

## Development of Long Basal Spacings in Chlorites by Thermal Treatment

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### Abstract

Alterations of micas, vermiculite, and smectites, mainly montmorillonite, have provided numerous examples of the development of long spacings, but such spacings have not been developed previously from chlorites by laboratory processes. Magnesian chlorites, both natural and synthetic materials, are shown to develop long spacings of about 27 Å when the hydroxide interlayers are decomposed (dehydroxylated). A model is developed with a regular alternating sequence of A- and B-type interlayers, and with small displacements of the talc-like layers which gives calculated X-ray (001) intensities in general agreement with the observed peak intensities. Broadened odd-order reflections from the long spacing are thought to indicate "mistakes" in the modified layer sequence, while the even orders, corresponding to the usual 14 Å spacing, show sharp reflections.

### Introduction

Numerous examples are known of layer silicates having basal spacings greater than 20 Å. These long spacings are produced by regular successions of layers of two kinds, generally in a 1:1 ratio. Typical examples are rectorite (allewardite), corrensite, tosudite, and tarasovite. The component layers are usually similar to those in micas, smectites, vermiculite, chlorite; *i.e.*, they are 2:1 type layers with various interlayer arrangements. Many laboratory experiments have been made to develop similar long-spacing structures from micas, smectites, and vermiculites, but to the writers' knowledge no chlorites, although they are also 2:1 type layer silicates, have been so modified experimentally until now.

The development of a long-spacing modification of vermiculite was described by Walker (1956) who found during the final stages of dehydration of vermiculite a 20.6 Å phase consisting of an alternating sequence of 11.6 and 9.0 Å components. Evidently the residual water in this structure preferred to occupy every second interlayer rather than to be randomly distributed over all interlayers. Bassett (1959) described the progressive replacement of K<sup>+</sup> ions in biotite by hydrated Mg<sup>2+</sup> or Ca<sup>2+</sup> ions to form vermiculite, with hydrobiotite developing as an intermediate phase with alternating K<sup>+</sup> and hydrated R<sup>2+</sup> interlayers. Sawhney (1967, 1972) obtained similar results when a Ca-vermiculite was exchanged pro-

gressively with K<sup>+</sup> or Cs<sup>+</sup> ions; long spacings were developed with Ca<sup>2+</sup> and K<sup>+</sup> (or Cs<sup>+</sup>) ions in alternate layers.

Many authors have discussed the influence of OH dipole orientation on the stability of interlayer cations in mica structures. Bassett (1960), following the earlier work of Tsuboi (1950) and of Serratosa and Bradley (1958a,b), correlated the stabilities of muscovite, biotite, and phlogopite with OH dipole orientations. The increased chemical stability of biotites when oxidized also may be related to a re-orientation of the internal OH dipoles (Barshad and Kishk, 1968, 1970; Juo and White, 1969), and the tendency of high-iron biotites to form long-spacing structures when oxidized may involve a similar mechanism (Weed and Leonard, 1968; Farmer and Wilson, 1970). Norrish (1972) has described a mechanism by which changes in one interlayer may influence adjacent interlayers through changes in OH dipole orientation within the 2:1 layers. Thus a considerable body of opinion, supported by many experiments, has developed around the idea that a long-range influence can be transmitted through the 2:1 layer structure by the OH dipoles.

An alternative view, put forward by Sudo, Hayashi, and Shimoda (1962), is that structures containing alternating layers are influenced by a polarity of layer charge distribution in the 2:1 silicate layers. Long basal spacings in micas have been developed

by Sudo and his colleagues using various techniques, including acid treatment of preheated mica (Tomita and Sudo, 1968), treatment of sericite with molten lithium nitrate, either alone or with NaCl present (Tomita and Sudo, 1971), and sericite dehydroxylated at 800°C and treated with sodium tetraphenylboron to remove potassium (Tomita and Dozono, 1972). If the initial layer structure has features which alternate from layer to layer, then the alternation may become more evident after appropriate treatments. This kind of explanation moves the basic question one step further back, namely: how the mineral itself initially acquired alternating structural or compositional features.

Lippmann and Johns (1969) advanced an argument which seemed to support Sudo's point of view. From cation exchange data obtained by Brown and Weir (1963; 1965) to determine the partition of alkali ions between interlayer exchangeable and non-exchangeable sites in rectorite, Lippmann and Johns considered that the tetrahedral sheets adjacent to the exchangeable cations carried a smaller net negative charge than the tetrahedral sheets adjacent to the non-exchangeable cations. The consequence is that each 2:1 silicate layer has a high-charge and a low-charge surface. They go on to say: "The same sort of polarity must characterize also the so-called chlorite and expandable units in corrensite and tosudite," as mentioned also by Frank-Kamenetski, Logrinenko, and Drits (1965).

A different view put forward by Brindley and Sandalaki (1963) invoked a redistribution of cations between exchangeable and non-exchangeable sites, with Na<sup>+</sup> and H<sup>+</sup> (or H<sub>3</sub>O<sup>+</sup>) as exchangeable ions and K<sup>+</sup> and Ca<sup>2+</sup> as non-exchangeable ions. This suggestion was based on earlier work of Mering and Glaeser (1954) on the de-mixing of cations in montmorillonite. Similar experiments with hectorite have been made by Glaeser (1958).

The development of long spacing regularities in chlorites provides yet another example which can be considered in relation to these various hypotheses.

### Experimental Materials and Results

#### Materials

A number of different chlorites have been studied, but most observations have been made using a recently discovered, almost pure, micro-crystalline magnesian chlorite from Omeo, Victoria, Australia, a brief description of which has been given by Segnit

and Holland (1971). A sample of this material, kindly provided by Dr. W. F. Cole, was almost pure white in color and showed only a minor amount of a dark colored impurity which we still have not identified with certainty. A sample crushed to pass a 200 mesh sieve contained very little of the dark impurity, and a complete separation of the chlorite from the heavier impurity was achieved by flotation in bromoform-acetone mixtures.

#### Chemical Analysis and Structural Formula of Omeo Chlorite

Table 1 records a chemical analysis by atomic absorption of the purified material dried at 110°C (Dr. N. Suhr, analyst). The H<sub>2</sub>O+ content was taken as the weight loss of a sample dried at 110°C and then heated overnight at 1000°C. The analysis differs appreciably from that reported by Segnit and Holland. Table 1 gives the structural formula derived on the basis of 18 oxygen ions per formula unit; on this basis the hydrogen content is 7.98 H, essentially in perfect agreement with the ideal anion ratio O<sub>10</sub>(OH)<sub>8</sub>. Iron, measured as Fe<sub>2</sub>O<sub>3</sub>, is practically absent; this is consistent with the fired material remaining almost colorless. The formula lies in or

TABLE 1. Chemical Composition\* and Structural Formula\*\* of a Chlorite from Omeo, Victoria, Australia

	Weight per cent	Atomic proportions	
SiO <sub>2</sub>	28.9	Si 2.66	
TiO <sub>2</sub>	0.10	Ti 0.00	4.00
		Al 1.33 <sub>5</sub>	
Al <sub>2</sub> O <sub>3</sub>	25.6	Al 1.44	
Fe <sub>2</sub> O <sub>3</sub>	0.16	Fe 0.01 <sub>5</sub>	5.94
MgO	32.7	Mg 4.48 <sub>5</sub>	
MnO	0.00	--	
CaO	0.00	--	
Na <sub>2</sub> O	0.00	--	
K <sub>2</sub> O	0.00	--	
H <sub>2</sub> O+***	13.0	O 10.02	
		OH 7.98	
Total	100.46		

\*Atomic absorption analyses by Dr. Norman Suhr, Mineral Constitution Laboratories, Pennsylvania State University.

\*\*Normalized with respect to total oxygen = 18.

\*\*\*Weight loss from 110°C-1000°C.

near the clinocllore range and the octahedral cations total 5.94.

#### *X-ray Powder Diffraction Data for Omeo Chlorite*

Random powder samples gave a type IIb (Bailey and Brown, 1962) X-ray pattern. Basal reflections up to 00,12 gave  $d(001) = 14.15 \pm 0.02$  Å after calibration of the diffractometer with respect to the quartz pattern of Swanson, Fuyat, and Ugrinic (1954). The  $b$ -parameter, taken as  $6d(060)$ , was found to be  $9.19 \pm 0.01$  Å. It is of interest to compare the X-ray data and the chemical composition with the determinative relations given by Brindley (1961) and by Bailey (1972). If  $x$  = number of Al atoms in four tetrahedral sites, then

$$d(001) = 14.55 - 0.29x \text{ (Brindley, 1961)} \quad (1)$$

or

$$d(001) = 14.648 - 0.378x \text{ (Kepezhinskas, 1965; Bailey, 1972)} \quad (2)$$

With  $d(001) = 14.15$ ,  $x = 1.38$  (Eq. 1) and 1.32 (Eq. 2); chemical analysis gives  $x = 1.34$ . The agreements are excellent. Various equations have been given relating  $b$  to the number of Fe ions in octahedral positions; for zero octahedral Fe, the  $b$ -parameter is given mainly as 9.20 – 9.21 Å. The observed value of  $9.19 \pm 0.01$  is consistent with a negligible amount of iron in this chlorite.

#### *X-ray and Thermogravimetric Data for Heated Omeo Chlorite*

Samples of about 200 mg were heated in platinum thimbles overnight in air at constant temperatures at intervals of about 50°C. One sample was used for weight determinations and a second sample for X-ray powder diffraction after cooling to room temperature in a desiccator. Figure 1 shows both series of measurements.

Dehydroxylation began at 500°C, and the first stage was complete at 600°C, with a 9.3 percent weight loss which corresponds with the 'water' associated with the hydroxide interlayers ( $3/4$  of maximum weight loss =  $0.75 \times 13.0\% = 9.7\%$ ). Dehydroxylation of the 2:1 talc-like layers took place progressively from about 700° to 950°C, and the total weight loss was 13.0 percent.

The basal spacings, measured at room temperature, increased from 14.15 Å to 14.20 Å on heating to 500°C, then diminished sharply to about 14.05 Å with the first stage of dehydroxylation. Marked

changes in basal intensities were observed at this stage of reaction as described earlier by Brindley and Ali (1950), and additional reflections from a long spacing of about  $2 \times 14.0$  Å also were observed. The limitations of powder photography ruled out the clear observation of a 28 Å reflection in the earlier work, but reexamination of old photographs showed that it was probably present just at the cut-off angle. The long-spacing phase persisted without further change through the temperature range 550–725°C.

Above 725°C, the basal reflections diminished rapidly in intensity and at 800°C forsterite reflections were observed. Heating above 1000°C gave a strong forsterite pattern and the spacing of the 130 reflection, recorded at  $0.5^\circ (2\theta)/\text{min}$ , 2.767 Å, agreed closely with that of the magnesian end member of the olivine series,  $d = 2.7659$  Å, as given by Yoder and Sahama (1957). Reflections from a spinel phase, which presumably accommodates the Al ions, were also observed.

#### *The long-spacing phase*

This phase is developed at the first stage of dehydroxylation of the chlorite. It evidently is a modification of the normal chlorite structure, since the 14

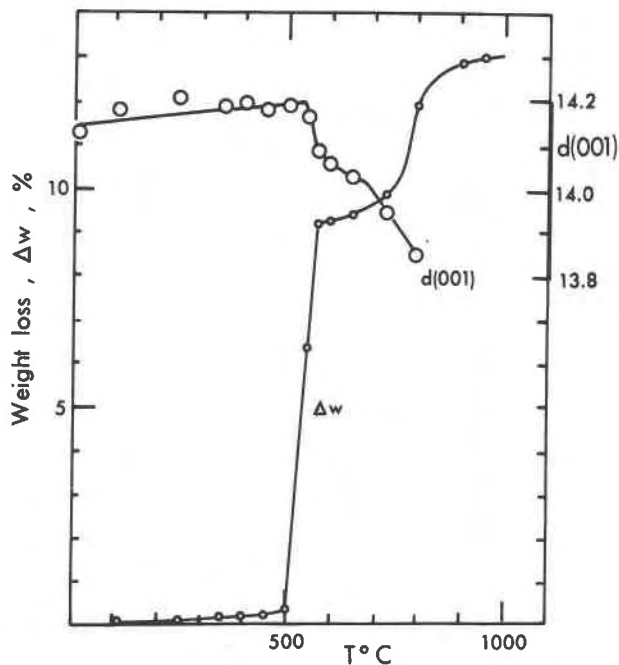


FIG. 1. Weight loss,  $\Delta w$ , and basal spacing  $d(001)$  in Å of Omeo chlorite heated overnight at successively higher temperatures.

A basal reflection and its higher orders persist though their intensities are changed, as Brindley and Ali (1950) have discussed previously. Figure 2 shows a diffractometer pattern (A) obtained with filtered  $\text{CuK}\alpha$  radiation, a  $1/4^\circ$  slit system, a specimen holder 4.5 cm long and a recording rate  $1^\circ(2\theta)/\text{min}$ . Pattern (B) was obtained by changing to a  $1^\circ$  slit system at  $2\theta = 16^\circ$ . All measurements have been made on more slowly recorded patterns ( $0.5^\circ(2\theta)/\text{min}$ ).

The first observed reflection corresponds to a spacing of about 27 Å. This reflection and its odd orders are appreciably broader than the 14 Å reflection and its higher orders. The long spacing is not exactly  $2 \times 14$  Å, but the precise value is difficult to obtain. Correction for the combined Lorentz-polarization factor leads to a smaller spacing of about 26 Å, but a further correction for diffractometer errors at small angles brings the spacing up to near 27 Å. The latter correction has been made using the extended series of basal reflections from long-chain normal primary alcohols,  $\text{C}_{14}$ ,  $\text{C}_{16}$ ,  $\text{C}_{18}$ , and  $\text{C}_{20}$ . The breadth of the long spacing reflection and the fact that it is not an exact multiple of 14 Å suggests that it may arise from an imperfect alternation of two kinds of layers of somewhat different thickness.

#### Formation of long spacings from other chlorites

To check whether the formation of a long spacing is a general property of chlorites, the following were examined after heating in the temperature range  $500^\circ\text{--}750^\circ\text{C}$ .

(i) A chlorite from the Sierra Talc and Clay Company supplied by Dr. J. A. Pask, and described by Pask and Warner (1954, Sample A) and Brindley and Gillery (1956). The chemical formula on the basis of 18 anions is



(ii) A penninite from Rimfischwänge, Zermatt, Switzerland, supplied by Dr. R. C. Mackenzie, chemical analysis not available.

(iii) A sheridanite from St. Coloman, Savoy, supplied by Mlle. S. Caillère from the Museum d'histoire Naturelle, Paris (No. 124, 257). Specimens (ii) and (iii) were used by Brindley and Ali (1950).

(iv) A ripidolite from Flagstaff Hill, El Dorado County, California, donated by Dr. J. L. Post (See Post and Plummer, 1972). The formula of a ripido-

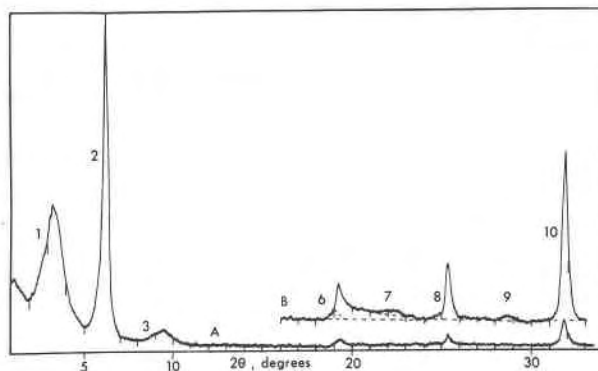
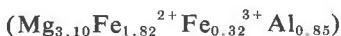


FIG. 2. Diffractometer traces of Omeo chlorite after heating to  $650^\circ\text{C}$ , filtered  $\text{CuK}\alpha$  radiation. Trace (A) recorded with  $1/4^\circ$  slit system and scanning speed  $1^\circ(2\theta)/\text{min}$ . Trace (B) recorded with  $1^\circ$  slit system. Numbers at peaks indicate value of  $l$  in  $00l$ .

lite from the same area is given as:



on the basis of a total anion valence of 28; on this basis  $\text{O} + \text{OH} = 17.14$ .

(v) A corundophilite, donated by Dr. F. A. Bannister, from the British Museum, sample No. 40261.

(vi) and (vii) Two synthetic chlorites, donated by Dr. H. Shirozu and described by Shirozu and Momoi (1972). They contained respectively  $(\text{Si}_3\text{Al})$  and  $(\text{Si}_{2.5}\text{Al}_{1.5})$  in tetrahedral positions and were prepared at  $630^\circ\text{C}$  and 30,000 or 35,000 psi water vapor pressure.

(viii) A synthetic chlorite with theoretical composition  $(\text{Mg}_5\text{Al})(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$ , prepared at  $660^\circ\text{C}$ , 30,000 psi, for 12 weeks, by Dr. D. M. Roy.

The development of a spacing of about 27 Å was observed with all these chlorites and most of them showed a weak third order. A second order is not distinguishable from the normal first order reflection at 14 Å, which has increased intensity after dehydroxylation. If the 27 Å reflection from the Omeo chlorite is described as having medium intensity, then sample (viii) also gave medium intensity, whereas samples (i), (ii), and (iii) gave medium-weak intensity, and samples (iv), (v), (vi), and (vii) gave weak intensity. In all cases, the 27 Å reflection and its third order were broader than the 14 Å reflection.

All eight chlorite samples were of the structural variety IIb as described by Bailey and Brown (1962). Additionally a number of samples of types Ia and Ib were generously provided by Dr. J. B. Hayes (see

Hayes, 1970). These were all iron-rich samples and with the available X-radiations gave rather poor diffraction patterns. After heat-treatment, these samples did not give observable long spacings.

### Discussion

The results show that a long spacing of about 27 Å develops in the (001) planes of magnesian chlorites when the hydroxide interlayers are dehydroxylated. The regularity of this spacing seems to be somewhat variable from one chlorite to another as shown by the variable intensities and broadened reflections. Any simple model, such as will be suggested below, will be an idealized model.

The occurrence of a long spacing suggests that dehydroxylation in one interlayer influences the process in adjacent interlayers so that an -A-B-A-B-A-type alternation is created. To develop a model for this alternation, one can begin with the conclusions established by Brindley and Ali (1950) by a one-dimensional Fourier synthesis, namely: (i) The talc-like layers remain unchanged in composition and structure. (ii) The two (OH) planes and one Mg, Al, . . . plane comprising the hydroxide interlayers transform into two diffuse levels of electron density

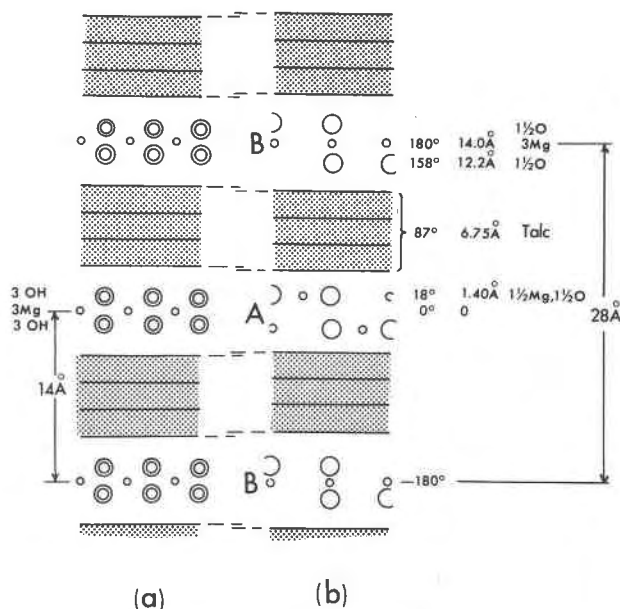


FIG. 3. Schematic diagram to illustrate the proposed modification of the initial chlorite structure (a), when the modulated structure (b) is formed by dehydroxylation of the hydroxide interlayers.

Shaded areas represent the talc-like layers considered to be the same in (a) and (b). Double circles represent (OH) ions; large single circles, O ions; and small circles, Mg ions.

with the cations moving partly or mainly away from their original central positions.

We now suppose that the hydroxide interlayers, following their dehydroxylation, become oxide interlayers of either the type designated A in Figure 3b—that is, the cations move, more or less, into the same levels as the oxide ions—or the type designated B wherein the cations maintain their pre-hydroxylation levels. The A-type oxide interlayers will thus exhibit a greater electrostatic attraction for the talc-like layers, which are negatively charged because of Al for Si replacement, than will the B-type interlayers. The interaction from A-type to B-type interlayers may be a direct electrostatic effect, or may be transmitted by the action of the OH dipoles as discussed earlier. At the present stage, it is premature to consider such details.

Figure 3 presents an idealized picture of the suggested A- and B-type interlayers, with the talc-like layers drawn towards the A-type interlayers. Certain general remarks can be made in defense of this model. In the first place, it agrees with the 001 synthesis based on a 14 Å spacing, in that oxygen ions are left in two planes between the talc-like layers, and half the cations are moved away from their central positions. In the second place, it is necessary to maintain a sequence of spacings near 14 Å as shown by the data in Figure 1.

The breadth of the 27 Å reflection suggests that the A, B alternation is imperfect, such as



with about equal numbers of A and B, but with many mistakes. The frequency of the mistakes may be related to the weak interactions between interlayers. Such a succession is equivalent to small domains exhibiting a long spacing and giving broad reflections, and a longer sequence corresponding to the usual spacing and giving relatively sharp reflections but with reduced intensities because of the small displacements of the talc-like layers.

Reflected intensities have been calculated on the basis of the idealized model shown in Figure 3, using atomic scattering factors from the *International Tables for X-ray Crystallography*, Vol. 2, with a temperature factor  $B = 1.0$ , together with the structure factors for a talc layer given by Cole and Lancucki (1966), also with a temperature factor of  $B = 1.0$  applied, and with

$$I(\text{calc}) = F^2(1 + \cos^2 2\theta)/(\sin \theta \sin^2 \theta).$$

TABLE 2. Observed and Calculated Intensities of Basal Reflections from Omeo Chlorite After Development of a Long Basal Spacing,  $\sim 2 \times 14 \text{ \AA}$

$h$ index	I (peak), obs	I calculated*	
		(1)	(2)
1	21	13.5	23
2	100	100	100
3	4	1.1	1.6
4	--	0	0
5	--	2.2	3.1
6	0.6	1.1	1.0
7	0.4	2.0	2.3
8	2.3	2.3	1.8
9	0.2	0.0	0.3
10	7.0	4.9	4.1

\*Parameters as in Figure 3 but with talc layer at  $87^\circ$  for column (1) and at  $86^\circ$  for column (2).

With the  $z$  coordinates shown in Figure 3b, the calculated intensities given in Table 2 were obtained. Observed peak intensities from patterns recorded at  $0.5^\circ(2\theta)/\text{min}$  also are given. The agreement between observed and calculated values is reasonable, but must be accepted cautiously because of the disorder in the long-range structure. As regards the particular  $z$  parameters shown in Figure 3b, the following statements can be made: (1) The talc-like layers cannot be displaced from the  $z = 90^\circ$  position by more than about  $4^\circ$  at the most. (2) In the A-type interlayers, the Mg, Al . . . ions must lie near the level of the oxygen ions. Further displacement of the cations towards the talc-like layers gives poorer intensity agreement. (3) The possibility that the B-type interlayers are highly disorganized, effectively amorphous, seems unlikely.

The fact that the long spacing periodicity appears to be near 27 Å while the second order reflection is very close to 14 Å is most probably an indication that the modified structure has some degree of random interstratification of the component layers.

### Conclusions

Magnesian chlorites, both natural and synthetic, develop a long-spacing regularity of about  $2 \times 14 \text{ \AA}$  when the hydroxide interlayers are dehydroxylated. A model is developed with two kinds of dehydroxylated interlayers such that the talc-like layers move slightly towards one type of interlayer and away from the other. The sequence is not strictly regular, and mistakes occur, leading to a broadening of odd-order reflections from the long-range spacing and to

the long-range spacing appearing at about 27 Å rather than 28 Å.

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### Postscript

A referee has pointed out the possibility that the modified chlorite may consist of a matrix of B-type layers with a 14 Å spacing, containing laterally-restricted domains of alternating A- and B-type layers. This model, like the one proposed, is consistent with the broadened reflections from the long-spacing component. An inhomogeneous model of this type is not easily excluded; however, it does not readily permit calculation of basal intensities because of the unknown ratio of the matrix to the modified domains. If a long-range interaction causes one type of modified interlayer to influence adjacent interlayers, as suggested in the paper, then a quasi-homogeneous model seems more reasonable. The short-range of . . . ABABA . . . regular ordering can be compared with the order-disorder state developed in annealed copper-gold alloys in which "mistakes" give rise to anti-phase domains and broadened superlattice lines.

### References

- BAILEY, S. W. (1972) Determination of chlorite compositions by x-ray spacings and intensities. *Clays Clay Minerals*, **20**, 381-388.
- , AND B. E. BROWN (1962) Chlorite polytypism: I. Regular and semi-random one-layer structures. *Am. Mineral.* **47**, 819-850.
- BARSHAD, I., AND F. M. KISHK (1968) Oxidation of ferrous iron in vermiculite and biotite alters fixation and replaceability of potassium. *Science*, **162**, 1401-2.
- , AND ——— (1970) Factors affecting potassium fixation and cation exchange capacities of soil vermiculite clays. *Clays Clay Minerals*, **18**, 127-137.
- BASSETT, W. A. (1959) Origin of vermiculite deposit at Libby, Montana. *Am. Mineral.* **44**, 282-299.
- (1960) Role of hydroxyl orientation in mica alteration. *Geol. Soc. Am. Bull.* **71**, 449-456.
- BRINDLEY, G. W. (1961) Chlorite minerals. Chap. VI in *X-ray Identification and Crystal Structures of Clay Min-*

- erals, Ed. G. Brown. London, Mineralogical Society, pp. 242-296.
- , AND S. Z. ALI (1950) X-ray study of thermal transformations in some magnesian chlorite minerals. *Acta Crystallogr.* **3**, 25-30.
- , AND F. H. GILLERY (1956) X-ray identification of chlorite species. *Am. Mineral.* **41**, 169-186.
- , AND Z. SANDALAKI (1963) Structure, composition and genesis of some long-spacing mica-like minerals. *Am. Mineral.* **48**, 138-149.
- BROWN, G., AND A. H. WEIR (1963, 1965) The identity of rectorite and allewardite. *Proc. Int. Clay Conf. Stockholm*, **1**, 27-35; **2**, 87-90.
- COLE, W. F., AND C. J. LANCUCKI (1966) Tabular data of layer structure factors for clay minerals. *Acta Crystallogr.* **21**, 836-838.
- FARMER, V. C., AND M. J. WILSON (1970) Experimental conversion of biotite to hydrobiotite. *Nature*, **226**, 341-2.
- FRANK-KAMENETSKI, V. A., N. V., LOGVINENKO, AND V. A. DRITS (1965) Tosudite, a new mineral forming the mixed-layer phase in alushite. *Proc. Int. Clay Conf., Stockholm*, **2**, 181-186.
- GLAESER, R. (1958) Détection de la démixtion des cations Na,Ca dans une hectorite bi-ionique. *C. R. Acad. Sci., Paris*, **246**, 2909-2912.
- HAYES, J. B. (1970) Polytypism of chlorite in sedimentary rocks. *Clays Clay Minerals*, **18**, 285-306.
- JUO, A. S. R., AND J. L. WHITE (1969) Orientation of the dipole moments of hydroxyl groups in oxidized and unoxidized biotite. *Science*, **165**, 304-5.
- KEPEZHINSKAS, K. B. (1965) Compositions of chlorites as determined from their physical properties: *Dokl. Akad. Nauk S.S.S.R., Earth Sci. Sec.* **164**, 126-129 (English translation).
- LIPPMANN, F., AND W. D. JOHNS (1969) Regular interstratification in rhombohedral carbonates and layer silicates. *Neues Jahrb. Mineral. Monatsh.* 212-221.
- MERING, J., AND R. GLAESER (1954) Sur le rôle de la valence des cations échangeables dans la montmorillonite. *Bull. Soc. franç. Minéral. Cristallogr.* **77**, 519-530.
- NORRISH, K. (1972) Factors in the weathering of mica to vermiculite. *Int. Clay Conf., Madrid* (preprints), **2**, 83-101.
- PASK, J. A., AND M. F. WARNER (1954) Fundamental studies of talc: I. Constitution of talcs. *J. Am. Ceram. Soc.* **37**, 118-128.
- POST, J. L., AND C. C. PLUMMER (1972) The chlorite series of Flagstaff Hill area, California; a preliminary investigation. *Clays Clay Minerals*, **20**, 271-284.
- SAWHNEY, B. L. (1967) Interstratification in vermiculite. *Clays Clay Minerals*, **15**, 75-84.
- (1972) Selective sorption and fixation of cations by clay minerals: A review. *Clays Clay Minerals*, **20**, 93-100.
- SEGNIT, E. R., AND A. E. HOLLAND (1971) Formation of cordierite from clinocllore and kaolinite. *J. Aust. Ceram. Soc.* **7**, 43-46.
- SERRATOSA, J. M., AND W. F. BRADLEY (1958a) Infra-red absorption of OH bonds in micas. *Nature*, **181**, 111.
- , AND ——— (1958b) Determination of the orientation of OH bond axes in layer silicates by infrared absorption. *J. Phys. Chem.* **62**, 1164-1167.
- SHIROZU, H., AND H. MOMOI (1972) Synthetic Mg-chlorite in relation to natural chlorite. *Mineral. J.* **6**, 464-476.
- SUDO, T., H. HAYASHI, AND S. SHIMODA (1962) Mineralogical problems of intermediate clay minerals. *Clays Clay Minerals*, **9**, 378-392.
- SWANSON, H. E., R. K. FUYAT, AND G. M. UGRINIC (1954) Standard X-ray Powder Patterns. *Nat. Bur. Stand. Circ.* **539**, **3**, p. 25.
- TOMITA, K., AND M. DOZONO (1972) Formation of an interstratified mineral by extraction of potassium from mica with sodium tetraphenylboron. *Clays Clay Minerals*, **20**, 225-231.
- , AND T. SUDO (1968) Interstratified structure formed from preheated mica by acid treatments. *Nature*, **217**, 1043-4.
- , AND ——— (1971) Transformation of sericite into an interstratified mineral. *Clays Clay Minerals*, **19**, 263-270.
- TSUBOI, M. (1950) Positions of the hydrogen atoms in the crystal structure of muscovite as revealed by the infra-red absorption study. *Bull. Chem. Soc. Japan*, **23**, 83-88.
- WALKER, G. F. (1956) Mechanism of dehydration of Mg-vermiculite. *Clays Clay Minerals*, **4**, 101-115.
- WEED, S. B., AND R. A. LEONARD (1968) Effect of K<sup>+</sup>-uptake by K<sup>+</sup>-depleted micas on the basal spacing. *Soil Sci. Soc. Am. Proc.* **32**, 335-340.
- YODER, H. S., AND TH. G. SAHAMA (1957) Olivine X-ray determinative curve. *Am. Mineral.* **42**, 475-591.

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