American Mineralogist, Volume 75, pages 1443–1446, 1990

LETTER

Alkylammonium ion treatment of clay minerals in ultrathin section: A new method for HRTEM examination of expandable layers

HOJATOLLAH VALI, REINHARD HESSE
Department of Geological Sciences, McGill University, 3450 University Street, Montreal, Quebec H3A 2A7, Canada

ABSTRACT

Intercalation of *n*-alkylammonium ions in the interlayers of clay minerals in ultrathin sections after section preparation permits a rapid estimation of the interlayer charge of clay mineral particles using HRTEM. The layer structures of illite, vermiculite, and smectite were studied on the same section before and after *n*-alkylammonium treatment within a period of 3–4 h. The difference between smectite (13-Å layer spacing) and vermiculite layers (17-Å layer spacing) is clearly observed.

INTRODUCTION

Ion exchange of *n*-alkylammonium (Lagaly and Weiss, 1969; Lagaly, 1981) coupled with HRTEM has proved to be a useful technique in investigations of the expandability behavior of 2:1 layer silicates (Bell, 1986; Ghabru et al., 1989; Lee and Peacor, 1986; Vali and Köster, 1986). Although *n*-alkylammonium ion exchange is an elegant technique for accurate determination of the interlayer charge of clay minerals by XRD (Häuser and Stanjek, 1988; Ghabru et al., 1989; Olis et al., 1990; Rühlicke and Kohler, 1981), it has not yet been used for the same purpose in HRTEM studies of clay-mineral particles, probably because of the large amount of labor and and time involved in sample preparation. The purpose of this paper is to outline a new technique of sample preparation of HRTEM, which will allow the investigation of the layer structure of mixed-layer clays on the same ultrathin section before and after *n*-alkylammonium ion treatment within a short period of time.

METHODS

Marblehead illite (Wisconsin), Jefferson vermiculite (Brinton's Quarry, Pennsylvania) and Fe-rich smectite (Grand County, Washington) were disaggregated and fully dispersed in distilled H_2O by shaking and ultrasonic treatment. The grain-sized fractions <0.6 μm and <1.0 μm were separated by centrifugation, freeze-dried, and then embedded in a low-viscosity resin (Spurr, 1969), following the embedding procedure described by Vali and Köster (1986).

The embedding blocks were trimmed to a cutting-face size of 0.15 × 0.2 mm. Ultrathin sections (700–800 Å thick) were prepared with an ultramicrotome using a Diatome diamond knife. One ribbon, consisting of 3–5 sections, was selected and transferred onto the center of the 200- or 300-mesh TEM grids, without a support film as a substrate.

The ultrathin sections were treated with *n*-alkylammonium ions of various chain-lengths ($n_C = 7$ to $n_C = 18$; *n* equals the number of c atoms in the alkyl chains). The *n*-alkylammonium chloride is prepared by treating alkylamines with hydrochloric acid. To prevent the reaction of hydrochloric acid with the Cu grids, the addition of excess hydrochloric acid should be avoided. An aqueous solution was prepared with an *n*-alkylammonium concentration that was 30–40% of that used in the conventional method (Lagaly et al., 1976), and stored in closed glass flasks at 60 °C. Higher concentrations produced sample contamination.

For TEM studies, 0.5 mL of the alkylammonium solutions was transferred to 1.5-mL polypropylene Eppendorf microtest tubes. The section mounted on a TEM grid, which had already been investigated by TEM as untreated sample, was dropped into the *n*-alkylamine solution. The tubes were then closed and stored in an oven at 60 °C. During the treatment, the samples were shaken every 5 min for the first 30 min and then every 60 min. After *n*-alkylamine treatment, the grids were dipped into a 20-mL beaker of distilled H_2O at 60 °C. The excess mixture of *n*-alkylamine and H_2O on the grids was removed with filter paper. The washing procedure was repeated three times for short chains and five times for long chains. The grids, which were held with tweezers during the washing procedure, were dipped for approximately 10 s in distilled H_2O in separate beakers heated to 60 °C.

The prepared ultrathin section should cover at least one whole mesh and should be devoid of large holes or

0003–004X/90/1112–1443$02.00

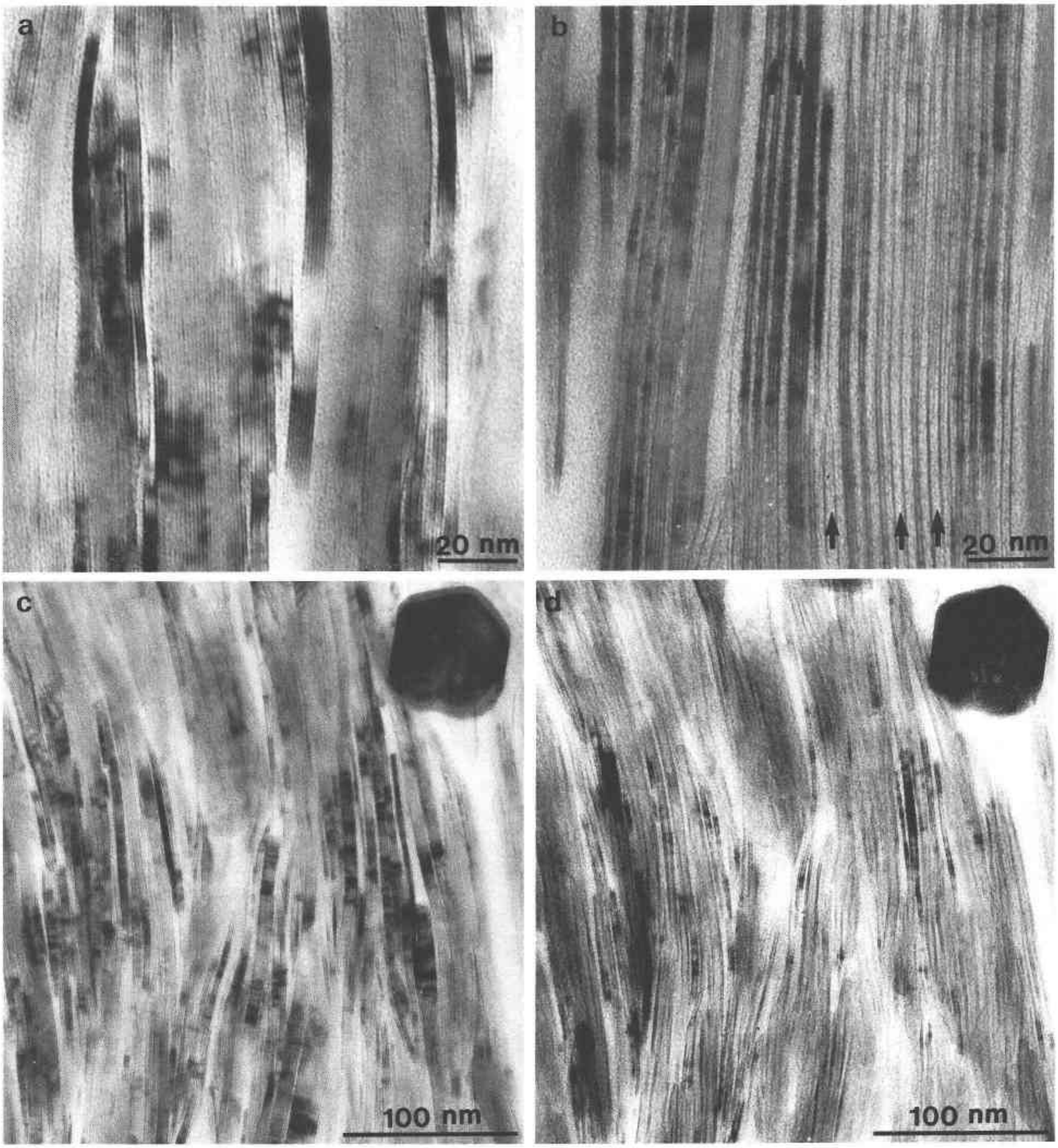

Fig. 1. HRTEM images of Marblehead illite in ultrathin sections. (**a**) Untreated section showing stacks of packets measuring 30–200 Å made up of nonexpanded 10-Å layers. (**b**) Section treated with octadecylammonium showing nonexpanded (10 Å) and expanded layers with layer spacings of 16–17 Å (top arrows) and layer spacings of 24–25 Å (bottom arrows). (**c**), (**d**) Ultrathin section of the same particles imaged on the same spot showing the layer structure before treatment (**c**) and after treatment (**d**) with octadecylammonium ions.

folds. The particles should be well impregnated and have a uniform distribution. In order to minimize the problem of radiation damage to clay minerals under the electron beam, it is advantageous to have an identical aggregate of particles occurring in two adjacent ultrathin sections. Thus one ultrathin section can be imaged before *n*-alkylammonium treatment and the other after. In order to observe the same particles before and after treatment, the position of particles can be identified by counting the mesh intersections from the center of the grids to the location of the section of interest. Alternatively, one can use index grids. HRTEM imaging and selected-area dif-

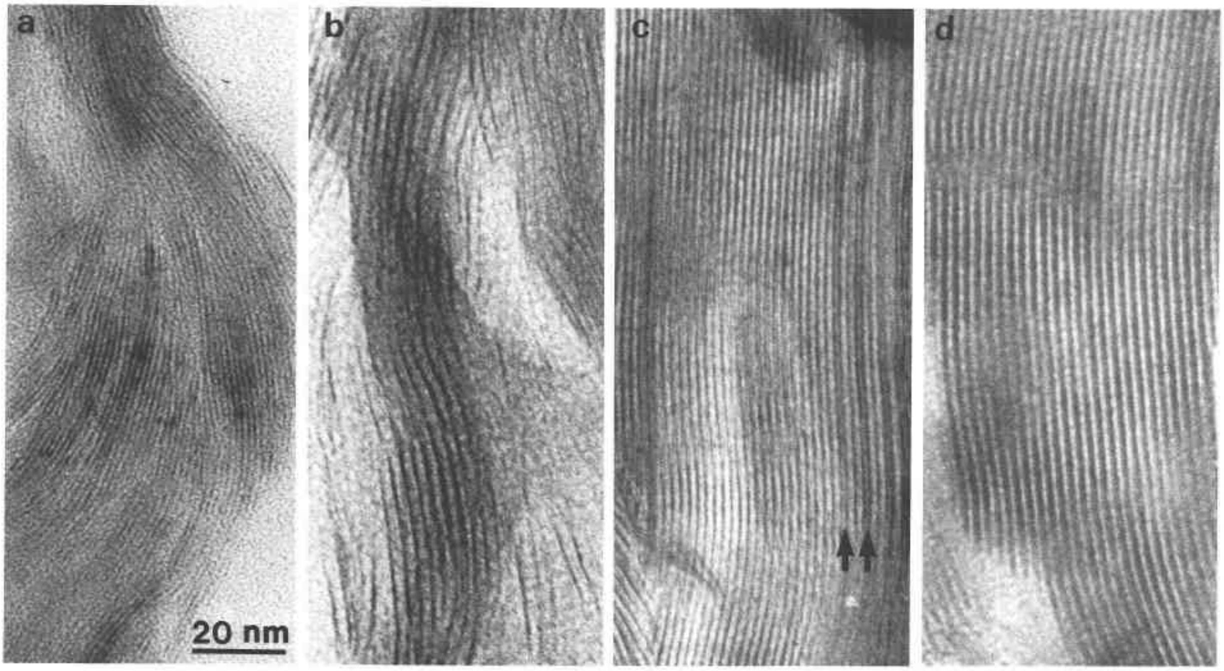

Fig. 2. HRTEM images of Fe-rich smectite and Jefferson vermiculite. (**a**) The smectite treated with heptylammonium ions showing short stacks of uniformly expanded layers with a 13-Å layer spacing. (**b**) Same specimen treated with octadecylammonium ions, showing large variation in layer spacing (20–28 Å), and random ordering. (**c**) The vermiculite treated with heptylammonium ions, showing perfect ordering of expanded layers with 17-Å layer spacing. Occasional nonexpanded 10-Å layers can be observed, however (arrows). (**d**) Same specimen treated with octadecylammonium ions showing uniformly expanded layers with 25-Å layer spacing. Same scale bar for **a**–**d**.

fraction (SAD) were performed using a JEOL 100CX TEM at 100 kV with focus conditions approximating the Scherzer defocus.

RESULTS AND DISCUSSION

A comparison of ultrathin sections obtained from the Epon 812 epoxy resin (Luft, 1961) and the ERL 4206 low-viscosity epoxy resin (Spurr, 1969) revealed that the latter is more suitable for the purpose of this study. The sections obtained from this resin are resistant to the electron beam and can be used on TEM grids without any supporting film. Routine observations at 100 kV reveal no visible damage to sections even after *n*-alkylammonium treatment for 1 week. Experiments on vermiculite and smectite indicate that 3–4 h of *n*-alkylammonium ion treatment are sufficient for full expansion of interlayers of these minerals. In most illitic materials, a significant change in layer structure could not be observed even after 24 h of treatment.

Figures 1a and 1b show the layer structure of Marblehead illite before and after treatment with octadecylammonium ions ($n_C = 18$), as imaged at different spots. Figures 1c and 1d are images of the same particles before and after the treatment. Note that particles, which are imaged at high magnification (>50000 ×) before treatment, do not respond in a consistent way to the treatment because of radiation damage to the specimen. According to Amos et al. (1982), "normal exposure in HRTEM (200–500 electrons/Å^2 to locate, focus and image a specimen at high magnification) results in radiation doses to the specimen of 10^{10}–10^{11} rads." Figures 2a–2d show the smectite and the vermiculite after treatment with octadecylammonium ions ($n_C = 18$) and heptylammonium ions ($n_C = 7$). The expansion of interlayers in clay minerals is dependent on their interlayer charge and reflects the arrangement of *n*-alkylammonium ions in interlayer spaces (Ghabru et al., 1989; Lagaly, 1981).

The results concerning the expandability behavior of 2:1 layer silicates obtained from this study agree with the results obtained from the conventional method (treatment of the samples with *n*-alkylammonium ion before embedding; Vali and Köster, 1986). With both methods, the expansion of the basal spacing is 5–10%, depending on chain arrangement, smaller than that measured by XRD. This difference may be due to radiation damage of the *n*-alkylammonium under the electron beam.

Treating Marblehead illite with $n_C = 18$ reveals two sets of expandable layers (Fig. 1). One has layer spacings of 16–17 Å corresponding to a bilayer arrangement of $n_C = 18$ in a low-charge smectite. The other has layer spacings of 24–25 Å corresponding to a paraffinlike layer configuration in vermiculite or a highly charged smectite with a pseudotrimolecular arrangement of $n_C = 18$ (Ghabru et al., 1989; Lagaly, 1981). Using X-ray powder diffraction patterns, Środoń (1984) described this illite as consisting of I + ISII mixed layers.

By treating both the smectite and the vermiculite with heptylammonium ions, the difference between smectite (13-Å layer spacing) and vermiculite layers (17-Å layer spacing) can be clearly observed. According to Lagaly et al. (1976), the heptylammonium ions in smectite are arranged in monolayers (13.5-Å layer spacing) up to an interlayer charge of 0.46 per [$O_{10}(OH)_2$]. In vermiculite they are arranged in paraffinlike layers (18-Å layer spacing; Ghabru et al., 1989; Lagaly, 1981). With $n_C = 18$ the vermiculite shows a uniform expansion of layers (25-Å layer spacing), whereas the smectite displays a large and random variation in layer spacing (20–28 Å).

Although the *n*-alkylammonium treatment of samples enables the charge density of expandable layer components in illitic materials by TEM to be estimated, the nature of these layers remains unclear. An overlap of interlayer charges between 0.53 and 0.8 per $O_{10}(OH)_2$ typical of natural vermiculite (Suquet and Pezerat, 1988) and between 0.3 and 0.7 per $O_{10}(OH)_2$ in the smectite component of I/S mixed layers (Velde and Brusewitz, 1986) has been reported. If true, a precise distinction between smectite-like and vermiculite-like layers requires further attention. However, the untreated smectite layers with TEM layer spacings of approximately 13 Å (Ahn and Peacor, 1986; Bell, 1986; Huff et al., 1988; Środoń et al., 1990; Vali and Köster, 1986) appear to behave differently compared to the so-called collapsed 10-Å interlayers in I/S mixed layers (Veblen et al., 1990). Their behavior is more like that of untreated vermiculite, with a TEM layer spacing of 9.6–10 Å (Vali and Köster, 1986; Ghabru et al., 1989). It is of course important also to study ion-milled specimens with this technique, and to observe the structural make-up of the clay minerals in the original fabric.

This new technique offers a great advantage over the conventional method because of the labor and time required for sample preparation.

ACKNOWLEDGMENTS

This research was supported by a strategic grant from the Natural Science and Engineering Research Council (NSERC) of Canada, and by Petroleum Research Fund Grant ACS-PRF 21730-AC8, administered by the American Chemical Society. R.F. Martin is thanked for reviewing an early version of this manuscript. We thank D. Peacor, W. Johns, and R. Freed for reviewing the manuscript and for their valuable suggestions. We also thank S. Aja for discussion and supplying the sample of Marblehead illite.

REFERENCES CITED

Ahn, J.H., and Peacor, D.R. (1986) Transmission and analytical electron microscopy of the smectite-to-illite transition. Clays and Clay Minerals, 34, 165–179.

Amos, L.A., Henderson, R., and Unwin, P.N.T. (1982) Three-dimensional structure determination by electron microscopy of two-dimensional crystals. Progress. Biophysics Molecular Biology, 39, 183–231.

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.

Ghabru, S.K., Mermut, A.R., and St. Arnaud, R.J. (1989) Layer-charge and cation-exchange characteristics of vermiculite (weathered biotite) isolated from a gray luvisol in northeastern Saskatchewan. Clays and Clay Minerals, 37, 164–172.

Häuser, W., and Stanjek, H. (1988) A refined procedure for the determination of the layer charge with alkylammonium ions. Clay Minerals, 23, 333–337.

Huff, W.D., Whiteman, J.A., and Curtis, C.D. (1988) Investigation of a K-bentonite by X-ray powder diffraction and analytical transmission electron microscopy. Clays and Clay Minerals, 36, 83–93.

Lagaly, G. (1981) Characterization of clays by organic compounds. Clay Minerals, 16, 1–21.

Lagaly, G., and Weiss, A. (1969) Determination of the layer charge in mica-type layer silicates. Proceedings of the International Clay Conference, Tokyo, 1, 61–80.

Lagaly, G., Gonzalez, F.M., and Weiss, A. (1976) Problems in layer charge determination of montmorillonites. Clay Minerals, 11, 173–187.

Lee, J.H., and Peacor, D.R. (1986) Expansion of smectite by laurylamine hydrochloride: Ambiguities in transmission electron microscope observations. Clays and Clay Minerals, 34, 69–73.

Luft, J.H. (1961) Improvements in epoxy resin embedding method. Journal of Biophysical Biochemical Cytology, 9, 409.

Olis, A.C., Malla, P.B., and Douglas, L.A. (1990) The rapid estimation of the layer charges of 2:1 expanding clays from a single alkylammonium ion expansion. Clay Minerals, 25, 39–50.

Rühlicke, G., and Kohler, E.E. (1981) A simplified procedure for determining layer charge by the n-alkylammonium method. Clay Minerals, 16, 305–307.

Spurr, A.R. (1969) A low-viscosity epoxy resin embedding medium for electron microscopy. Journal of Ultrastructure Research, 26, 31–43.

Środoń, J. (1984) X-ray powder diffraction identification of illitic minerals. 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. Clay and Clay Minerals, 38, 373–379.

Suquet, H., and Pezerat, H. (1988) Comments on the classification of trioctahedral 2:1 phyllosilicates. Clays and Clay Minerals, 36, 186–188.

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.

Veblen, D.R., Guthrie, G.D., Jr., Livi, K.J.T., and Reynolds, R.C. (1990) High-resolution transmission electron microscopy and electron diffraction of mixed-layer illite/smectite: Experimental results. Clays and Clay Minerals, 38, 1–13.

Velde, B., and Brusewitz, A.M. (1986) Compositional variation in component layers in natural illite/smectite. Clays and Clay Minerals, 34, 651–657.

MANUSCRIPT RECEIVED SEPTEMBER 13, 1990
MANUSCRIPT ACCEPTED NOVEMBER 7, 1990