# LAYER CHARGE CHARACTERISTICS OF SMECTITES IN SALT-AFFECTED SOILS IN ALBERTA, CANADA

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**Abstract**—The layer charge characteristics of expanding phyllosilicates in four salt-affected soils in Alberta, Canada were investigated using X-ray diffraction analysis of alkylammonium saturated samples. The layer charge was found to be lower and more heterogeneous than previously reported for non-saline Alberta soils, with the mean layer charge ranging between 0.261 to 0.339 mol $(-)/O_{10}(OH)_2$. Layer charge characteristics varied inconsistently with location, depth and particle size, likely the result of both different origins and weathering processes. Different degrees of K depletion from the micaceous component after equilibration with alkylammonium compounds may also account for some variability between samples. Extreme broadening and essential disappearance of smectite diffraction maxima was noted for some samples after intercalation with alkylammonium cations of all carbon chain lengths, indicating unusual alteration of the layer charge characteristics in some salt-affected soils.

**Key Words**—Layer charge, Salinity, Smectite.

## 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 numerically 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 (e.g., 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 layer charge of smectites in the province is lacking except for work done by Warren *et al* (1992), who calculated 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 using the alkylammonium method.

It is unclear as to 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 (Kohut and Dudas 1994a). 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 investi-

gations of the porewater chemistry in Alberta saline soils (Kohut and Dudas 1994a) 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.

## MATERIALS AND METHODS

Four salt-affected soils, located near Hanna, Nobleford, Provost, and Wainwright, Alberta 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. Salt efflorescences, composed primarily of thenardite ($Na_2SO_4$), were present on the surface at the time of sampling as a result of upward capillary movement of groundwater and its subsequent evaporation. The soils were classified as Typic Cryaquents (Rego Gleysols) because of minimal pedogenesis and saturation during at least parts of the year. Since horizon development was very weak or non-existent, samples were taken approximately every 20 cm unless differences in texture or color were noted.

Particle size distribution and $CaCO_3$ equivalents of the bulk soil samples, and pH and electrical conductivity (EC) of immiscibly displaced soil solutions were determined as described in Kohut and Dudas (1994a). Soil sub-samples were ultrasonified for 3 minutes at 400 W, and the clay fraction ($<2.0\ \mu m$) separated using sedimentation techniques after soluble salts, primarily sodium sulfates, had been removed by repeated deionized water washings and decantations. The $<2.0\ \mu m$ fraction was then further subdivided by centrifugation into coarse ($2$–$0.2\ \mu m$), fine ($0.2$–$0.08\ \mu m$) and very fine ($<0.08\ \mu m$) size fractions (Jackson 1979). The amount of fine or very fine clay was low in many samples and therefore layer charge analysis was only conducted for samples where adequate quantities of the solids could be separated. Samples were treated with sodium hypochlorite to remove organic matter (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.

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 seven pretreatments. 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. 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 for 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 (Thiesen 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 two seconds $step^{-1}$. The relative humidity in the sample chamber was maintained at 0% RH during analysis.

The layer charge characteristics of the soil smectites were examined by analyzing the increase in basal spacings with alkylammonium chain length within the monolayer/bilayer transition range. Monolayer arrangements were recognized by d(001) values of 1.36 nm and bilayer arrangements indicated by d(001) values of $>1.77$ nm. 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 chain lengths using peak migration curves as described by Lagaly (1981). The weighted mean values for the smectite layer charge were then calculated based on the resulting frequency distributions. Corrections for particle size effects were made for each size fraction as described by Lagaly (1992).

Table 1. Particle size distribution,[1] CaCO$_3$ equivalents and selected chemical properties of the study soils.

| Sampling depth (cm) | Sand | Silt | Clay | CaCO$_3$ g kg$^{-1}$ | pH | EC dS m$^{-1}$ |
|---|---|---|---|---|---|---|
|  |  | % |  |  |  |  |
| *Wainwright* | | | | | | |
| 0–20 | 68 | 17 | 15 | 76 | 9.6 | 24 |
| 20–28 | 34 | 35 | 31 | 106 | 9.6 | 13 |
| 28–42 | 92 | 4 | 4 | 56 | 9.3 | 6 |
| 42–70 | 71 | 15 | 14 | 101 | 9.1 | 7 |
| >70 | 79 | 11 | 10 | 74 | 9.0 | 12 |
| *Hanna* | | | | | | |
| 0–23 | 72 | 13 | 15 | 47 | 9.9 | 45 |
| 23–50 | 66 | 17 | 17 | 45 | 9.9 | 41 |
| 50–80 | 26 | 27 | 47 | 63 | 9.6 | 40 |
| >80 | 22 | 30 | 48 | 55 | 9.8 | 42 |
| *Nobleford* | | | | | | |
| 0–20 | 39 | 40 | 21 | 10 | 8.3 | 34 |
| 20–40 | 46 | 30 | 23 | 0.7 | 7.8 | 37 |
| 40–60 | 47 | 32 | 21 | 7.1 | 8.2 | 35 |
| >60 | 34 | 39 | 27 | 234 | 8.4 | 44 |
| *Provost* | | | | | | |
| 0–15 | 54 | 16 | 31 | 167 | 8.1 | 37 |
| 15–40 | 71 | 8 | 21 | 84 | 8.0 | 44 |
| >40 | 64 | 10 | 26 | 115 | 8.1 | 35 |

[1] Sand (2.0–0.05 mm), silt (50–2.0 $\mu$m), clay (<2.0 $\mu$m).

## RESULTS AND DISCUSSION

Selected characteristics of the soils in this study are summarized in Table 1. The study soils were highly saline and sodic, with the chemistry of the soil solutions dominated by Na and SO$_4$ ions (Kohut and Dudas 1994b). 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 and Hanna soils. Detailed information on the clay mineralogy has been documented in Kohut and Dudas (1994a).

Most samples showed similar X-ray diffraction characteristics after saturation with n-alkylammonium compounds, with broad low angle reflections indicative of smectites containing monolayer or bilayer alkylammonium complexes in the interlayer region and peaks at 1.0 nm and 0.72 nm characteristic of discrete mica and kaolinite respectively. Some broadening and reduction in the intensity of the 1.0 nm mica peak was
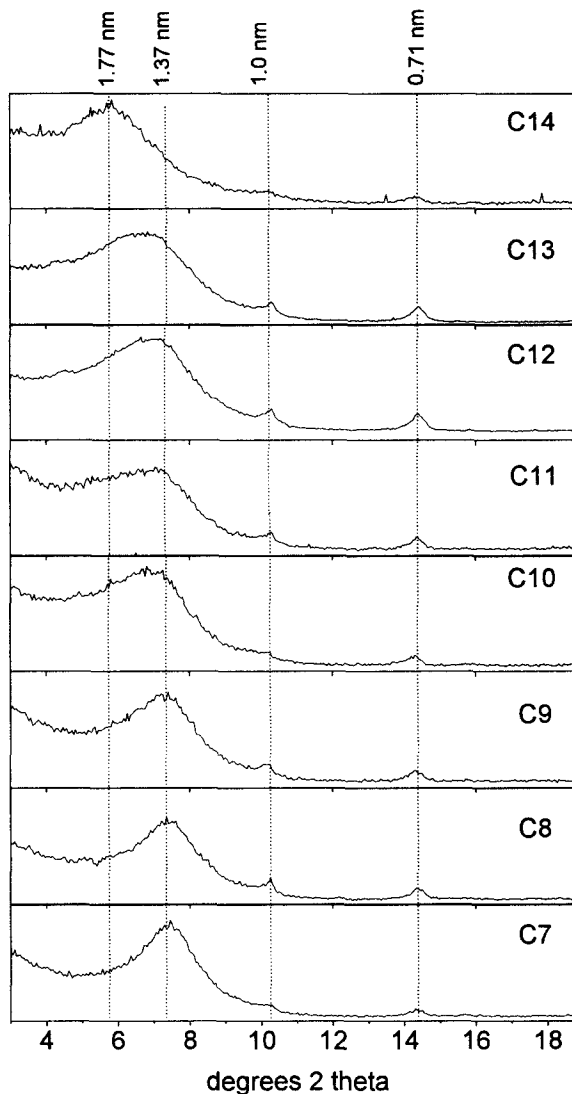


Figure 1. X-ray diffraction patterns for the alkylammonium saturated <2.0 $\mu$m fraction of the <70 cm layer in the Wainwright soil. C$_n$ refers to the number of carbons in the alkylammonium chain.

usually noted after alkylammonium treatments when compared to XRD patterns obtained after traditional pretreatments, indicating partial replacement of interlayer K by alkylammonium cations.

A typical series of X-ray patterns showing the gradual increase in d-spacings with increasing alkylammonium chain length is shown in Figure 1. The calculated mean layer charge density of the expanding clay minerals ranged from 0.261 to 0.339 mol($-$) per half unit cell (Table 2), with the charge assumed to be predominantly in the octahedral layer because of the lack of expansion of Li-saturated samples after heating and glycerol solvation (Kohut and Dudas 1994a). These

values are considerably lower than previously reported for soil material in Alberta (Warren *et al* 1992). Lower smectite layer charge in saline soils has also been reported by Reid (1992), who suggested that this may be due to neoformation of low-charged smectites under conditions of high salinity. This is likely not a major factor in this study, since the amount of fine clay found in the majority of the samples is low (Kohut and Dudas 1994a) and the relationship between clay size fractions and layer charge inconsistent.

The transition from a monolayer to bilayer took place over a number of different alkylammonium chain lengths for all samples, indicating considerable charge heterogeneity. This appears to be a characteristic feature of soil smectites (Stul and Mortier 1974, Lagaly and Weiss 1976, Lagaly 1981) and may be attributed to different charges along a given silicate layer or different charges between layers. Most samples in this study showed a charge distribution that remained approximately the same with decreasing particle size, implying that the latter condition existed. The charge distribution in the Nobleford samples was seen to increase as particle size decreased (data not shown), suggesting that only a small region at crystal edges contributed most to charge heterogeneity.

Although some variation in layer charge existed between sites, and between depths and size fractions for a given soil, no consistent patterns were seen when looking at the variation of mean layer charge with depth and particle size for each soil. The variability between samples in a single pedon was unexpected and may be the result of differences in smectite origins or in weathering processes occurring within the profile. 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. Since all of the soils in the study are saturated with water during at least part of the year and showed characteristics of either periodic or prolonged reducing conditions, we speculate that the reduction and oxidation of structural iron may also account for some differences in layer charge between samples at different depths and locations.

Reduction of the intensity of the 1.0 nm peak in many samples after equilibration with alkylammonium compounds 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

Table 2. Mean layer charge[1] of smectites from salt-affected soils.

| Sample (cm) | Size fraction ($\mu$m) | | |
|---|---|---|---|
| | 2 to 0.2 | 0.2 to 0.08 | <0.08 |
| 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 |
| Hanna | | | |
| 0–23 | 0.317 | 0.312 | 0.301 |
| 23–50 | 0.282 | 0.309 | nd[2] |
| 50–80 | 0.276 | 0.299 | 0.309 |
| >80 | 0.280 | 0.292 | 0.299 |
| Nobleford | | | |
| 0–20 | 0.324 | nc[3] | nc |
| 20–40 | 0.323 | 0.309 | 0.312 |
| 40–60 | 0.339 | 0.308 | nd |
| >60 | 0.338 | nd | nd |

[1] Expressed as mol($-$) per mol $O_{10}(OH)_2$.
[2] Not determined because of insufficient amounts of samples.
[3] Not calculated because of extreme peak broadening (see text).

vermiculite was noted in this study, the partial replacement of K from micaceous layers could potentially affect the calculated mean layer charge by increasing the proportion of higher charge layers. Different degrees of K depletion between samples can also likely be expected because of differences in the amount and characteristics of the micaceous component. A charge reduction with decreasing particle size in soil clays has been previously interpreted as indicating transformation of illite into smectite (Lagaly 1981), but may be at least partially due to the removal of K from micas by alkylammonium compounds.

Unusual X-ray diffraction characteristics were seen in 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. No layer charge density values could be calculated for these samples because of the difficulty of identifying smectite diffraction peaks. For example, although the 0.2 to 0.08 $\mu$m fraction from the Nobelford surface sample is predominantly composed of smectite (Figure 2), 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 (Figure 3). Similar behavior was seen after analysis of the <0.08 $\mu$m fraction of this sample (Figure 4). Previous X-ray diffraction analysis of these samples after traditional pretreatments (Figures 2 and 4b) shows smectite diffraction peaks that, while although broad, are fairly typical of finely crystalline montmorillonite in the In-
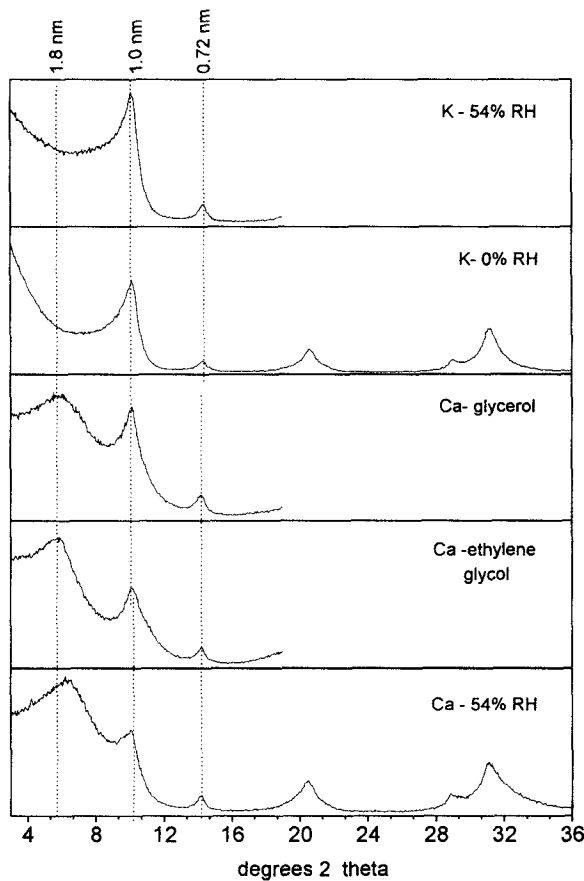
Figure 2. X-ray diffraction patterns of the 0.2 to 0.08 μm fraction of the 0 to 20 cm layer in the Nobleford soil after traditional pretreatments.



Figure 3. X-ray diffraction patterns for the alkylammonium saturated 0.2 to 0.08 μm fraction of the 0 to 20 cm layer in the Nobleford soil. $C_n$ refers to the number of carbons in the alkylammonium chain.

terior Plains region of western Canada (Mills and Zwarich 1972, Dudas and Pawluk 1982, Ross and Kodama 1993). Rehydration after K-saturation results in a very broad elevation of the baseline rather than an expected distinct diffraction maxima between 1.2 and 1.4 nm, and would imply that the layer charge density is extremely heterogeneous. However, this diffraction behavior on K-54% RH treatment is not restricted to these samples alone, and was seen for other samples from the Nobleford and Hanna soils which showed more typical behavior after alkylammonium saturation.

This extreme broadening and essential disappearance of smectite diffraction maxima 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 is remote because all samples were treated in exa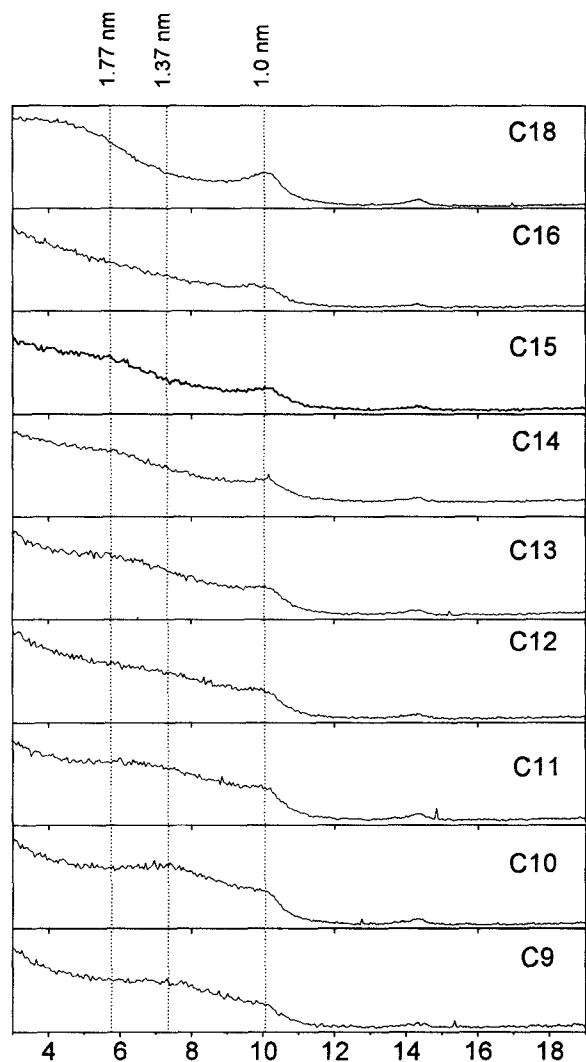ctly the same way. Basal reflections are normally weakened and broadened only in the transition range; this may suggest that charge characteristics of some samples may always cause the smectites to appear to be in transition from a monolayer to bilayer of alkylammonium molecules. Similar characteristics after traditional XRD analysis of untreated soil clays was suggested to be the result of interaction with soil organic matter (Kohut and Dudas 1994a), but it is unclear as to why the phenomenon is only seen in some saline soil clay fractions.

## 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
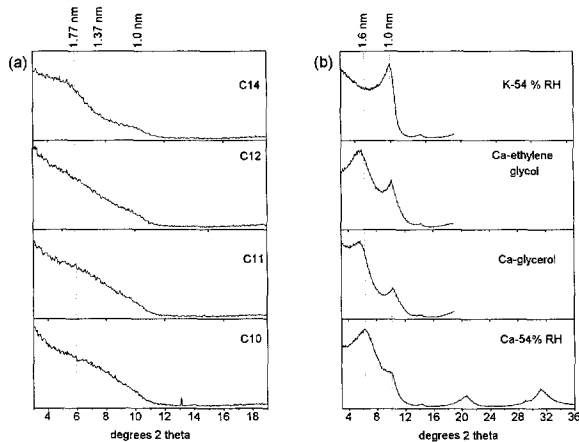
Figure 4. X-ray diffractograms of (a) alkylammonium saturated and (b) traditional pretreatments of the <0.08 μm fraction of the 0 to 20 cm layer at Nobleford.

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, or may also be due to variable K depletion of the micaceous component. The lack of any consistent relationships between samples and the possible addition of clay particles from other locations through physical processes complicates potential explanations. It is probable that the alternating redox conditions or strongly reducing environments present in the study soils influence the oxidation state of structural Fe, and hence play a major role in determining smectite layer charge.

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 soil 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.

## ACKNOWLEDGMENTS

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