

A TEM-based definition of 2:1 layer silicates and their interstratified constituents

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ABSTRACT

The layer structure and chemical composition of individual packets of 2:1 layer silicates in illitic materials from various environments have been studied with analytical high-resolution electron microscopy using ultrathin sections treated with *n*-alkylammonium. Individual packets consist of a polar or nonpolar structure, as judged by the response to treatment with *n*-alkylammonium. The status of illite-smectite mixed-layers attributed to these materials is found to reflect the composition and arrangement of polar and nonpolar 2:1 layer silicates. The nature of the 2:1 mixed-layer silicate thus cannot be ascribed to a mixture of illite and smectite layers. In our opinion, a definition based on TEM reflects the true nature of mixed-layer materials more accurately than one based on XRD: it leads us (1) to distinguish among different types of expandable and nonexpandable components; (2) to document variations in the density of interlayer charge of the expandable components, which are not detectable by XRD; (3) to distinguish between expandable and nonexpandable illite, which do not respond differently to ethylene glycol treatment; (4) to distinguish between fundamental particles and short-range ordered structures; (5) to relate the ordering of the T-O-T layers to the chemical composition, as measured directly by TEM (XRD study of oriented samples gives information on the interlayer spacing only); and (6) to characterize all types of particles present (not only the coherent sequences, as given by XRD).

INTRODUCTION

Questions concerning the classification and nomenclature of 2:1 layer silicates evidently remain topical and unsettled in the light of conflicting results from XRD and TEM studies of mixed-layer clay minerals (Reynolds, 1992; Środoń et al., 1990). Środoń et al. (1992) combined many lines of evidence, such as bulk chemical analysis, determination of ion-exchange capacity (CEC), X-ray diffraction (XRD), measurement of the thickness of fundamental particles by transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), measurement of expandability, and wetting and drying experiments, in an attempt to establish the chemical composition of illite-smectite mixed layers formed by the conversion of volcanic materials in hydrothermal and diagenetic environments. These authors proposed an interlayer charge of 0.89 per $O_{10}(OH)_2$ for illite and 0.4 per $O_{10}(OH)_2$ for smectite [with an accuracy of $\pm 1\%$ for smectite and ± 0.01 per $O_{10}(OH)_2$ for illite components]. In addition, they sought to explain the systematic discrepancy between XRD and TEM measurements of illite-smectite expandability (Środoń et al., 1990, 1992) by comparing the results of conventional XRD with the expandability inferred from the distributions of fundamental particle thickness, as measured by shadowing techniques in TEM.

Do the techniques applied by these authors allow the conclusion that such "illite-smectite" mixed-layer sam-

ples consist of interlayered illite and smectite phases? Ransom and Helgeson (1989) have stressed the need to rely on strictly mineralogical and chemical criteria in any scheme of classification. In their opinion, expandability behavior upon glycolation, as measured by XRD, should not be taken as de facto evidence for the presence of a smectite-group phase in the interstratified 2:1 layer silicates (I/S), because of inherent ambiguities in the interpretation of the results. These authors recommended that species labels like IS, IIS, and ISII should be avoided unless the actual mineral and chemical contents of the components of a mixed-layer material can be determined. In addition, the common presence of impurities and the limited precision of the analytical techniques applied (Mackinnon, 1987; Warren and Ransom, 1992; Peacor, 1992a; Vali et al., 1993) make the bulk-chemical characterization of clay minerals of questionable value.

In support of the point made by Ransom and Helgeson (1989), the data presented in the literature, as reviewed by Peacor (1992b) and Allen (1992), concerning the classification of minerals of 2:1 layer silicates and related I/S mixed-layer minerals, do not necessarily reflect the true nature of the individual clay-mineral phases, in our opinion. So far in the literature, illite-smectite has been assigned a definite structure such as ISIS ($R = 1$ ordered), ISIIISII ($R = 3$ ordered), and end-member illite. However, use of a group name such as smectite or illite to describe a single phase obviously is misleading. The individual components in a mixed-layer structure must be

determined, as a contribution to a full understanding of the thermodynamic definition of this very widespread species (Ransom and Helgeson, 1993).

A solution to the dilemma, and one that does provide reliable chemical and structural data, involves treating the clay-mineral samples with *n*-alkylammonium (Lagaly and Weiss, 1969), followed by imaging and analyzing selected areas using analytical HRTEM. This approach leads to an improved characterization of individual clay-mineral components, and thus to a more reliable classification of 2:1 mixed-layer phases.

Terminology and definition

In this study, the term layer represents the tetrahedral-octahedral-tetrahedral (T-O-T) part of the crystal structure in 2:1 layer silicates. The layers are described as polar and nonpolar with respect to the charge distribution within the layer structures. Mixed layering here is considered to involve a mixture of polar and nonpolar layers. Ordering of sequences is expressed with the *R* notation, which describes stacking order in the *c*-direction with respect to the interlayers without characterizing the nature of layers. Expandable components present in individual samples, with respect to the *n*-alkylammonium treatment, are designated as (1) low-charge and high-charge smectite (present in diagenetic samples), (2) vermiculite-like (expandable component in soil samples), (3) expandable illite [sequence of illite layers displaying expanded interlayers (Laird et al., 1987; Vali et al., 1991)]. (In contrast to vermiculite and high-charge smectite, expandable illite does not respond either to treatment with ethylene glycol or to *n*-alkylammonium exchange for $n_c < 12$, where n_c represents the number of C atoms in the alkyl chain.) We use the term smallest unit rather than the fundamental particle of Nadeau and coworkers. The smallest unit in smectite-group minerals is a single 2:1 layer silicate; in a rectorite-like ($R = 1$) structure there are two such units; in higher-ordered mixed-layer structures and illite there are three. A coherent sequence measured by XRD on oriented clay mineral samples, or imaged in ultrathin section by TEM, is considered here as an apparently coherent sequence, because the crystallographic orientation is evident in one direction only. Crystallographic orientation in more than one direction is expressed by the term crystallographic coherence, which is evident in two-dimensional HRTEM images (e.g., Ahn and Buseck, 1990; Veblen et al., 1990) or observed in the freeze-etch replicas of free particles in dispersion (Vali et al., 1991).

MATERIALS AND METHODS

The samples used in this study have been described as consisting of "illite-smectite" mixed layers in the literature cited and are taken from different environments of formation: (1) Zempleni, Hungary (hydrothermal; Środoń, 1984; Veblen et al., 1990; Ahn and Buseck, 1990), (2) Reindeer D-27 and Kumak E-58 oil wells in the Beaufort-Mackenzie

basin, Canada (Vali et al., 1992a; Ko, 1992; Ko and Hesse, 1992), and (3) samples SMJ9 (Kodama and Brydon, 1968) and the Ae soil horizon, New Brunswick, Canada, and E4, from the Ae soil horizon, Aylesford Lake, Nova Scotia, Canada (Ross and Kodama, 1993). In addition, muscovite from Wacker Chemie, Germany (Valie and Köster, 1986), was used as a reference sample.

A Na-saturated dispersion of the samples was dehydrated with propylene oxide and embedded in a low-viscosity epoxy resin (Spurr, 1969). Ultrathin sections (50–100 nm thick) were treated with *n*-alkylammonium solutions (Lagaly and Weiss, 1969) at 60 °C for 3 h (a significant change in layer structure cannot be observed even after 24 h of such treatment) and studied in TEM according to the conditions of sample preparation and TEM-imaging described by Vali and Hesse (1990). In all cases, the images were obtained under condition of Scherzer underfocus. Semiquantitative chemical analyses were performed by scanning transmission electron microscopy (STEM) at 100 kV. The JEOL 100 CX instrument used is equipped with an ultrahigh-resolution scanning system (EM-ASID-4D) using a transmitted electron beam and an X-ray energy-dispersion system (PGT IV), with an analyzable area of $\sim 50 \text{ nm}^2$. We used the reference muscovite to standardize the conditions of analysis. For the purpose of this study, we made use of raw data on proportions of Si, Al, Fe, Mg, and K, corrected for background and normalized to 100%, to construct the diagrams.

RESULTS

HRTEM

Our TEM investigation of 2:1 mixed-layer silicates from various environments reveals distinct differences in stacking order and chemistry. The hydrothermal sample from Zempleni, treated with *n*-alkylammonium, shows an $R = 3$ structure with packets (i.e., sequences of coherent layers of uniform spacing; Vali et al., 1991) consisting of three to six 2:1 layers having nonexpandable interlayers that are stacked in an apparently coherent sequence (Fig. 1a). XRD results of the same sample also indicate the presence of an $R = 3$ ordered structure (Środoń, 1984). The interface between adjacent packets within a coherent sequence does not respond consistently to *n*-alkylammonium treatment: some of these packets ($\sim 20\%$) show uniform expansion (Fig. 1b; here referred to as expandable illite). A small proportion (10%) are sequences of a few layers that seem disorganized and bent (Fig. 1c). TEM images of the same sample were obtained by Veblen et al. (1990) under conditions of overfocus. They interpreted the interface between adjacent packets of illite (apparently expanded interface between packets in Fig. 1a) to have a smectitic composition (dark fringes in Fig. 6 of Veblen et al., 1990). Note that such boundaries between the packet are not detectable in underfocus imaging in TEM without treatment with *n*-alkylammonium. The layer structure and stoichiometry of the hydrothermal sample are distinct from those of muscovite, diagenetic, and soil samples (see below).

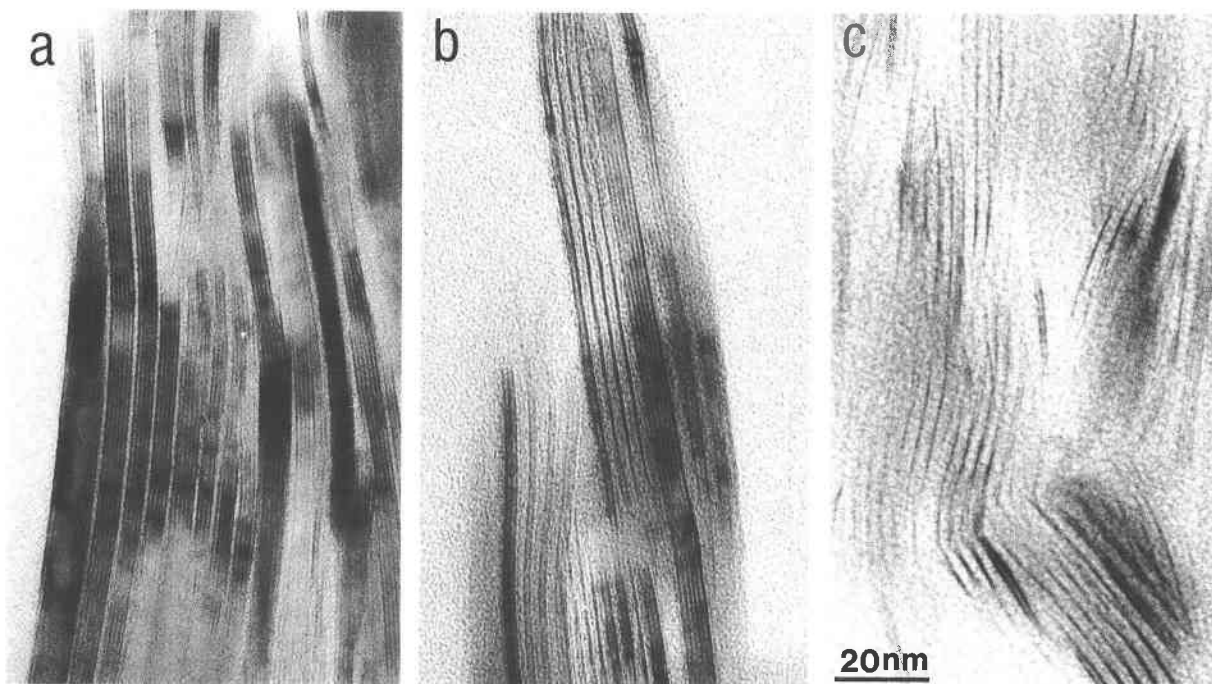


Fig. 1. TEM images of ultrathin sections of the $<0.2\text{-}\mu\text{m}$ fraction of the Zempleni illite treated with octadecylammonium. (a) A stack of packets having nonexpandable interlayers. Spacing between adjacent packets varies between 1.2 and 1.5 nm. (b) Packets of coherent expanded (2.5 nm) and nonexpanded (1.0 nm) illite components. (c) Disorganized and bent expanded layers.

Progressive illitization with depth was observed in the samples from the Beaufort-Mackenzie basin (Sears, 1993; Ko, 1992; Ko and Hesse, 1992). At shallow depths, single units of 2:1 layer silicate that represent a smectite-group phase are curved and of short length and do not seem to form coherent sequences (sample Kumak E-58, 1313, Fig. 2a). Discrete packets of illite, between three and ten layers thick, are present as isolated particles at the same depth (Fig. 2a). At greater depth of burial, packets of illite are present as isolated particles (sample Reindeer D-27, 3833 m: Fig. 2b) or as apparently more coherent sequences with a $R > 1$ structure (Fig. 2c), as was also documented by XRD (Sears, 1993; Ko, 1992; Ko and Hesse, 1992). The interface between adjacent packets, in contrast to that in the Zempleni sample, has expanded up to 2.5 nm, which indicates an interlayer charge-density > 0.6 per $\text{O}_{10}(\text{OH})_2$ (Vali and Hesse, 1990).

As Figure 3a–3c show, different types of mixed-layer structures of 2:1 phyllosilicates are present in the weathering environment of soils. The thickness of the particles in our soil samples is greater than in the hydrothermal and diagenetic samples, as is the degree of order of the apparently coherent sequences. Figure 3a represents a random mixed-layer structure (polar and nonpolar layers) having expandable and nonexpandable interlayers, whereas Figure 3b illustrates a $R = 1$ ordered structure (polar layers), and Figure 3c is a fully and uniformly expanded sequence consisting of nonpolar layers typical of vermiculite and weathered micaceous minerals (Vali and Hesse, 1992; Vali et al., 1992b). The spacing of the ex-

panded interlayers in both the random and the $R = 1$ ordered structures shows considerable variation (Fig. 3a, 3b), indicating extensive variation in the density of interlayer charge, which is a result of variation in the extent of isomorphous substitution within the T-O-T part of the 2:1 layer silicates. The number of expanded interlayers is lower in samples treated with $n_c = 7$ than in those treated with $n_c = 18$. This observation indicates that the soil sample also contains expandable illite. Note that neither variation in the charge density nor the occurrence of different types of expandable component can be detected by ethylene glycol treatment in XRD (Kodama and Brydon, 1968; Ross and Kodama, 1993).

AEM

An attempt was made to assess the relationship between the degree of expandability caused by reaction with n -alkylammonium and the extent of the isomorphous substitution of Al for Si within the T-O-T sequences of the samples characterized above. The percentage of expandable interlayers is inferred from its expected inverse relationship with the amount of K fixed in the interlayer (Fig. 4). The particles consisting predominantly of nonexpandable packets reveal high K and Al contents, whereas the particles in which the interlayer had become expanded with n -alkylammonium ions have a lowered concentration of K and Al (Fig. 4). The variation noted cannot be attributed to the presence of impurities in the samples, to chemical pretreatment of the samples (e.g., Na saturation of n -alkylammonium exchange), or to analytical

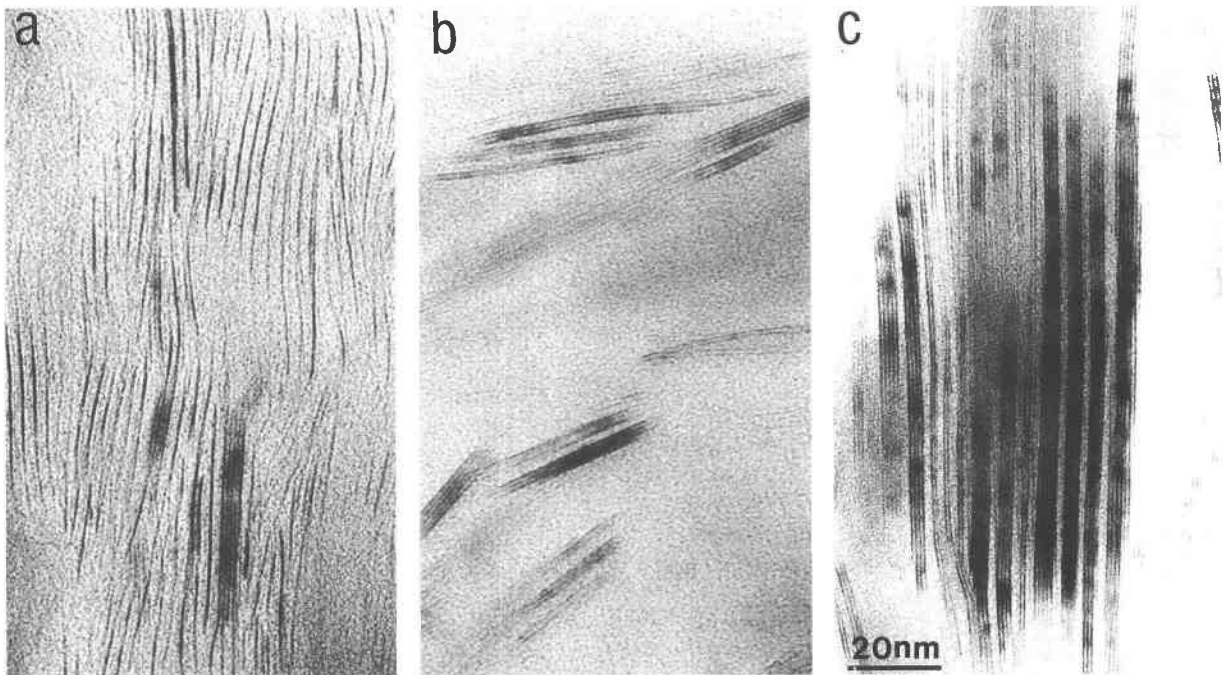


Fig. 2. TEM images of ultrathin sections of the $<0.1\text{-}\mu\text{m}$ fraction of diagenetic samples of Beaufort-Mackenzie basin treated with octadecylammonium. (a) A shallow sample (Kumak E 58, 1313 m) composed of isolated 2:1 layer silicates (smectite-group phases) and packets of discrete illite consisting of three to ten layers. (b and c) A sample from greater depth (Reindeer D-27, 3833 m) showing isolated packets of illite and units of two layers (b) or sequences with $R > 1$ and $R = 1$ order (c). Spacing between adjacent packets has a value of ~ 2.5 nm.

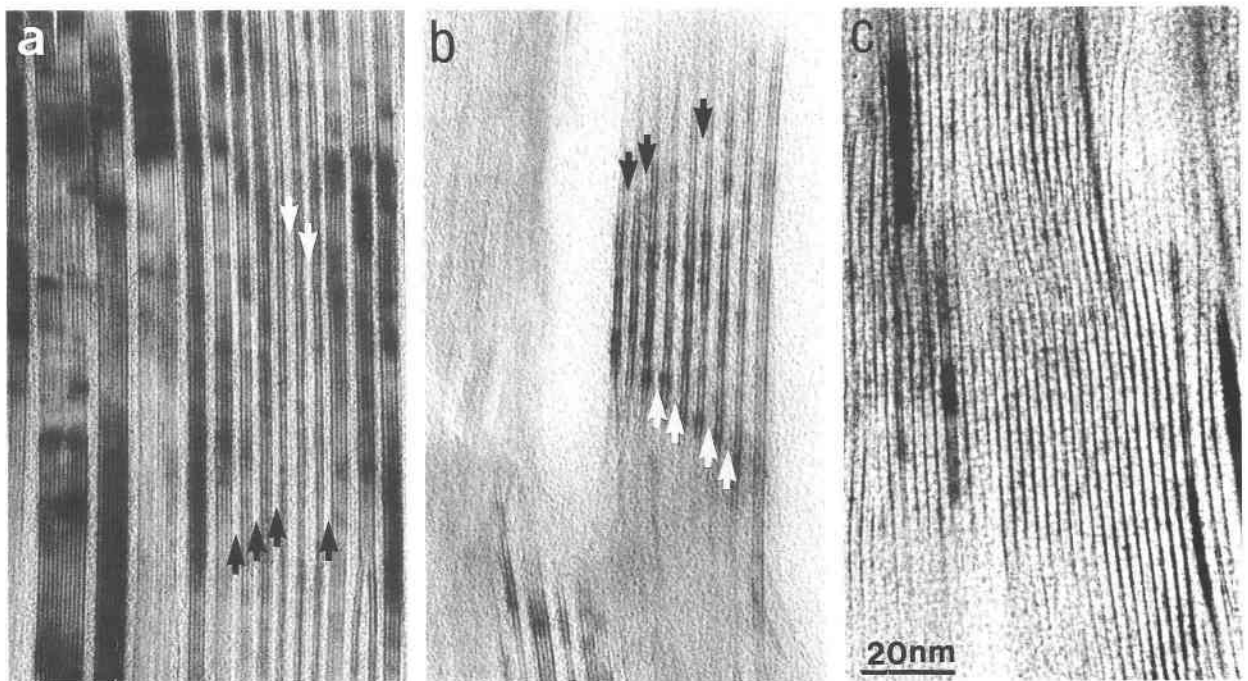


Fig. 3. TEM images of ultrathin sections of soil samples from the Ae horizon treated with octadecylammonium. (a) SMJ9 from the fraction from 2 to $0.2\ \mu\text{m}$ showing packets consisting of mostly nonexpanded interlayers (left side) and random mixed-layer structure [right side; black arrows indicate the expanded component with smaller spacing (~ 2.0 nm), and white arrows indicate those with a larger spacing (~ 2.8 nm)]. (b and c) E4

from the $<2\text{-}\mu\text{m}$ fraction showing sequences of an $R = 1$ ordered structure consisting of domains with a distinct expanded inter-layer spacing; black arrows indicate ~ 2.5 -nm spacing and white arrows indicate ~ 3.0 -nm spacing (b), and coherent sequences of 2:1 layer silicates with uniformly expanded interlayers have ~ 2.5 -nm spacing (c).

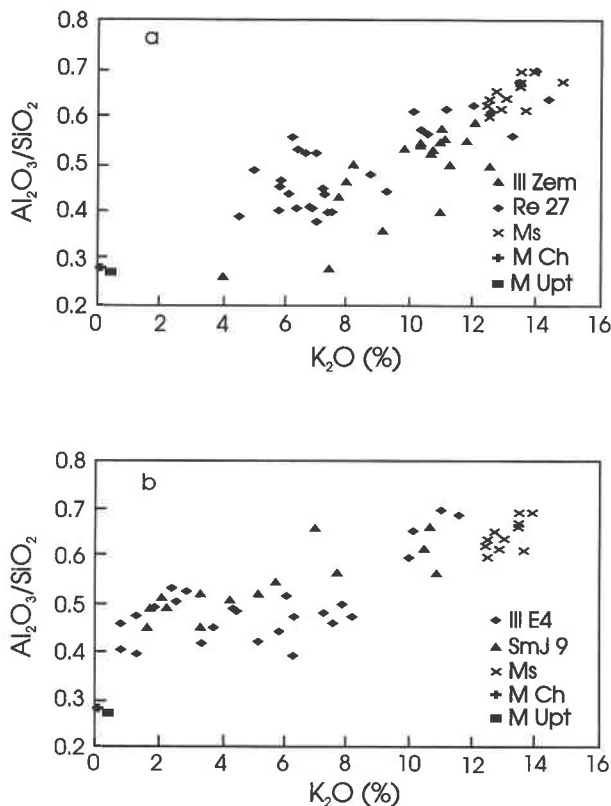


Fig. 4. Plots of chemical composition of 2:1 mixed-layer silicates, expressed in terms of $\text{Al}_2\text{O}_3/\text{SiO}_2$ vs. K_2O content. (a) Data on Zempleni illite (Ill Zem), Reindeer D-27 (Re 27). (b) Data on soil samples SMJ 9, Ill E4. The reference samples, muscovite (Ms), Upton montmorillonite (M Upt), and Chisholm montmorillonite (M Ch), were described by Vali and Köster (1986). There is a direct relationship between expandability and the K_2O content of the samples. The expandability increases from 0 (muscovite, right side) to 100% (montmorillonite, left side).

error (Warren and Ransom, 1992; Peacor, 1992a; Vali et al., 1993). Unfortunately, the spot size of the electron beam exceeds the size of the sequences of apparently coherent expanded and nonexpanded components within isolated particles in both hydrothermal and diagenetic samples (Vali et al., 1993). Thus the direct microanalysis of discrete expanded and nonexpanded components, coherently intergrown in these samples (Figs. 1b, 1c, 2a, and 2b), is not possible. In our opinion, it is because of the small scale of domain size that the amount of K (Fig. 4a) in diagenetic and hydrothermal samples seems much higher than that expected from a sequence consisting of expanded interlayers only. Nevertheless, there is extensive variation in chemical composition among the particles. In contrast, in the soil samples (Fig. 4b), the dimensions of the sequences associated with the different types of structure are sufficiently large to allow the chemical composition of discrete expandable (Figs. 3c, left side of 4b), nonexpandable (Figs. 3a, right side of 4b), and mixed-layer components (Figs. 3b, center of 4b) to be determined.

The values so obtained plot in three distinct areas. Muscovite, which shows no expansion upon treatment with *n*-alkylammonium, has the highest $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio and K_2O content. The amount of K_2O and the ratio of Al_2O_3 to SiO_2 decrease with increasing proportion of expandable interlayers. Generally, the $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio of the expandable component is higher than that of low-charge smectite-group minerals (Fig. 4; Upton montmorillonite and Chisholm montmorillonite were described by Vali and Köster, 1986), which suggests that the expandable component may be vermiculite-like or a high-charge smectite. In addition, Figure 4 shows extensive variation in the range of $\text{Al}_2\text{O}_3/\text{SiO}_2$ values that is independent of K_2O content; the depletion of K thus can also take place in interlayers characterized by a relatively high $\text{Al}_2\text{O}_3/\text{SiO}_2$ value (expandable illite). The presence of structural defects or of multiple polytypes within a mixed-layer structure (Baronnet, 1992; Lonker and Fitz Gerald 1990; Vali and Hesse 1992) also could contribute to this behavior. It is important to emphasize that the extensive variation noted among the data in Figure 4 represents a mixture of particles having different structures and stoichiometries present in the same sample. In some cases, individual particles consisting of apparently coherent sequences of different types of structure and having distinct stoichiometries also were present.

DISCUSSION

Interpretation of mixed-layer structure using Markovian and fundamental-particle models

The Markovian crystallite model and the fundamental-particle concept currently are employed to characterize "illite-smectite" mixed-layer structures. In our opinion, neither is completely satisfactory to account for findings based on TEM. In the Markovian model (Fig. 5a), structural units (smectite and illite) are considered for convenience to extend from one sheet of octahedra to the next, and the interlayer sites thus are located within the structural units. Cations of the interlayer are easily exchangeable; thus, chemical composition and structural arrangement, as well as the expandability of these units, which is important in the evaluation of the mixed-layer structures, strongly depend on the interlayer charge, type of interlayer cation, and relative humidity (Środoń, 1980). According to this model, the dispersion of illite-smectite mixed-layer samples results in the disruption of the crystal structure. In other words, the expandable and nonexpandable components would not be expected to occur as individual 2:1 layer silicates.

The *n*-alkylammonium treatment allows the identification of the T-O-T layers and interlayers of the crystal structure without image simulation (Guthrie and Veblen, 1989, 1990). In TEM images obtained under conditions of underfocus, the dark fringes represent the T-O-T layers, whereas the bright fringes represent the expandable or nonexpandable interlayers (Figs. 1, 2, and 3). Isolated particles of 2:1 layer silicate (smectite-group mineral) and

Characterization of the expandable component in 2:1 layer silicates: Treatment with *n*-alkylammonium vs. ethylene glycol treatment

On the basis of XRD measurements, the interface between the polar layers in an ordered sequence ($R = 1$, $R > 1$, or $R = 3$) responds to ethylene glycol or glycerol treatment in the same manner as in smectite-group or vermiculite phases. For this reason, these minerals are identified as illite-smectite by XRD analysis (Nadeau et al., 1987). However, a reliable description of the mixed-layer structure must be based on the characterization of the T-O-T layers they contain rather than on the response of their interlayers to the ethylene glycol or glycerol treatment. Also, a distinction between smectitic and illitic layers, as practiced by Amouric and Olives (1991) and Murakami et al. (1993), cannot be made on the basis of their apparent thickness in TEM images. According to Guthrie and Veblen (1990), great care is required in the interpretation of TEM images of layer silicates using conventional techniques of preparation and operating conditions of the TEM.

Although available analytical techniques do not permit a direct analysis of the structure and chemical composition of the individual T-O-T sequences, we contend that our approach of combined *n*-alkylammonium exchange (Lagaly and Weiss, 1969) and analytical TEM offers a unique opportunity to characterize the types of 2:1 layer silicates involved in the mixed-layer clay minerals.

At present, in the classification of ordered illite-smectite based on ethylene glycol treatment, one assumes that (1) these materials are composed of one type of nonexpandable illite (1.0 nm) and an expandable smectite component (1.7 nm) and (2) there is one pattern of order present in the individual samples. However, our TEM results on mixed-layer materials treated with *n*-alkylammonium from different environments revealed that different types of particles with distinct patterns of order do occur in a single sample; thus more than one type of expandable component is involved in the mixed-layer structure in 2:1 mixed-layer silicates. As an example, rectorite from Little Rock, Arkansas, shows a sharp peak at 2.7 nm upon treatment with ethylene glycol. However treatment of the same sample with *n*-alkylammonium (Fig. 2e in Lagaly, 1979) reveals the presence of domains with distinctly different values of charge density of the expandable component. Short-range order of coherent sequences with different spacings of the expanded interlayers also is observed in the $R = 1$ ordered structure in ultrathin sections of soil samples (Fig. 3b). These differences in expansion behavior cannot be detected in XRD analysis of specimens treated with ethylene glycol. In addition to the expandable components with low charge, illitic materials also contain expandable components with high charge, such as expandable illite and vermiculite-like layers (Fig. 4, left side). These components do not respond to treatment with ethylene glycol upon K saturation and mimic a true illitic component in XRD anal-

yses. The illitic interlayers in illite-smectite produced by the wetting and drying of smectite-group minerals in a K-saturated environment (Środoń et al., 1992; Eberl et al., 1993) may be of a similar nature.

A multistep mechanism, involving the coalescence of smectite layers by K fixation or the dissolution of metastable illite and the precipitation of more stable illite, has been proposed to explain the formation of illite during burial diagenesis or metamorphism (Eberl, 1993). However, there is a significant difference in morphology between illite formed from smectite by K fixation (Ko, 1992; Eberl et al., 1993) and authigenic illite formed by means of dissolution and reprecipitation (Freed and Peacor, 1992). Both samples may show the same response to the ethylene glycol, and, therefore, both may be designated as illite in terms of XRD evidence. However, it is most likely that the chemistry and structure of these two types of illite differ significantly, as do their morphological features. In addition, it is evident that K is irreversibly fixed by the illite component produced by K saturation (Eberl et al., 1987). Note that the degree of expansion with *n*-alkylammonium ions depends mostly on structural arrangement and chemical composition rather than being a function of time or kinetics of reaction (Vali and Hesse, 1990, 1992).

TEM images obtained under conditions of overfocus suggest that the interface between adjacent packets of illite in ordered 2:1 mixed-layer silicates has a smectitic composition (Ahn and Peacor, 1989; Veblen et al., 1990). However, results of our TEM investigation revealed that there is no such smectite phase in ordered illite-smectite mixed-layer silicates, in agreement with what has previously been suggested by Nadeau et al. (1984a, 1984b, 1984c) on the basis of thickness measurements using the Pt-C shadowing technique. If the expandable component in ordered mixed layers were to behave as a true smectite phase, as Altaner et al. (1988) suggested, one would expect the mixed-layer structure (Figs. 1a, 3c) to disaggregate upon dispersion. However, three-dimensional XRD patterns of disaggregated illite-smectite samples (Reynolds, 1992) and a TEM investigation of illitic materials in dispersion (Vali et al., 1991) revealed that the stacking order of 2:1 mixed-layer materials is preserved upon chemical treatment and dispersion.

There is additional evidence supporting the concept that 2:1 mixed-layer silicates have a distinct composition and structure (characterized by P layers) and are not a collage of illite and smectite phases: (1) Thermodynamic studies of Ransom and Helgeson (1993) revealed that illite and smectite do not form a mutual solid solution corresponding to mixed-layer illite-smectite. (2) Image simulation of calculated two-component systems in ordered illite-smectite mixed layers shows significant differences among smectite and illite components, whereas structural imaging of natural samples does not reveal any differences among interlayers within a coherent sequence of illite-smectite mixed layers (Ahn and Buseck, 1990). Although this difference could be explained by the im-

aging conditions not being optimal (Guthrie and Veblen, 1990), we consider the difference as evidence that the expandable component is not truly smectitic. (3) Smectite-group minerals observed in TEM show a larger spacing (11–13 Å), in specimens prepared either by microtomy or by ion-milling, than illite (10 Å) observed in TEM (Ahn and Peacor, 1986a; Vali and Köster, 1986; Środoń et al., 1990), whereas the expandable component in ordered illite-smectite mixed layers shows a spacing of 10 Å (Ahn and Peacor, 1989; Veblen et al., 1990; Ahn and Buseck, 1990; Środoń et al., 1990; Vali and Hesse, 1990; Vali et al., 1991). For a number of reasons, therefore, it is obvious that ordered illite-smectite (XRD definition) does not consist of illite and smectite phases. On the other hand, a smectite-group phase and illite may occur as distinct phases in a random mixed-layer arrangement (Fig. 3a). Ahn and Peacor (1986a) noted that in the early stage of diagenesis, smectite and illite are morphologically and chemically distinct.

The nature of 2:1 layer silicates and the status of mixed layering: A definition based on TEM

The different responses of interlayers to treatment with *n*-alkylammonium are a result of differences in the nature of isomorphous substitution within the T-O-T sequences. With increasing proportions of expandable interlayers within a mixed-layer structure, the Al-Si ratio gradually decreases. This suggests a lower density of interlayer charge in the expandable component (Lagaly, 1979) and implies a composition different from that in the nonexpanded component (Fig. 4). However, variation in Al₂O₃-SiO₂ ratio of samples having a similar expansion and K content (Fig. 4, left side) indicates the presence of both low-charge (smectitic) and high-charge (expandable illite or vermiculite?) expandable components in those samples.

The occurrence of different types of 2:1 layer silicate (Figs. 1, 2, and 3) with distinct stoichiometries (Fig. 4) is in agreement with the solubility data of Aja and Rosenberg (1992) and Aja et al. (1991), which revealed the existence of "multiple, stoichiometric mica-like phases" in illitic materials. However, it seems more likely to us that phases of distinct stoichiometry are associated with the arrangement and ratio of different types of polar and nonpolar layers present in the samples rather than related to different stacking sequences (S, IS, ISII, I), as was assumed by these authors.

Stacking order in a mixed-layer structure can best be described by the P-layer concept proposed by Güven (1991). Smectite-group layers (Figs. 2a, 5c), nonexpandable mica-like layers (Fig. 3a, left side), expandable illite (Fig. 1b), and vermiculite-like layers (Fig. 3c) have a single type of nonpolar 2:1 layer structure and represent distinct single phases. The rectorite-like $R = 1$ ordered structure (Figs. 3b, 5a) is composed of polar 2:1 layers only (Lagaly 1979; Ahn and Peacor, 1986b) and should be described as a single phase. This is in agreement with the structural model of Jiang et al. (1990) that rectorite-like illite-smectite has a unique structure and chemistry, thus

contradicting a model that proposes equal proportions of illite- and smectite-like layers. Randomly ordered structures ($R = 0$; Fig. 4a, right side) and $R > 1$ ordered structures (Figs. 1a, 2c) are composed of both types of layer (polar and nonpolar). It is most likely that the outer layers of individual packets of nonexpandable illite (Figs. 1b, 2a, 2b, and 5d) are polar. If these packets, which are composed of sequences of nonpolar (inner) and polar (outer) 2:1 layers, can be described as a distinct thermodynamic phase, then a coherent sequence of such packets (Figs. 1a, 2c) also should be treated as a single phase. Since there is no discrete smectite-group phase associated with the ordered 2:1 mixed-layer structures, the mixed-layer status of 2:1 layer silicates depends only on the composition and arrangement of polar and nonpolar layers. We propose that stacking order be denoted by terms such as $R = 0$, $R = 1$, $R > 1$, and $R = 3$ in the classification of mixed-layer minerals rather than by the notation IS, ISII, etc. $R = 0$ represents a random mixed-layer structure; $R = 1$ stands for rectorite-like structures; $R = 3$ refers to a sequence consisting of packets having between three and six layers of illite; and $R > 1$ is a structure intermediate between that of $R = 1$ and that of $R = 3$.

A definition of mixed-layer structure based on TEM observations reflects more accurately the true nature of mixed-layer material than one based on other techniques. In contrast to treatment with ethylene glycol, expandability measurement based on treatment with *n*-alkylammonium allows distinction among different types of layer having expandable and nonexpandable interlayers (Lagaly and Weiss, 1969; Lagaly, 1979; Vali and Hesse, 1990). Extensive variations in chemical composition noted among the sequences (Fig. 4) are consistent with a suggestion that illitic materials consist of mixtures instead of being monomineralic. This recognition has important implications for a reliable evaluation of diagenetic and weathering processes involving phase transitions, radiometric dating, crystal growth, and pseudomorphism.

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REFERENCES CITED

- Ahn, J.H., and Buseck, P.R. (1990) Layer-stacking sequences and structural disorder in mixed-layer illite/smectite: Image simulation and HRTEM imaging. *American Mineralogist*, 75, 267–275.
- Ahn, J.H., and Peacor, D.R. (1986a) Transmission and analytical electron microscopy of the smectite-to-illite transition. *Clays and Clay Minerals*, 34, 165–179.
- (1986b) Transmission electron microscope data for rectorite: Implications for the origin and structure of "fundamental particles." *Clays and Clay Minerals*, 34, 180–186.
- (1989) Illite/smectite from Gulf Coast shales: A reappraisal of transmission electron microscope images. *Clays and Clay Minerals*, 37, 542–546.
- Aja, S.U., and Rosenberg, P.E. (1992) The thermodynamic status of com-

- positionally variable clay minerals: A discussion. *Clays and Clay Minerals*, 40, 292–299.
- Aja, S.U., Rosenberg, P.E., and Kittrick, J.A. (1991) Illite equilibria in solutions. I. Phase relationships in the system $K_2O-Al_2O_3-SiO_2-H_2O$ between 25° and 250 °C. *Geochimica et Cosmochimica Acta*, 55, 1353–1364.
- Allen, F.M. (1992) Mineral definition by HRTEM: Problems and opportunities. In *Mineralogical Society of America Reviews in Mineralogy*, 27, 289–333.
- Altaner, S.P., Weiss, C.A., Jr., and Kirkpatrick, R.J. (1988) Evidence from ^{29}Si NMR for the structure of mixed-layer illite/smectite clay minerals. *Nature*, 331, 699–702.
- Amouric, M., and Olives, J. (1991) Illitization of smectite as seen by high-resolution transmission electron microscopy. *European Journal of Mineralogy*, 3, 831–835.
- Baronnet, A. (1992) Polytypism and stacking disorder. In *Mineralogical Society of America Reviews in Mineralogy*, 27, 231–288.
- Bell, T. E. (1986) Microstructure in mixed-layer illite/smectite and its relationship to the reaction of smectite to illite. *Clays and Clay Minerals*, 34, 146–154.
- Corbato, C. E., and Tettenhorst, R.T. (1987) Analysis of illite-smectite interstratification. *Clay Minerals*, 22, 269–285.
- Eberl, D.D. (1993) Three zones for illite formation during burial diagenesis and metamorphism. *Clays and Clay Minerals*, 41, 26–37.
- Eberl, D.D., Środoń, J., Lee, M., Nadeau, P.H., and Northrop, H.R. (1987) Sericite from the Silverton caldera, Colorado: Correlation among structure, composition, origin, and particle thickness. *American Mineralogist*, 72, 914–935.
- Eberl, D.D., Velde, B., and McCormick, T. (1993) Synthesis of illite-smectite from smectite at Earth surface temperatures and high pH. *Clay Minerals*, 28, 49–60.
- Freed, R.L., and Peacor, D.R. (1992) Diagenesis and formation of authigenic illite-rich I/S crystals in Gulf Coast shales: TEM study of clay separates. *Journal of Sedimentary Petrology*, 62, 220–234.
- Guthrie, G.D., Jr., and Veblen, D.R. (1989) High-resolution transmission electron microscopy of mixed-layer illite/smectite: Computer simulations. *Clays and Clay Minerals*, 34, 1–11.
- (1990) Interpreting one-dimensional high-resolution transmission electron micrographs of sheet silicates by computer simulation. *American Mineralogist*, 75, 276–288.
- Güven, N. (1991) On a definition of illite/smectite mixed-layer. *Clays and Clay Minerals*, 39, 661–662.
- Jiang, Wei-Teh, Peacor, D.R., Merriman, R.J., and Roberts, B. (1990) Transmission and analytical electron microscopic study of mixed-layer illite/smectite formed as an apparent replacement product of diagenetic illite. *Clays and Clay Minerals*, 38, 449–468.
- Ko, J. (1992) Illite/smectite diagenesis in the Beaufort-Mackenzie Basin, Arctic Canada, 184 p. Ph.D. thesis, McGill University, Montreal, Canada.
- Ko, J., and Hesse, R. (1992) Illite/smectite diagenesis in overpressured and normally pressured environments. Beaufort-Mackenzie Basin, Arctic Canada. In Y.K. Kharaka and A.S. Meast, Eds., *Proceedings of the 7th International Symposium on Water-Rock Interaction*, p. 1173–1176. Park City, Utah, 13–18 July, 1992.
- Kodama, H., and Brydon, J.E. (1968) A study of clay minerals in podzol soils in New Brunswick, Eastern Canada. *Clay Minerals*, 7, 295–309.
- Lagaly, G. (1979) The “layer charge” of regular interstratified 2:1 clay minerals. *Clays and Clay Minerals*, 27, 1–10.
- Lagaly, G., and Weiss, A. (1969) Determination of the layer charge in mica-type layer silicates. *Proceedings of the International Clay Conference*, Tokyo, 1969, 1, 61–80.
- Laird, D.A., Scott, A.D., and Fenton, T.E. (1987) Interpretation of alkylammonium characterization of soil clays. *Soil Science Society of America Journal*, 51, 1659–1663.
- Lonker, S.W., and Fitz Gerald, J.D. (1990) Formation of coexisting 1M and 2M polytypes in illite from an active hydrothermal system. *American Mineralogist*, 75, 1282–1289.
- Mackinnon, I.D.R. (1987) The fundamental nature of illite/smectite mixed-layer clay particles: A comment on papers by P.H. Nadeau and co-workers. *Clays and Clay Minerals*, 35, 74–76.
- Murakami, T., Sato, T., and Watanabe, T. (1993) Microstructure of interstratified illite/smectite at 123 K: a new method for HRTEM examination. *American Mineralogist*, 78, 465–468.
- Nadeau, P.H., Tait, J.M., McHardy, W.J., and Wilson, M.J. (1984a) Interstratified XRD characteristics of physical mixtures of elementary clay particles. *Clay Minerals*, 19, 67–76.
- Nadeau, P.H., Wilson, M.J., McHardy, W.J., and Tait, J.M. (1984b) Interparticle diffraction: A new concept for interstratified clays. *Clay Minerals*, 19, 757–769.
- (1984c) Interstratified clays as fundamental particles. *Science*, 225, 923–925.
- (1987) The fundamental nature of interstratified illite/smectite clay particles: A reply. *Clays and Clay Minerals*, 35, 77–79.
- Peacor, D.R. (1992a) Analytical electron microscopy: X-analysis. In *Mineralogical Society of America Reviews in Mineralogy*, 27, 113–140.
- (1992b) Diagenesis and low-grade metamorphism of shales and slates. In *Mineralogical Society of America Reviews in Mineralogy*, 27, 335–380.
- Ransom, B., and Helgeson, H.C. (1989) On the correlation of expandability with mineralogy and layering in mixed-layer clays. *Clays and Clay Minerals*, 37, 189–191.
- (1993) Compositional end members and thermodynamic components of illite and dioctahedral aluminous smectite solid solutions. *Clays and Clay Minerals*, 41, 537–550.
- Reynolds, R.C., Jr. (1985) NEWMOD: A computer program for the calculation of one-dimensional diffraction patterns of mixed-layer clays. R.C. Reynolds, 8 Brook Road, Hanover, New Hampshire 03755, U.S.A.
- (1992) X-ray diffraction studies of illite/smectite from rocks, <1 μm randomly oriented powders, and <1 μm oriented powder aggregates: The absence of laboratory-induced artifacts. *Clays and Clay Minerals*, 40, 387–396.
- Ross, G.J., and Kodama, H. (1993) X-ray diffraction characteristics and related properties of smectite in some Canadian soils. *Canadian Journal of Soil Sciences*, 73, 93–102.
- Sears, S.K. (1993) Effects of sample treatment on mixed-layer illite/smectite in X-ray diffractograms and transmission electron micrographs, 178 p. M.Sc. thesis, McGill University, Montreal, Canada.
- Spurr, A.R. (1969) A low-viscosity epoxy resin embedding medium for electron microscopy. *Journal of Ultrastructure Research*, 26, 31–43.
- Środoń, J. (1980) Precise identification of illite/smectite interstratifications by X-ray powder diffraction. *Clays and Clay Minerals*, 28, 401–411.
- (1984) X-ray powder diffraction identification of illitic materials. *Clays and Clay Minerals*, 32, 337–349.
- Środoń, J., Andreoli, C., Elsass, F., and Robert, M. (1990) Direct high-resolution transmission electron microscopic measurement of expandability of mixed-layer illite/smectite in bentonite rock. *Clays and Clay Minerals*, 38, 373–379.
- Środoń, J., Elsass, F., McHardy, W.J., and Morgan, D.J. (1992) Chemistry of illite-smectite inferred from TEM measurements of fundamental particles. *Clay Minerals*, 27, 137–158.
- Tettenhorst, R.T., Corbato, C.E., and Haller, R.I. (1990) The I-S contact in 10 Å–17 Å interstratified clay minerals. *Clay Minerals*, 25, 437–445.
- Vali, H., and Hesse, R. (1990) Alkylammonium ion treatment of clay minerals in ultrathin sections: A new method for HRTEM examination of expandable layers. *American Mineralogist*, 75, 1443–1446.
- (1992) identification of vermiculite by transmission electron microscopy (TEM) and X-ray diffraction. *Clay Minerals*, 27, 185–192.
- Vali, H., and Köster, H.M. (1986) Expanding behaviour, structural disorder, regular and random irregular interstratification of 2:1 layer-silicates studied by high-resolution images of transmission electron microscopy. *Clay Minerals*, 21, 827–859.
- Vali, H., Hesse, R., and Kohler, E.E. (1991) Combined freeze-etch replicas and HRTEM images as tools to study fundamental-particles and the multi-phase nature of 2:1 layer silicates. *American Mineralogist*, 76, 1973–1984.
- Vali, H., Hesse, R., and Ko, J. (1992a) Transmission electron microscopic (TEM) study of illite-smectite (I/S) diagenesis in the Beaufort-Mackenzie Basin, Arctic Canada. American Association of Petroleum Geologists, Annual Convention, p. 133–134. Calgary, June 21–24, 1992.
- Vali, H., Hesse, R., and Kodama, H. (1992b) Arrangement of *n*-alkylam-

- monium ions in phlogopite and vermiculite: An XRD- and TEM-study. *Clays and Clay Minerals*, 40, 240–245.
- Vali, H., Martin, R.F., Amaratidis, G., and Morteani, G. (1993) Smectite-group minerals in deep-sea sediments: Monomineralic solid-solution or multiphase mixtures? *American Mineralogist*, 78, 1217–1229.
- Veblen, D.R., Guthrie, G.D., Jr., Livi, K.J.T., and Reynolds, R.C., Jr. (1990) High-resolution transmission electron microscopy and electron diffraction of mixed-layer illite/smectite: Experimental results. *Clays and Clay Minerals*, 38, 1–13.
- Warren, E.A., and Ransom, B. (1992) The influence of analytical error upon the interpretation of chemical variations in clay minerals. *Clay Minerals*, 27, 193–209.

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