REACTIONS OF MOLTEN SALTS WITH LAYER-LATTICE SILICATES[1]

By

JOE L. WHITE

Agronomy Department, Purdue University, Lafayette, Indiana

ABSTRACT

A preliminary x-ray diffraction study of the effect of treatment of typical layer-lattice silicates with molten lithium, sodium, and potassium nitrates has been made. Treatment of Wyoming bentonite (Upton, Wyoming) with molten lithium nitrate produced random interstratification of spacings of 9.6 and 17.8 A when specimens were glycerol-solvated, with approximately 20 percent expanded layers. Treatment with sodium nitrate at 320° C produced a very high degree of preferred orientation in film specimens dried from water, whereas treatment with molten potassium nitrate produced a more random orientation in the specimen. The bentonite treated with molten sodium nitrate expanded completely to 17.8 A with glycerol; treatment with potassium nitrate resulted in a small amount of random interstratification, the proportion of expanded layers being about 80 percent.

Treatment of the $<5\mu$ fraction of Delamica (muscovite) with molten lithium nitrate removed a large portion of the potassium from the mica, and lithium was fixed in a not readily exchangeable manner. When barium-saturated and glycerol-solvated, the treated material gave an 001 spacing of 17.8 A, the basal spacing for glycerol-montmorillonoids. The amount of potassium removed from the muscovite varied with the muscovite/lithium-nitrate ratio and length of treatment.

INTRODUCTION

Layer-lattice silicates such as montmorillonite, illite, vermiculite, etc., have cation-exchange properties which are attributed largely to isomorphous substitutions within the various structures (Hendricks, 1942; Hofmann and Wilm, 1933; Maegdefrau and Hofmann, 1937; Marshall, 1935). Edelman and Favejee (1940) proposed montmorillonite and halloysite structures without ionic substitutions. They suggested that cation-exchange capacity results from dissociation of certain projecting OH groups. The artificial production of ionic entrance or substitution and consequent changes in the electrical properties of clay minerals would aid in evaluating these proposed structures.

Thilo's (1933) studies of the high-temperature reactions of pyrophyllite with metallic oxides and chlorides indicated that magnesium could be introduced into positions of six-fold coordination. However, the effect of these reactions on the structure, cation-exchange capacity and other electrical properties of the pyrophyllite were not reported.

The salts used by Thilo had melting points of 600° C or higher; these temperatures are sufficiently high to result in the partial or complete destruction of a number of clay minerals. For the present study salts having melting points below the decomposition temperatures of clay minerals were chosen. Lithium

133

nitrate (m.p., 255° C), potassium nitrate (m.p., 334° C), and sodium nitrate (m.p., 307° C) were used.

Lithium is the only cation in the above group small enough to occupy the octahedral position in layer-lattice silicates. Lithium also occurs in tetrahedral coordination in certain aluminosilicate minerals (Winkler, 1954). It has been shown that montmorillonite saturated with lithium is difficult to rehydrate after being dried at moderate temperatures (Greene-Kelly, 1952a, 1952b; Hofmann and Klemen, 1950). Hofmann and Klemen (1950) suggested that lithium ions migrated into the vacant octahedral positions with a consequent neutralization of charge. Greene-Kelly (1955) found a correlation between the percentage of octahedral substitution and the loss of expansion. He concluded that the results could be explained if it were assumed that migration is permissible only when the silicate sheet charge is due to octahedral substitution.

The fundamental properties of molten salt systems have received increasing attention in recent years (Van Artsdalen and Yaffe, 1955). Barrer (1950) used the fusion method, i.e., molten salts, in studying ion-exchange processes in crystalline zeolites. White (1954) has recently reported preliminary studies of the reactions between molten lithium nitrate and certain mica minerals.

EXPERIMENTAL

The reactions with molten salts were carried out in both porcelain and platinum crucibles in muffle furnaces. Reactions were studied in the range 280° to 350° C.

Cation-exchange capacities of the minerals were measured by saturation with ammonium acetate and determination of adsorbed ammonia with a micro-distillation apparatus (Mackenzie, 1952).

Total lithium and potassium were determined on samples which had been saturated with calcium or ammonium. The samples were decomposed with HF, and an Eel Flame Photometer was used for determination of potassium and lithium.

Reactions were followed by means of x-ray diffraction photographs and diffractometer tracings. Copper, cobalt, and molybdenum Ka radiation was used.

Electron micrographs of treated materials were made by Mr. Harry Fisher of the Electron Microscopy Laboratory, Rothamsted Experimental Station.

The salts used were of AnalaR Reagent grade.

Minerals studied included Wyoming bentonite (Upton, Wyoming), Delamica (a finely divided mica separated from Cornish china clay), illite (Fithian, Illinois), a micaceous subsoil clay on basement Carboniferous sandstone from North Wales, paragonite (British Museum specimen, Simplon, Switzerland), and biotite (Gold Coast specimen, Dr. I. Stephens).

RESULTS

Reaction of Wyoming Bentonite with Lithium, Sodium, and Potassium Nitrates

Treatment of $<0.2\ \mu$ Wyoming bentonite with lithium nitrate at 320° C for 21 hours resulted in a decrease in the exchange capacity from 97.5 meq/100 g

to 22 meq/100 g. The amount of lithium retained in the structure against extraction with 1 N ammonium acetate was 76 meq/100 g.

X-ray diffraction patterns of glycerol-solvated specimens of bentonite treated with lithium nitrate at 300° C for 15 hours had peaks at 9.40 A and 17.8 A, indicating random interstratification with about 20 percent expanded layers (Table 1). Greene-Kelly (1955) reported no expansion for Wyoming bentonite saturated with lithium and dried at 200° to 300° C. A D. T. A. curve for the lithium-treated Wyoming bentonite is shown in Figure 1C. The absence of interlayer water is indicated by the lack of an endothermic peak in the range 100° to 200° C.

TABLE 1. — EFFECT OF MOLTEN SALT TREATMENTS ON THE EXPANSION OF WYOMING BENTONITE WHEN GLYCEROL-SOLVATED.

| Treatment	001/002, A	p^1
KNO_3 at 350° C	9.02	0.8
$NaNO_3$ at 320° C	8.89	1.0
$LiNO_3$ at 300° C	9.40	0.2

[1] p—proportion of expanded layers expressed as a decimal.

X-ray diffraction patterns and tracings produced from oriented aggregates or slides of <0.2 μ Wyoming bentonite treated with sodium nitrate at 320° C for 50 hours indicated a very high degree of orientation. Solvation with glycerol or ethylene glycol produced a rational sequence of $00l$ reflections indicating complete expansion of the clay. Electron micrographs revealed the particles to be well-dispersed thin platelets.

Treatment of Wyoming bentonite with potassium nitrate at 350° C and glycerol solvation produced a specimen which gave an x-ray pattern indicating greater random orientation than the sodium-nitrate treatment. The 001/002 spacing in the 9 A region indicated some random interstratification. The proportion of expanded layers was estimated to be 80 percent (Table 1) using the data of Brown and Greene-Kelly (1954) with slight corrections for the c values of the two components.

Reaction between Molten Lithium Nitrate and Delamica

Delamica is a delaminated muscovite obtained from English Clays Lovering Pochin & Co., Ltd., St. Austell, Cornwall, England. The muscovite is a by-product of china clay manufacture and contains about 5 percent kaolinite. The delamination is an entirely mechanical process. A considerable proportion of the Delamica is finer than 5 μ. The chemical composition of Delamica is as follows: SiO_2, 46.60 percent; Al_2O_3, 32.69 percent; Fe_2O_3, 4.0 percent; TiO_2, 0.43 percent, MgO, 0.8 percent; CaO, 0.06 percent; K_2O, 9.1 percent; Na_2O, 0.7 percent; loss on ignition, 5.35 percent.[1] The calculated formula for the muscovite in Delamica with a correction for the presence of approximately 5 percent kaolinite is

$$X_{0.93}$$
$$\uparrow$$
$$(Al_{1.71}Fe_{0.21}Mg_{0.08}) (Al_{0.85}Si_{3.15}) O_{10} (OH)_2$$
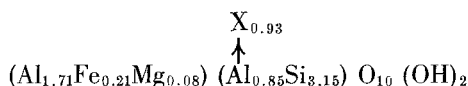
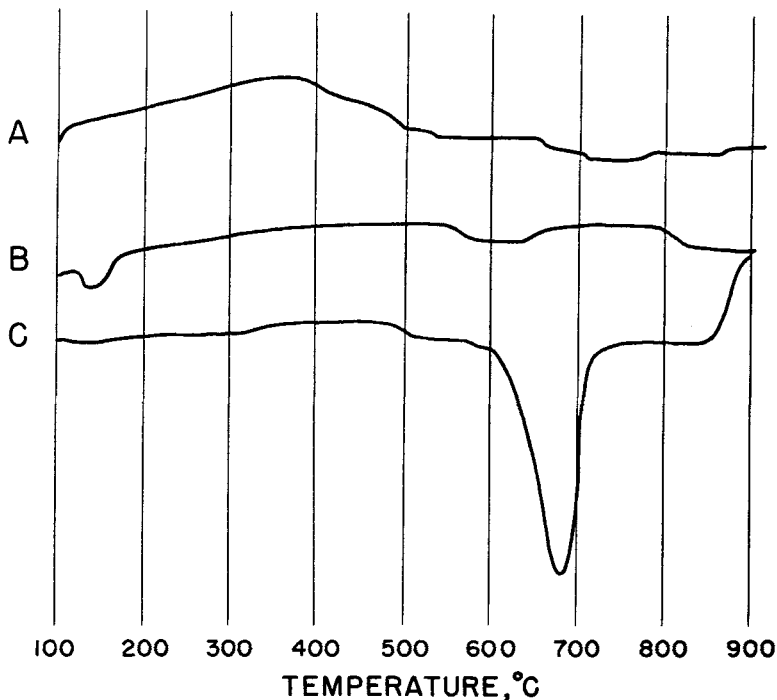[1] Courtesy of T. W. Parker, English Clays Lovering Pochin & Co., Ltd.

FIGURE 1. — Differential thermal analysis curves of (A) untreated Delamica (5 to 2 μ);
(B) Delamica (5 to 2 μ) treated with LiNO$_3$ (1:120 ratio) for 480 hours at 300° C; and
(C) Wyoming bentonite (<0.2 μ) treated with LiNO$_3$ for 15 hours at 300° C.

Thus, Delamica is representative of the muscovite group, being dioctahedral and having practically all isomorphous substitution in the tetrahedral position. The 060 reflection at 1.504 A further confirms the dioctahedral nature of the Delamica.

Powder diffraction data for the 5 to 2 μ fraction of Delamica are given in Table 2. The pattern was recorded using a chart operation with the Philips high-angle x-ray diffractometer. The settings were as follows: scale factor, 8; multiplier, 0.6; time constant, 2 seconds; divergence slit, 1°; receiving slit, 0.006 inch; scatter slit, 1°; scanning speed, $\frac{1}{4}$° per minute; radiation, filtered Cu. Instrumental corrections were applied from a smooth $\Delta 2\theta$ curve obtained by exposing a silicon standard.

The d$_{(001)}$ dimension was derived from the third, fourth and fifth orders of the (00l) series. A value of 9.974 A was obtained.

Differential thermal analysis curves for the untreated Delamica (5 to 2 μ) and for the same size fraction treated with molten lithium nitrate for 480 hours are shown in Figure 1A and 1B. The shape of the curves in the high-temperature region is typical of muscovite, as evidenced by little loss of hydroxyl water

below 800° C. The presence of interlayer water in the lithium-treated Delamica is clearly shown.

Fractions of $<5\ \mu$ Delamica were separated by dispersion with Calgon and sedimentation and/or centrifugation.

The effect of temperature of the molten lithium nitrate on removal of potassium from Delamica (5 to $2\ \mu$) was studied by treating the Delamica with $LiNO_3$ ($1:120$ ratio) for 12 hours at 280° C and 350 ° C. At 280° C, 45 meq potassium per 100 g was removed; and at 350° C, 108 meq per 100 g was removed.

The effect of reaction time with molten $LiNO_3$ on the chemical composition of Delamica was studied using the 1 to $0.2\ \mu$ fraction and $1:60$ ratio of Delamica to $LiNO_3$ at a temperature of 300° C. Table 3 shows the changes in potassium, lithium, and cation-exchange capacity for reaction times of 0.3 hours to 18 hours. The summation of potassium, lithium, and cation-exchange capacity is relatively constant at about 250 meq/100 g.

The removal of potassium and increase in lithium content and cation-exchange capacity with time of reaction for this experiment are shown in Figure 2. The lithium here is that which is not replaced by ammonium and is assumed to be nonexchangeable. There is rather rapid removal of potassium and increase in lithium and cation-exchange capacity up to 6 hours. After this the reaction goes much more slowly.

It is postulated that two factors are largely responsible for this sudden and marked change in reaction rate; (1) a critical potassium concentration being attained in the melt, and (2) the charge on the mineral being reduced to a critical value.

Considering the first factor, the potassium concentration in the melt can be approximated if it is assumed that the amount of potassium removed from the

TABLE 2. — X-RAY DIFFRACTION DATA (POWDER) FOR DELAMICA (5 TO 2μ).

d (A)	Relative intensity	d (A)	Relative intensity
9.974	100	2.794	24
4.988	28	2.788	25
4.469	40	2.594	20
4.323	12	2.566	52
4.300	12	2.492	11
4.115	8	2.463	12
3.975	4	2.446	8
3.883	23	2.383	19
3.738	23	2.149	13
3.575	19	2.131	14
3.570	18	2.031	7
3.494	37	1.9949	30
3.481	39	1.9646	12
3.340	59	1.6632	13
3.326	76	1.6477	18
3.201	41	1.5240	7
3.116	8	1.5045	14
2.989	40	1.3517	9
2.863	30	1.3396	8

λ Cu Ka ($= 1.5418$ A) used below 25° 2θ and λ Cu Ka_1 ($= 1.54051$ A) above 25° 2θ.
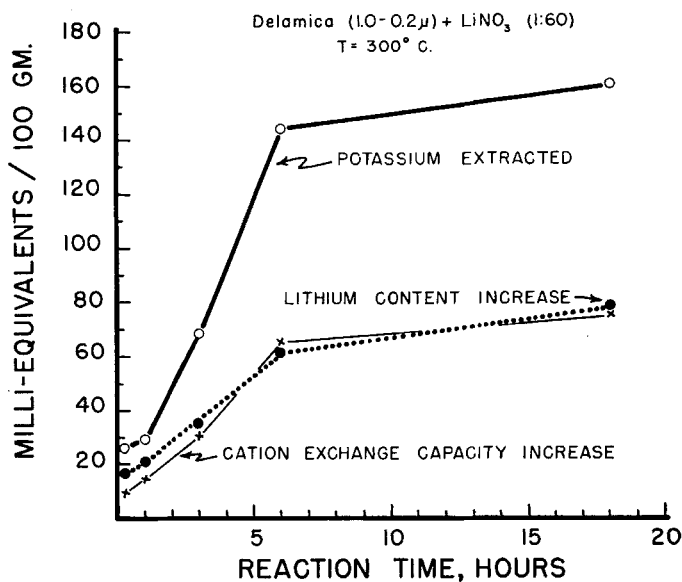
FIGURE 2. — Variation in potassium removed, lithium content, and cation-exchange capacity with reaction time in the treatment of Delamica (1 to 0.2 μ) with $LiNO_3$ (1:60 ratio) at 300° C.

Delamica is uniformly distributed throughout the melt. The density of lithium nitrate at 300° C was found to be 2.22. The molecular volume was calculated to be 31.08 cc; this would give a normality of 32.1 for molten lithium nitrate at this temperature. The normality of the lithium nitrate melt with respect to potassium was calculated for the various reaction times. The normality of potassium in the melt increased from zero up to 0.053 N at the end of six hours.

To check this further, a melt of lithium nitrate was prepared so as to be 0.055 N with respect to potassium. The melt was agitated frequently over a period of 12 hours to insure thorough mixing; then the 1 to 0.2 μ fraction of Delamica was added to the lithium nitrate melt in a ratio of 1:60 and the crucible heated at 300° C overnight. X-ray photographs of glycerol-solvated specimens from this treatment showed no expansion of the mica spacing. This indicates that a concentration of 0.055 N potassium (0.16 percent with respect to concentration of lithium ions) is sufficient to prevent or greatly to inhibit removal of inter-layer potassium from muscovite. The second factor involved in the rate change, the attainment of a critical charge on the clay, is important because of its role in the expansion of the lattice of the mica and subsequent release of potassium. It appears that interlamellar expansion is associated with a layer charge in the range of 160 to 150 meq/100 g and lower (Barshad, 1954). Above this value the minerals do not expand or expand only with difficulty. Assuming that lithium enters the lattice and reduces the charge on the layer by an equivalent amount, the total charge would be given by the summation of potassium and cation-exchange capacity. From Table 3 it can be seen that the charge has been

TABLE 3. — CHEMICAL COMPOSITION OF DELAMICA (1 TO 0.2μ) AS AFFECTED BY
REACTION TIME WITH MOLTEN LiNO$_3$ (1:60 RATIO) AT 300° C.

Reaction time, hours	meq/100 g			
	K	Li	C.E.C.	Σ K, Li, C.E.C.
Untreated	223	15	15	253
0.3	197	31	25	253
1.0	193	36	30	259
3.0	155	50	46	251
6.0	82	77	81	240
18.0	63	94	92	249

reduced from 238 meq/100 g in the untreated Delamica to $(82+81)=163$ meq/100 g at a reaction time of six hours. It is suggested that this permits expansion of the layers with a very sudden increase in potassium-ion concentration in the vicinity of the mica surface and the reaction is driven in the reverse direction with a marked decline in rate of removal of potassium. X-ray diffraction patterns indicated that practically all the Delamica expanded at a reaction time of six hours.

Previous experiments indicated that a large proportion of the lithium reacting with the Delamica was not replaced by ammonium or calcium. It was assumed that this lithium was not held on external surfaces, but in view of the relatively weak replacing power of the ammonium ion further confirmatory evidence was sought. Duplicate samples of the 5 to 2 μ and 2 to 1 μ fractions were treated with lithium nitrate at 320° C for 130 and 106 hours, respectively. The excess lithium nitrate was removed by washing with distilled water, and then the samples were washed five times with 2 N BaCl$_2$ or 6 N H$_2$SO$_4$ and the lithium and potassium remaining in the mica were determined (Table 4). Even after these drastic treatments, 90 to 117 meq/100 g of lithium remain. It seems unlikely that lithium could be held so tenaciously on external surfaces.

Electron micrographs of the treated Delamica are shown in Figures 3 to 7. The expanding properties of the lithium-treated Delamica are illustrated vividly in these micrographs.

From the chemical data one is led to conclude that the lithium held by the Delamica is internal. A logical place to expect migration of lithium ions would be into empty octahedral positions. If lithium ions move into empty octahedral positions in a dioctahedral mineral one might assume an increase in the 060 spacing from 1.50 A in the direction of 1.53 A as the trioctahedral member is

TABLE 4. — LITHIUM CONTENT OF DELAMICA TREATED WITH LiNO$_3$ (1:120 RATIO) (AT
320° C (5 TO 2 μ FRACTION TREATED 130 HOURS, 2 TO 1 μ FRACTION TREATED 106 HOURS
AFTER FIVE EXTRACTIONS WITH 2 N BaCl$_2$ OR 6 N H$_2$SO$_4$)

Treatment		Lithium content, meq./100 g
5 to 2 μ	6 N H$_2$SO$_4$	111
	2 N BaCl$_2$	117
2 to 1 μ	6 N H$_2$SO$_4$	91
	2 N BaCl$_2$	95

approached (Grim, Bradley, and Brown, 1951). However, the 060 spacing of Delamica treated with $LiNO_3$ was found to 1.50 A, the same as that of the untreated Delamica.

X-ray diffraction patterns and diffractometer tracings were made of glycerol- and ethylene glycol-solvated Delamica samples treated with lithium nitrate and saturated with various ions. When saturated with barium or cesium and glycerol-solvated the treated material gives a rational series of reflections corresponding to a $d_{(001)}$ of 17.8 A on x-ray analysis. Figure 8 shows a diffractometer tracing of treated Delamica saturated with barium and solvated with ethylene glycol; a powder-pattern tracing of the untreated Delamica is included for comparison.

Fourier syntheses were made following a procedure similar to that of Brown (1950) and the resulting electron density projections are shown in Figures 9 and 10. The peaks at about 5.5 A from the origin are assumed to be due to potassium ions which have not been exchanged. The barium-saturated material (Figure 9) was treated for a longer time and contained less potassium than the cesium-saturated material (Figure 10). The 5.5 A peak is considerably smaller in Figure 9 than in Figure 10. The presence of difficultly exchangeable potassium at the surface of the expanded Delamica would emphasize the role of tetrahedral charge in potassium "fixation" (Wear and White, 1951).
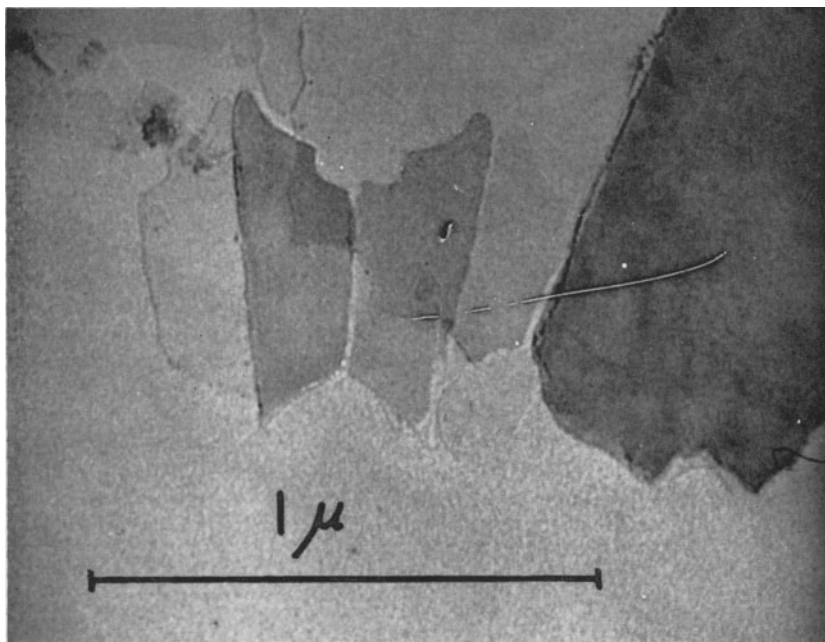
Figure 3. — Electron micrograph of Delamica (5 to 2 μ) treated with $LiNO_3$ at 320° C. Note cleavage of a flake with initial separation at top of packet, then further separation at bottom of each half to unfold somewhat like a road map.
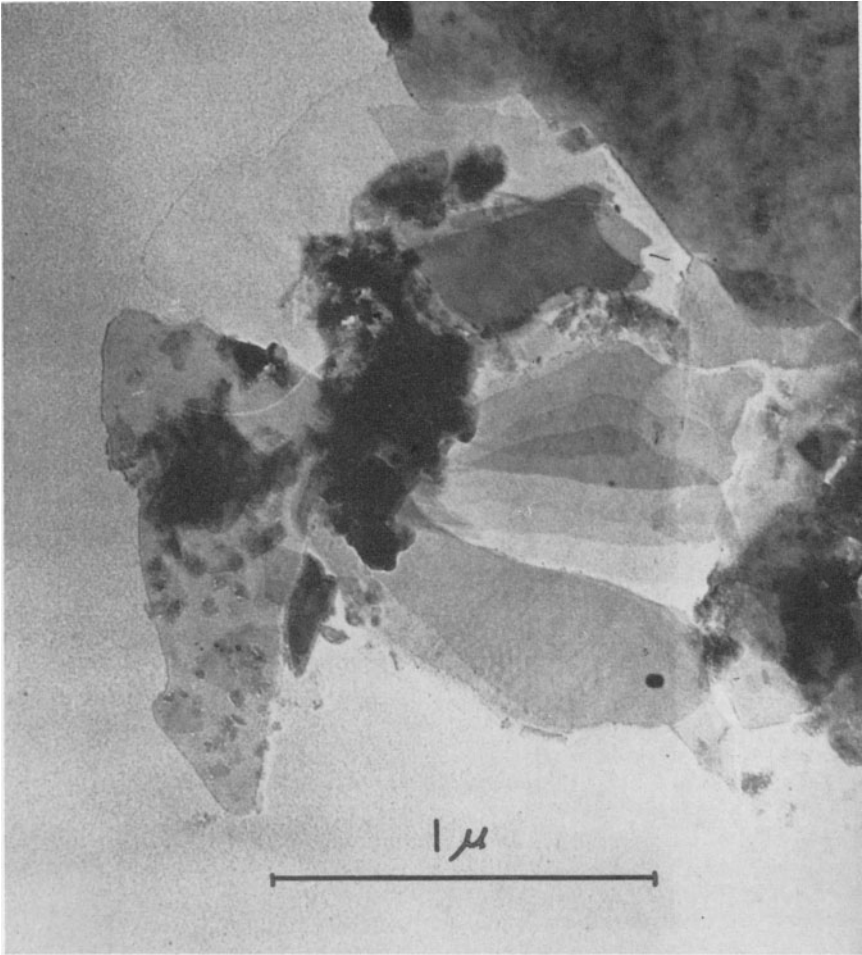
FIGURE 4. — Electron micrograph of Delamica (5 to 2 μ) treated with $LiNO_3$ at 320° C. Note cleavage of flakes on micro scale with plates superimposed in a staggered arrangement.

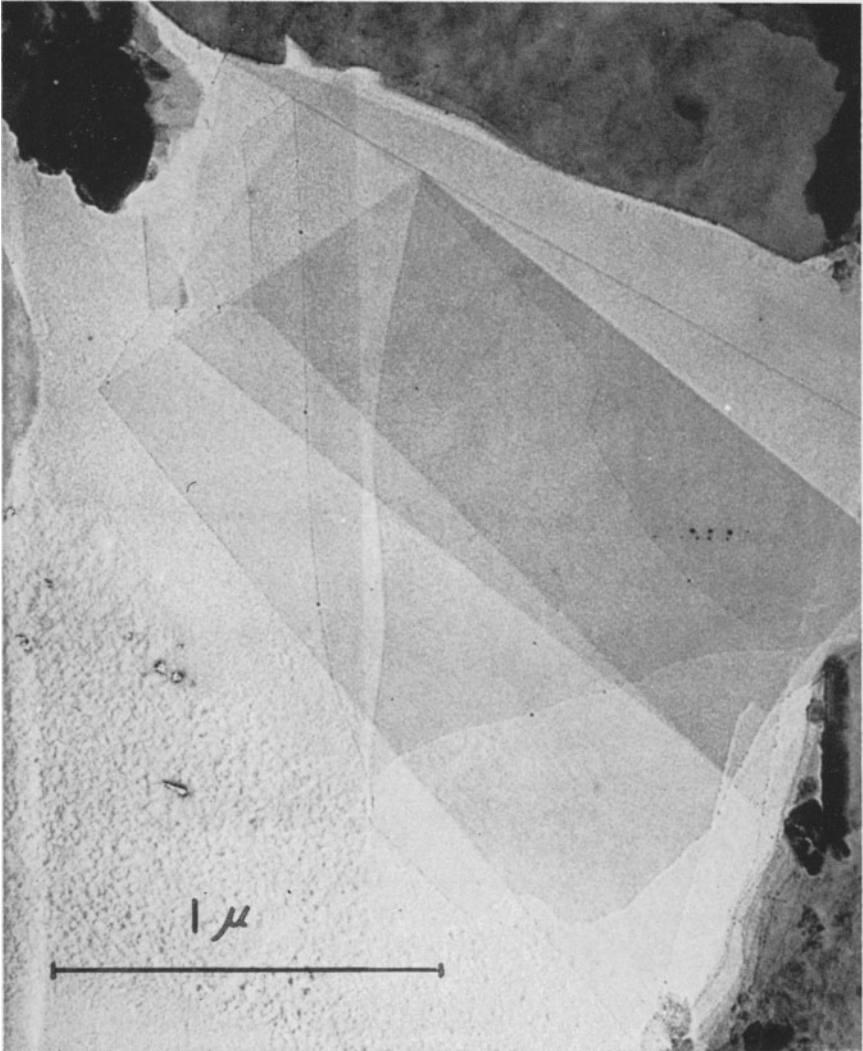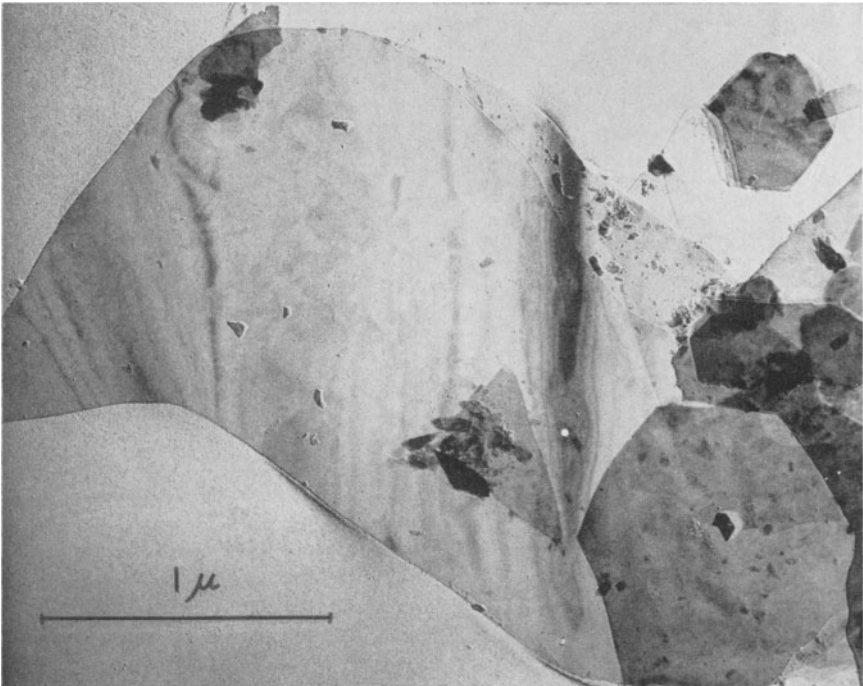FIGURE 5. — Electron micrograph of Delamica (5 to 2 μ) treated with $LiNO_3$ at 320° C; showing very extensive sheets folded upon themselves.

FIGURE 6. — Electron micrograph of Delamica (5 to 2 μ) treated with LiNO$_3$ and saturated with barium. Measurement of shadow length indicates that top layer is one layer thick (10 A).

Attempts to react molten lithium nitrate with large particle-size fractions of Delamica or small flakes of muscovite were not successful.

Other dioctahedral micas, including an illite from Fithian, Illinois, a micaceous subsoil clay on basement Carboniferous sandstone from North Wales, and paragonite, reacted in a manner similar to the Delamica. Biotite, a trioctahedral mica, was not expanded by treatment with molten lithium nitrate.

ACKNOWLEDGMENTS

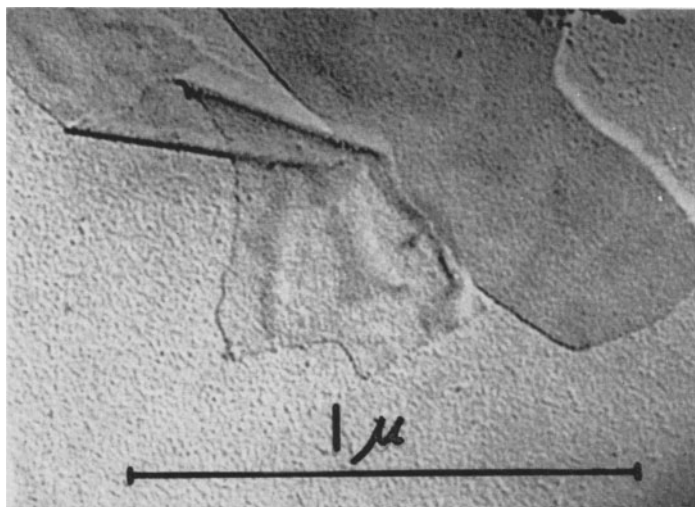FIGURE 7. — Electron micrograph of Delamica (5 to 2 μ) treated with $LiNO_3$ and washed with H_2SO_4. The thin, sharply folded flake is a single layer (10 A) and the larger flake is six or seven layers thick.
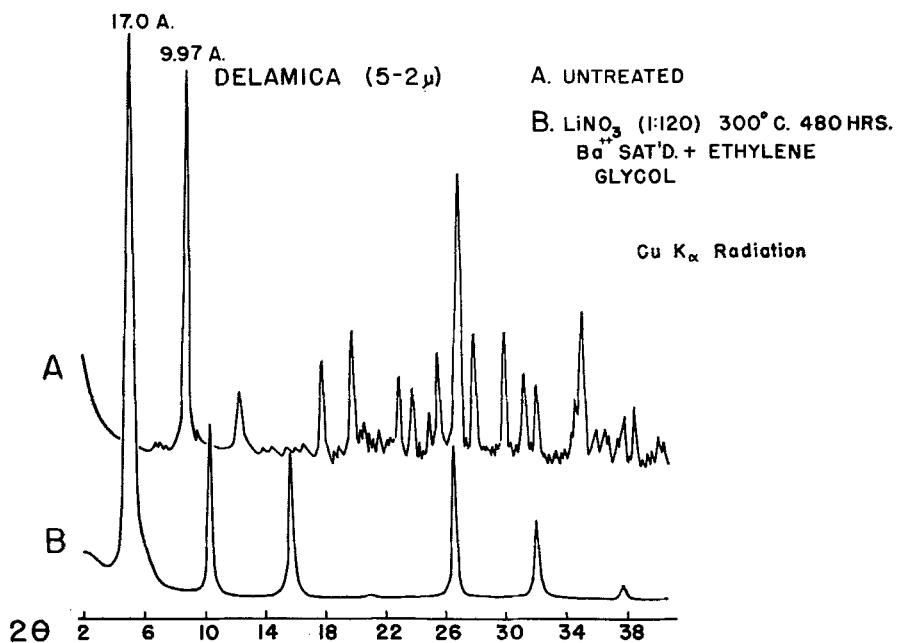

FIGURE 8. — X-ray diffraction patterns of Delamica (5 to 2 μ): (A) Powder specimen of untreated Delamica; (B) oriented specimen after treatment with $LiNO_3$.
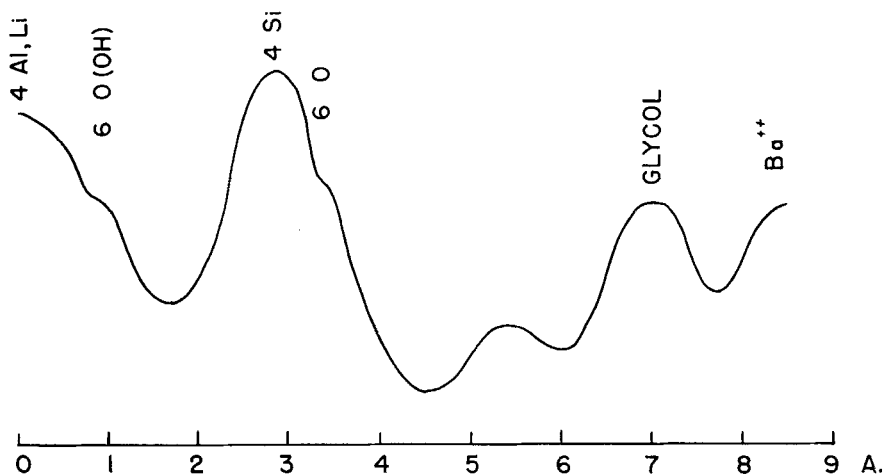
DELAMICA (5-2μ) + LiNO₃
Ba⁺⁺, ETHYLENE GLYCOL

FIGURE 9. — Fourier summation of 00*l* reflections of Delamica (5 to 2 μ) treated with LiNO₃; specimen saturated with barium and solvated with ethylene glycol.
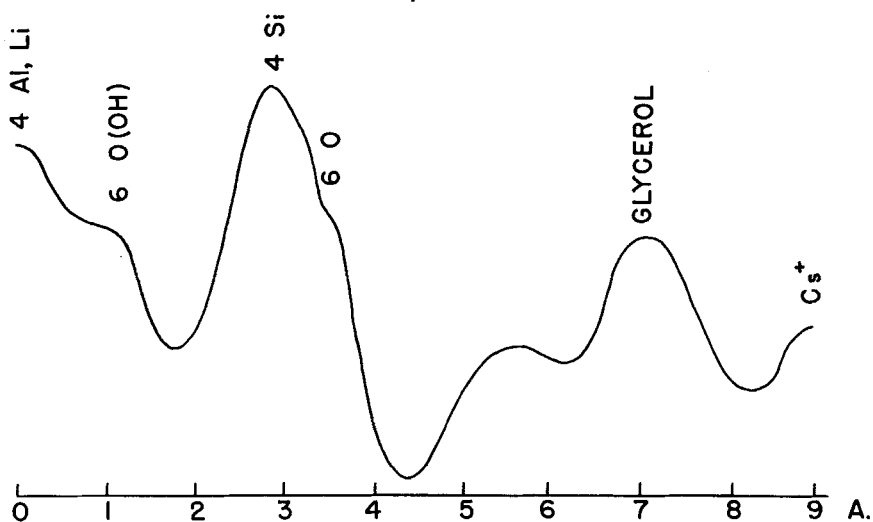
DELAMICA (5-2μ) + LiNO₃
Cs⁺, GLYCEROL

FIGURE 10. — Fourier summation of 00*l* reflections of Delamica (5 to 2 μ) treated with LiNO₃; specimen saturated with cesium and solvated with glycerol.

REFERENCES

Barrer, R. M., 1950, Ion-exchange and ion-sieve processes in crystalline zeolites: J. Chem. Soc., v. 481, p. 2342-2350.

Barshad, Isaac, 1954, Cation exchange in micaceous minerals. II. Replaceability of ammonium and potassium from vermiculite, biotite and montmorillonite: Soil Sci., v. 78, p. 57-76.

Brown, George, 1950, A Fourier investigation of montmorillonite: Clay Minerals Bull., v. 1, p. 109-111.

Brown, George, and Greene-Kelly, R., 1954, X-ray diffraction by a randomly interstratified clay mineral: Acta Cryst., v. 7, p. 101-103.

Edelman, C. H., and Favejee, J. C. L., 1940, On the crystal structure of montmorillonite and halloysite: Z. Krist., v. 102, p. 417-431.

Greene-Kelly, R., 1952a, Irreversible dehydration in montmorillonite: Clay Minerals Bull., v. 1, p. 221-227.

——, 1952b, A test for montmorillonite: Nature, v. 170, p. 1130.

——, 1955, Dehydration of the montmorillonite minerals: Min. Mag., v. 30, p. 604-615.

Grim, R. E., Bradley, W. F., and Brown, George, 1951, The mica clay minerals: in X-ray identification and crystal structures of clay minerals, Mineralogical Society, London, p. 138-172.

Hendricks, S. B., 1942, Crystal structure of clay minerals and some properties of clays: J. Geol., v. 50, p. 276-290.

Hofmann, U., Endell, K., and Wilm, D., 1933, Kristallstruktur und Quellung von Montmorillonit: Z. Krist., v. 86, p. 340-348.

Hofmann, U., and Klemen R., 1950, Verlust der Austäuschfahigkeit von Lithiumionen an Bentonit durch Erhitzung: Z. anorg. Chem., v. 262, p. 95-99.

Mackenzie, R. C., 1952, A micro method for determination of cation-exchange capacity of clay: Clay Minerals Bull., v. 1, p. 203-205.

Maegdefrau, E., and Hofmann, U., 1937, Die Kristallstruktur des Montmorillonits: Z. Krist., v. 98. p. 299-323.

Marshall, C. E., 1935, Layer lattices and base-exchange clays: Z. Krist., v. 91, p. 433-449.

Thilo, E., 1933, Chemische Untersuchungen von Silikaten. I und II: Z. anorg. Chem., v. 212, p. 369-384.

Van Artsdalen, E. R., and Yaffe, I. S., 1955, Electrical conductance and density of molten salt systems: KCl-LiCl, KCl-NaCl and KCl-KI: J. Phys. Chem., v. 59, p. 118-127.

Wear, J. I., and White, J. L., 1951, Potassium fixation in clay minerals as related to crystal structure: Soil Sci., v. 71, p. 1-14.

White, J. L., 1954, Reactions of molten salts with layer-lattice silicates: Nature, v. 174, p. 799.

Winkler, H. G. F., 1954, Struktur und Polymorphie des Eukryptits (Tief-LiAlSiO$_4$) (Betrachtungen zur Polymorphie II.) : Heidelberger Beiträge zur Mineralogie und Petrographie, v. 4, p. 233-242.