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EFFECTS OF ACIDIFICATION ON THE CHEMICAL COMPOSITION AND LAYER CHARGE OF SMECTITE FROM CALCAREOUS TILL

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Abstract—The objectives of the study were to determine the chemical composition and layer charge of smectite found in calcareous till of the Interior Plains region of western Canada and to examine the effects of acidification on alteration of the smectite. Samples of acidified and non-acidified (calcareous) late-Wisconsin till were obtained from four soil pits located immediately adjacent to an elemental sulfur block located in southern Alberta. Samples of the surface material (0–10 cm depth) had been subjected to extreme acidity for 25 years due to the oxidation of elemental sulfur and displayed pH values of about 2.0. Samples of the till obtained at depth (65–75 cm) remained calcareous with pH values between 7.3 and 7.6. A combination of analytical methods was used to determine the chemical composition of the smectite found in the samples. The layer charge of the smectite was determined independently using X-ray diffraction data for n-alkylammonium saturated specimens. Smectite found in the non-acidified calcareous material was characteristic of montmorillonite with a low content of Fe and very little substitution of Al for Si in the tetrahedral sheet. The smectite had a structural formula of $M^{+}_{0.40}(Si_{3.96}Al_{0.04})(Al_{1.56}Fe^{3+}_{0.10}Mg_{0.33})O_{10}(OH)_2$, which compared well with a mean value for layer charge of 0.399 mol(−)/$O_{10}(OH)_2$ determined using X-ray diffraction data for n-alkylammonium treated specimens. Smectite remaining in the till material subjected to extreme acidity underwent incongruent dissolution with a net loss of layer charge and preferential loss of octahedral Mg.

Key Words—Layer charge, Smectite, Soil acidity, Structural formula, Weathering.

INTRODUCTION

Soil parent materials from the Interior Plains region of western Canada are primarily composed of thick deposits of clay-rich calcareous till of continental origin. The clay-size fraction is commonly dominated by admixtures of discrete smectite and clay-sized mica, with lesser amounts of kaolinite, chlorite, and quartz (Rice *et al.,* 1959; Pawluk, 1961; Kodama, 1979; Dudas and Pawluk, 1982; Spiers *et al.,* 1989). The clays are allogenic, derived mainly from underlying Cretaceous sedimentary rocks. The relative proportions of the clays are generally uniform throughout the region, with smectite accounting for the largest fraction. Details on the chemical characteristics of the phyllosilicates, most notably the smectites, are lacking.

Smectite is usually considered unstable in acidic environments (Kittrick, 1971), yet it is commonly identified in acidic soils (Pawluk, 1971; Karathansis and Hajek, 1984; Curtin and Mermut, 1985). Montmorillonite is the common smectite in western Canadian soils with beidellite frequently identified as a minor phase (Dudas and Pawluk, 1982). One possible explanation for the presence of beidellite in these soils is alteration and weathering of montmorillonite under acidic conditions (Karathanasis and Hajek, 1983). The octahedral layers of 2:1 phyllosilicates are preferentially attacked under acidic conditions and dissolve more rapidly than the tetrahedral layers (Novak and Cicel, 1978). Acidification may thus result in the evolution of the composition of smectite towards beidellite. The specific behavior of the soil smectite subjected to acidic conditions *in situ* warrants detailed examination.

Values for the layer charge of smectites have been reported for only a few sample sites in western Canada. Mermut and coworkers (1984) reported a layer charge of 0.49 mol(−)/$O_{10}(OH)_2$ for iron-rich montmorillonite found in the parent materials of southern Saskatchewan soils. This value for layer charge is high compared to typical values for natural smectites. A layer charge of 0.36 mol(−)/$O_{10}(OH)_2$, more typical of most smectites, was reported for a monomineralic sample of smectite found in an acidic marine shale in Saskatchewan (Curtin and Mermut, 1985). Layer charge values for smectites in Alberta soils have not been reported previously, and the effects of acidity on layer charge have not been examined.

Separation of smectite from the clay-size fraction of multimineralic soils poses a barrier to characterization. Rare occurrences of monomineralic samples of smectite in western Canadian soils have been characterized (e.g., Curtin and Mermut, 1985), but the chemical composition may not be representative of smectite found in soils containing mixtures of clay minerals. The relative abundance of phyllosilicates varies with particle size within the clay-size fraction. Separation on the basis of particle size using sedimentation methods (e.g., McKeague, 1978; Jackson, 1979), does not produce pure monomineralic separates. Interstratification of different clay minerals within single particle domains also obstructs separation of monomineralic fractions by sedimentation. Magnetic separation of iron-containing fractions (ferromagnetic and paramagnetic) is also constrained because iron is usually not restricted to one type of clay mineral in a natural mixture (Berry and Jorgensen, 1969; Schulze and Dixon, 1979). New and innovative approaches are, therefore, required to characterize the clays that occur within such soil mixtures to study the response of soil clays to changing chemical environments such as acidification.

For the current study, the objectives were to determine the chemical composition and layer charge of smectite common to calcareous till of the Interior Plains region of western Canada and to examine the effects of acidification on the composition and layer charge of the smectite. A combination of analytical methods were used in an attempt to determine, by difference, the chemical composition of smectite found within a mixture of other soil clays in the <2 μm size-fraction. X-ray diffraction analyses of n-alkylammonium saturated specimens were used to independently determine the layer charge of the smectites.

MATERIALS AND METHODS

Samples used in this study were collected beside a 25-year-old elemental sulfur block located on the site of a sour natural gas refinery. Before construction of the sulfur block, the soil solum had been removed to expose the underlying calcareous parent material. The field site was used to take advantage of the extended time the clays had been exposed to extreme acidity. At the time of sampling, the surficial material was extremely acidic to a depth of 45 cm, while material at depths greater than 65 cm remained calcareous (Warren and Dudas, 1992). Samples were collected from four replicate pits, spaced five meters apart, located two meters from the side of the sulfur block. Samples of approximately 5 kg each representative of the 0–10 cm depth—identified here as the acidified material—and the 65–75 cm depth—identified here as the calcareous or non-acidified material—were obtained from each pit. These sample depths were chosen in an effort to examine the effects of the greatly different pH environments on the soil minerals. All samples were air dried prior to analysis. The pH values for the bulk samples were determined in 0.01 $mol \cdot dm^{-3}$ $CaCl_2$ (McKeague, 1978). Total content of inorganic carbon (carbonate) was determined using the procedure of Bundy and Bremner (1972).

The samples of the acidified and calcareous materials obtained from each pit were dispersed in distilled water using ultrasonic vibration (Genrich and Bremner, 1972). The clay-size fraction (<2 μm diameter) was obtained by repeated gravity sedimentation (Jackson, 1979). No attempt was made to concentrate the smectite in a smaller particle size fraction. A pure monomineralic smectite fraction could not be separated, and corrections for the composition of clays other than smectite in the samples were required. It was felt that the accuracy of the calculated smectite composition would not be improved by further concentration because the compositions for the clays other than smectite were based on documented values and the assumed compositions might not hold for smaller size fractions.

Subsamples of the separated clay-size fractions were saturated with Ca^{2+} or K^+ by repeated treatments with 1 $mol \cdot dm^{-3}$ solutions of the respective chloride salts followed by repeated washing with distilled water to remove excess electrolyte. Phyllosilicate minerals present in the clay separates were identified from X-ray diffractograms of orientated Ca-saturated and K-saturated specimens (Warren and Dudas, 1992). Separate subsamples of electrolyte free Ca-saturated clays were dissolved in HF and HNO_3 (Warren *et al.,* 1990) and the digests analyzed for total content of Si, Al, Fe, Mg, K, Ca, Na, Mn, and Ti by inductively coupled plasma atomic emission spectrometry (ICP-AES). Subsamples were also extracted using acid ammonium oxalate (McKeague, 1978) and the extracts analyzed by flame atomic absorption spectrophotometry for content of Fe and Si.

The composition and quantities of kaolinite, clay-sized mica, and chlorite in the samples were determined primarily from X-ray diffraction and chemical data. Kaolinite identified in the clay fraction was assumed to be of uniform crystallinity and composition (Chittleborough and Walker, 1988) and quantified based on the area under the (001) reflections in the X-ray diffraction patterns for the oriented K-saturated specimens (Warren and Dudas, 1992). The clay-sized mica in the samples was dioctahedral (Warren and Dudas, 1992), derived primarily from plutonic micas of the Canadian shield, and incorporated into the till during glaciation (Kodama 1979; Miller *et al.* 1981). The quantity of mica in the samples was calculated based on a total content of 100 $g \cdot kg^{-1}$ K_2O for pure mica (Mehra and Jackson, 1959). The proportional contents of Fe_2O_3 and MgO in the clay-sized mica were based on mean values for documented samples representative of muscovite derived from the Canadian shield (Miller *et al.,* 1981). The composition of the chlorite in the calcareous sample was derived from the X-ray diffraction data obtained for the oriented K-saturated specimens. The mean d-spacing values for chlorite in the calcareous till material was 1.414 nm (± 0.003) based on the peak positions of the d(003) and d(004) reflections (Warren and Dudas, 1992). Content of total Al, Al in tetrahedral coordination (Al^{IV}), and, by difference, Al in octahedral coordination (Al^{VI}) in the chlorite were calculated using the equations of Bailey (1972):

$$d(001) = 1.455 - 0.029(Al^{IV}) \quad (1)$$

$$d(001) = 1.452 - 0.014(Al^{IV} + Al^{VI} + Cr) \quad (2)$$

where d(001) is the basal spacing for chlorite measured in nm. The contribution of Cr to the peak positions for the chlorite was assumed to be negligible. The total content of Mg in the chlorite was derived from the relationship (Foster, 1962, cited by Bailey, 1988):

$$Si^{4+}(IV) + Mg^{2+}(VI) = Al^{3+}(IV) + Al^{3+}(VI) \quad (3)$$

The remaining component of the chlorite was assumed to be Fe. Most chlorites found in soil are trioctahedral and inherited from the parent material (Bailey, 1988). The mean octahedral cation site occupation for natural trioctahedral chlorites was taken as 5.75 (range = 5.45–6.05; Foster, 1962, cited by Newman and Brown, 1987). Chlorite was present as a minor phase in the calcareous layer and absent in the acidified material (Warren and Dudas, 1992). The differences in the total amounts of Fe_2O_3 and MgO between the acidified and calcareous samples, after accounting for clay-sized mica and acid ammonium oxalate extractable fractions, were allocated to chlorite. The fraction of total Fe_2O_3 allocated to chlorite structure as FeO was converted on a molar basis.

Structural formulae for the smectites were calculated using the computer program CLAYFORM (Bodine, 1987). For the calculations it was assumed initially that all structural Fe occurred in the oxidized (expressed as Fe_2O_3) form (Rozenson and Heller-Kallai, 1978). The interlayer charge for the calculated structures were based on oxygen equivalency (Gast, 1977; Bodine, 1987).

The layer charge of 2:1 expandable phyllosilicates in the samples were determined from X-ray diffractograms of n-alkylammonium saturated specimens (Weiss, 1963; Rühlicke and Kohler, 1981; Rühlicke and Niederbudde, 1985; Häusler and Stanjek, 1988; Laird, 1987; Laird *et al.*, 1988) prepared using the method described by Laird *et al.* (1989). The number of carbon atoms (C_n) in the n-alkylammonium cations ranged from 6 to 18. The n-alkylammonium saturated clays were prepared through treatment with aqueous solutions of n-alkylamine hydrochlorides synthesized from the reaction of the alkylamines with gaseous HCl (Laird, 1987). Oriented specimens of the n-alkylammonium saturated clays were prepared on glass slides by the paste technique (Theissen and Harward, 1962; Laird, 1987; Laird *et al.*, 1988).

Layer charge values (σ) for the smectites were calculated as a function of C_n based on an empirically derived mathematical relationship (Laird *et al.*, 1989):

$$\sigma = \frac{38.88}{5.67(C_n) + 14} - 0.078 \quad (4)$$

where σ is expressed in units of moles of charge per structural formula ($mol(-)/O_{10}(OH)_2$). The fraction of the total amount of expandable 2:1 clay (p) assigned to each layer charge range was calculated using the following third order polynomial equation:

$$p = -86691 + 16672(d) - 1072.7(d)^2 + 23.203(d)^3 \qquad R^2 = 0.9994 \quad (5)$$

based on the data of Lagaly (1981) for d-spacings (d) between 1.36 and 1.77 nm. Weighted mean values for the layer charge of the smectites were calculated based on the resulting frequency distributions.

Potential variations in the predicted composition of the smectites with respect to variability in the analytical values were examined through a sensitivity analysis. Coefficients of sensitivity (S) were calculated (Villeneuve *et al.*, 1988):

$$S = \frac{\partial P/P}{\partial a/a} \quad (6)$$

where $\partial P/P$ is the relative variation of the response and $\partial a/a$ is the relative variation of the parameter. Values of S equal to zero indicate no effect of the variant on the response parameter; values equal to 1.0 indicate a parallel response of the parameter to the variant; and values of S greater than 1.0 indicate larger relative variations in the response parameter compared to the change in the variant. Values of S in the order of 10.0 indicate extreme sensitivity of the response parameter to the variant.

RESULTS AND DISCUSSION

The clay-sized fraction (<2 μm diameter) of the samples was dominated by smectite and clay-sized dioctahedral mica with lesser quantities of kaolinite, chlorite, and quartz (Warren, 1991) typical of soils from the Interior Plains region of western Canada (Kodama, 1979; Dudas and Pawluk, 1982). The samples of the acidified material displayed pH values of about 2.0 in 0.01 $mol \cdot dm^{-3}$ $CaCl_2$ and contained precipitated gypsum. The non-acidified calcareous material displayed pH values between 7.3 and 7.6 in 0.01 $mol \cdot dm^{-3}$ $CaCl_2$ and contained an average $CaCO_3$ equivalent of 100 $g \cdot kg^{-1}$. The clay content of the acidified material was 301 ± 23 $g \cdot kg^{-1}$ and the calcareous material contained 295 ± 33 $g \cdot kg^{-1}$.

Layer charge

The X-ray patterns for the n-alkylammonium saturated specimens from the acidified material (Figure 1) were similar to those of the calcareous material. All samples displayed broad reflections with low angle peaks (<9°2θ CoKα radiation) indicative of the presence of expandable 2:1 clays containing monolayer or bilayer alkylammonium complexes in the interlayer region (Lagaly and Weiss, 1969; Lagaly, 1981). The diffractograms also displayed strong sharp reflections with peaks at 0.715 nm, indicative of the presence of ka-

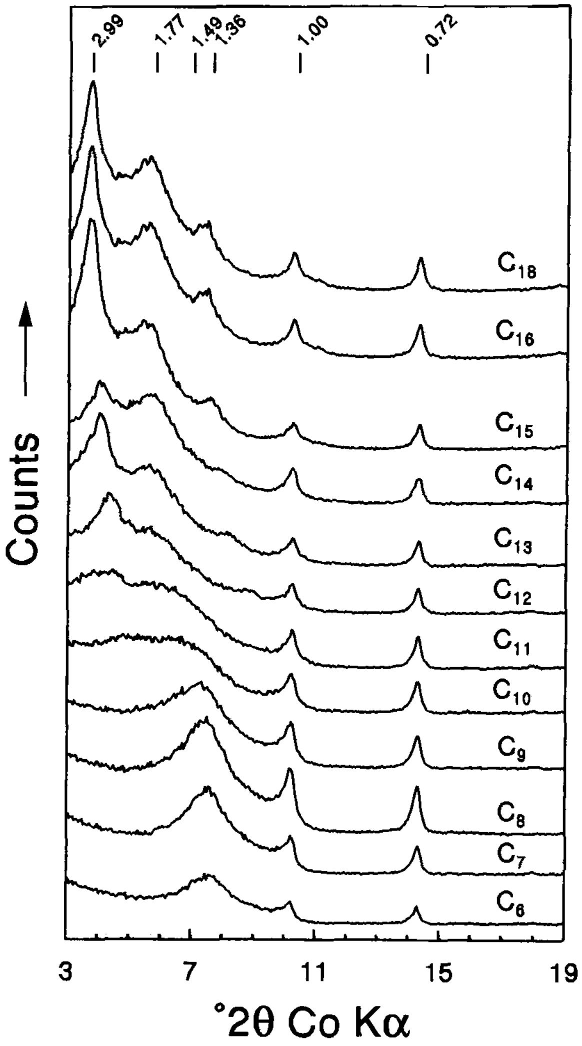

Figure 1. X-ray diffraction patterns for the alkylammonium saturated clay separates from the acidified material. Values along the top indicate d-spacings in nm.

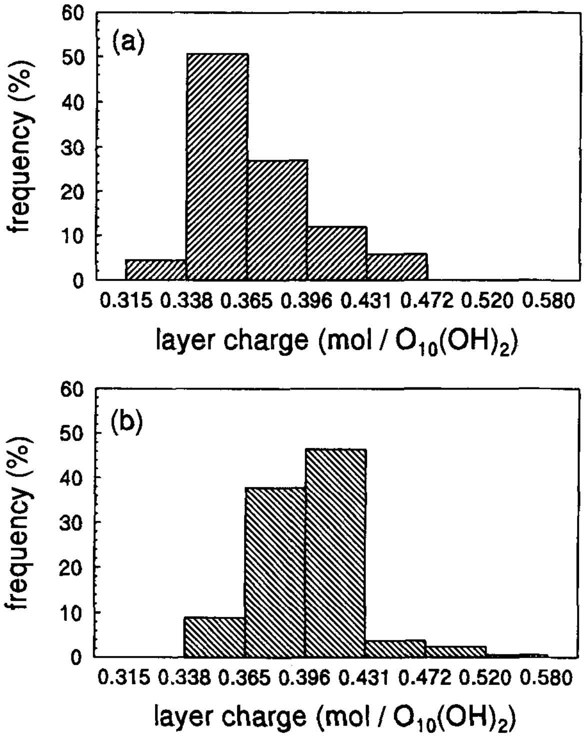

Figure 2. Histograms for the distribution of layer charge (σ) for smectite from the acidic (a) and calcareous (b) materials.

olinite, and 0.997 nm, indicative of the presence of discrete mica. The X-ray diffractograms for the specimens treated with short chain (C_n = 6 to 9) alkylammonium derivatives displayed broad peaks with maxima corresponding to basal spacings of 1.34 to 1.36 nm (Figure 1), indicating the presence of 2:1 expandable phyllosilicates containing monolayers of straight chain hydrocarbons in the interlayer region. Diffractograms for specimens treated with alkylammonium derivatives containing more than nine carbon atoms ($C_n > 9$) displayed two broad peaks at low 2θ angles (Figure 1). The more diffuse of the two peaks, located at higher angles, corresponded to basal spacings that increased from 1.36 to 1.77 nm for carbon chain lengths of 10 to 14, which indicated the formation of a monolayer-bilayer transition (Lagaly, 1981). For carbon chains with $C_n > 14$, d-spacings remained at 1.77 nm corresponding to the presence of bilayers in the interlayer region. The sharper reflections observed at angles less than 5°2θ (CoKα) in diffractograms for $C_n > 9$ displayed maxima that increased linearly from about 2.0 nm for C_n = 10 to 2.99 nm for C_n = 18. Second order reflections for the more intense low angle peaks were also observed in specimens for $C_n > 11$.

Histograms representing the calculated frequencies for layer charge ranges for the smectites from the acidified and calcareous samples were normally distributed with a single mean (Figure 2). Acidification produced a significant shift in the distribution of smectite layer charge towards lower values. Layer charge values for the smectites from the acidified material (Figure 2a) ranged from 0.315 to 0.472 mol(−)/$O_{10}(OH)_2$ with a weighted mean of 0.372 mol(−)/$O_{10}(OH)_2$. The smectites from the calcareous material had σ ranging from 0.338 to 0.580 mol(−)/$O_{10}(OH)_2$ with a weighted mean of 0.399 (Figure 2b).

The presence of reflections at angles less than 5°2θ (CoKα) for the n-alkylammonium saturated clays (Figure 1) with d-spacings values that increased as a linear function of C_n suggested the presence of 2:1 expandable clay minerals with σ greater than 0.6 mol(−)/$O_{10}(OH)_2$ characteristic of vermiculite (Lagaly, 1982; Bailey *et al.*, 1980). The presence of vermiculite in the samples was not supported by previous observations (Warren and Dudas, 1992), and vermiculite has not been iden-

Table 1. Mean analytical values for chemical compositions ($g \cdot kg^{-1}$) and relative standard deviations (RSD) for the bulk clay and the calculated composition of smectite from the acidic material and the calcareous material.

	Bulk clay					
	Acidic		Calcareous		Smectite composition	
Component	Mean	RSD[1]	Mean	RSD[2]	Acidic	Calcareous
SiO_2	656	1.9	568	2.8	617	636
TiO_2	9.4	4.1	6.1	3.8	0	0
Al_2O_3	215	4.8	230	2.8	221	218
Fe_2O_3[2]	23.6	8.2	66.0	12	20.7	21.5
CaO	11.1	11	10.5	10	30.3	25.9
MgO	12.4	6.6	20.8	2.1	16.3	35.7
MnO	0.1	12	0.2	58	0	0
K_2O	32.1	3.3	29.2	4.9	0	0
Na_2O	4.6	14	1.9	11	0	0
LOI[3]	64.7	12	63.8	20	94.7	63.4
Total	1029		996		1000	1000

[1] Expressed as percent (%).
[2] Total Fe expressed as Fe_2O_3.
[3] LOI = Loss on Ignition at 850°C.

tified in samples from other studies of similar soils (e.g., Dudas and Pawluk, 1982). X-ray diffraction data and the ability of the clays to fix only 4 $g \cdot kg^{-1}$ (0.4%)K^+ (Warren and Dudas, 1992) indicated the absence of significant quantities of vermiculite in the samples. The detection of vermiculite-like structures in the clay sized fractions by the alkylammonium technique may have been due to the increased sensitivity of the method (Lagaly, 1981), enabling detection of small amounts (<5%) of vermiculite. The appearance of vermiculite-like structures was more likely an artifact resulting from the removal of interlayer K^+ from clay-sized mica in the sample (Ross and Kodama, 1986; Laird *et al.,* 1987). The presence of the second order peaks for $C_n > 11$ suggested that the vermiculite-like structure had few crystalline defects, further suggesting that the structures were derived from mica that had been depotassified during the alkylammonium treatment.

Chemical composition

The chemical composition of the <2 μm size fraction acidified and calcareous samples and the calculated composition for the smectites after correcting for the elemental composition of all other minerals in the clay sized fraction are presented in Table 1. Silicon and Al were the major components of the clay fraction with lesser amounts of Fe, Mg, Ca, K, Na, Ti, and Mn. Acidification reduced the amount of total Al, Fe, Mg, Mn, and Na in the clay fraction. The total contents of K and Ca in the acidified material were not significantly different (Warren and Dudas, 1992) from the calcareous material. Contents of Si and Ti in the acidified material were enriched relative to the calcareous material.

Kaolinite accounted for 119 $g \cdot kg^{-1}$ of the calcareous material and 111 $g \cdot kg^{-1}$ of the acifidied material (Table 2). The amount of clay-size mica in the samples accounted for 292 $g \cdot kg^{-1}$ of the calcareous material which was not significantly different (95% level) from the 321 $g \cdot kg^{-1}$ found in the acidic material. The mean d-spacing values for chlorite in the calcareous till material was 1.414 nm (±0.003), and the calculated content of chlorite in the clay fraction of the calcareous layer was 65 $g \cdot kg^{-1}$. The calculated composition of the chlorite in the calcareous sample (Table 2) indicated that it was Fe rich, which is consistent with observations for chlorite in other Alberta soils (Pawluk and Lindsay, 1964; Spiers, 1982). The calculated content of total Fe in the chlorite was greater than 40 $g \cdot kg^{-1}$ exceeding the requirements for classification as a ferrous chlorite (Bailey, 1988).

The total amount of MnO and TiO_2 in the clay fractions were minor (Table 1) and collectively, including all other minor elements, accounted for 15 $g \cdot kg^{-1}$ (1.5%) of the total clay fraction in the acidic material and 9 $g \cdot kg^{-1}$ (0.9%) in the calcareous material. Much of the TiO_2 in the samples was attributed to the presence of resistant minerals such as rutile in the clay-sized fraction. It was assumed that the total quantities of Mn, Ti, Na, and all other minor and trace elements were distributed among all minerals in the samples and did not significantly affect the calculated composition for the smectite. These elements were therefore excluded from the calculations for the structural formulae.

After accounting for the quantities and compositions of the above mentioned minerals, the remaining fraction of the bulk composition was rich in SiO_2. Preliminary calculations for the structural formula of smectite, which included the high content of SiO_2, indicated that the amount of Si present was far in excess of the requirements to fill all tetrahedral sites in an ideal dioctahedral smectite structure. The calculated amount of SiO_2 in the samples allocated to smectite was, therefore, reduced such that the corresponding content of

Table 2. Structural formulae and quantities (g·kg^{-1}) of minerals and amorphous phases in the <2 μm size fraction separated from the acidic and calcareous materials.

Mineral	Structural formula	Quantity (g·kg^{-1})	
		Acidic	Calcareous
Kaolinite	$Al_4Si_4O_5(OH)_4$	111	119
Mica	$K_{0.85}[Si_{3.35}Al_{0.65}][Al_{1.55}Fe^{3+}{}_{0.25}Mg_{0.10}]O_{10}(OH)_2$	321	292
Chlorite	$[Si_{2.59}Al_{1.41}][Al_{1.30}Fe^{2+}{}_{4.32}Mg_{0.13}]O_{10}(OH)_8$	0	65
Fe_2O_3	Acid ammonium oxalate extractable Fe_2O_3	0	11
SiO_2	Quartz + amorphous SiO_2	217	95
Smectite	$M^+{}_{0.34}[Si_{3.98}Al_{0.02}][Al_{1.66}Fe^{3+}{}_{0.10}Mg_{0.16}]O_{9.92}(OH)_{2.08}$	365	—
Smectite	$M^+{}_{0.40}[Si_{3.96}Al_{0.04}][Al_{1.56}Fe^{3+}{}_{0.10}Mg_{0.33}]O_{10}(OH)_2$	—	404
Other	$TiO_2 + MnO + Na_2O$	15	9
Total		1029	996

Al, Fe, and Mg in the structure increased until the requirements for an ideal dioctahedral structure 2:1 phyllosilicate structure were met. Further decreases in the content of SiO_2 resulted in calculated structural formulae that exceeded 2.00 octahedral sites required for a dioctahedral structure and a net positive structural charge for the smectite. The excess SiO_2 was attributed to amorphous silica and clay-size quartz. The acidified material contained 57.1 g·kg^{-1} amorphous SiO_2 and the calcareous material contained 29.7 g·kg^{-1} as determined from acid ammonium oxalate extracts. The remaining excess SiO_2 was assumed to be clay-sized quartz. The total amount of quartz plus amorphous SiO_2 (expressed as SiO_2) in the acidified and calcareous materials accordingly accounted for 217 and 95 g·kg^{-1}, respectively (Table 2). The high amount of quartz calculated for the acidified material was consistent with the higher intensities of the 0.426 and 0.334 nm peaks for α-quartz relative to the peaks for the phyllosilicates observed in the acidified material compared to the calcareous material. The increased content of quartz in the acidified material compared to the calcareous material was attributed to enrichment resulting from the dissolution of other minerals (Warren and Dudas, 1992).

Sensitivity analysis of the data indicated that the calculated composition of the smectite was insensitive to changes of up to 10% in the analytical values. Potential variations in the predicted composition of the smectites included the quantities of kaolinite, K_2O (mica), SiO_2, Al_2O_3, Fe_2O_3, MgO, and CaO. Response parameters included the stoichiometric coefficients for the composition of the smectite, total charge, and content of SiO_2 allocated to quartz. Extreme changes (e.g., 100% variation) in the variants resulted in absurd predictions for the composition of the smectite. Changes of up to 20% of the measured means for most variants usually resulted in absolute values of S (Equation 6) between 0 and 1, which is considered insensitive. Any given variant usually produced the largest values for S in the corresponding structural coefficient (e.g., a ±20% variation in the amount of MgO produced S values of ±4.0 for the coefficient for Mg). The largest S values among the response parameters were observed in the coefficient for tetrahedral Al. However, an increase or decrease of 0.01 units in the coefficient for tetrahedral Al represented a 25% change in the value for the smectite in the calcareous material and a 50% change for the smectite in the acidified material. Variation in the total content of Al_2O_3 in the bulk clay produced greatest amount of variation among response parameters; therefore, the accuracy of the analytical data for Al in digests of the bulk clay should receive careful attention, as this value has the greatest impact on the predicted composition of the smectite.

The calculated total content of smectite in the acidified material decreased to 365 g·kg^{-1} (36%) compared to 404 g·kg^{-1} (40%) in the calcareous samples. The resultant calculated structural formulae for the smectites in the acidified and calcareous materials (Table 2) indicated that the 2:1 expandable clays were characteristic of montmorillonite. The calculated structural formula for the smectite in the calcareous material was $M^+{}_{0.40}[Si_{3.96}Al_{0.04}][Al_{1.56}Fe^{3+}{}_{0.10}Mg_{0.33}]O_{10}(OH)_2$. This formula was taken to be representative of smectite found in the acidified material prior to acidification. The calculated formula indicated that smectite found in the till had very little tetrahedral substitution of Al for Si with almost all permanent charge sites originating within the octahedral sheet. The layer charge for the structure determined from the chemical data (0.40 mol(−)/$O_{10}(OH)_2$) was very similar to the mean value of 0.399 mol(−)/$O_{10}(OH)_2$ determined using the n-alkylammonium method. The calculated compositions for the clays from the calcareous and acidified materials were also very similar except for reduction in the amount of Mg in the smectite from the acidified material. Calculations for the smectite in the acidified material provided a formula of $M^+{}_{0.42}[Si_{3.98}Al_{0.02}][Al_{1.66}Fe^{3+}{}_{0.10}Mg_{0.16}]O_{10}(OH)_2$. Reduction in the total amount of structural Mg, relative to the other component elements, indicated incongruent dissolution of the smectite structure with preferential attack of octahedral Mg, resulting in the loss of permanent structural charge. The layer charge based on the calculated chemical composition was higher (0.42 $mol(-)/O_{10}(OH)_2$) than layer charge for smectite in the calcareous material and much higher than the value of 0.372 $mol(-)/O_{10}(OH)_2$ determined using the n-alkylammonium technique. The layer charge determined using the n-alkylammonium method was taken as the more accurate value. The sum of the number of cations in the octahedral layer was 1.92, which was lower than the assumed value of 2.00 for an ideal dioctahedral 2:1 layer structures. The apparently vacant octahedral sites in the calculated structure for the smectite from the acidified material may have been occupied by minor and trace metals (e.g., Mn, Cr, Zn, and Cu) or H^+, not included in the calculations for composition. Inclusion of enough H^+ in the structural formula to satisfy the 0.08 deficit sites in the octahedral sheet would reduce the layer charge to 0.34 $mol(-)/O_{10}(OH)_2$, which agreed more closely with the values for structural charge of 0.372 $mol(-)/O_{10}(OH)_2$ determined using the n-alkylammonium method. This suggested that a large number of structural defects may have been introduced into the smectite during weathering in the acidified material and that the mode of acid attack was through neutralization of structural negative charges in the octahedral sheet and exchange for structural metals.

The amount of permanent charge allocated to the tetrahedral sheet, total structural charge, and the amount of Fe in the calculated structural formula for smectite in the calcareous till (Table 2) were low compared to the average chemical composition for smectites reported for some Saskatchewan soils: $M_{0.49}{}^+(Si_{3.86}Al_{0.14})(Al_{1.00}Fe^{3+}{}_{0.68}Mg_{0.31})O_{10}(OH)_2$ (Mermut *et al.*, 1984). Except for the amount of Al substitution in the tetrahedral sheet the composition of the smectite in the calcareous material was closer to the composition of smectite separated from the C horizon of an acid sulfate soil in Saskatchewan developed in a marine shale $M_{0.36}{}^+(Si_{3.87}Al_{0.13})(Al_{1.72}Fe_{0.06}{}^{3+}Mg_{0.22})O_{10}(OH)_2$ (Curtin and Mermut, 1985) suggesting that the smectite observed in the calcareous till in the present study may have been derived from the same shale formation.

The reduced layer charge for smectite from the acidified material compared to the calcareous material indicated that, although smectite initially in the calcareous till had not been totally dissolved during acidification of the surface material (Warren and Dudas, 1992), the smectites had been chemically attacked, resulting in the reduction in the amount of Mg in the octahedral sheet and a reduction in the total layer charge. The content of tetrahedral Al was initially low and the structural content did not increase due to preferential dissolution of other components during weathering under acidic conditions. Under the chemical conditions in the acidified material, weathering of the smectite occurred through acid attack of charge sites in the octahedral sheet, resulting in evolution of the composition toward that of pyrophyllite. The transformation of the montmorillonite towards a structure containing higher layer charge density, such as beidellite or vermiculite, was not evident.

CONCLUSIONS

A combination of analytical methods were used to characterize and quantify the clay minerals in the <2 μm size fractions of a calcareous till and the same till material subjected to acidification. The structural formula of the smectite clays in the samples were calculated after allocating and accounting for the compositions of all other minerals in <2 μm size fraction. The results of this study indicated that smectite clays found in the calcareous till had a calculated structural formula of $M^+{}_{0.40}(Si_{3.96}Al_{0.04})(Al_{1.56}Fe_{0.10}{}^{3+}Mg_{0.33})O_{10}(OH)_2$. The layer charge for the structure calculated from the chemical composition compared well with values for layer charge (0.399 $mol(-)/O_{10}(OH)_2$) calculated from X-ray diffraction data for n-alkylammonium saturated specimens. The value for layer charge determined using the n-alkylammonium method was considered more accurate and easier to obtain compared to the chemical method. The smectite in the calcareous till had a lower content of tetrahedral Al and total content of Fe compared to smectites characterized for other sites in western Canada. The calculated structural formula also had a lower layer charge compared to smectites found in Saskatchewan soils (Mermut *et al.*, 1984) but was closer to the composition of smectite from an acidic marine shale found in Saskatchewan (Curtin and Mermut, 1985). The smectites from the till material of the current study were montmorillonites possibly derived from similar Cretaceous shales.

The total content of smectite in the acidified material had decreased to 36% compared to 40% of the total clay content in the calcareous samples. The smectite in the acidified material had undergone incongruent dissolution with a net loss of layer charge due to preferential loss of octahedral Mg and apparent formation of cation vacancies in the octahedral sheet. Reduction in the layer charge, as determined by alkylammonium treatment of the clays, indicated that weathering occurred primarily as a result of the dissolution of the octahedral layer and subsequent disintegration of the mineral structure. Dissolution of the clay under acidic conditions resulted in the evolution of the composition of the smectite towards that of pyrophyllite. This may have been related to the low tetrahedral charge on the initial smectite structure. Evolution towards beidellite or vermiculite structures may be possible if tetrahedral substitution in the parent montmorillonite was higher.

The data and computations of the current study provided a method for determining the composition and structural formula of smectite in soil material containing three other common phyllosilicates. The main limitations of the approach are that it requires analytical values from a large number of different types of analyses, and assumptions. Accuracy of the elemental content for the clay digests, particularly for Al, should be given careful consideration. Variation in the analytical value for Al had the greatest impact on the predicted composition for the smectite. The approach is also very tedious and computationally intensive. However, the results provide reasonable estimates for the chemical composition and structural formulae of phyllosilicates where few or none existed before. The technique also identifies some weaknesses and deficiencies in current knowledge available on soil clays and the methods for their identification and quantification. More detailed data on the chemical composition of all clay minerals found in these soils are required before more accurate predictions can be made about the chemical composition of the smectite and the behavior of the clay minerals subjected to different chemical environments.

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