

## Cation Ordering and Pseudosymmetry in Layer Silicates<sup>1</sup>

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### Abstract

The particular sequence of sheets and layers present in the structure of a layer silicate creates an ideal symmetry that is usually based on the assumptions of trioctahedral compositions, no significant distortion, and no cation ordering. Ordering of tetrahedral cations, as judged by mean T-O bond lengths, has been found within the constraints of the ideal space group for specimens of muscovite-3T, phengite-2M<sub>2</sub>, 1a-4 Cr-chlorite, and vermiculite of the 2-layer *s* type. Many ideal space groups do not allow ordering of tetrahedral cations because all tetrahedra must be equivalent by symmetry. This includes the common 1M micas and chlorites. Ordering of tetrahedral cations within subgroup symmetries has not been sought very often, but has been reported for anandite-2Or, 11b-2 prochlorite, and 1a-2 donbassite.

Ordering of octahedral cations within the ideal space groups is more common and has been found for muscovite-3T, lepidolite-2M<sub>2</sub>, clintonite-1M, fluoropolythionite-1M, 1a-4 Cr-chlorite, 1b-odd ripidolite, and vermiculite. Ordering in subgroup symmetries has been reported for anandite-2Or, 11b-2 prochlorite, and 11b-4 corundophilite. Ordering in local out-of-step domains has been documented by study of diffuse non-Bragg scattering for the octahedral cations in polythionite according to a two-dimensional pattern and for the interlayer cations in vermiculite over a three-cell superlattice. All dioctahedral layer silicates have ordered vacant octahedral sites, and the locations of the vacancies change the symmetry from that of the ideal space group in kaolinite, dickite, nacrite, and 1a-2 donbassite.

Four new structural determinations are reported for margarite-2M<sub>1</sub>, amesite-2H<sub>2</sub>, cronstedtite-2H<sub>2</sub>, and a two-layer cookeite. Mean bond lengths indicate ordering of tetrahedral cations in all four minerals and ordering of octahedral cations in amesite and cookeite. Lower subgroup symmetries were found for margarite-2M<sub>1</sub> and amesite-2H<sub>2</sub>. The conclusion is reached that if a structure determination results in a disordered cation distribution on the assumption of an ideal space group, then evidence for a domain structure should be sought or the structure should be refined in subgroup symmetry.

### Introduction

When one atom or ion substitutes for another in a crystal structure, it may do so in several different structural ways. It may do so in disordered fashion, *i.e.*, atom *A* substitutes for atom *B* randomly at different but structurally equivalent locations in adjacent unit cells. This is our standard view of substitutional solid solution, in which the average unit cell is considered to contain "half-breed" atoms that are statistically part *A* and part *B*. For favorable ratios of *A* to *B* atoms, and if *A* and *B* are of different sizes or bonding tendencies, the substitution may take the form of a partly or completely regular, ordered distribution of *A* and *B* atoms over the available atomic positions. Ordered structures are of special interest to mineralogists and petrologists because they represent stable structures of low struc-

tural energy that may contain clues to the conditions of crystallization.

Atomic ordering may take place on a strict unit-cell-by-unit-cell basis in a true single crystal. The resultant space group may be the same as that of the disordered crystal or lowered to that of a subgroup. If the subgroup belongs to a different crystal system, the crystal often simulates the higher symmetry of the parent disordered structure, sometimes by twinning, with the result that detection of ordering is made more difficult unless a superlattice is evident. An alternative or concurrent form of ordering is within local out-of-step domains, usually with different directions of ordering patterns in adjacent domains. The ordering patterns within domains may be repetitive on a unit cell scale or may create a superlattice in one or more directions. Ordering within local domains can be studied by means of diffuse non-Bragg spots or streaks that occur between the normal Bragg reflections on monochromatized X-ray patterns or, if the domains repeat on a regular basis, by

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means of non-Bragg satellite reflections. These ordering possibilities are summarized below.

- A. Ordering within an homogeneous single crystal
  1. Space group and unit cell of disordered structure are retained
  2. Symmetry is lowered to that of a subgroup of disordered structure
    - a) Superlattice present
    - b) No superlattice
- B. Ordering within local domains
  1. Unit cell is same as that of disordered structure
  2. Unit cell is superlattice relative to disordered structure
  3. Non-Bragg satellite reflections are present

This paper will review known ordering patterns of tetrahedral, octahedral and interlayer cations within the hydrous layer silicate minerals, with special reference to the results from several previously unpublished structural determinations. Examples of all the ordering possibilities listed in the preceding table exist and have been recognized in these minerals. A major point of this paper will be, therefore, that if a structure determination results in a disordered cation distribution on the assumption of an ideal space group, then evidence for a domain structure should be sought or the structure should be refined in subgroup symmetry. This has not been done in many cases in the literature.

### Ordering Within the Ideal Symmetry

#### *Ideal Space Groups*

The particular sequence of sheets and layers present in a layer silicate structure is said to have an ideal symmetry that is usually based on the assumptions of trioctahedral compositions, no significant distortion, and no cation ordering. Ideal space groups of this sort have been worked out for the simple mica polytypes that are theoretically possible by Smith and Yoder (1956), for chlorites by Bailey and Brown (1962) and Lister and Bailey (1967), for 1:1 layer silicates by Zvyagin (1962) and by Bailey (1963, 1969), and for talc-pyrophyllite by Zvyagin, Mishchenko, and Soboleva (1968). Dioctahedral compositions have been considered for 1:1 layer silicates by Newnham (1961) and Zvyagin (1962) and for chlorites by Drits and Karavan (1969).

Probably the majority of the structural determinations of layer silicates have been made on the assumption that the ideal space group is valid for the natural crystal. Undoubtedly this assumption is cor-

rect in many cases. But it should be realized that this assumption automatically precludes the finding of cation ordering in certain space groups. For example, one-layer monoclinic (1M) micas, some of the one-layer chlorites, and several 1:1 layer minerals have only one independent tetrahedron in the asymmetric unit (Table 1), so that all tetrahedral cations must be equivalent to one another on a statistical basis, *i.e.* disordered, for the ideal symmetry. Octahedral ordering, on the other hand, is possible in the ideal space groups of most layer silicates, only some of the 1:1 layer polytypes being exceptions. Table 2 summarizes those layer silicates in which ordering has been confirmed by use of the ideal space groups.

#### *Micas*

Ordering of tetrahedral cations, as judged by differences in mean *T-O* bond lengths for non-equivalent tetrahedra, has been found within the constraints of the ideal space groups only in muscovite-3*T* and phengite 2*M*<sub>2</sub>. The pattern of ordering, which is the same for all layer silicates discussed here, is regular alternation of *T*(1) and *T*(2) tetrahedra around each 6-fold ring of the sheet (Fig. 1). Although muscovite-2*M*<sub>1</sub> has two independent tetrahedra, all well-refined structures for this mica show relatively small differences in mean *T-O* bond lengths for the two tetrahedra. In contrast to the

TABLE 1. Layer Silicate Polytypes for which Ideal Space Groups Do Not Permit Cation Ordering in the Sites Listed

Tetrahedral	Octahedral	Interlayer
<u>Micas</u>		
1M		1M
2Or		2M <sub>1</sub>
6H	no restrictions	2M <sub>2</sub>
		2Or
		3T
		6H
<u>1-Layer Chlorites</u>		
Ia-2		
Ib-1		
IIa-1	no restrictions	no restrictions
IIb-2		
<u>1:1 Layer Silicates</u>		
1T	1T	
1M	2T	
2Or	2H <sub>1</sub>	
2H <sub>1</sub>	2H <sub>2</sub>	not appropriate
	3R	
	6R	

TABLE 2. Cation Ordering within Ideal Space Groups

Space Group	Mean bond lengths in Å	
	T--O	M--O,OH*
MICAS		
muscovite-3T (Güven & Burnham, 1967)		
$(K_{0.9}Na_{0.06}R_{0.02}^{2+})Al_{1.83}Fe_{0.04}^{3+}Mg_{0.09}Fe_{0.04}^{2+}Ti_{0.01}-$ $(Si_{3.11}Al_{0.89})O_{10}(OH)_{1.98}F_{0.03}$		
P3 <sub>1</sub> 12	1.670, 1.603	1.973, 1.913, □
phengite-2M <sub>2</sub>		
(Zhoukhlistov, Zvyagin, Soboleva, & Fedotov, 1973)		
$\sim(K_{0.68}Na_{0.09})Al_{1.93}(Si_{3.5}Al_{0.5})O_{10.06}(OH)_{1.94}$		
c2/c	1.619, 1.653	1.956x2, □
clintonite-1M (Takéuchi & Sadanaga, 1966)		
Ca <sub>1.1</sub> (Mg <sub>2.18</sub> Al <sub>0.72</sub> )(Si <sub>1.05</sub> Al <sub>2.95</sub> )O <sub>10</sub> (OH) <sub>2</sub>		
c2/m	1.725x2	2.019, 2.050x2
lepidolite-2M <sub>2</sub> (Takeda, Haga & Sadanaga, 1971)		
$(K_{0.87}Na_{0.12}Rb_{0.06}Ca_{0.02})(Li_{1.05}Al_{1.4}R^{2+})-$ $(Si_{3.39}Al_{0.61})O_{10}(OH)_{0.8}F_{1.2}$		
c2/c	1.620, 1.632	2.144, 1.967x2
lepidolite-2M <sub>2</sub> (Sartori, Franzini & Merlino, 1973)		
$(K_{0.88}Na_{0.06}Rb_{0.05}Ca_{0.01})(Li_{1.69}Al_{1.31})-$ $(Si_{3.36}Al_{0.64})O_{10}(OH)_{0.47}F_{1.53}$		
c2/c	1.630, 1.627	2.123, 1.980x2
synthetic fluoro-polyolithionite-1M		
(Takeda & Burnham, 1969)		
K(Li <sub>2</sub> Al)Si <sub>4</sub> O <sub>10</sub> F <sub>2</sub>		
c2/m	1.619x2	2.106, 1.981x2
CHLORITES		
kämmererite Ia-4 (Brown & Bailey, 1963)		
$(Mg_{5.05}Fe_{0.14}^{2+}Cr_{0.75}Al_{0.07})(Si_{3.15}Al_{0.85})O_{18}H_{7.9}$		
c1	1.685, 1.636	2.082, 2.074x2 2.011, 2.068x2

TABLE 2, Continued

c2/m	1.670x2	2.102x3 2.050x3
VERMICULITE		
2-layer s type (Shirozu & Bailey, 1966)		
$(Mg_{2.83}Fe_{0.01}^{3+}Al_{0.15})(Si_{2.86}Al_{1.14})O_{10}(OH)_{2}^{-}$ $Mg_{0.48}K_{0.01}(H_2O)_{4.72}$		
c2/c	1.673, 1.641	2.084, 2.075, 2.088 2.073, □, □

\* For chlorites and vermiculite the first line refers to octahedra in the 2:1 layer, the second line to the interlayer.

order found in phengite-2M<sub>2</sub>, two determinations of the structure of lepidolite-2M<sub>2</sub> show no tetrahedral ordering. As mentioned previously, tetrahedral ordering is impossible in 1M micas of space group C2/m. This includes most of the trioctahedral micas.

Octahedral cation ordering, based either on differences in mean M-O,OH bond lengths or on refinement of octahedral scattering powers, is more common and has been found within the ideal space groups for muscovite-3T, fluoropolyolithionite-1M, clintonite-1M (= xanthophyllite), and two different specimens of lepidolite-2M<sub>2</sub>. Monoclinic micas have two independent types of octahedra; M(1), which lies

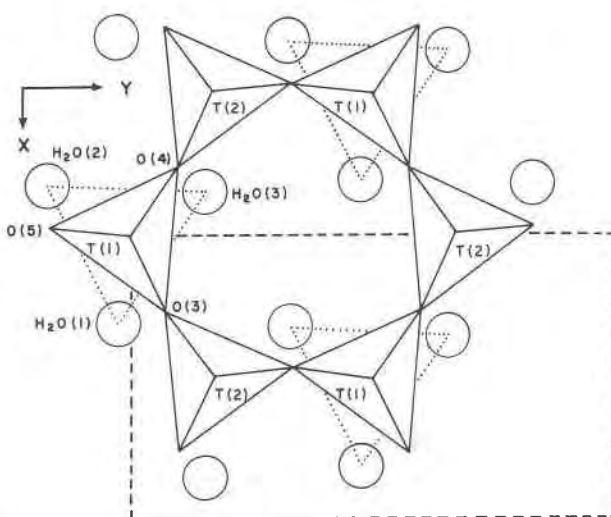


FIG. 1. Ordering pattern in vermiculite from Llano County, Texas. Tetrahedral Al concentrates primarily in T(1) rather than in T(2). Exchangeable Mg<sup>2+</sup> cations concentrate only in interlayer octahedral sites vertically adjacent to T(1) (under dotted triangles) rather than T(2).

ripidolite Ib-odd (Shirozu & Bailey, 1965)

$(Fe_{3.30}^{2+}Mg_{1.32}Mn_{0.05}^{2+}Al_{1.25})(Si_{2.91}Al_{1.09})O_{10}(OH)_8$

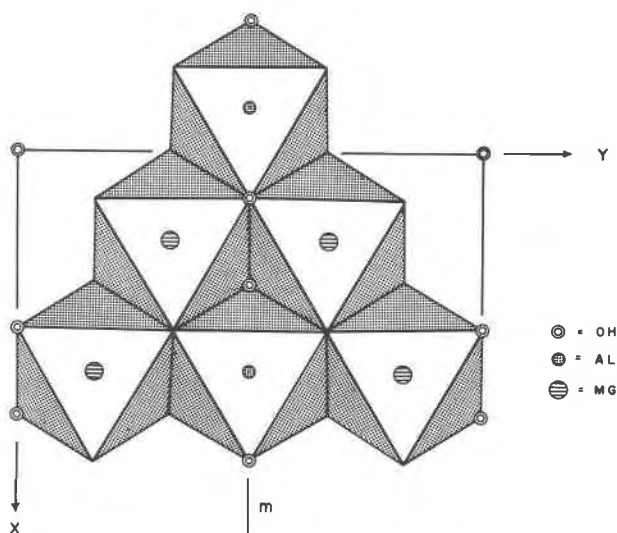


FIG. 2. Octahedral ordering pattern in clintonite-1M. Octahedral Al is concentrated in  $M(1)$  on the mirror plane and Mg in the two  $M(2)$  sites.

on a center of symmetry on the mirror plane for space group  $C2/m$  or on a center of symmetry for  $C2/c$ ; and a pair of equivalent  $M(2)$  octahedra related to each other by these symmetry elements. The two OH groups of each octahedron lie on the symmetry plane of each individual layer, but occupy different octahedral corners in  $M(1)$  and  $M(2)$ . The OH of  $M(1)$  are in the *trans* orientation, whereas those of  $M(2)$  are in the *cis* orientation and form a shared edge between adjacent symmetry-related  $M(2)$  octahedra (Fig. 2). The patterns of octahedral ordering found are primarily with  $M(1)$  larger than  $M(2)$ . The one exception to this rule found to date is clintonite-1M, in which  $M(1)$  is smaller than  $M(2)$ . The relative ratio of large to small octahedra, however, is not always in accord with the ratio of large to small octahedral cations present. For example, in fluoropolyolithionite-1M there are two large octahedral Li ions and one smaller Al ion. Yet the ordering pattern creates one larger octahedral site at  $M(1)$  on the mirror plane and two smaller symmetry-related  $M(2)$  sites. The compositions inferred from refinement of scattering powers in these sites are  $M(1) = \text{Li}_{0.89}\text{Al}_{0.11}$  and  $M(2) = \text{Li}_{0.55}\text{Al}_{0.45} \times 2$ . Similar octahedral ordering patterns were observed in two specimens of lepidolite-2M<sub>2</sub>. But in clintonite-1M the 2:1 ratio of large to small octahedral cations present is mirrored in the structure by the same ratio of large to small octahedra.

Diocahedral layer silicates can be assumed to have ordering of the vacant octahedral site relative to the occupied sites. Lindqvist (1962) has shown that dis-

ordering of the two cations over the three octahedral positions induced by heating at 600°C causes  $d(060)$  to increase to such an extent that the mineral would not be recognizable by this criterion as diocahedral.

In micas the vacant octahedral site always has been found to be located on the mirror plane of each 2:1 layer, *i.e.* at  $M(1)$ . For this reason there is no reduction in symmetry relative to the ideal trioctahedral analogs assumed for the derivation of polytype space groups. This will not be true for some of the kaolin and chlorite structures to be discussed later. Because of the linkage of tetrahedral and octahedral sheets by sharing of apical oxygens, the location of a large octahedron on the symmetry plane of the 2:1 layer means that the stagger between the two tetrahedral sheets within the layer is necessarily greater than the ideal value of  $a/3$ . Observed values of intralayer shift range from  $-0.365a_1$  in phengite-1M (Soboleva and Zvyagin, 1968) to  $+0.386a_{2,3}$  in phengite-2M<sub>1</sub> (Güven, 1971a) for diocahedral species with a vacancy at  $M(1)$  and from  $-0.351a_1$  for fluoropolyolithionite-1M to  $+0.364b_{2,3}$  for lepidolite-2M<sub>2</sub> for ordered trioctahedral species with the larger ion at  $M(1)$ . Clintonite-1M with a smaller ordered octahedral site at  $M(1)$  has a correspondingly reduced intralayer shift of  $-0.321a_1$ . Celadonite-1M does not show the usual diocahedral distortion because the vacant and occupied octahedral sites are nearly identical in size (Zvyagin, 1967).

Deviations of intralayer shift from the ideal value of  $a/3$  may lead to deviations of one to two degrees from the ideal  $\beta$  value. Two factors may tend to mask the effect of intralayer shift on  $\beta$ , however, and thereby diminish the usefulness of the latter as a predictor of octahedral ordering. Firstly, the directions of intralayer shift may not be parallel to the resultant XZ plane, for example as in the 2M<sub>1</sub> and 2M<sub>2</sub> structures. Secondly, adjacent 2:1 layers may be offset, as measured between tetrahedral cations in adjacent 2:1 layers, so that the coordination around the interlayer cation is asymmetric. This layer offset, first noted by Radoslovich (1960), has been found to vary between values of  $+0.035a_1$  in potassian paragonite (Burnham and Radoslovich, 1964) and  $-0.025a_1$  in phengite-1M (Soboleva and Zvyagin, 1968) and may cancel or enhance the effect of intralayer shift deviation.

#### Chlorites

Ordering of tetrahedral cations within the ideal space group has been confirmed for a one-layer Cr-chlorite that has 1a layer-interlayer structural units in

the terminology of Bailey and Brown (1962; Table 2). Chlorites have two octahedral sheets, one within the 2:1 layer and the other comprising the hydroxide interlayer sheet. All chlorites must have ordering of octahedral cations between the two sheets in order to insure a positive charge on the interlayer, and this has been observed in all structural analyses. In addition there may be ordering of cations within each octahedral sheet. The *Ia* structural unit is characterized by positioning certain interlayer octahedral sites vertically between tetrahedral sites in the tetrahedral sheets of the layers above and below. A unique type of local charge balance is found in the *Ia-4* Cr-chlorite, in which all of the  $\text{Cr}^{3+}$  is concentrated in the interlayer in the one octahedron that is between the ordered Al-rich tetrahedra of layers above and below. Thus, the source of positive charge on the interlayer is immediately adjacent to the sources of negative charges on the 2:1 layers.

An orthohexagonal ( $\beta = 90^\circ$ ) ripidolite (or brunsvigite in Foster's 1962 classification) of the *1b* structural type and having semi-random stacking of structural units has been refined by use of only the sharp  $k = 3n$  reflections. This type of analysis, in which the streaked  $k \neq 3n$  reflections are ignored, only gives the details of an average layer of symmetry  $C2/m$  and does not permit determination of any Si, Al ordering that may be present or of any ordering within octahedral sheets. Electron density peak heights indicated that 60 percent of the iron is concentrated in the octahedral sheet of the 2:1 layer. Smaller mean  $M\text{-OH}$  distances in the interlayer suggest that most of the octahedral Al is in the interlayer. This is confirmed by the relative thicknesses of the octahedral sheets in the interlayer and the 2:1 layer (1.98 Å versus 2.18 Å, respectively).

### Vermiculite

The well-known trioctahedral vermiculite from Llano County, Texas, with two planes of water molecules in the interlayer (14.36 Å phase) has been shown to have a two-layer structure of the *s* type, in which there are *L* type intralayer shifts of  $a/3$  parallel to the resultant *XZ* plane, incomplete *Ia* type interlayers of  $\text{Mg}^{2+}$  and  $\text{H}_2\text{O}$  molecules, and shifts of  $\pm b/3$  between adjacent 2:1 layers (Fig. 3). The structure is similar to that of the Cr-chlorite mentioned previously in that the small number of  $\text{Mg}^{2+}$  exchangeable cations present are concentrated in the one interlayer position where they are vertically between partly ordered Al-rich tetrahedra in the layers above and below (Fig. 1). Thus, the ex-

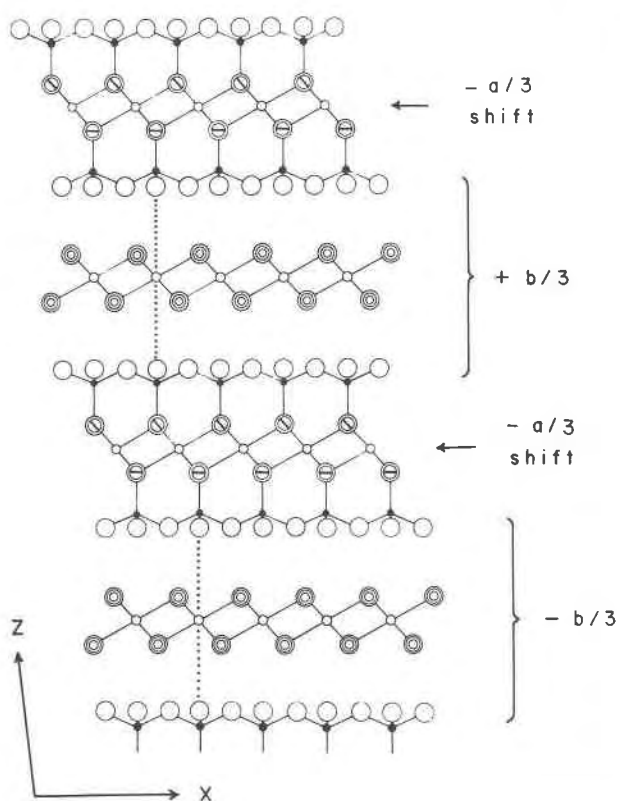


FIG. 3. Layer sequence in *s* type vermiculite from Llano County, Texas. Dots illustrate vertical alignment of exchangeable  $\text{Mg}^{2+}$  cations between Al-rich *T*(1) tetrahedra of 2:1 layers above and below to give local charge balance.

changeable cations are attracted to the loci of negative layer charges. There are only 0.41 atoms of exchangeable cations per formula unit in the specimen analyzed, and it is likely that there is further superlattice ordering on a local domain scale of both tetrahedral and interlayer cations, as discussed later.

### Ordering Within Subgroup Symmetry

#### Micas

Perhaps the most impressive example of the influence of cation ordering in decreasing the ideal space group symmetry to that of a subgroup is in anandite, the rare Ba-Fe brittle mica. Anandite has the  $2Or$  structure in the terminology of Smith and Yoder (1956), in which the intralayer shifts are  $\pm a_1/3$  with alternation of the I and II sets of octahedral positions within adjacent layers. The ideal space group for this structure is  $Ccmm$ , but the symmetry of anandite is lowered by ordering of tetrahedral Si and Fe to  $Pnmm$  (Table 3). A large number of weak reflections are observed that violate the *C*-cell centering. The octahedral cations are predominantly  $\text{Fe}^{2+}$ , but

TABLE 3. Cation Ordering within Subgroups

Space Groups		Mean bond lengths in Å	
Ideal	Actual	T-O	M-O, OH*
MICAS			
anandite-20r (Giuseppetti & Tadini, 1972)			
(Ba <sub>0.87</sub> Mn <sub>0.04</sub> K <sub>0.05</sub> Na <sub>0.04</sub> )(Fe <sub>2.46</sub> <sup>2+</sup> Mg <sub>0.48</sub> Mn <sub>0.06</sub> ) <sup>-</sup>			
(Si <sub>2.64</sub> Fe <sub>0.70</sub> <sup>3+</sup> Fe <sub>0.58</sub> <sup>2+</sup> Al <sub>1.08</sub> )O <sub>10</sub> (OH)(S <sub>0.85</sub> Cl <sub>0.15</sub> )			
C2/m	Pnmm	1.675, 1.766	2.105, 2.250x2, 2.268, 2.096x2
CHLORITES			
prochlorite I1b-2 (Steinfink, 1958a)			
(Mg <sub>2.69</sub> Fe <sub>0.02</sub> <sup>2+</sup> Mn <sub>0.02</sub> Al <sub>1.66</sub> Fe <sub>1.46</sub> <sup>3+</sup> )(Si <sub>2.48</sub> Al <sub>1.52</sub> )O <sub>10</sub> (OH) <sub>8</sub>			
C2/m	C2	1.726, 1.633	2.121, 2.084, 2.035 2.121, 2.101, 1.873
corundophilite I1b-4 (Steinfink, 1958b)			
(Mg <sub>4.69</sub> Fe <sub>0.11</sub> <sup>2+</sup> Ni <sub>0.01</sub> Al <sub>0.67</sub> Fe <sub>0.26</sub> <sup>3+</sup> Cr <sub>0.15</sub> )(Si <sub>3.02</sub> Al <sub>0.98</sub> )O <sub>10</sub> (OH) <sub>8</sub>			
C1	C1	1.677, 1.673, 1.683, 1.677	2.050, 2.052, 2.067 2.047, 2.023, 1.995
donbassite Ia-2 (Aleksandrova, Drits & Sokolova, 1972)			
(Al <sub>4.1</sub> Fe <sub>0.04</sub> <sup>3+</sup> Fe <sub>0.01</sub> <sup>2+</sup> Mg <sub>0.08</sub> Li <sub>0.26</sub> )(Si <sub>3.14</sub> Al <sub>0.86</sub> )O <sub>10</sub> (OH) <sub>8</sub>			
C2/m	C2	1.675, 1.618	1.913, 1.927, □ 1.897, 1.933, 2.180

\*For chlorites the first line refers to octahedra in the 2:1 layer, the second line to the interlayer.

scattering factor refinements and temperature factors suggest the small amount of Mg present is located mainly in one octahedral site. Anandite is unusual also in that one of the OH anion groups has been replaced by (S<sub>0.85</sub>Cl<sub>0.15</sub>), which lies close enough (3.2 Å) to the interlayer Ba to be considered as a 13th coordinating anion.

### Chlorites

One-layer chlorites of the common I1b structural type may be either monoclinic or triclinic. A monoclinic I1b-2 prochlorite (or ferrian sheridanite in Foster's classification) was found to belong to space group C2, rather than the ideal C2/m, as a consequence of tetrahedral and octahedral cation ordering. Based on differences in mean T-O bond lengths, nearly all of the tetrahedral Al present is concentrated in the T(1) tetrahedron. T(1) and T(2) would be equivalent in the ideal space group. From the heights of the electron density peaks and from the mean M-O, OH bond lengths it could be determined also that most of the iron is concentrated in the octahedral sheet within the 2:1 layer and that the octahedral Al is in the interlayer sheet. There is preferential ordering of Mg, Fe, and Al over the six cation sites of the 2:1 octahedral sheet and the interlayer. A triclinic I1b-4 corundophilite (or sheridanite in Foster's classification) was refined in space group C1 instead of the ideal C1. Although no

tetrahedral ordering was found, smaller M-O, OH bond lengths indicate that the octahedral Al is concentrated in the interlayer and that there is preferential ordering of cations over the three octahedral interlayer sites (Table 3). In this case, therefore, the reduction in symmetry is due to octahedral cation ordering in the interlayer.

Chlorites with two dioctahedral sheets are termed donbassites. In such chlorites the octahedral cations are primarily Al and the positive charge on the interlayer sheet arises from the presence of Al cations in excess of 2.0 in that sheet. A one-layer Ia-2 donbassite has been found to be reduced to symmetry C2 from the ideal C2/m. The reduction in symmetry has two causes. Firstly, although the vacant octahedral site in the 2:1 layer lies on the symmetry plane of the layer, the partly vacant octahedral site in the interlayer lies off the projection of the mirror plane (thereby eliminating the mirror for the crystal as a whole). Secondly, mean T-O bond lengths for the two tetrahedra that would be equivalent in the ideal space group are statistically different and indicate that all of the tetrahedral Al is concentrated in one tetrahedron. Local charge balance between the interlayer cations and adjacent loci of negative charge on the 2:1 layers of the sort found in the Ia Cr-chlorite and vermiculite structures is not realized in this Ia donbassite, however, because it is the partly vacant interlayer site that is positioned vertically between ordered Al-rich tetrahedra in the layers above and below.

### 1:1 Layer Silicates

Kaolinite, dickite, and nacrite all have symmetries that differ from those of the ideal space groups as a consequence of the particular locations of the vacant octahedral sites in each mineral. Kaolinite and dickite both are based on the 1M stacking sequence of layers, and would be identical and of space group Cm if they were trioctahedral. In kaolinite the vacant octahedral site is in the same place in each layer, and can be located either at site B or site C of Figure 4. Kaolinite with site B vacant is a mirror image of kaolinite with site C vacant. Location of the vacant site at either B or C imposes triclinic symmetry on the structure due to loss of the mirror plane that normally relates B to C in a trioctahedral structure. Ionic interactions also distort the structure to triclinic geometry as a separate anorthic effect. In dickite the vacant octahedral site alternates between B and C in successive layers to create a two-layer structure. The alternation of vacant sites creates monoclinic glide

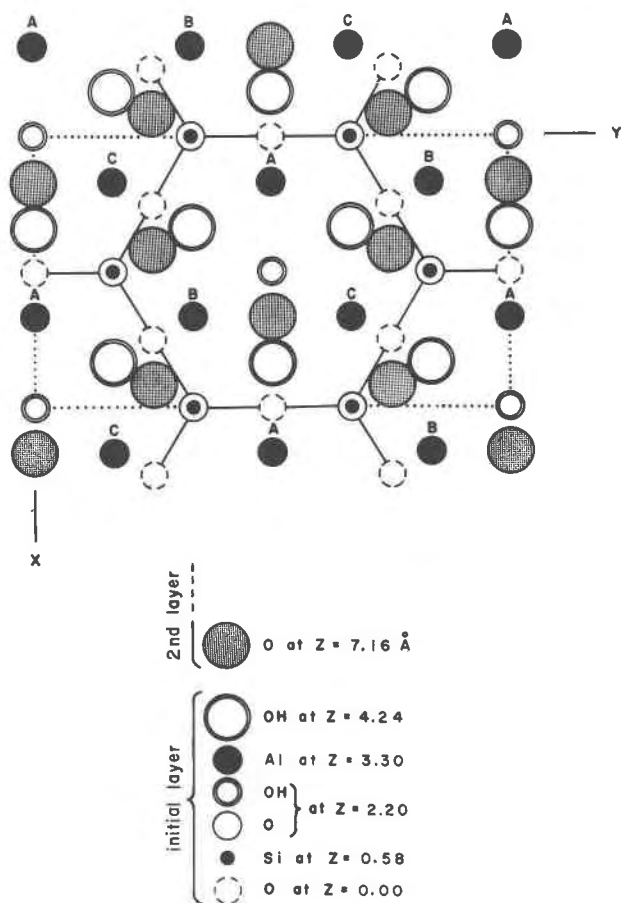


FIG. 4. Ideal structure of 1:1 layer in 1M polytype. Mirror planes parallel to (010) extend through octahedral site A and inner OH of each 6-fold ring.

planes parallel to (010) and balances the stress distribution so that the cell shape remains monoclinic also. Thus, dickite can be considered as a regular alternation of right- and left-handed kaolinite layers, in one sense, or as a superstructure of the ideal 1M polytype due to a particular ordering pattern of octahedral cations and vacancies. Nacrite, on the other hand, is based on an entirely different stacking sequence of layers—that of the ideal trioctahedral 6R structure. The vacant octahedral sites vary regularly in successive layers so that the resultant symmetry is reduced from rhombohedral to monoclinic, and an inclined Z axis can be selected along which there is true two-layer periodicity.

#### Regularly Interstratified Clay Minerals

A few clay minerals are known that show a reasonably regular alternation of 1:1 and 2:1 layers, which can be considered as a different kind of ordering. Examples of clays of this type are kaolin-

smectite interstratifications (Altschuler, Dwornik, and Kramer, 1963; Wiewióra, 1973) and serpentine-chlorite interstratifications (Brindley and Gillery, 1954). The latter specimen actually is a random interstratification, but it is reasonable to expect that regular alternations may be found in the future. Much more common are 2:1 layers with a regular alternation of different sorts of interlayer materials, some of which are listed in Table 4. Although the exact space groups of these clays usually are not known, it is likely that their symmetries are lower than those of the individual 1:1 or 2:1 layers. It is important to note here that one interpretation of the regular alternation of different interlayers in these minerals is that the layer charges differ either on alternate tetrahedral sheets or on alternate 2:1 layers.

#### Cation Ordering Within Local Domains

##### Micas

Despite the apparent lack of long-range tetrahedral cation order in muscovite- $2M_1$ , Gatineau (1964) has reported the presence of an unusual type of short-range order from study of diffuse scattering in the regions between the normal Bragg reflections on single crystal X-ray photographs. The distribution and intensity of these diffuse streaks have been interpreted as due to concentration in local small domains of Al in zigzag chains within the tetrahedral sheet. In a given domain the direction of chain alignment may be along any one of the three pseudohexagonal X axes of the crystal. Chains of pure Al are said to alternate along the Y direction in partly ordered fashion with chains of pure Si. This type of short-range order is unusual in that it grossly violates the principle of avoidance of Al-Al neighbors postulated by Loewenstein (1954) and found to be obeyed in a large number of cases of long-range ordering in aluminosilicates. The interpretation must be viewed with some caution because of the later finding by Kodama, Alcover, Gatineau, and Mering (1971) that in the local domains of other layer silicates the tetrahedral networks are distorted in linear waves characterized by alternating rows of tetrahedra of slightly differing dimensions even in the absence of any tetrahedral substitution (e.g., as in pyrophyllite, talc, and saponite). Further study appears required to sort out the contributions to the diffuse scattering of Si,Al ordering as contrasted to that of the oxygen network distortion. Similar comments apply to the structures of phlogopite and biotite, as Gatineau and Mering (1966) have observed diffuse scattering in these minerals very similar to that in muscovite- $2M_1$ .

TABLE 4. Examples of Regular Interstratifications of 2:1 Layers with Different Interlayer Materials

Component minerals	Ratio of components	Reference
paragonite-smectite = rectorite	1:1	Brown & Weir (1963)
dioctahedral mica-smectite = tarasovite	3:1	Lazarenko & Korolev (1970); Reynolds & Hower (1970)
illite-smectite	1:1	Bonorino (1959); Reynolds & Hower (1970)
biotite-vermiculite = hydrobiotite	variable	Gruner (1934); Bassett (1959)
talc-saponite = aliettite	1:1	Veniale & van der Marel (1969)
trioctahedral chlorite-"swelling chlorite" = corrensite	1:1	Lippmann (1954)
trioctahedral chlorite-saponite	1:1	Veniale & van der Marel (1969)
trioctahedral chlorite-dioctahedral smectite	1:1	Blatter, Roberson & Thompson (1973)
trioctahedral chlorite-vermiculite	1:1	Drits & Kossovskaya (1963)
dioctahedral chlorite-smectite = tosudite	1:1	Frank-Kamenetskii, Logvinenko & Drits (1963)
dioctahedral chlorite-"swelling chlorite"	1:1	Heckroodt & Roering (1965)
vermiculite dehydrate-hydrate	1:1	Walker (1956)
K <sup>+</sup> -vermiculite-Ca <sup>2+</sup> -vermiculite	1:1	Sawhney (1967, 1972)

Gatineau and Mering (1966) also have studied the diffuse X-ray scattering for a lepidolite of unstated structural type. The composition is not given, but by implication is that of polyolithionite. Diffuse spots are observed at positions that are satellitic ( $\pm a^*/3$ ) to the positions of certain of the  $h + k = \text{odd}$  Bragg reflections that are forbidden by  $C$  centering. The spots are interpreted to indicate short-range octahedral ordering of  $1\text{Al} + 2\text{Li}$  in local domains. The ordering takes the form of rows of pure Al and pure Li aligned along one or the other of the three pseudohexagonal  $Y$  axes  $[01]$ ,  $[31]$ , or  $[3\bar{1}]$ , such that each domain is characterized by only one ordering direction. The ordering is two-dimensional in that the Al rows are spaced regularly within a layer at intervals of  $3a/2$  (every third row), but irregularly between layers. The extent of each domain is small, perhaps due to antiphase relations.

#### Vermiculite

The  $14.36 \text{ \AA}$  phase of vermiculite that is stable under atmospheric humidity conditions has an incomplete interlayer sheet, relative to a chlorite interlayer, in that only about  $1/6$  to  $1/10$  of the possible cation sites are occupied by exchangeable cations and only about  $2/3$  of the possible "anion" sites are oc-

cupied by water molecules. The question then arises as to the distribution of exchangeable cations and water molecules over the available sites in adjacent unit cells. The structure determination by Shirozu and Bailey (1966) of Llano vermiculite found that 0.41 atoms of  $\text{Mg}^{2+}$  occupy statistically one of the three available octahedral interlayer sites, and under the relative humidity conditions of the laboratory at the time of investigation that 0.62  $\text{H}_2\text{O}$  statistically occupy each of the six interlayer "anion" sites for a total of 3.72  $\text{H}_2\text{O}$  per formula unit. No long-range ordering of the interlayer cations and  $\text{H}_2\text{O}$  over adjacent unit cells was noted by Shirozu and Bailey in their study.

Mathieson and Walker (1954) suggested a dynamic interlayer system should exist that would allow cation and water migration between the available positions. They further suggested a tendency to maintain a regular, hexagonal distribution of the occupied cation sites over three unit cells as a result of mutual repulsion, with the water clustering around the occupied cation sites as octahedral hydration shells. Bradley and Serratosa (1960) have suggested another modification of the interlamellar region in which a  $C$ -centered superstructure would extend laterally over three unit cells for the lower observed level of ex-



changeable cations and a regular array over one cell for the highest level of exchange. The orderly arrays were not believed to extend throughout the entire crystal. Alcover, Gatineau, and Mering (1973) have confirmed existence of a three-cell superstructure in local domains by study of diffuse reflections present on single crystal X-ray patterns of Kenya vermiculite. The abnormal scattering is concentrated along lines parallel to  $Z^*$  and disappears upon dehydration at  $500^\circ\text{C}$ , so that it must be attributed to the arrangement of the interlayer materials. The interpretation by Alcover *et al* confirms the general outline of the local ordering patterns predicted by Mathieson and Walker and by Bradley and Serratosa in which exchangeable  $\text{Mg}^{2+}$  and associated water molecules are distributed over the lattice points of a large  $C$ -centered cell having dimensions  $3a \times b$ , where  $a$  and  $b$  are the dimensions of the normal vermiculite unit cell. The ordering is two-dimensional in that there is no coupling between successive interlayers. The possible positions for the exchangeable cations in the local supercell are divided into three sets, as shown in Figure 5. Only one set can be occupied in a given domain, but different sets can be occupied in different domains. Full occupancy of one set of possible positions requires  $2 \text{ Mg}^{2+}$  per supercell interlayer, or  $0.33 \text{ Mg}^{2+}$  per formula unit. The precise distribution of the interlayer water molecules over the three cells, which would be required to distinguish between the Mathieson-Walker and Bradley-Serratosa models, was not determined in this study. It is inferred, but not demonstrated, by the authors that local Si,Al ordering accompanies the interlayer  $\text{Mg}^{2+}$  ordering so that the local charge balance is retained. It should be noted in this connection that the amount of *long-range* Si,Al order found in Llano vermiculite by Shirozu and Bailey [*average* composition of tetrahedron  $T(1) = \text{Si}_{0.65}\text{Al}_{0.35}$ ] is almost ideally suited for an additional *short-range* order in which one set of  $T(1)$  positions in each supercell domain (adjacent to the positions occupied by the exchangeable cations) is occupied only by Al and the other two sets of  $T(1)$  only by Si.

### Test Structures

In order to test the concept that ordering may be a more common phenomenon in layer silicates than previously suspected because of the difficulty in detection due to reduced symmetry or domain structure, three minerals were selected as test examples. Margarite, amesite, and cronstedtite were selected because all (1) have favorable tetrahedral ratios near

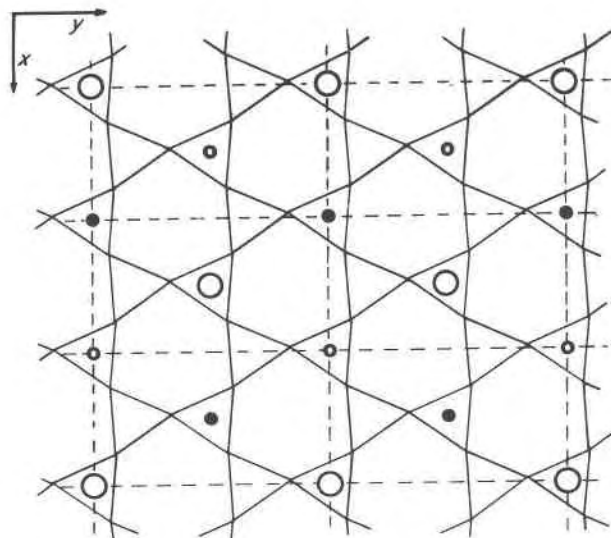


FIG. 5. Distribution of exchangeable  $\text{Mg}^{2+}$  over sites of a  $C$ -centered superlattice ( $3a \times b$ ) in Kenya vermiculite. Interlayer sites occupied by  $\text{Mg}^{2+}$  in the three domain types are indicated by three different symbols. From Alcover *et al* (1973).

1 : 1 of Si to Al or  $\text{Fe}^{3+}$ , (2) have been reported previously as disordered within their ideal space groups, and (3) can be obtained in good crystals. A fourth structure, that of a two-layer cookeite, also was selected because the ideal space group imposes very few constraints on ordering.

Although refinement of two of these structures has not been completed, the residual values ranging from  $R = 7.5$  to 10.9 percent with isotropic  $B$  values suggest the structural details are essentially correct. The results indicate that ordering of tetrahedral cations exists in all four minerals. Evidence for domain structure has not been investigated, but non-Bragg satellites were observed in cronstedtite. More detailed results will be presented in later publications, but are summarized below and also in Table 5.

### Margarite

Takéuchi (1965) found the brittle mica margarite- $2M_1$  from Chester, Massachusetts,  $[(\text{Ca}_{0.87}\text{Na}_{0.13})\text{Al}_2(\text{Si}_2\text{Al}_2)\text{O}_{10}(\text{OH})_2]$  to be disordered with respect to tetrahedral cations within its ideal space group  $C2/c$ , despite the favorable 1 : 1 ratio of tetrahedral cation species. Since then, Gatineau and Mering (1966) from the absence of diffuse X-ray scattering and Farmer and Velde (1973) from the sharp infrared spectra and the absence of Al-O-Al vibrations have suggested that margarite should be ordered.

Margarite- $2M_1$  from Chester County, Pennsylvania, was selected to test the possibility of ordering in a lower symmetry. As a first step, refinement

TABLE 5. Results of Test Structures

Mineral	Reflections used	Method	Residual (%)	Mean bond lengths	
				T--O (Å)	M--O,OH (Å)
margarite- $2M_1$	1,071	Counter	7.5 (iso. B)	1.747, 1.624 1.640, 1.730	1.910, 1.900, □
amesite- $2H_2$	722	Counter	10.9 (iso. B) (in progress)	1.671, 1.717 1.736, 1.649	2.064, 2.073, 1.977 2.062, 1.988, 2.060
cronstedtite- $2H_2$	300	Film, visual	10.2 (iso. B)	1.617, 1.801	2.097 x 3
cookeite	900	Film, visual	10.3 (iso. B) (in progress)	1.622, 1.620 1.652, 1.673	1.932, 1.906, □ 1.892, 1.928, 2.125

of the structure in the ideal space group  $C2/c$  confirmed Takéuchi's finding of tetrahedral disorder (Guggenheim and Bailey, in preparation). Because of systematic absences, the only possible subgroup is  $Cc$  and Farmer and Velde (1973) have suggested this may be the true space group. In this lower symmetry, the two tetrahedral sheets within the 2:1 layer no longer are equivalent, and two different ordering models may be postulated that are consistent with disorder in the parent space group but full order in the subgroup. Because of the high pseudosymmetry, initial attempts to refine the ordered structure starting from the coordinates of the disordered phase and varying the coordinates of one sheet at a time proved unsuccessful. It was necessary to model the coordinates for the two possible ordered structures by using the distance least squares program OPTDIS of Dollase. For one model, refinement of coordinates predicted by OPTDIS from assumed bond lengths and bond strengths converged smoothly to a satisfactory structure with consistent bond lengths and angles. Refinement of the second model was unsatisfactory in that bonds around the postulated  $Al^{IV}$  became smaller and around the postulated  $Si^{IV}$  became larger, thus proving an incorrect model. Application of Hamilton's (1965) residual ratio test indicates that the successful ordered model is a significant improvement over the disordered model at better than the 1 percent significance level.

The resultant mean T-O bond lengths of 1.624, 1.747, 1.640, and 1.730 Å in the successful  $Cc$  model suggest nearly complete ordering for the indicated electron probe composition of  $(Ca_{0.81}Na_{0.19}K_{0.01})(Al_{1.99}Mg_{0.03}Fe_{0.01})(Si_{2.11}Al_{1.89})O_{10}(OH)_2$ . The ordering pattern is illustrated in Figure 6. Tetrahedra in the lower tetrahedral sheet that would be related by inversion centers to tetrahedra in the upper sheet of

the same 2:1 layer in the ideal space group  $C2/c$  prove to be compositionally different when refined in subgroup  $Cc$ . A lateral (pseudo) two-fold axis normal to the direction of intralayer shift and passing through the two octahedral Al atoms can be seen to relate compositionally similar tetrahedra in the two sheets instead. Güven (1971b) has pointed out for muscovite- $2M_1$  that ordering may be inhibited in the ideal space group  $C2/c$  because ordering would cause two apical oxygens (of Al-rich tetrahedra) along the same octahedral shared edge to be electrostatically unbalanced. This unstable situation is avoided in

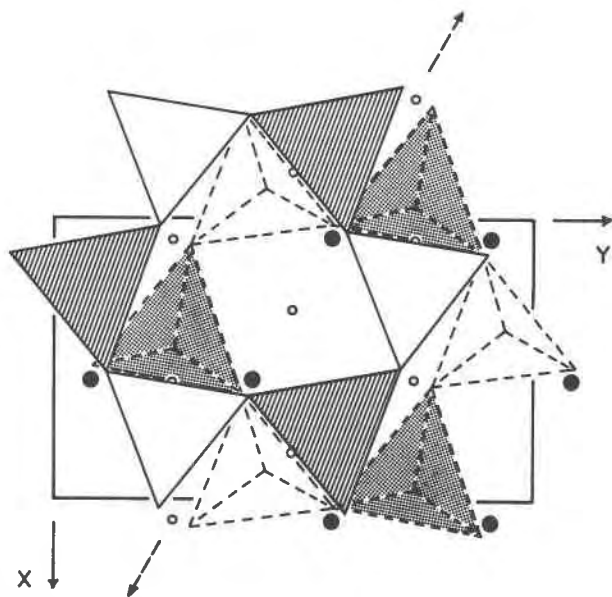


FIG. 6. Tetrahedral ordering pattern within 2:1 layer of margarite- $2M_1$  in subgroup  $Cc$ . Al-rich tetrahedra = ruled lines and dots; octahedral Al = solid circles; inversion centers of ideal space group = small open circles; pseudo 2-fold axis = dashed arrows.

muscovite-3*T*, where the two tetrahedral sheets are related by a true two-fold axis instead of by inversion centers and where ordering of tetrahedral cations has been confirmed within the ideal space group  $P3_112$  (Table 2). The *Cc* ordered pattern in margarite-2*M*<sub>1</sub> also avoids two unbalanced oxygens on the same octahedral shared edge, but the two-fold axis relating compositionally similar tetrahedra in the two tetrahedral sheets does not hold for the structure as a whole.

In the case of muscovite-2*M*<sub>1</sub>, where the Si:Al ratio is 3:1, only one ordered model is possible in subgroup *Cc* that would be disordered in the ideal space group. This is the same ordered model found to be present in margarite-2*M*<sub>1</sub>, except that the maximum order possible is alternation of Si and Si<sub>0.5</sub>Al<sub>0.5</sub> tetrahedra. Refinement of the neutron diffraction data of Rothbauer (1971) according to this model proved unsuccessful, and it can be concluded that the ordered model of margarite-2*M*<sub>1</sub> does not extend to muscovite-2*M*<sub>1</sub>.

#### Amesite

Prismatic single crystals of the aluminian serpentine amesite [(Mg<sub>2</sub>Al)(SiAl)O<sub>6</sub>(OH)<sub>4</sub>] usually crystallize as the 2*H*<sub>2</sub> polytype and exhibit apparent hexagonal diffraction symmetry. Partial refinement within the ideal space group  $P6_3$  by Steinfink and Brunton (1956) indicated both tetrahedral and octahedral disorder for amesite from the Ural Mountains. Microscopic observation, however, invariably shows that amesite crystals are composed of six-fold biaxial twin sectors on (001). Individual twin sectors cut from the larger aggregate have 2*V* optic angles near 20°, slightly triclinic unit cell geometry, and triclinic diffraction symmetry. Refinement in progress by S. H. Hall of the structure of a sector cut from a previously unreported amesite from Antarctica, kindly provided by T. S. Laudon, indicates both tetrahedral and octahedral cation ordering in subgroup *P1* (actually refined in *C1* for convenience). The pattern of tetrahedral ordering is such that tetrahedra of adjacent layers that should be equivalent to each other in the ideal  $P6_3$  symmetry actually have different Si,Al contents, as judged by the differences in mean *T*-O bond lengths (Table 5). Of the six independent octahedra in the two-layer structure, two are observed to be smaller than the other four and are interpreted as Al-rich and Mg-rich, respectively. Although this refinement is not complete, no structural features exist that would explain the observed triclinic symmetry and geometry other than ordering.

#### Cronstedtite

The iron-rich 1:1 layer silicate cronstedtite [(R<sup>2+</sup><sub>3-x</sub>Fe<sup>3+</sup><sub>x</sub>)(Si<sub>2-x</sub>Fe<sup>3+</sup><sub>x</sub>)O<sub>6</sub>(OH)<sub>4</sub>] with  $x \sim 0.5$  to 1.0] shows a great variety of layer stacking sequences. Partial refinement of several of these by Steadman and Nuttall (1963, 1964) showed no evidence of ordering of tetrahedral or octahedral cations. For comparison with the amesite-2*H*<sub>2</sub> structure, a cronstedtite-2*H*<sub>2</sub> crystal from Příbram, Bohemia, kindly provided by C. Frondel, was selected for study. This particular polytype had not been refined previously by Steadman and Nuttall.

Because of its jet-black color, optical search for (001) twin sectors similar to those in amesite proved difficult, but no clear evidence for sectors was obtained either by reflection microscopy or by transmission microscopy with ultra-thin sections. Refinement by Henry and Bailey (in preparation) in the ideal space group  $P6_3$  indicated ordering of tetrahedral Si and Fe<sup>3+</sup> according to mean *T*-O bond lengths of 1.62 and 1.80 Å. Ordering is confirmed also by observation of 06*l* reflections with *l* odd (as indexed on an orthohexagonal cell). Radoslovich and Norrish (1962) have shown that these reflections should have zero intensities in a truly hexagonal structure in which the tetrahedral cations have *y* coordinates that are exact multiples of *b*/12 and are disordered. Cronstedtite-2*H*<sub>2</sub> appears truly hexagonal, and calculations show that the observed intensities of the 06*l* reflections with *l* odd must be due to differences in X-ray scattering powers of ordered tetrahedral Si and Fe<sup>3+</sup> plus the differences in position of their coordinating oxygens as a consequence of ordering. Ordering of octahedral Fe<sup>2+</sup> and Fe<sup>3+</sup> is not possible in the ideal space group.

Non-Bragg satellites were observed on X-ray films of nine cronstedtite crystals of several different polytypes, including the 2*H*<sub>2</sub> crystal used for refinement. The satellites are associated with only a few Bragg reflections on *hk0* Weissenberg photographs, and do not conform to hexagonal symmetry. The satellites vary in position and sharpness from crystal to crystal, and some are connected by diffuse streaks. They cannot be accounted for by physical imperfections or twinning in the crystal. Although not investigated further, they presumably represent some non-hexagonal modulation of the structure that is not reflected in the average refinement of the structure reported here.

#### Cookeite

Cookeite is a di,triocahedral chlorite in which the 2:1 layer is dioctahedral and the interlayer sheet is

trioctahedral. Bailey and Brown (1962) and Lister (1966) have shown that cookeite usually adopts one of two stacking sequences based on the *Ia* structural unit. The regular 2-layer variety from North Little Rock, Arkansas, [ $\sim(\text{Al}_{4.02}\text{Li}_{0.86})(\text{Si}_{3.02}\text{Al}_{0.97})\text{O}_{10}(\text{OH})_8$ ], kindly supplied by C. G. Stone, was chosen for study because of its good crystals and relatively rare occurrence in nature.

Initial study (Lister, 1966) showed the 2-layer structure to be of the *r*-type (Mathieson and Walker, 1954), for which the ideal space group is *Cc*. This space group imposes few constraints on cation ordering and allows the two tetrahedral sheets within a 2:1 layer to be non-equivalent. Refinement (Table 5) suggests both tetrahedral and octahedral ordering have taken place in this specimen. The Li is localized primarily in one position in the interlayer sheet ( $M\text{-O,OH} = 2.125 \text{ \AA}$ ). The pattern of tetrahedral ordering is surprising in that mean *T-O* bond lengths suggest one tetrahedral sheet contains only Si in tetrahedral coordination and that all of the tetrahedral Al is concentrated in the other tetrahedral sheet of the same 2:1 layer. This is such a surprising and interesting result that it is being checked presently by a second refinement based on densitometer measurement of the film data rather than the original visual measurement. If verified, this result will have implications as to the origin of regular interstratifications of the type listed in Table 4 because it will mean asymmetric distributions of negative charge are possible in 2:1 layers. Assumption of a centrosymmetric space group, as in many previous studies of 2:1 layer silicates, necessarily precludes determination of such asymmetry.

### Conclusions

The finding of cation order in all four test structures lends support to the view that ordering is more common in layer silicates than previously believed. Structures previously determined as disordered in their ideal space groups merit reexamination for lower symmetry or for non-Bragg scattering. It should be kept in mind that, as for margarite- $2M_1$ , successful refinement in subgroup symmetry by least squares procedures may require modeling of all possible ordered structures.

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