

Combined freeze-etch replicas and HRTEM images as tools to study fundamental particles and the multiphase nature of 2:1 layer silicates

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ABSTRACT

Comparative studies of illite and glauconite dispersions ($<1.0\ \mu\text{m}$ fraction) using transmission electron microscopy on freeze-etch replicas and ultrathin sections provide detailed information on surface morphology and layer structure of these 2:1 layer silicates. Results show that the arrangement of layer packets observed in ultrathin section is both a clumping artifact caused by dehydration required for embedding and a primary structure. Adjacent packets (40–150 Å) of 2:1 layers usually do not split along joint interfaces even in dilute and Na-saturated dispersions. The thickness of these packets imaged on ultrathin sections is in agreement with the size of illite “fundamental particles.” However, they do not usually occur as free particles in dispersion. The thickness of individual free particles observed in freeze-etch replicas varies between 50 and 500 Å. Thus most free particles of illite and glauconite are composed of several packets.

Treatment of samples with octadecylammonium ions reveals three different types of interlayer spacings corresponding to (1) a high-charged nonexpandable component (10 Å in XRD and HRTEM), (2) a high-charged expandable component (29–30 Å in XRD; 24 Å in HRTEM), and (3) a low-charged expandable component as single interlayers between adjacent packets and as expandable components in the 1:1 ordered mixed layers (no XRD peak; 16–17 Å in HRTEM). It is concluded that the illitic materials contain at least three distinct phases: a nonexpandable illite phase, an expandable illite phase, and a 1:1 ordered mixed-layer phase. The IIS or IIIS structures identified in XRD are due to interparticle diffraction. The smectite-like interlayers in ordered mixed-layer clays do not represent a separate phase.

INTRODUCTION

Comparison of the surface morphology of naturally occurring clay particles with their detailed layer structures has important implications for the fundamental particle hypothesis and the multiphase nature of illitic clays. This paper reports the results of a comparative study of the surface morphology, layer structure, and crystallite size of illite and glauconite particles using freeze-etch replicas and ultramicrotome sections.

The surface morphology of clay minerals can be studied in dispersed systems. For the investigation of dilute aqueous dispersions, the advanced cryofixation technique (Robards and Sleytr, 1985; Bachmann, 1987) followed by freeze etching (Moor and Muehlethaler, 1963) has great advantage over conventional preparation methods such as sample drying and impregnation. These techniques enable the observation of detailed surface features of clay mineral particles dispersed in H_2O (Vali and Bachmann, 1988). Since they do not dehydrate samples as occurs during conventional shadowing (Baronnet, 1972; Nadeau et al., 1984a, 1984b, 1984c), the true surface morphology of clay minerals can be studied. Furthermore, the TEM

resolution of platinum-carbon-shadowed replicas (approximately 10 Å for layer silicates, Baronnet, 1972) is much higher than that achieved with scanning electron microscopy (SEM).

High-resolution transmission electron microscopy (HRTEM) allows the direct observation of illite and smectite layers as well as their stacking sequence. However, comparison with computer-simulated images shows that determination of smectite layers in illitic material is possible only under certain TEM focus conditions; thus, prudence is required in the interpretation of HRTEM images (Guthrie and Veblen, 1989, 1990; Veblen et al., 1990; Ahn and Peacor, 1989).

Application of the alkylammonium ion-exchange method of Lagaly and Weiss (1969) to XRD (Lagaly, 1979, 1982; Rühlcke and Kohler, 1981; Stanjek and Friedrich, 1986; Laird et al., 1987; Olis et al., 1990; Vali, 1983) and to TEM investigations (Ahn and Peacor, 1986a; Lee and Peacor, 1986; Vali and Köster, 1986; Bell, 1986; Klimentidis and Mackinnon, 1986; Marcks et al., 1989; Ghabru et al., 1989) has had great impact on the characterization of expandable and nonexpandable layer sil-

icates and made HRTEM investigations of these minerals most profitable. Using this method, Vali and Hesse (1990) introduced a new preparation technique for HRTEM, which allows the estimation of interlayer charge in expandable clay minerals on ultrathin sections.

An important aspect of clay minerals is particle thickness. Besides being needed for the calculation of simulated X-ray diffraction patterns (e.g., Reynolds, 1989; Bethke and Altaner, 1986; Inoue et al., 1989), clay particle thickness is critical for the fundamental particle hypothesis of Nadeau et al. (1984a, 1984b, 1984c) and Nadeau (1985); this hypothesis provides a conceptual interpretation for the difference in origin between random and ordered smectite/illite mixed layers (S/I). To understand the origin of these interstratified clays, however, it is necessary to determine whether fundamental clay particles occur commonly in nature (Mackinnon, 1987; Altaner et al., 1988). More recently, the multiphase nature of illitic materials has been the subject of extensive discussions by Altaner and Vergo (1988), Eberl et al. (1988), and Rosenberg et al. (1990), which again center on the problem of the existence of fundamental particles for different phases. In HRTEM images of illite and glauconite, Vali and Köster (1986) observed successive stacks of layers with varying swelling capabilities. They could not determine, however, whether the different packets were parts of the same crystal or whether they belonged to different crystals that, upon desiccation, became stacked by chance.

These problems are here further pursued with a combination of newly developed methods for the study of the surface morphology and ultrafine structure of 2:1 layer silicates.

Terminology

The terms for various components of layer silicate structures used in this paper are applied in the sense of Brown (1984). In addition, the term "packet" is used to describe a coherent sequence of 2:1 layers in ultrathin section. The term "free particle" is used for a particle observed in freeze-etch replica. In colloid chemistry, the term "free particle" applies to particles that, in dispersion, behave kinetically independently (Hiemenz, 1986). The cooling rate of the applied cryo-technique is high enough to prevent phase separation and to preserve the random distribution of particles in dispersion because the ice crystals formed remain significantly smaller than the objects to be studied (Vali and Bachmann, 1988). Therefore the particles shown in freeze-etch replicas represent free particles in dispersion in the sense of the colloid chemist's definition. The term "unit" is used as an equivalent of packets for lath-shaped and platy morphological entities, which are visible in freeze-etch replicas on the surface of a free particle as coherent surface elements surrounded by steps or furrows. A free particle can be composed of numerous units. "Particle" is the general term that applies to all types of particles occurring in both freeze-etch replicas and ultrathin sections. "Fundamental particle" is a term introduced by Nadeau et al. (1984b,

1984c) and Nadeau (1985) for the smallest units of smectite and illite in mixed-layer clays. Fundamental particles of smectite consist of single 2:1 layers 10 Å thick. Fundamental particles of illite consist of two or more such layers which are 20, 30, or up to 90 Å thick, all coordinated by planes of K interlayer ions. A "phase" is "a state of matter that is uniform throughout, not only in chemical composition but also physical state" (Gibbs, quoted in Atkins, 1978; Eberl et al., 1988). In the following, we use the acronym ODAT as an abbreviation for octadecylammonium treatment or octadecylammonium treated (R. Reynolds, Jr., personal communication).

MATERIAL AND METHODS

Samples

Illite from Füzerradvany, Hungary, which formed by hydrothermal alteration of feldspar (Nemez, 1973); glauconite from Bichl, Bavaria, which formed from gel-like hydroxide precipitates and amorphous biogenic silica under reducing conditions (Kohler and Köster, 1976); and an epimetamorphic slate from the northern Appalachians in Quebec, Canada, were selected for this study. The samples were treated with a 0.1 M solution of di-sodium-ethylenediamine-tetracetic acid (EDTA-Na₂) three times for 24 h at room temperature for carbonate removal and Na saturation; they were then washed with distilled H₂O until all excess EDTA Na₂ was removed (Köster et al., 1973). After dispersion, the fraction of the samples that was <1.0 μ was separated with a centrifuge.

Ultrathin sectioning

Fifty milligrams of freeze-dried sample material were embedded in 1 mL of a low-viscosity resin (Spurr, 1969) for HRTEM study (Lee and Jackson, 1975; Vali and Köster, 1986). To preserve the uniform distribution of the clay mineral particles, the samples were carefully stirred until the resin became highly viscous. Ultrathin sections were then prepared using an ultramicrotome (Reichert-Jung Ultracut E). For the examination of expandability, the samples were treated with octadecylammonium ions before resin impregnation for 2 d at 60 °C, following the method of Lagaly and Weiss (1969) and Vali and Köster (1986). The sample from Quebec was treated after section preparation (Vali and Hesse, 1990). The ultrathin sections were studied with a JEOL 100 CX transmission electron microscope (TEM) at 100 kV. Focus conditions approximated the Scherzer defocus, depending on the thickness of the sections, which varied between 500 and 700 Å.

Cryofixation and freeze etching

For cryofixation and freeze etching, the samples were frozen following the spray method of Bachmann and Schmitt (1971). Suspensions of 5% illite and glauconite were prepared using different electrolytes. To obtain complete dispersion of the particles, the Na-saturated 5% suspensions were prepared at least 1 week before investiga-

tion and were ultrasonicated periodically (two times per day for 3 min). Approximately 300 μL of the suspension were sprayed with a commercial retouching air brush into a propane-propylene mixture (temperature of 77 K or -196°C) from a distance of 20 cm at a pressure of 1.5 kp/cm^2 . The perfectly dispersed particles were frozen without cryo-artifacts at a cooling rate of 10^5 K/s in droplets of fluid 10–50 μm in diameter. The liquid propane-propylene mixture, which served as a cryomedium, was evaporated in a preparation box under slightly reduced pressure at 187 K (-86°C). The frozen clay suspension was then mixed with one or two drops of ethyl benzene at 187 K and transferred onto a Au specimen holder. In the freeze-etch unit (Balzer's model BAF 400T), the samples were fractured in a vacuum of 10^{-6} torr at a temperature of 173 K (-100°C). The fractured surfaces were etched by ice sublimation for 1 min at 173 K and 10^{-6} torr. They were then platinum-carbon shadowed at an angle of 45° and coated with a C layer 100 $\text{\AA}$ thick for stabilization. A more detailed description of the process is given by Moor and Muehlethaler (1963) and Robards and Sleytr (1985). The replica was floated in distilled H_2O and kept for 24 h in 6% HF to dissolve adhering silicate particles. Replicas were imaged with a JEOL 100 CX at 100 kV TEM.

RESULTS

XRD patterns of ethylene-glycol-saturated Hungary illite of this study indicated the presence of R3-ordered mixed layers with about 10% smectite-like expandable layers, estimated by comparison with the patterns of Reynolds and Hower (1970) and Środoń (1984). Before glycolation, the (001) reflection of Hungary illite gave a d value of 10.3 $\text{\AA}$, which after glycolation split into a 9.8 $\text{\AA}$ and a 11.0–11.6 $\text{\AA}$ reflection (Fig. 1, sections a and b). The 11.6- and 9.8- $\text{\AA}$ peaks indicate R3-ordered mixed layers. The XRD pattern of this illite (Fig. 1, section b) is similar to that of the Kalkberg bentonite (Fig. 2 in Reynolds and Hower, 1970) and the Devonian bentonite (Fig. 6 in Nadeau et al., 1984b). After glycolation, the 10.2- $\text{\AA}$ peak of the Bavaria glauconite changed to 10.0 $\text{\AA}$ and broadened (Fig. 1, sections c and d). The XRD pattern of illite from Quebec did not change upon glycolation (Fig. 1, sections e and f). This sample also contained about 50% chlorite. Figure 2, sections a–i show X-ray diffraction patterns of the same samples described above together with some reference samples after ODAT.

Comparison of freeze-etch replicas and ultrathin sections

Replicas of spray-frozen and freeze-etched clay mineral dispersions allowed the observation of free particles in TEM. It is of interest to compare the surface morphology and thickness of these particles with the layer structure observed in ultrathin sections. Measurement of the thickness of free particles from freeze-etch replicas poses problems because the angle of observation in TEM is not precisely known. Determination of the thickness was possible,

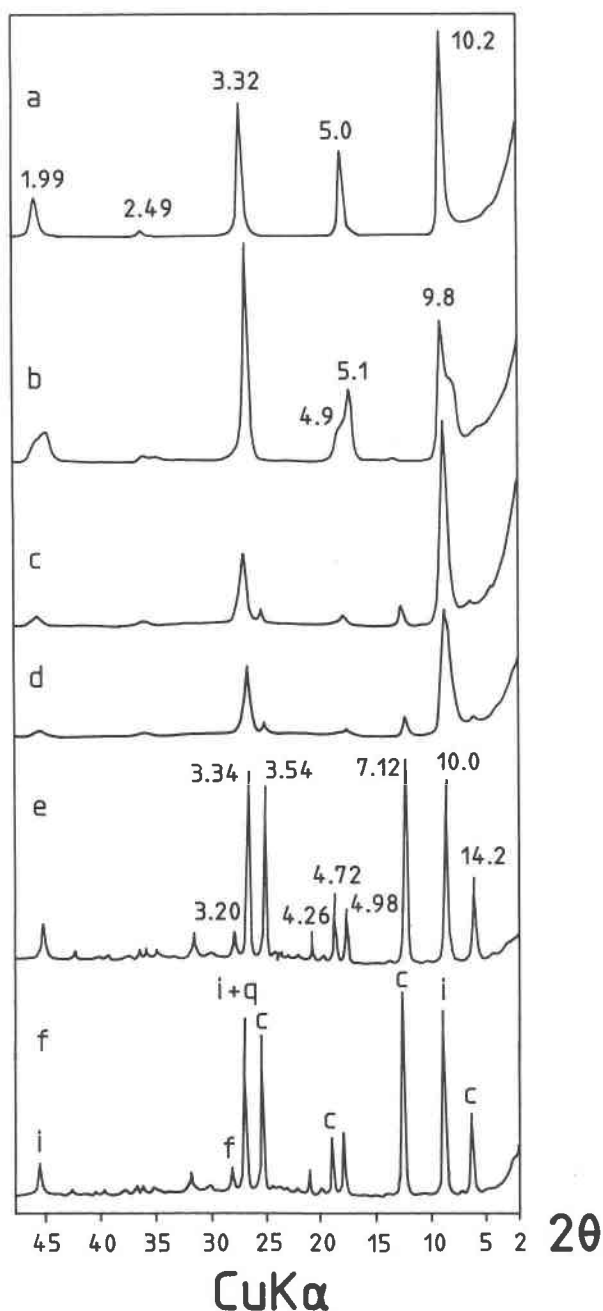


Fig. 1. X-ray diffraction patterns: a = Hungary illite (Füzervány), air dried. b = The same specimen after glycolation. The (001) reflection at 10.3 $\text{\AA}$ (before glycolation) splits into a 9.8- $\text{\AA}$ peak and a peak at 11.0–11.6 $\text{\AA}$ after glycolation. c = Bavaria glauconite (Bichl), air dried. d = The same specimen after glycolation. The 10.2- $\text{\AA}$ peak changes to 10.0 $\text{\AA}$ and broadens. e = Quebec illite (northern Appalachians), air dried. f = the same specimen after glycolation does not show any changes in its XRD pattern. All samples are fractions $<1.0 \mu\text{m}$. Ethylene glycol solvation accomplished by exposure to the vapor at 60°C for 24 h. Abbreviations are c = chlorite; i = illite; q = quartz; f = feldspar.

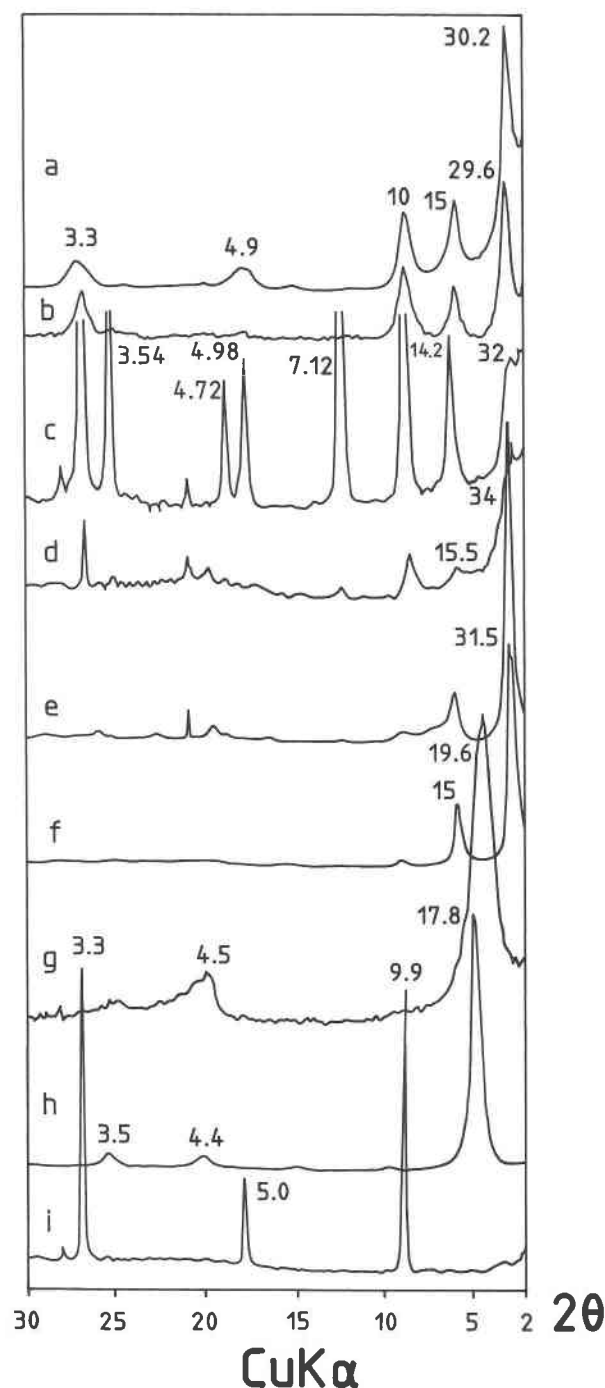


Fig. 2. X-ray diffraction patterns of ODAT (octadecylammonium treatment) samples: a = Hungary illite; b = Bavaria glauconite; c = Quebec illite; d = S/I mixed-layer clays, Mancos Shale (CMS sample ISTM-1); e = rectorite, Little Rock, Arkansas; f = vermiculite, Llano, Texas; g = calcium montmorillonite, Polkville, Mississippi (API standard 21); h = sodium montmorillonite, Upton, Wyoming (API standard 25); i = finely ground muscovite, Wacker Chemie, Munich. All samples (fraction $<1.0 \mu\text{m}$) were treated two times for 24 h (for preparation method, see Rühlicke and Kohler, 1981).

however, for particles that were oriented perpendicularly to the freeze-etched surface and parallel to the direction of shadowing (arrows in Fig. 3b). In this case, thickness could be measured with a precision of at least $10 \text{ \AA}$.

Figure 3a shows an overview of an ultrathin section of a 5% dispersion of Hungary illite ($<1 \mu\text{m}$ fraction). Most of the particles embedded in epoxy resin were distinctly aggregated. This aggregation probably resulted from dehydration required for impregnation. In contrast, the freeze-etch replica of the same 5% dispersion (Fig. 3b) showed that the silicate particles were perfectly dispersed in H_2O as free particles. The thickness of these particles ($50\text{--}500 \text{ \AA}$) was 1–2 orders of magnitude smaller compared with the aggregates (up to $0.5 \mu\text{m}$) shown in ultrathin section (Fig. 3a). Higher magnification of the same material in ultrathin section revealed that the particles embedded in epoxy resin consisted of numerous packets stacked on top of one another (Fig. 4a). The thickness of individual packets within the stacks varied between 40 and $150 \text{ \AA}$ and was comparable to that of some free particles in the freeze-etch replicas. Single isolated packets were rarely encountered in ultrathin sections.

The surface of most free particles in freeze-etch replicas (Fig. 4b) showed a layered or terraced structure, indicating that these particles were composed of many units. Under the experimental conditions applied here, observation of $10\text{-\AA}$ steps (= thickness of a single 2:1 layer) on freeze-etch replicas is difficult (see Fig. 8 in Vali and Bachmann, 1988). Therefore the height of these steps (= thickness of the units) must be more than $10 \text{ \AA}$. If so, these units may represent the packets observed in ultrathin sections. In other words, a complete disintegration of all particles into individual packets did not occur in dispersion. The shape and diameter of the stacked units varied considerably and included both euhedral laths and plates. Laths and plates usually occurred within the same free particle (Figs. 4b and 5b). In some cases, the laths in two adjacent units are interlaced parallel to their long axes. The contacts between adjacent units were clearly visible on crystal surfaces in the freeze-etch replicas (arrows in Fig. 5b). The ultrathin section shown in Figure 5a may represent a cross section, perpendicular to the basal plane, through a particle that is similar to the one imaged in Figure 5b. The steps along the outer edges of the particle (arrows in Fig. 5a) may correspond to the contacts between adjacent units visible in the freeze-etch replica (arrows in Fig. 5b).

Particles of glauconite showed terracelike margins in ultrathin section (solid arrows in Fig. 6a). The 2:1-layer packets ($50\text{--}200 \text{ \AA}$ thick) were not always stacked parallel and their thicknesses were not always constant. Some of the packets appear to be tilted and wedge out (open arrows within particle of Fig. 6a). Freeze etching revealed that both irregular platy crystals and very well developed pseudo-hexagonal crystals commonly occur in the same particle. Figure 6b shows surface features of the glauconite particles that display well-developed crystal edges stacked in a coherent crystallographic orientation. Aggregates of extremely small platy crystallites ($<100 \text{ \AA}$ thick

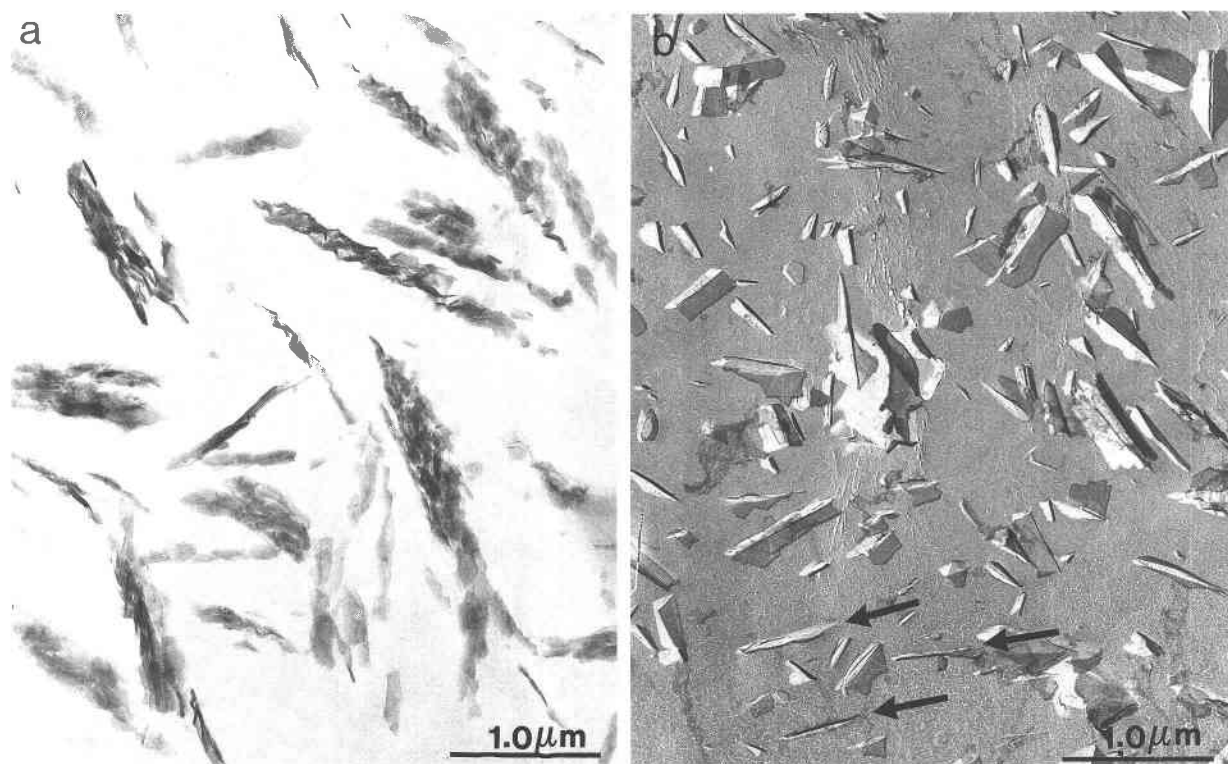


Fig. 3. Low-magnification images of 5% suspensions of Hungary illite, $<1.0 \mu\text{m}$ fraction. (a) Ultrathin section showing particle aggregates in epoxy resin. (b) Freeze-etch replica representing dispersed free particles of the same material embedded in ice. Arrows point to particles oriented perpendicularly to freeze-etched surface and parallel to direction of shadowing. (Note: shadows are white.)

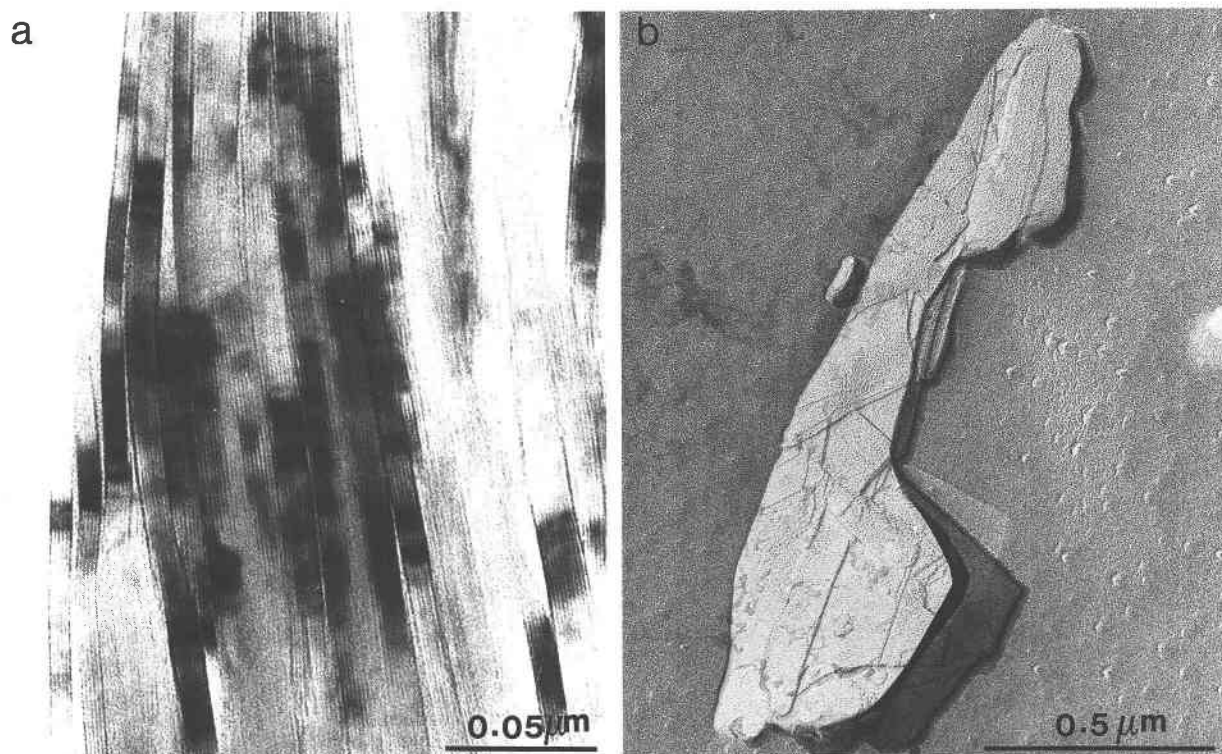


Fig. 4. High-magnification images of Hungary illite. (a) Ultrathin section showing stacking of individual layer packets. (b) Freeze-etch replica of a free particle. The surface structure indicates that this free particle is composed of numerous units. Part a could be a typical cross section of a particle similar to the one shown in b.

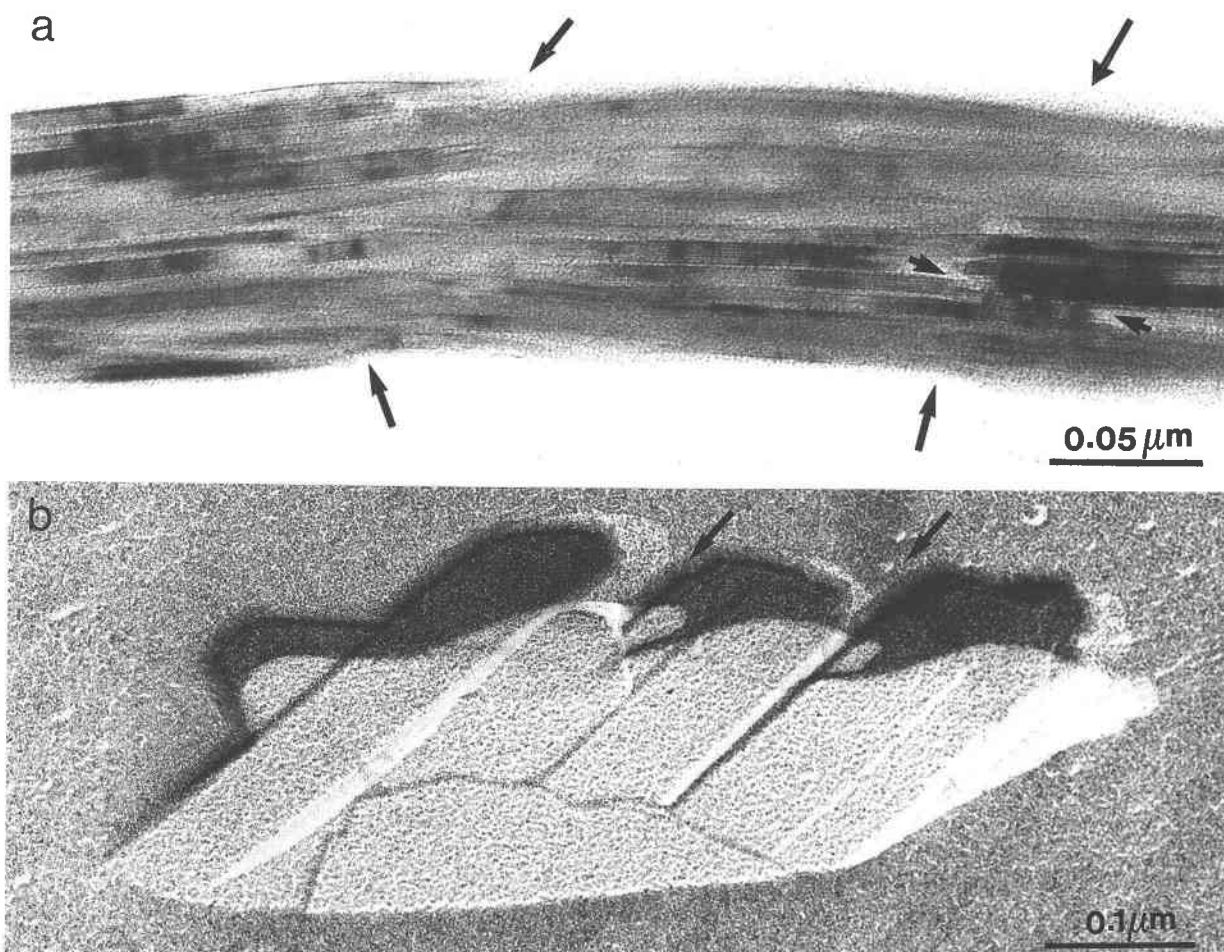


Fig. 5. High magnification of Hungary illite exhibiting intergrowth structure. (a) Ultrathin section showing stacks of packets with wedged intergrowth structure (arrows within particle). Arrows indicate the positions of contacts between adjacent packets. (b) Freeze-etch replica showing intergrowths of laths and irregular plates within an individual particle. Arrows denote contacts between adjacent laths. Part a could be a typical cross section of a particle similar to the one shown in b.

and <1000 Å in diameter) were also observed, but these were irregular in both shape and stacking arrangement.

ODAT of illite and glauconite

A stable expansion of expandable interlayers in illite and glauconite was achieved by treating the samples with octadecylammonium ions ($n_c = 18$). Two sets of expanded interlayer spacings were observed in HRTEM: one with an average 24-Å (range: 22–25 Å) layer spacing (solid diamonds in Figs. 7a and 7b) corresponding to a paraffinlike layer configuration in a high-charge expandable component (Lagaly, 1979; Vali and Hesse, 1990); the other with spacing of 16–17 Å corresponding to a bilayer arrangement of $n_c = 18$ in a low-charge component (open arrows in Figs. 7a and 7b). The proportion of expandable components was estimated by counting the number of interlayers. The proportion of expanded interlayers in glauconite determined in HRTEM after ODAT was approximately 20% greater than in illite. Whereas the estimates of Środoń et al. (1990) and Veblen et al. (1990) are

based on an assumed two-component system of expandable smectite and nonexpandable illite, our material revealed the presence of more than two components. Since the ODAT measures the interlayer charge generated in adjacent layers (Lagaly, 1979), the true structure and composition of individual 2:1 layers in each of the components could not be determined. However, different responses to ODAT indicated the presence of several distinct phases in the same sample, at least three of which could be characterized as follows:

The first phase was a nonexpandable component (40–50% of all layers), and therefore its layer charge could not be measured directly. Average layer charges calculated from the chemical compositions of the Hungary illite, $K_{0.76}Na_{0.02}Ca_{0.02}(Al_{1.79}Mg_{0.19})_{1.98}[Al_{0.57}Si_{3.43}O_{10}(OH)_2]$ and the glauconite from Bavaria, $K_{0.72}Na_{0.05}(Al_{0.46}Fe_{1.02}^{3+}Fe_{0.15}^{2+}Mg_{0.33})_{1.97}[Al_{0.20}Si_{3.80}O_{10}(OH)_2]$, are 0.82 and 0.77, respectively, per $[O_{10}(OH)_2]$ (Vali and Köster, 1986). The layer charges of the first phase in both minerals must be greater than these values because the second phase has charges

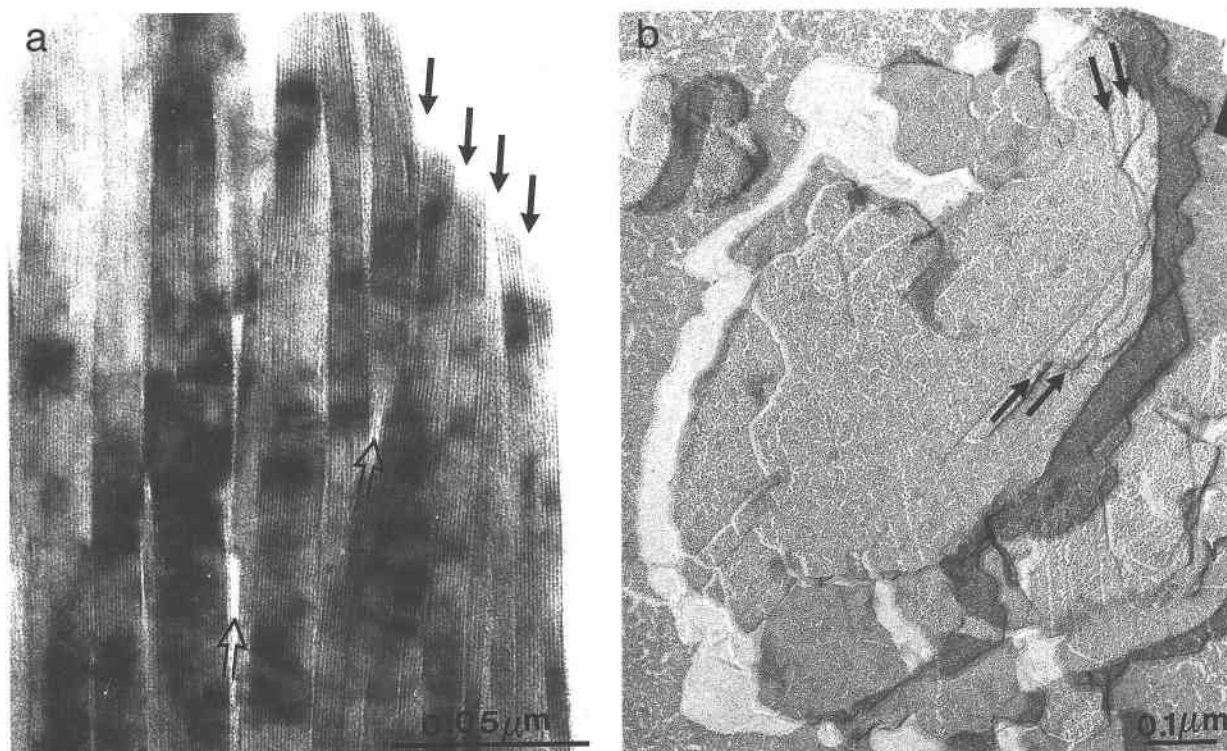


Fig. 6. High-magnification images of Bavaria glauconite exhibiting intergrowth structure. (a) Ultrathin section showing packets with stacking disorder (open arrows within particle). Solid arrows point to the terracelike margins of particle as well as the interfaces between adjacent packets. (b) Freeze-etch replica of a crystal with well-developed crystal faces showing pseudo-hexagonal symmetry (solid arrows). Part a could be a typical cross section of a particle similar to the one shown in b.

less than these averages (see below). The interlayer positions of this phase must be largely filled with K because the layers did not expand even after ODAT for 6 weeks. Such behavior has been observed only in muscovite (Fig. 2, section i; Vali and Köster, 1986) and biotite (Ghabru et al., 1989). This phase was identified in HRTEM images as nonexpanded packets of varying thickness after ODAT (Figs. 7a, 7b, 8a, and 8b). The 10-Å peak on X-ray diffraction patterns (Fig. 2, sections a–c) probably received a contribution from thicker packets (>60 Å) of this phase and also from the (003) reflection of the second phase (see below). Packets consisting of four to six nonexpanded 2:1 layers were predominant in the Hungary illite (Fig. 7b). These packets may represent a 47-Å or 57-Å superstructure of the type IIIS or IIIS, which causes the superlattice reflections at 9.8 and 11.0–11.6 in glycolated XRD patterns (Fig. 1, section b; R. C. Reynolds, Jr., personal communication, 1991). In the glauconite and illite from Quebec, thicker packets containing 10 or more 2:1 layers predominated (Figs. 7a and 8).

The second phase (20–30% of all layers) was an expandable high-charge component. An accurate determination of mean interlayer charge from XRD analysis (following the method of Olis et al., 1990) yielded values of 0.74 and 0.70 per $[\text{O}_{10}(\text{OH})_2]$ for illite and glauconite, respectively. The interlayers of this phase expanded after 2 d of ODAT, giving an XRD peak of 30.2 Å for illite and

29.2 Å for glauconite (Fig. 2, sections a and b). In HRTEM images, this phase appeared as sequences of coherent-appearing layers with a 24-Å spacing (Figs. 7a and 7b). This difference may be due to radiation damage of the *n*-alkylammonium ions under the electron beam (Vali and Hesse, 1990). Similar expansion behavior is shown by vermiculite (weathered biotite) and standard “Llano vermiculite” (Ghabru et al., 1989; Vali and Hesse, 1990; Vali and Köster, 1986). Laird et al. (1987) observed analogous XRD behavior for some illite using alkylammonium exchange and XRD techniques, and they described the expandable component as “expanded illite layers.”

The third phase (5–10% of all layers) consisted of 1:1 ordered mixed layers, which occurred as thin packets of a few nonexpandable double layers sandwiched between expandable smectite-like interlayers (16–17 Å) or as single nonexpandable double layers (Figs. 7a and 7b). Ordered mixed layers of this kind were also imaged in Marblehead illite (Vali and Hesse, 1990).

In addition, 5–10% of all layers in ultrathin sections were single 2:1 layers or thin packets of expanded layers, which occur either isolated or within larger particles (Fig. 7a). Their main characteristic is that they are short and bent. Aggregates of very fine particles were also observed in freeze-etch replicas that might represent this material. These layers appear to be smectite-like, but it was not possible to identify the mineral. Their morphology hinted

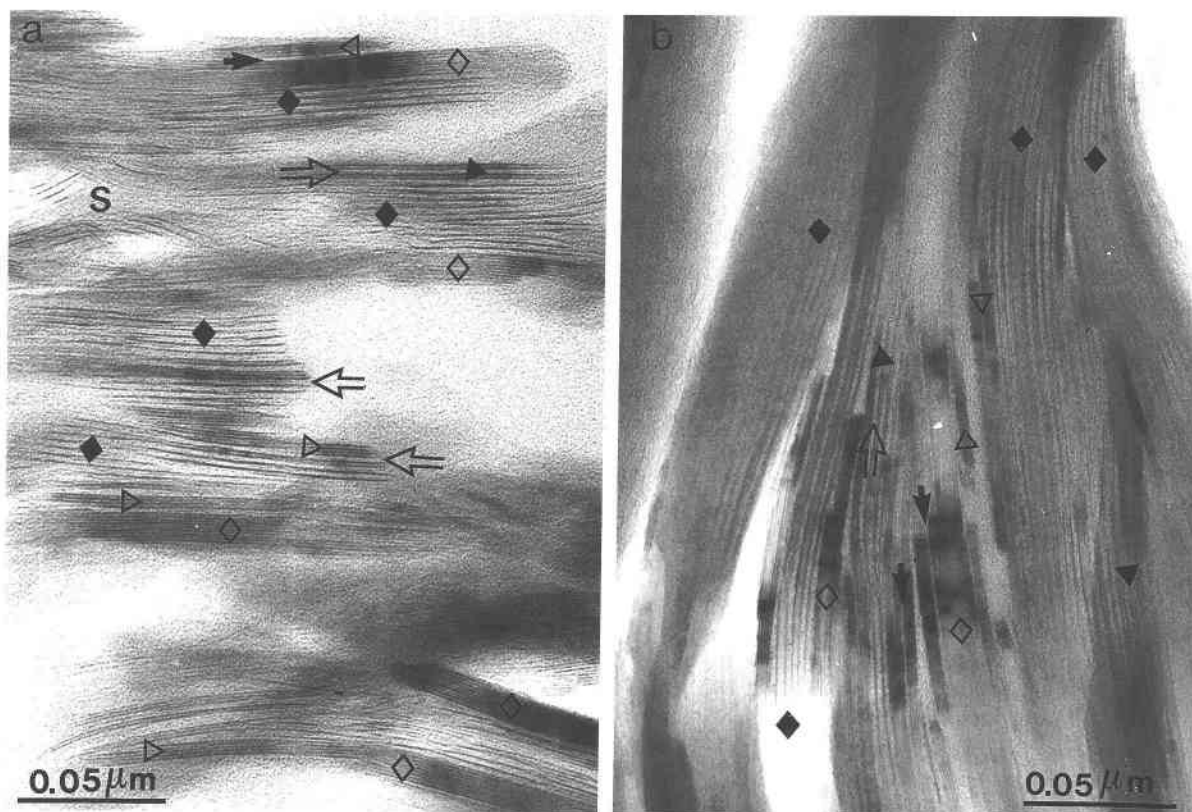


Fig. 7. Ultrathin sections of (a) Bavaria glauconite and (b) Hungary illite, showing stacked nonexpanded and expanded components after treatment with octadecylammonium ions. Open diamonds = packets of 2:1 layers with a 10-Å spacing (first phase); solid diamonds = packets of 2:1 layers with an average 24-Å spacing (second phase); open arrows = interlayer spacing of 16–17 Å; solid triangles = 1:1 ordered-mixed layers (R1 structure, third phase); S = short and bent 2:1 layers of a smectite-like component (fourth phase?); open triangles = thin packets of four to six 2:1 layers (R3 structure); black arrows = interfaces between adjacent packets.

at smectite, which would represent an additional separate phase.

ODAT provides characteristic XRD patterns for well-defined minerals such as rectorite, vermiculite, montmorillonite, and muscovite (Fig. 2, sections e–i), which can be correlated with HRTEM images as well as X-ray data on glycolated specimens. We want to emphasize, however, that for illitic material such as illite, smectite/illite, and glauconite the X-ray data on glycolated materials did not correlate with ODAT results obtained from XRD or HRTEM. The Bavaria glauconite and the Quebec illite did not reveal interstratification with smectite after glycolation, whereas the Hungary illite did (Fig. 1, sections a–f). However, after ODAT all three samples showed expansion (Fig. 2, sections a–c, Figs. 7a, 7b, 8a, and 8b). It is obvious that some 10-Å layers, which were nonexpandable after glycolation, did expand by ODAT, as seen on HRTEM images (the second phase in Figs. 7a, 7b, 8a, and 8b). ODAT apparently exerts a stronger expanding force than glycol treatment. It is most likely that the peaks corresponding to d -values around 30 Å, 15 Å, and 10 Å in ODAT X-ray diffraction patterns (Fig. 2, sections a–c) represent this type of layer [i.e., the (001), (002), and (003)

reflections of this expanded phase], whereas the strong 10-Å reflection (compared to rectorite, Fig. 2, section e, or vermiculite, Fig. 2, section f) also includes a contribution from the nonexpandable illite phase, as mentioned above (Figs. 7a, 7b, 8a, and 8b).

The reproducibility of ODAT results depends largely on uniform experimental conditions such as washing and drying (under a 10^{-4} -bar vacuum for at least 12 h) procedures, use of the same particle size-fraction, and duration of treatment. The similarity in the appearance of the ODAT X-ray pattern of the interstratified Hungary illite and the noninterstratified Bavaria glauconite (Fig. 2, sections a and b) indicates that the original structure of these materials may be modified during ODAT. The sharpness of the 30-Å peak indicates that the expanded layers indeed occur as coherent sequences, as is visible in HRTEM (Figs. 7a and 7b). In contrast, the diffuse reflection in the Quebec illite at 31–32 Å (Fig. 2, section c) indicates the presence of stacking disorder of expandable and nonexpandable layers in this sample, as can also be seen in HRTEM images (Figs. 8a and 8b). Although some other illite and glauconite samples show similar behavior (Vali, 1983; Vali and Köster, 1986), a detailed compar-

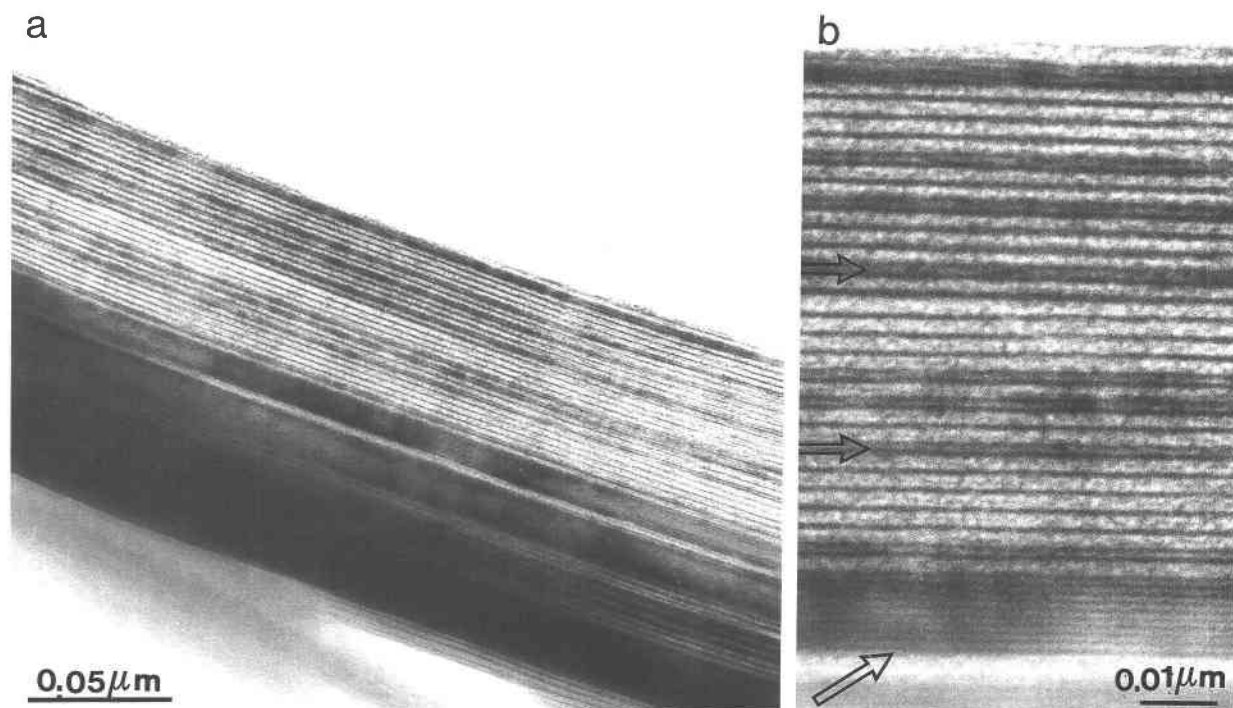


Fig. 8. Ultrathin section of Quebec illite treated with octadecylammonium ions. (a) Stacked nonexpanded layers (10 Å) and expanded layers (25 Å). (b) Close-up of a showing that both packets as well as single double layers (20 Å) of nonexpandable 2:1 layers are present (open arrows).

ative XRD and HRTEM investigation of ODAT samples of these materials was beyond the scope of this study.

As mentioned above, the HRTEM images of the first and second phases of illite and glauconite after ODAT (Figs. 7a and 7b) could be correlated with their ODAT X-ray patterns (Fig. 2, sections a and b). However, the third phase as well as the smectite-like phase could not be differentiated in diffraction patterns because of (1) possible peak overlap, (2) the small amounts present of these phases, and (3) the random distribution of very thin packets or layers. For comparison, an ordered 1:1 mixed-layer mineral (rectorite) produced a series of XRD peaks that overlapped those of the expanded phase in illite and glauconite (compare Fig. 2, sections a and b, with Fig. 2, section e) and could not be detected by XRD even if present in sufficient quantity. Vermiculite has the same expanded reflections as those of the second phase (at 29–30 Å in XRD, Fig. 2, section f, and 24 Å in HRTEM, Vali and Hesse, 1990). The presence of vermiculite can be excluded, however, because of the absence of characteristic XRD reflections for this mineral in glycolated material (Fig. 1, sections b and c). Absence of a 17–20 Å peak which is characteristic of ODAT smectite (Fig. 2, sections g and h), confirms that the expanded phase is not smectite. Therefore the second phase is interpreted as expandable illite in the sense of Laird et al. (1987).

Preliminary HRTEM investigation of the illite from Quebec revealed that both thin (<100 Å) and thick packets (>100 Å) were stacked together. After ODAT, ap-

proximately 20% of the interlayers were expanded in both types of packets. Figures 8a and 8b show nonexpanded (10-Å) and expanded (25-Å) interlayers alternating in a random array.

DISCUSSION

Combination of cryofixation and freeze-etching techniques with ultrathin sections and XRD methods is a potentially powerful tool that may hold a key to the solution of controversial issues concerning the natural occurrence of fundamental particles and the multiphase nature of illitic materials.

Free particles vs. fundamental particles

Free particles observed in freeze-etch replicas are thicker (average thickness of 200 Å) than the packets of 2:1 layers imaged in ultrathin section (average thickness of 100 Å). The former are composed of several units as evidenced by their surface structure (Figs. 4b, 5b, and 6b). These units correspond to the packets seen in ultrathin section (Figs. 4a, 5a, and 6a). In some cases, the well-developed edges of units that repeat consistent crystallographic orientations suggest that the free particles display primary growth features (Fig. 6b). The results of freeze etching combined with those from ultrathin sectioning thus reveal that the stacking arrangement of the packets (Fig. 4a) can be a primary feature of these materials in both organic resins and aqueous dispersion and is not only a clumping artifact. Under the applied experimental con-

ditions it is not possible to tell whether the stacking arrangements and surface features of the particles in dispersion are the same as those existing in the original in situ mudrock fabric.

Thin packets (30–50 Å) observed in ultrathin sections (Figs. 7a and 7b) have the thickness of fundamental illite particles in an R3-ordered mixed-layer clay. However, they do not occur as individual free particles in dispersion. This observation confirms Ahn and Buseck's (1990) conclusion that the crystallites (= stacks of packets in our terminology) in R1- and R3-ordered S/I mixed-layer clays are thicker than the fundamental particles of Nadeau and coworkers. The free particles of illite and glauconite (50–500 Å) are considerably larger than fundamental particles of illite in S/I mixed layers described by Nadeau et al. (1984a) and Nadeau (1985). Thus the natural occurrence of fundamental illite particles in the materials studied is unlikely.

In contrast, preliminary freeze-etching results of the Wyoming sodium montmorillonite show that, in this sample, free particles may exist as single dispersed smectite 2:1 layers (Vali and Bachmann, 1988). This observation supports the definition of fundamental particles for smectite by Nadeau et al. (1984a, 1984c) and Nadeau (1985). Thus in the case of smectite, the size of free particles can be the same as that of fundamental smectite particles.

Nature of bounding faces of packets

It has been suggested that natural S/I mixed-layer clays consist of thicker particles, which may split into fundamental particles because of osmotic swelling along their smectite interlayers during the sample preparation procedure (Altaner and Bethke, 1988; Altaner et al., 1988; Ahn and Peacor, 1986b; Veblen et al., 1990; Ahn and Buseck, 1990). Altaner and Vergo (1988) and Altaner et al. (1988) viewed such smectite interlayers as a separate phase. If smectite layers are present as individual layers, they can be imaged in ultrathin sections (Shomer and Mingelgrin, 1978; Środoń et al., 1990; Vali and Köster, 1986) and in dispersions after platinum-carbon shadowing (Nadeau et al., 1984a, 1984b, 1984c) or freeze-etching (Vali and Bachmann, 1988). In this case, they form a separate phase. However, single expanded interlayers between illitic packets (solid arrows in Figs. 7a and 7b) in our illite and glauconite do not represent a separate smectite phase. As mentioned, freeze etching reveals that most free particles do not split into units in H₂O, even in dilute and Na-saturated suspensions. Moreover, the interfaces of adjacent packets within some particles do not respond in a consistent way to ODAT (solid arrows in Figs. 7a and b). This observation tends to support the model of Eberl and Środoń (1988) that the basal surfaces of "short stacks" are nonswelling "stacking faults." The problem of characterization of interlayers between the packets is closely related to the question of what the basal surfaces of these packets are. Determination of their chemical composition is not yet possible. However, the top and bottom

layers of individual packets of illite and glauconite of this study do not appear to be smectite.

Multiphase nature of illitic materials

Illitic materials commonly contain a smectite component and these smectite/illite mixed layers are considered by some as members of a continuous series of single-phase solid solutions or by others as mixtures of two or more thermodynamically distinct phases. This difference in opinion is highlighted by a recent animated discussion concerning the multiphase nature of hydrothermal sericite from the Silverton Caldera, Colorado, by Altaner and Vergo (1988), Altaner et al. (1988), Eberl et al. (1987, 1988), and Rosenberg et al. (1990). The answer to this long-debated problem (Lippmann, 1977, 1982; Garrels, 1984; Velde, 1985) has important repercussions for (1) the solution chemistry of H₂O/solid-silicate systems, (2) the mechanism of the smectite-to-illite transformation during burial diagenesis, and (3) the evolution of mica polytypes during advanced-level diagenesis and low-grade metamorphism.

As far as solution chemistry is concerned, a two-phase system restricts the composition of an aqueous solution coexisting in equilibrium with the solid phase more than a single-phase solid solution does. This consequence of the phase rule has been used in the design of equilibration experiments by Rosenberg et al. (1990). Their results suggest that, in the illitization process of smectite under hydrothermal conditions, at least four discrete mica-like phases appear.

Morphological studies by Inoue et al. (1987, 1988) of the smectite-to-illite conversion and the transformation of the 1*M* to 2*M* polytype of illite from the Shinzan hydrothermal alteration area of Japan, on the other hand, revealed the occurrence of three distinct morphologic types of mica-like minerals that appear successively in the illitization process: flakelike (1*Md*), lathlike (1*M*) and platelike (2*M*) crystallites. There is considerable overlap in the chemical composition of the different morphologic types, which the authors attribute to a dissolution-recrystallization mechanism corresponding to an Ostwald maturation process. Eberl et al. (1987, 1988) also prefer Ostwald ripening of a single-phase solid-solution S/I in the course of which larger particles with lower surface energies grow at the expense of smaller particles. The fundamental-particle concept of Nadeau et al. (1984a, 1984b) and Nadeau (1985) is well in line with such a mechanism.

Our results support the suggestion of Aja et al. (1991) and Rosenberg et al. (1990) that illitic materials consist of several thermodynamically distinct phases. In the illite and glauconite studied, the different phases exist within the same free particles. If the thermodynamic definition of a phase given in the introduction is followed, then the three types of layer stacks identified in this study by their different expansion response to ODAT can be interpreted as three distinct phases in illitic materials. However, no evidence was found for the presence of smectite as a sep-

arate phase in ordered mixed layers, contrary to Altaner et al. (1988).

Illitic materials that are composed of more than one phase occur in a variety of different environments. They form authigenically (Bavarian glauconite), hydrothermally (Hungarian illite), and during burial diagenesis and metamorphism (Quebec illite). In this study, we have shown that the freeze-etch and ultrathin section techniques together with the *n*-alkylammonium method enable the particle size and the multiphase nature of illitic materials to be investigated. Further work may unravel important details of the phase transformations of clay minerals during progressive burial diagenesis and metamorphism.

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