Clays and Clay Minerals. Vol. 23, pp. 161–166. Pergamon Press 1975. Printed in Great Britain

NOTES

CRITICAL POINT DRYING OF ELECTRON MICROSCOPE SAMPLES OF CLAY MINERALS

(*Received* 22 *June* 1974)

The technique of critical point drying of samples for investigation in the electron microscope is not new (Anderson, 1952), but has not been applied previously to the study of clay minerals. A variety of methods have been used (Gal and Rich, 1972; Güven, 1972; Güven and Grim, 1972; Jonas and Oliver, 1967; Mering and Oberlin, 1967; Roberson *et al.*, 1968; Uyeda *et al.*, 1973; Warren and McAtee, 1968) in preparing samples of clay minerals, but as has been pointed out (Anderson, 1952; Mering and Oberlin, 1967; Jonas and Oliver, 1967) all of the methods tend to cause aggregation and orientation of particles during the drying process. With the smectite minerals, the tendency toward aggregation has been said to be due to edge-to-edge forces (Mering and Oberlin, 1967) producing associations. However, any type of sample may be artificially oriented in any drying process which causes an interfacial boundary to pass through the sample during the drying process (Anderson, 1952). The most common preparation method used (Mering and Oberlin, 1967; Roberson *et al.*, 1968; Uyeda *et al.*, 1973; Warren and McAtee, 1968) has been ultrasonic dispersion of the sample in water followed by air drying of a drop of the suspension over a coated microscope grid. However, in this technique, as well as in freeze drying (Gal and Rich, 1972), spray drying (Jonas and Oliver, 1967), and others, the interfacial tension effect as the solvent is dried is not eliminated. Anderson (Anderson, 1952) has studied, in particular, the effect of this interfacial tension in flattening and distorting biological samples. In this note, critical point drying has been used and is compared to air drying to demonstrate that aggregation, particle orientation and distortion may be minimized by this technique.

Approximately 40 ml of a 0·1 per cent suspension of the various samples in amyl acetate was prepared by means of ultrasonic dispersion. The time of sonication was four minutes. At the end of this time, carbon coated copper grids (400 mesh) in a special holder supplied with the critical point drying apparatus were placed in the dispersion such that the grids were located in the upper one-third of the suspension. The grids and holder were allowed to remain in the dispersion for fifteen minutes. Immediately upon removal from the dispersion, the grids were placed in the cylinder of the critical point drying apparatus and the drying procedure begun. Amyl acetate was chosen as the solvent both because of the nature of the samples, and because amyl acetate is miscible with the liquid CO_2 used in critical point drying.

The clay minerals studied were dimethyldioctadecylammonium–montmorillonite (BENTONE 34) and dimethyldioctadecylammonium–hectorite (BENTONE 38) obtained from Baroid Corporation, NL Industries. Also studied were tris(ethylenediamine)copper(II)–montmorillonite, tris(ethylenediamine)nickel(II)–montmorillonite, tris(ethylenediamine)chromium(III)–montmorillonite, and tris(ethylenediamine)cobalt(III)–montmorillonite.

Critical point drying was performed with the DCP-1 Critical Point Dryer (Denton Vacuum, Inc., Cherry Hill, New Jersey). After placing the grids and holder in the cylinder the exit valve to the cylinder was closed and the inlet valve opened to allow liquid CO_2 to fill the cylinder at a pressure of 900 psi. The exit valve was then opened slightly to allow a steady flow of liquid CO_2 to escape the drying chamber. The liquid CO_2 was allowed to flow through the chamber for 15–20 minutes, or until no odor of amyl acetate could be detected in the escaping CO_2. The exit and inlet valves were then closed to isolate the chamber and a container of water heated to 50°C was brought up around the drying chamber. Within a few minutes the pressure increased from 900–1500 psi approx. At approximately 1060 psi the liquid CO_2 passed through the critical point. With the temperature maintained at 45°C, the exit valve was opened and the CO_2 allowed to escape the drying chamber. The dried samples were then removed and examined in the Hitachi HU-11A microscope at an accelerating voltage of 75 kV.

All these samples were also investigated after drying in air. In this case the sample was prepared in an identical manner to that described with the exception that the grids in the holder were placed in air to dry after being in the dispersion for 15 min.

Figures 1 and 2 show typical electron photomicrographs of dimethyldioctadecylammonium–montmorillonite which has been prepared by critical point drying. These two figures are to be compared with Fig. 3 which is an electron micrograph of the same which has been allowed to air dry. Figures 1 and 3 are of the same magnification.

The most striking contrast between the critical point and air dried samples is in the degree of "curling" of sheets. In the critical point dried samples, curling was as extensive as shown in all cases. As can be seen, the air dried samples exhibit no such effect. As Anderson (1952) has discussed, air drying would be expected to flatten and orient any specimen which has an edge pointed upward through the liquid surface as the interfacial boundary moves downward. This being the case, then it must be concluded that the curling seen in Figs. 1 and 2 is the natural morphology of the sample as prepared.

For the dimethyldioctadecylammonium–montmorillonite samples the extent of the coverage of the grids in Figs. 1 and 2 does not allow any conclusions to be made with regard to the tendency toward aggregation of particles under the different drying conditions. However, in examining the other samples (dimethyldioctadecylammonium–hectorite, tris(ethylenediamine)copper(II)–montmorillonite, tris(ethylenediamine)nickel(II)–montmorillonite, tris(ethylenediamine)cobalt(III)–montmorillonite, and tris(ethylenediamine)chromium(III)–montmorillonite, Fig. 4), it was very obvious that critical point drying leads to a minimum of aggregation of particles. The air dried samples had large aggregates of smaller particles which obscured the detail of individual particles. The critical point dried samples showed uniform coverage of the grid with a large number of individual particles.

In all of the samples, air drying produced samples with strong orientation such that the basal plane was parallel to the grid surface. With critical point drying, orientation was more random and aggregates were found where the individual clay sheets had the basal plane perpendicular to or inclined with respect to the grid surface.

https://doi.org/10.1346/CCMN.1975.0230212 Published online by Cambridge University Press

Acknowledgement—The Robert A. Welch Foundation is recognized for its financial support of this research project.

Chemistry Department,
Baylor University,
Waco,
Texas 76703, *U.S.A.*

DONALD L. JERNIGAN
JAMES L. MCATEE, JR.

REFERENCES

Anderson, T. F. (1952) A method for eliminating gross artifacts in drying specimens: *Extrait du Congres De Microscopic Electronique, Editions de la Revue d'Optique.* Section **V,** 567–576.

Gal, M. and Rich, C. I. (1972) Selectivity effect of cesium on clay size weathered mica; transmission electron microscopy studies: *Clays and Clay Minerals* **20,** 175–179.

Güven, N. (1972) Electron optical observations on marblehead illite: *Clays and Clay Minerals* **20,** 83–88.

Güven, N. and Grim, R. E. (1972) X-Ray diffraction and electron optical studies on smectite and α-cristobalite associations: *Clays and Clay Minerals* **20,** 89–92.

Jonas, E. C. and Oliver, R. M. (1967) Size and shape of montmorillonite crystallites: *Clays and Clay Minerals* **15,** 27–33.

Mering, J. and Oberlin, A. (1967) Electron optical study of smectites: *Clays and Clay Minerals* **15,** 3–25.

Roberson, H. E., Weir, A. H. and Woods, R. D. (1968) Morphology of particles in size-fractionated Na-montmorillonites: *Clays and Clay Minerals* **16,** 239–247.

Uyeda, N., Hang, P. T. and Brindley, G. W. (1973) The nature of garnierites—II: electon optical study: *Clays and Clay Minerals* **21,** 41–50.

Warren, D. C. and McAtee, J. L., Jr. (1968) A morphological study of selected synthetic clays by electron microscopy: *Clays and Clay Minerals* **16,** 271–274.

EXCHANGE ION POSITIONS IN SMECTITE: EFFECTS ON ELECTRON SPIN RESONANCE OF STRUCTURAL IRON

(*Received* 13 *June* 1974)

The positions of exchange ions in smectite minerals depend in part on the hydration energies of the cations and hydration conditions. Under ambient conditions they may be solvated by one or two molecular layers of water as in $Cu(H_2O)_4^{2+}$ and $Cu(H_2O)_6^{2+}$ (Clementz *et al.*, 1973), whereas in the wet silicate they are generally present in greatly expanded interlayers as fully hydrated cations. Thermal dehydration of the cations allows the silicate layers to collapse as the ions move into hexagonal cavities formed by oxygen atoms on the interlayer surfaces. In these hexagonal sites, the dehydrated cations are adjacent to structural OH groups (McBride and Mortland, 1974). Since the dioctahedral smectites possess vacant octahedral positions, small cations such as Li^+ can migrate irreversibly at sufficiently elevated temperatures through the hexagonal cavities into the empty octahedral sites (Calvet and Prost, 1971). The present work demonstrates that the position of the interlayer cation can be readily determined from the nature of the electron spin resonance (ESR) signals of Fe^{3+} ions present in the aluminosilicate layers of the mineral.

Isolated structural Fe^{3+} ions in distorted tetrahedral or octahedral sites of silicate minerals (Matyash *et al.*, 1969; Kemp, 1971; Novozhilov *et al.*, 1970) and glasses (Castner *et al.*, 1960) commonly exhibit a broad signal with an isotropic g value near 4·3. Hydrated Na^+, Li^+ and Ca^{2+} exchange forms of the smectite in this study (Upton, Wyoming montmorillonite, $M^+_{0.64}$ $(Al_{3.06}$ $Fe_{0.32}$ $Mg_{0.66})$ $(Al_{0.10}$ $Si_{7.90})$ $O_{20}(OH)_4$) exhibit two Fe^{3+} signals near g = 4·4 as shown in Fig. 1(1). The authors suggest that the weak Fe^{3+} resonance may arise from ions adjacent to octahedra containing Mg^{2+}, while the more intense Fe^{3+} resonance is attributed to those ions adjoining octahedra which contain trivalent ions (mainly Al^{3+}). The Mg^{2+} ions are the source of net negative charge in the silicate structure, and this charge imbalance must cause the Fe^{3+} environment adjacent to Mg^{2+} to differ from that adjacent to Al^{3+}. Thus the

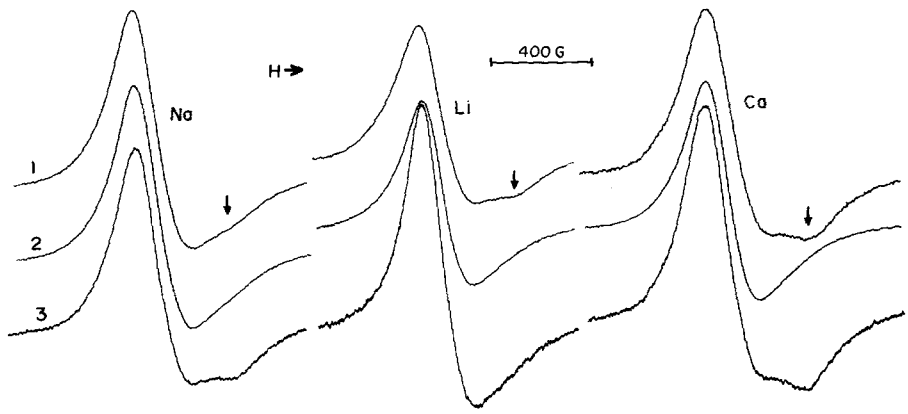


Fig. 1. Effects of thermal dehydration and resolvation of Na^+, Li^+, and Ca^{2+} smectites on the ESR signal of structural Fe^{3+}.
(1) Hydrated mineral under ambient conditions; (2) Mineral dehydrated at 205°C for 24 hr; (3) Mineral resolvated in ethanol after 205° heat treatment.
The arrows indicate the weak Fe^{3+} resonance.

https://doi.org/10.1346/CCMN.1975.0230212 Published online by Cambridge University Press