

# LAYER CHARGE AND INTERLAMELLAR EXPANSION IN A MUSCOVITE<sup>1</sup>

By

JOE L. WHITE

Purdue University, Lafayette, Indiana

## ABSTRACT

Treatment of a muscovite (Delamica) with molten lithium nitrate produced a lowering of the layer charge on the mica. By gradual reduction of the density of surface charge the dependence of interlamellar expansion on the attainment of a critical value of about  $6.7 \times 10^4$  e.s.u./cm<sup>2</sup> was demonstrated in a straightforward manner.

## INTRODUCTION

Interlamellar expansion of the 2:1-type clay mineral is related to the presence and hydration of interlamellar cations, the magnitude of the layer charge, and the dielectric constant of the medium (Brindley and MacEwan, 1953; Barshad, 1952, 1950; Norrish, 1954). The following tabulation from Brindley and MacEwan (1953) illustrates the relation of swelling properties to layer charge.

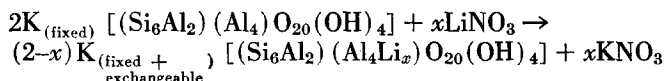
|   | Micas        |  | Vermiculite                 | Montmorillonite<br>Beidellite<br>Nontronite<br>Hectorite | Pyrophyllite<br>Talc |              |
|---|--------------|--|-----------------------------|--|----------------------|--------------|
|   | Margarite    | Muscovite<br>Paragonite<br>Biotite                                     | Hydrous<br>micas<br>Illites |  |                      |              |
| Negative charge on layer, per unit cell | 4            | 2  | 1.2<br>or more              | 1.4-0.9  | 1.0-0.6              | 0            |
| Swelling Properties                     | Nonexpanding | Expanding only with more or less drastic chemical treatment, if at all |                             | Expanding  | Readily Expanding    | Nonexpanding |

Barshad (1954) studied naturally occurring mixtures of vermiculite, biotite, and chlorite and on the basis of the estimated layer charge of the vermiculite constituent concluded that a crystal lattice with an interlayer charge greater than 150 meq/100 g will be contracted. Norrish (1954) has published a significant paper on the swelling of montmorillonite in which he considers the

<sup>1</sup> Journal Paper no. 994, Purdue University Agricultural Experiment Station, Lafayette, Indiana.

effect of surface density of charge as well as charge and hydration energy of cations in crystalline swelling.

In studies of the reaction of molten lithium nitrate with a muscovite, White (1956) found that lithium replaced a large proportion of the interlayer potassium and that lithium ions were fixed in a not readily exchangeable manner. Since the major portion of the fixed lithium could not be removed by washing with 6 *N* sulfuric acid or 2 *N* barium chloride it was concluded that the lithium had entered the lattice. The reaction can be represented by an equation like:



The net effect of this reaction would be to lower the layer charge. This paper reports the observations on the influence of the lowering of the layer charge on interlamellar swelling of the treated muscovite.

## EXPERIMENTAL

The 1.0 to 0.2 $\mu$  fraction of Delamica (a muscovite) was treated with molten lithium nitrate (1:60 ratio) at 300°C for periods of 0.3 to 36 hours. After each reaction period the excess lithium nitrate was removed by washing with distilled water and oriented specimens prepared using the procedure described by Brown (1953). X-ray diffraction photographs were then made of air-dry lithium-saturated flakes. Cu K $\alpha$  radiation was used.

Total potassium, lithium, and cation-exchange capacity were determined as previously reported (White, 1956).

## RESULTS

The postulated mechanism for the replacement of the potassium ion and subsequent migration of the lithium ion into the lattice would predict that the cation-exchange capacity should increase stoichiometrically with the amount of lithium migrating into the lattice. This follows from the assumption that the lithium ion replacing a potassium ion would migrate into the layer immediately above or below. This migration would leave, on the average, one exchange position on the layer opposite the one into which the lithium migrated. Thus, the layer charge on the treated mica can be computed by summation of the total potassium and cation-exchange capacity. This was done for the various reaction times and the results are shown in Figure 1. The layer charge is reduced rapidly until a reaction time of about 6 hours; after this time, there is apparently no further decrease. This may be due to attainment of a critical potassium content in the melt.

Tracings of the 001 and 002 reflections of the lithium-saturated air-dry specimens after the various reaction periods are shown in Figure 2. A small

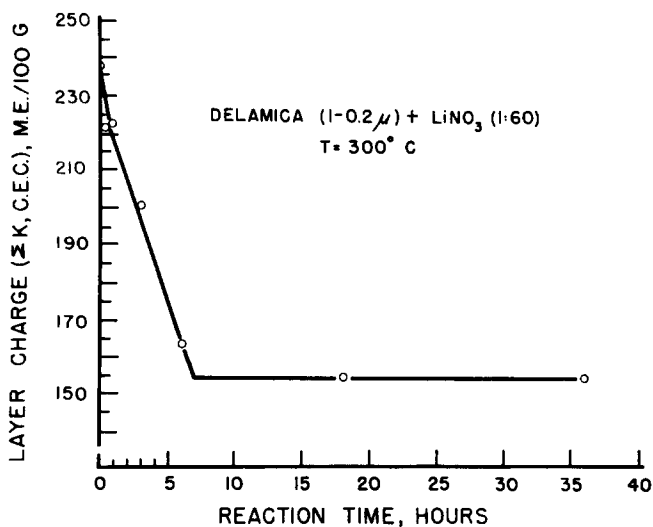


FIGURE 1.—Variation in layer charge ( $\Sigma$  K, C.E.C.) with reaction time in the treatment of Delamica (1-0.2 $\mu$ ) with LiNO<sub>3</sub> (1:60 ratio) at 300°C.

amount of expansion occurred as the layer charge was reduced from 238 meq/100 g to 201 meq/100 g. This expansion is due to the more rapid reaction of the lithium nitrate with the fine fraction of the material used. When the layer charge was further reduced to 163 meq/100 g a major portion of the mica expanded to 11.8A. The layer charge was reduced to a minimum of 155 meq/100 g and all the mica expanded to 11.8A. The 36-hour product contained 51 meq K/100 g and had a cation-exchange capacity of 104 meq/100 g.

The 11.8A reflection appears to have a second order at about 5.9A in the 36-hour curve (Fig. 2), which implies that nearly all layers reacted equally. This implication was confirmed by the glycerol reaction, which showed mostly 17.8A with only the tail toward 14A.

When the lithium-treated specimens were solvated with glycerol the finer particles that reacted rapidly showed expansion to 17.8A. At a reaction time of 3 hours a portion of the expanded layers gave a  $d_{001}$  of 14A. After the 6-hour reaction period virtually all the mica expanded and the diffraction pattern exhibited a very strong maximum at 17.8A with a slight tailing-off on the high-angle side toward 14A.

When flakes of the expanded material were placed in plastic tubes and brought to equilibrium with 0.01 N NaCl, x-ray diffraction patterns showed a  $d_{001}$  of 14.8A. This agrees with the value for sodium-saturated vermiculite given by Barshad (1950) and Walker and Milne (1950).

The average planar surface area for one face of particles of the 1.0-0.2 $\mu$  fraction of the Delamica was determined by measuring with a planimeter the average area of flakes in electron micrographs. This was found to be  $2.62 \times$

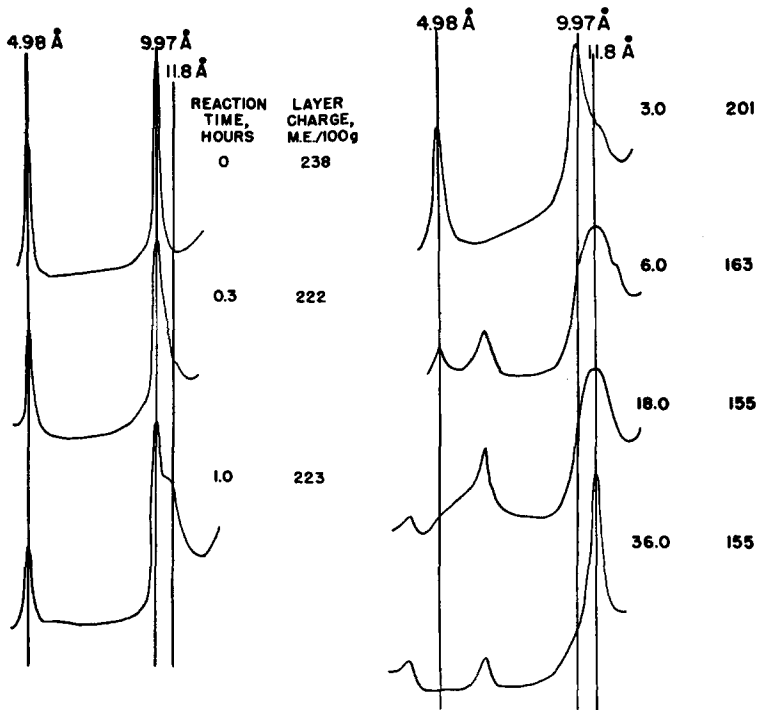


FIGURE 2. — Influence of layer charge ( $\Sigma$  K, C.E.C.) on the 001 and 002 reflections of lithium-saturated, air-dry specimens of Delamica (1–0.2 $\mu$ ).

$10^7 \text{Å}^2$ . The total planar surface area per each 10Å layer would be twice this or  $5.24 \times 10^7 \text{Å}^2$ . The average perimeter of these particles was determined to be  $2.07 \times 10^4 \text{Å}$ . For a plate thickness of 10Å this would give an edge area of  $2.07 \times 10^5 \text{Å}^2$ . The proportion of interlamellar to edge surface area would then be  $5.24 \times 10^7 \text{Å}^2$  to  $2.07 \times 10^5 \text{Å}^2$  or about 253 to 1. Thus no significant error is made in assigning the total charge to interlamellar exchange positions in the computation of surface density of charge for the mica.

The total interlamellar surface area of muscovite can be calculated on the basis of a unit cell having  $a = 5.18 \text{Å}$ ,  $b = 9.02 \text{Å}$  and having the formula



The interlamellar surface area for a unit weight (796 g) is

$$5.18 \times 9.02 \times 10^{-16} \text{ cm}^2 \times 2 \times 6.02 \times 10^{23} = 5.62 \times 10^9 \text{ cm}^2$$

This is equivalent to 707  $\text{m}^2/\text{g}$ .

The surface density of charge for a unit cell of muscovite having the above composition may be computed by multiplying the number of negative charges (two) times the electron charge ( $4.802 \times 10^{-10}$  e.s.u.) and dividing by the surface area per unit cell ( $2 \times 5.18 \times 9.02 \times 10^{-16} \text{ cm}^2$ ). This gives a value of  $1.03 \times 10^5$  e.s.u./ $\text{cm}^2$ .

Now, taking the summation of potassium and cation-exchange capacity of the treated Delamica as the layer charge, the surface density of charge ( $\sigma$ ) was computed for the various reaction periods. The results are shown in Table 1.

Recalling from Figure 2 that virtually all the Delamica expanded at a reaction time of 6 hours, it would appear that the critical value of surface density of charge for interlamellar expansion of the mica is about  $6.7 \times 10^4$  e.s.u./cm<sup>2</sup>. This is in good agreement with the values proposed by Brindley and MacEwan (1953) and Barshad (1954).

Thus, by reducing artificially the surface density of charge of Delamica it has been possible to demonstrate in a straightforward manner the dependence of interlamellar expansion on the attainment of a critical value of about  $6.7 \times 10^4$  e.s.u./cm<sup>2</sup>.

TABLE 1.—SURFACE DENSITY OF CHARGE ( $\sigma$ ) OF DELAMICA (1–0.2 $\mu$ ) AS AFFECTED BY REACTION TIME WITH MOLTEN LiNO<sub>3</sub> (1:60 RATIO) AT 300°C.

| Reaction Time,<br>Hours | $\sigma$ e.s.u./cm <sup>2</sup> |
|-------------------------|---------------------------------|
| 0                       | $9.8 \times 10^4$               |
| 0.3                     | $9.1 \times 10^4$               |
| 1.0                     | $9.1 \times 10^4$               |
| 3.0                     | $8.2 \times 10^4$               |
| 6.0                     | $6.7 \times 10^4$               |
| 18.0                    | $6.3 \times 10^4$               |
| 36.0                    | $6.3 \times 10^4$               |

### ACKNOWLEDGMENTS

Most of the experimental work described in this paper was carried out at Rothamsted Experimental Station, Harpenden, Herts., while the author was a Rockefeller Fellow in the Natural Sciences of the National Research Council. This assistance is gratefully acknowledged. The writer is indebted to George Brown and Dr. D. M. C. MacEwan for advice and generous assistance during the fellowship period.

### REFERENCES

- Barshad, Isaac, 1950, The effect of the interlayer cations on the expansion of the mica type of crystal lattice: *Amer. Min.* v. 35, p. 225–238.
- Barshad, Isaac, 1952, Factors affecting the interlayer expansion of vermiculite and montmorillonite with organic substances: *Soil Sci. Soc. Amer. Proc.*, v. 16, p. 176–182.
- 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.
- Brindley, G. W., and MacEwan, D. M. C., 1953, Structural aspects of the mineralogy of clays and related silicates: *Ceramics, A Symposium*, British Ceramic Society, p. 15–59.
- Brown, George, 1953, A semi-micro method for the preparation of soil clays for x-ray diffraction studies: *J. Soil Sci.*, v. 4, p. 229–232.

- Norrish, K., 1954, The swelling of montmorillonite: Faraday Soc. Discussion 18, p. 120-134.
- Walker, G. F., and Milne, A., 1950, Hydration of vermiculite saturated with various cations: Trans. 4th Intern. Congr. Soil Sci., v. 2, p. 62-67.
- White, Joe L., 1956, Reactions of molten salts with layer-lattice silicates: in Clays and Clay Minerals, Nat. Acad. Sci.—Nat. Res. Council pub. 456, p. 133-146.