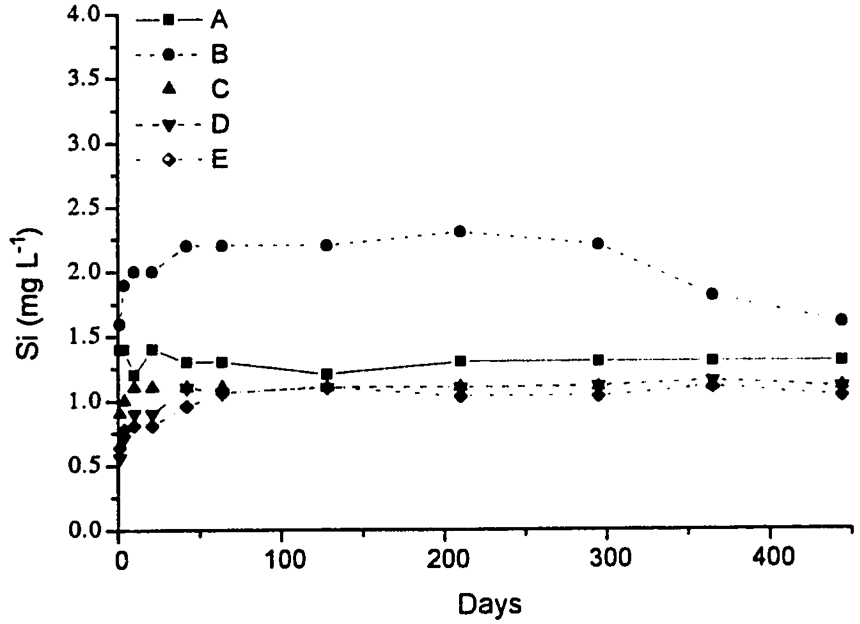


Silicon concentrations in solutions equilibrating with kaolinite.

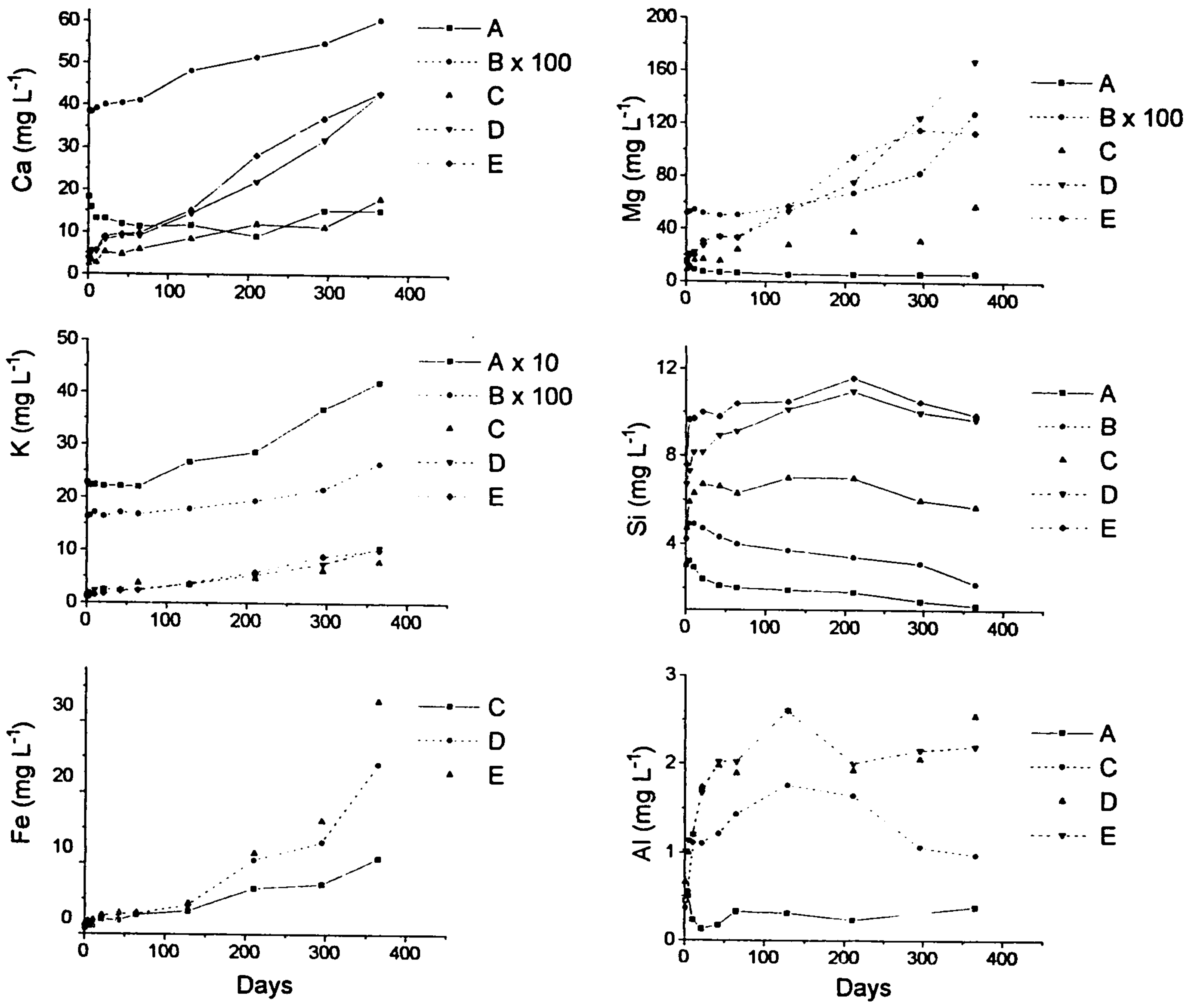


Concentrations of selected constituents in solutions equilibrating with muscovite.





Concentrations of selected constituents in solutions equilibrating with chlorite.



Concentrations of soluble constituents in solutions equilibrating with the clay mixture.