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ARRANGEMENT OF n-ALKYLAMMONIUM IONS IN PHLOGOPITE AND VERMICULITE: AN XRD AND TEM STUDY

Key Words—Alkylammonium, Layer charge, Phlogopite, Transmission Electron Microscopy, Vermiculite, X-ray diffraction.

The n-alkylammonium exchange method of Lagaly and Weiss (1969) has become a routine analytical technique for estimation of interlayer charge and characterization of expandable 2:1 layer silicates in soils and sediments. Rühlicke and Kohler (1981), Stanjek and Friedrich (1986), Ghabru *et al.* (1989); Olis *et al.* (1990), and Stanjek *et al.* (1991) have introduced improvements and simplifications of the method. However, there are considerable discrepancies in the interpretation of results in the literature (Ghabru *et al.,* 1989; Mermut and St. Arnaud, 1990).

Based on the model of Lagaly and Weiss (1969), in high-charge 2:1 layer silicates the alkylammonium chains are arranged in a monoparaffin-like array. There is a relationship between the tilt angle (α), which is the angle between the alkyl chain and the basal plane (001) of layer silicates, and the layer charge. By increasing the layer charge upward to 1 per $[O_{10}(OH)_2]$, the tilt angle, α, should increase to a maximum of 90°. In this case, the alkyl chains are arranged perpendicularly to the basal surface and the $\Delta d_{(001)}$ of a given alkyl chain to the next would increase by about 1.26 Å (Beneke and Lagaly, 1982; Ghabru *et al.,* 1989).

High-resolution transmission electron microscope (HRTEM) images of artificially K-depleted biotite treated with alkylammonium ions (Marcks *et al.,* 1989) show such a perpendicular arrangement of the alkyl chains in interlayer spaces. However, the X-ray diffraction (XRD) data of the same sample show basal spacings smaller than expected for such an arrangement. Beneke and Lagaly (1982) discuss the arrangement of alkyl chains in nickel arsenate ($KNiAsO_4$), which has a similar crystallography as brittle mica, and suggest that the alkyl chains in artificially-weathered mica (high-charge vermiculite) are arranged with a tilt angle of about 56°.

The present study compares the results of n-alkylammonium exchange on phlogopite, K-depleted phlogopite (vermiculite), and natural vermiculite. Based on XRD and HRTEM data, the reliability of layer-charge determination in high-charge 2:1 layer silicates by the n-alkylammonium exchange method is discussed.

MATERIALS AND EXPERIMENTS

Large crystals (25 × 20 cm) of phlogopite from a pegmatitic rock (Burgess, Ontario; Ward's Natural Science Est.) and Llano vermiculite (Texas, CMS source clay VTx-1), which is a weathering product of phlogopite, were wet-ground and dispersed in distilled water by shaking and ultrasonic treatment. The grain-size fraction 2.0–0.2 μm was separated by centrifugation and then freeze-dried. In addition, a finely-ground (<0.2 μm) muscovite (Wacker Chemie; Bavaria, Germany) was used as a reference sample.

To study alteration of the layer structure of phlogopite by artificial weathering under laboratory conditions by XRD and HRTEM, the original samples (2.0–0.2-μm fraction) were treated as a powder with $CaCl_2$ and n-alkylammonium solutions. For $CaCl_2$-treatment, a 40-mg sample was immersed in 200 ml of a 0.2 N solution at 80°C. The solution was renewed every two days and the reaction repeated until K was effectively depleted (22 days).

The original phlogopite, K-depleted phlogopite, and the original Llano vermiculite were treated with n-alkylammonium ions of the following chain lengths: heptylammonium ($n_c = 7$); pentadecylammonium ($n_c = 15$); hexadecylammonium ($n_c = 16$); and octadecylammonium ($n_c = 18$), where n is the number of C atoms in the alkyl chains. All samples were treated two times for 24 hours at 60°C. For XRD analysis the method of Rühlicke and Kohler (1981) was followed. The tilt angle was calculated from Δd between the (001) peaks of the $n_c = 16$- and $n_c = 18$-treated samples (for calculations, see Beneke and Lagaly, 1982 and Ghabru *et al.,* 1989). HRTEM studies were performed on ultrathin sections obtained from powders that were treated with alkylammonium ions before (Vali and Köster, 1986) as well as after section preparation (Vali and Hesse, 1990). There was no visible difference in the layer structure of particles between the two preparation techniques.

For K-depletion of phlogopite on ultrathin sections (Vali and Hesse, 1991), the sections were transferred onto grids with Formvar and carbon-supported film as a substrate and treated with a 0.1 N $CaCl_2$ solution for 2–12 hours at 60°C. The chemical composition of bulk samples was determined using wet-chemistry and X-ray fluorescence analysis. The exchange of interlayer cations and the chemical composition of individual particles were determined using a JEOL 100 CX TEM at 100 kV equipped with an energy-dispersive X-ray detector.

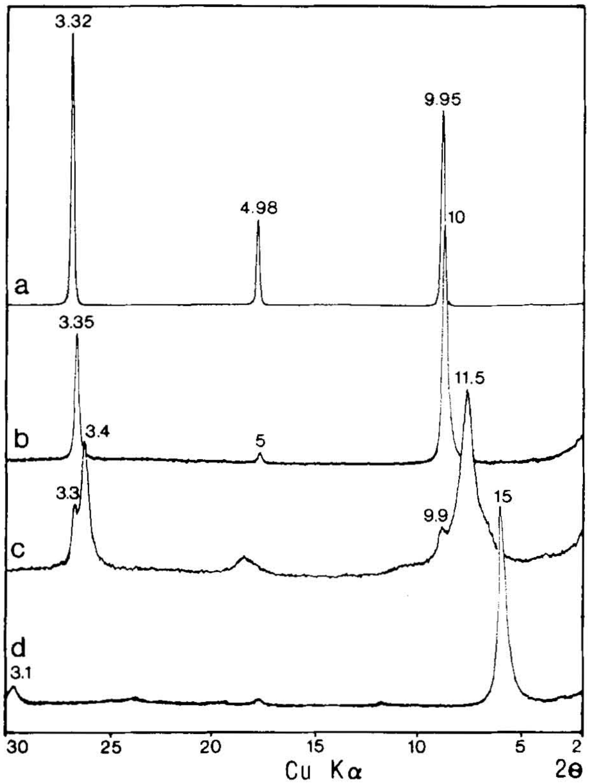

Figure 1. X-ray diffractograms of ethylene glycol-solvated samples vapor-exposed for 24 hr at 60°C: a) finely ground muscovite; b) Ontario phlogopite; c) 50% K⁺-depleted Ontario phlogopite; d) Llano vermiculite.

RESULTS AND DISCUSSION

XRD data of glycolated muscovite and phlogopite specimens (glycolation at 60°C for 24 hours) showed no changes on basal reflections (001) (Figures 1a, 1b). However, $CaCl_2$-treated phlogopite (50% K^+-depleted) revealed the presence of a mixed-layer structure between expanded Ca-layers and nonexpanded K-layers (Figure 1c). The peaks at 11.5 Å and 3.4 Å are probably caused by the expandable component (Ca-phlogopite), and the peaks at 9.9 Å and 3.3 Å by original phlogopite. Original Llano vermiculite showed an expanded (001) peak at 15 Å (Figure 1d).

After n-alkylammonium treatment phlogopite and vermiculite clearly expanded, whereas muscovite did not reveal any change. The original phlogopite sample showed two sets of basal reflections: one at 28.9 Å, 14.4 Å and 9.6 Å corresponding to the expandable component, the other at 10 Å and 3.5 Å corresponding to nonexpandable layers (Figures 2a–2d). The $CaCl_2$-treated sample showed the same X-ray pattern as the untreated sample. No changes in the shape and position of the peaks could be detected, except for a decrease in the proportion of nonexpandable components as seen in the 10 Å/9.6 Å peak ratio (Figures 2a, 2b).

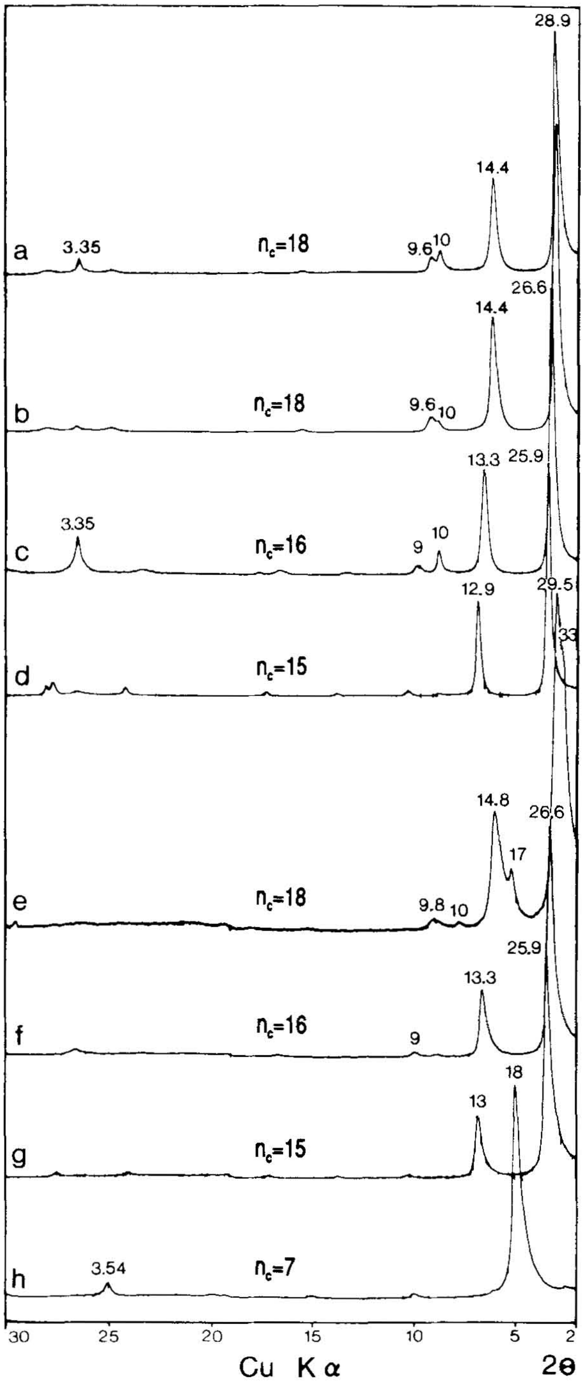

Figure 2. X-ray diffractograms of n-alkylammonium-treated Ontario phlogopite and Llano vermiculite: a) phlogopite (n_c = 18); b) artificially-weathered phlogopite (50% K⁺-depleted, n_c = 18 treated); c) phlogopite (n_c = 16); d) phlogopite (n_c = 15); e) vermiculite (n_c = 18); f) vermiculite (n_c = 16); g) vermiculite (n_c = 15); h) vermiculite (n_c = 7).

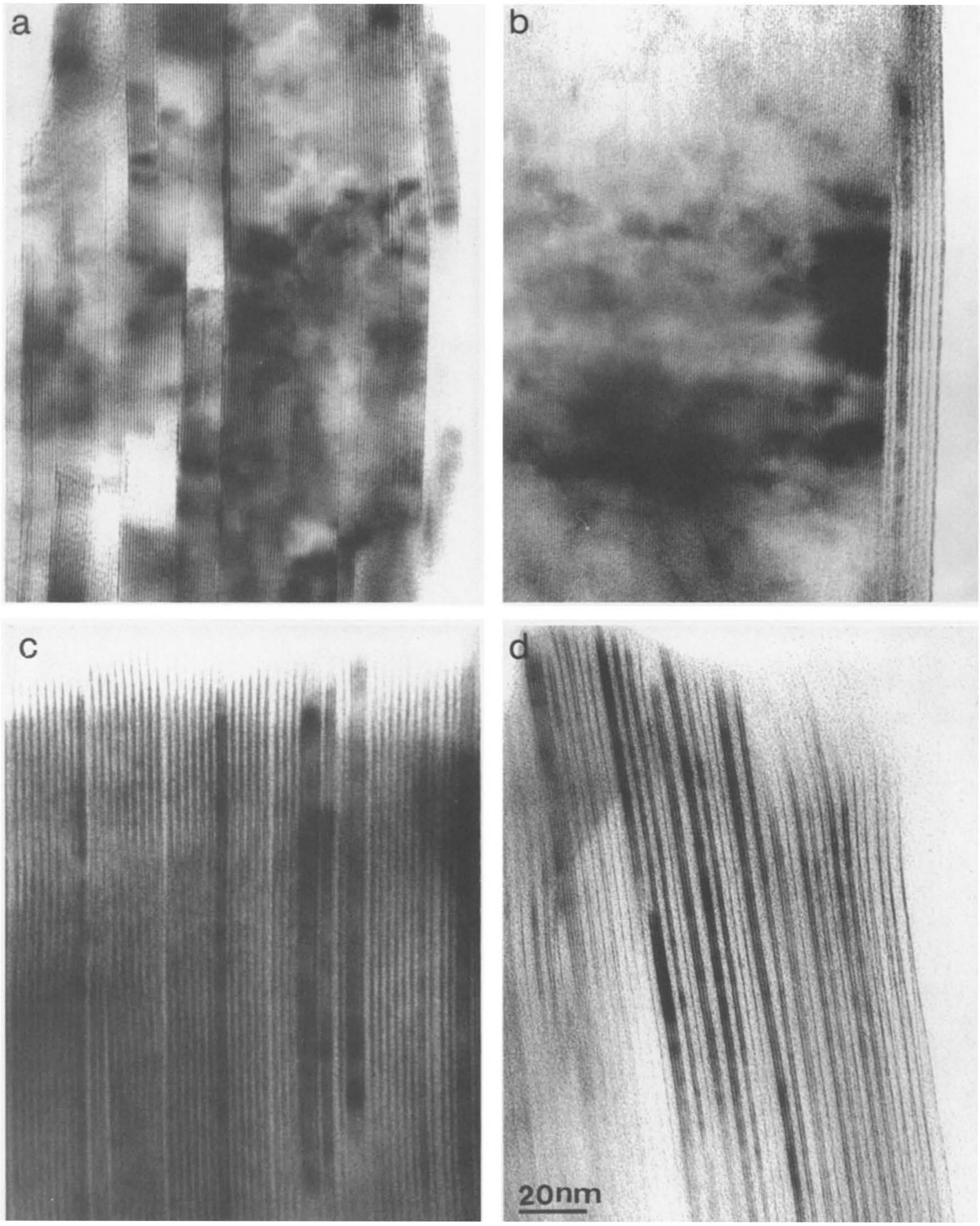

Figure 3. TEM images of Ontario phlogopite: a) untreated sample; b) particle treated with $n_c = 18$ for 1 hour in ultrathin section showing a thick crystal with a few expanded layers; c) particle consisting of coherent sequences of expanded layers (25–30 Å) and nonexpanded 10 Å layers after $CaCl_2$ treatment (for 12 hours at 60°C) and $n_c = 18$-treatment (for 3 hours at 60°C) in the same ultrathin section; d) particle with a random mixed-layer structure (same section as Figure 3c).

Therefore, the layer charge of the Ca-layers (Ca-phlogopite) and the K-layers (original phlogopite), shown in Figure 1c, appears to be the same. This suggests that depletion of K in phlogopite does not change the layer charge, as has also been observed in muscovite (Kodama and Ross, 1973). This phlogopite did not respond to the $n_c = 7$ treatment even after a 50% K-depletion.

Llano vermiculite showed two types of expandable layers following $n_c = 18$ treatment, but only one type after treatment with other alkyl chains (Figures 2e–2g). In contrast to phlogopite, this vermiculite expanded easily with $n_c = 7$ (Figure 2h).

HRTEM images of untreated samples revealed that the phlogopite was composed of packets of layers, 50 to 1000 Å thick, that were commonly stacked in a random arrangement (Figure 3a). It cannot be excluded that the shorter packets in this sample are a result of the grinding process.

After n-alkylammonium treatment both nonexpanded and expanded components occurred as apparently coherent sequences (Figures 3b, 3c). In some cases, packets consisting of hundreds of 10 Å-layers showed only a few expanded interlayers at the outer edge (Figure 3c). In addition, a random mixed-layer structure consisting of both types of layers was also observed (Figure 3d). This could not be detected in X-ray diffractograms of the same sample (Figure 2b). The proportion of expanded layers increased after $CaCl_2$ treatment. However, a complete expansion of all layers in ultrathin sections could not be achieved even after alkylammonium treatment for 12 hours. Apparently, no significant increase in the proportion of expanded interlayers occurred after a 3-hour treatment in ultrathin section. Approximately 30% of the layers remained nonexpanded. In contrast, Llano vermiculite showed complete expansion of the interlayers. There was also a significant difference in morphology between phlogopite and Llano vermiculite, i.e., the distribution of particle sizes, thickness of packets and stacking order (Vali and Hesse, 1992).

Since the microenvironmental conditions for all particles in an ultrathin section are about the same, different responses of individual layers to a given chemical reaction appear to be controlled more by variation in the chemistry of individual 2:1 layer silicates than by the kinetics of the reaction. Beneke and Lagaly (1982) suggested that structural bonding of K rather than high charge density in micas is responsible for the poor cation exchange reactivity of these minerals. Kodama *et al.* (1974) studied the rate of K exchange by Ca in phlogopite with a tetrahedral and octahedral ionic substitution, and with the same total layer charge. They concluded that mica layers are more expandable when their charge is located octahedrally. Indeed, the proportion of the expandable component in glauconite and celadonite with dominant octahedral substitution is higher than in illite and muscovite, which have a higher tetrahedral substitution (Vali, 1983; Vali *et al.*, 1991b). However, since some trioctahedral biotites also respond to alkylammonium treatment (as observed in Lake Clear biotite, Ontario, Canada; Vali and Hesse, 1992; Vali *et al.*, 1991a), a possible explanation for the unexpected expansion of phlogopite may be the trioctahedral nature of this mineral.

The chemical composition and charge distribution of Llano vermiculite $\{Mg_{0.44}(Al_{0.13}Fe_{0.02}Mg_{2.91})[Al_{1.15}Si_{2.85}O_{10}(OH)_2]\}$ is similar to Ontario phlogopite $\{K_{0.92}Na_{0.03}(Al_{0.09}Fe_{0.12}Mg_{2.77})[Al_{1.12}Si_{2.88}O_{10}(OH, F)_2]\}$. Based on electron microprobe analyses, Slade *et al.* (1987) give an interlayer charge for Na-saturated Llano vermiculite of 0.93 per $[O_{10}(OH)_2]$. This is similar to the interlayer charge of Ontario phlogopite (0.94), whereas our Llano vermiculite has an interlayer charge of 0.88, as shown above. Both samples also showed the same X-ray pattern after $n_c = 16$- and $n_c = 15$-treatment (Figures 2c, 2d, 2f, 2g). However, based on the model of Olis *et al.* (1990), using the single alkyl chain ($n_c = 18$) for estimation of layer charge, the vermiculite yielded a layer charge of 0.74 per $[O_{10}(OH)_2]$ and phlogopite 0.70 per $[O_{10}(OH)_2]$. On the other hand, using the relationship of the tilt angle as a function of layer charge, phlogopite gave a layer charge of 0.81 per $[0_{10}(OH)_2]$, if the diagram of Ghabru *et al.* (1989) is applied. The original diagram of Lagaly and Weiss (1969) had suggested a layer charge of 0.86 per $[O_{10}(OH)_2]$. The best approach was provided by using the curve suggested by Mermut and St. Arnaud (1990). This gave a layer charge of 0.9 per $[O_{10}(OH)_2]$ for phlogopite using the tilt angle ($\alpha = 64°$) derived from X-ray patterns from $n_c = 16$- and $n_c = 18$-treated samples. The tilt angle calculated from $\Delta d_{(001)}$ of even-numbered alkyl chains differs from that calculated from odd-numbered alkyl chains (Walker, 1967; Beneke and Lagaly, 1982). The $\Delta d_{(001)}$ of odd/even-numbered chains ($n_c = 15/n_c = 16$) is 0.7 Å both for phlogopite and vermiculite. The $\Delta d_{(001)}$ of even/even-numbered chains $n_c = 16/n_c = 18$) is 2.3 Å for phlogopite and 2.9 Å for vermiculite. Calculation of a layer charge based on tilt angle for the Llano vermiculite was not possible because the $\Delta d_{(001)}$ of 2.9 Å obtained from $n_c = 16$- and $n_c = 18$-treatment is unusually large.

It is obvious that the layer charge derived from the n-alkylammonium method is smaller than that calculated from chemical analyses. Beneke and Lagaly (1982) suggested that in high charge, 2:1 layer silicates, two-thirds of the interlayer cation sites are occupied by alkylammonium ions. Thus, a perpendicular arrangement of alkyl chains in weathered mica may not be possible. Slade *et al.* (1987) also reported that some interlayer sites in Llano vermiculite were still occupied by inorganic cations after intercalation of anilinium ions. However, energy-dispersive X-ray analysis of both phlogopite and K-depleted phlogopite (Ca-phlogopite) revealed that the remaining K was derived from nonexpanded K-layers in the alkylammonium-treated sample. The arrangement of alkyl chains may also be influenced by polytypism and interlayer shift in micas (Bailey, 1980).

The fact that the XRD patterns of $n_c = 16$- and $n_c = 15$-treated phlogopite and vermiculite are the same indicates that the arrangement and tilt angle in both minerals should be the same. This observation seems to confirm the suggestion of Beneke and Lagaly (1982), that in high-charge, 2:1 layer silicates the alkyl chains may form a tilt angle of $\alpha \approx 56°$. If so, the straight-line relationship between α and layer charge, as suggested by Ghabru *et al.* (1989), cannot be used for layer-charge estimation. On the other hand, the $\Delta d_{(001)}$ derived from $n_c = 16$- and $n_c = 18$-treated Ca-phlogopite and Llano vermiculite differ considerably from one another, indicating that natural vermiculite may respond differently from artificial vermiculite (Ca-phlogopite) to some alkylammonium chains.

CONCLUSIONS

This study reveals that great care is required in the investigation of clay minerals in soils and sediments using the n-alkylammonium method. The different response of muscovite and phlogopite to alkylammonium treatment provides evidence that the mechanism of alkylammonium exchange in mica-like 2:1 layer silicates is controlled more by structural type than by layer charge and K-content.

Estimation of layer charge from a single alkyl chain, as suggested by Olis *et al.* (1990), is inadequate for the characterization of high-charge expandable minerals. Distinction of vermiculite in soils and sediments from other 2:1 layer silicates, such as glauconite, illite, phlogopite, or biotite that show a similar response to long alkyl chains ($n_c > 12$) as vermiculite, is possible by treating the sample with short alkyl chains ($n_c < 12$) (Laird *et al.,* 1987; Vali and Hesse, 1992).

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