Polytypism in micas: A polyhedral approach to energy calculations

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ABSTRACT

There has been wide speculation about the structural factors responsible for the observed frequency of the different mica polytypes. The purpose of this investigation is to identify the important factors and to test the relevant ones by using calculated cohesive energies to discriminate between alternative model structures. Sets of structures were constructed, based on talc, pyrophyllite, muscovite, biotite, and anandite. Each model set was specifically designed so that all structures in a given set would have essentially the same short-range repulsive forces and essentially the same van der Waals forces. The difference between the cohesive energies of two structures could then be ascribed essentially entirely to long-range Coulomb electrostatic forces. The method is a natural extension of the polyhedral approach to crystal chemistry.

Of the various parameters designed to characterize deviations from structural ideality, only \( \Delta z \) and \( \alpha \) are specifically related to the articulation of the various coordination polyhedra. Other parameters measure the departure from ideal geometry of individual coordination polyhedra. We identify \( \Delta z \) as the best parameter for predicting the stable polytype. Most micas with \( \Delta z \) less than 0.1 Å are \( 1M \) polytypes, regardless of composition and other structural parameters. Most micas with \( \Delta z \) greater than 0.1 Å are \( 2M \) polytypes regardless of composition and other structural parameters. The conspicuous exceptions include the lithian micas and the brittle mica anandite, \([\text{Ba(Mg,Fe)}_8(\text{Si,Fe})_6\text{O}_{10}(\text{OH})_2]\). Though significantly variable, \( \alpha \) bears no apparent relationship to the stability of the \( 1M \) versus the \( 2M \) polytype.

The calculations support both theoretical and empirical observations regarding (a) the predominance of \( 1M \) and \( 2M \) polytypes and (b) the scarcity of \( 2O \) polytypes. Al-Si “disordering” in micas is subject to certain rules: (a) the principle of aluminum avoidance and (b) the same ratio of Al to Si in all tetrahedral sheets. The relative positioning of tetrahedral Al cations on opposite sides of the octahedral sheet seems not to be important. For muscovite-\( 2M_0 \), there are at least 48 crystal-chemically reasonable Al-Si orderings with very nearly the same low energy. The different orderings should be more or less equally represented in actual structures. Calculated energies are most sensitive to interlayer Al-Al separations. In \( 1M \) and \( 2M_1 \) polytypes, Al-Si orderings consistent with a \( 2 \), axis parallel to \( b \) are especially favorable.

INTRODUCTION

There are fundamental differences in the unit-layer structures of dioctahedral and trioctahedral micas (Bailey, 1984). The differences are in some combination responsible for the general observation that most dioctahedral micas are \( 2M_1 \) polytypes, using the notation of Ramsdell (1947), whereas most trioctahedral micas are \( 1M \) (Bailey, 1984). Other simple polytypes—\( 2M_2 \), \( 2O \), \( 3T \), and \( 6H \) (Smith and Yoder, 1956)—are comparatively rare or largely restricted to special compositions; for instance, anandite \([\text{Ba(Mg,Fe)}_8(\text{Si,Fe})_6\text{O}_{10}(\text{OH})_2]\), which is a \( 2O \) brittle mica, and the lithian micas, many of which are \( 3T \) or \( 2M_1 \) polytypes (Bailey, 1984). Although there are excellent crystal-chemical grounds for understanding the scarcity of \( 2M_2 \), \( 2O \), and \( 6H \) polytypes (Radoslovich, 1959, 1960; Güven, 1971; Thompson, 1981), there is little consensus and much speculation (Güven, 1971; Bailey, 1984) regarding the structural factors responsible for the overwhelming predominance of \( 2M_1 \)-dioctahedral and \( 1M \)-trioctahedral micas.

The purpose of this research is to identify the relevant structural factors controlling mica polytypism and to test the important ones by comparing calculated cohesive energies for appropriate model structures. Although the primary goal is a better understanding of polytypism, this end is not achieved without paying considerable attention to short-range ordering of tetrahedral cations (Abbott, 1984; Abbott et al., 1986). The calculations help to iden-
tify the direct and indirect influences on polytypism of the following factors: (1) OH = F exchange, (2) Al-Si ordering, and (3) M1 = vacancy exchange (trioctahedral vs. dioctahedral structures).

**RELEVANT STRUCTURAL PARAMETERS**

The differences in unit-layer structures of dioctahedral and trioctahedral micas can be quantified, for the purpose of comparison, in a number of ways. Several of the standard parameters for 69 structural determinations of dioctahedral and trioctahedral micas have been compiled by Bailey (1984). The parameters for 14 brittle micas have been compiled by Guggenheim (1984). The parameters measure the departure of a given structure from ideality (Pauling, 1930; Jackson and West, 1930; Gruner, 1934; Pabst, 1955). Table I presents the statistics on the structural parameters for 46 nonlithian and nongermanian micas from Bailey (1984). The parameters are explained in Figure I and include (1) the tetrahedral rotation, $a$ (0° < $a$ < 30°), (2) the octahedral flattening angle, $\psi$ ($\psi_{\text{ideal}} = 54°44'$), (3) the interlayer tetrahedral shift, $s$ (approximately 0.333$a$), and (5) the tetrahedral shift, $s$. (c) View of portion of unit-layer structure, looking down $I/M$ setting $a$ axis. The parameter $\Delta z$ is indicated.

Most of the parameters—$\psi$, $s$, $r$, $\Delta z$—are specifically related to the geometries of individual coordination polyhedra. These parameters are strongly dependent on cation substitution, hence on bulk composition. The mean T-O distance, for instance, is a measure of the ratio of Al to Si (Smith, 1954; Baur, 1970; Hazen and Burnham, 1973). The similarity in the averages of the T-O distances for the dioctahedral and trioctahedral micas simply reflects the common ratio of Al to Si (approx. 0.5). The value of $r$ is essentially the same for dioctahedral and trioctahedral micas by virtue of the inherent rigidity and incompressibility (Hazen and Fin-ger, 1982; Hazen, 1985) of Si and Al tetrahedra. The averages of the M-O distances are different for dioctahedral and trioctahedral micas, but this is merely a reflection of the size of the common M substituents, $M_2$: Al and $M_1$: vacancy in the former versus $M_1$: $M_2$: Mg or Fe$^{2+}$ in the latter. The average values for $r$ ($M_1$ or $M_2$) are directly proportional to the averages of the M-O distances ($M = M_1$ or $M_2$). The tetrahedral shift, $s$, is greater in the dioctahedral micas than in the trioctahedral micas because the disparity in the sizes of the $M_1$ (= vacant) and $M_2$ coordination polyhedra is greater in the former than in the latter.

Unlike the other parameters in Table 1, $a$ and $\Delta z$ are direct measures of the manner of articulation of the various coordination polyhedra. Both parameters are sensitive to variations in the other parameters. Hence, they happen to be distinctly different in the dioctahedral and trioctahedral micas, but only because of the differences in the common $M_1$ and $M_2$ substituents. Because they are not specifically related to the geometries of individual polyhedra, but rather to the way the polyhedra are connected, $a$ and $\Delta z$ share certain advantages in identifying causes underlying the obvious correlation between the
polytype and the occupancy of the octahedral sites (Table 1):

1. The value of $\alpha$ is independent of structural variations due to homogeneous size-scaling. Two structures that are distinguishable on the basis of T-O and M-O values may be the same in other respects if the ratios of T-O to M1-O and M2-O are the same in the two structures. One structure is simply homogeneously bigger than the other. Problems associated with size-scaling of this sort may be more insidiously embedded in the complex chemistries and structures of micas than might otherwise be indicated by a simple inspection of T-O and M-O distances. For this reason, we have avoided the size-dependent parameters, such as T-O and M-O, in order to avoid false or ambiguous conclusions based on distinctions between structures, or parts thereof, that differ only in size-scaling.

2. Though $\Delta z$ does vary in response to homogeneous size-scaling because it is a function of $c \sin \beta$, the dependency is small. This can be seen when it is considered that the percent variation in $\Delta z$, as measured for instance by $100 \sigma / \Delta z_{\text{mean}}$, where $\sigma$ is the standard deviation of the $z(O_{0,0})$ values, is very much greater than the anticipated percent variation in $(c \sin \beta)/n (=10 \text{ Å})$, where $n$ is the number of unit layers in one c translation, i.e., $n = 1$ for the $1M$ polytype, $n = 2$ for $2M_1$, etc. Consequently, variations in $\Delta z$ are largely independent of variations due to homogeneous size-scaling. A better definition for $\Delta z$ might be $n[z(O_{0,0})_{\text{max}} - z(O_{0,0})_{\text{min}}]$, which would be truly independent of homogeneous size-scaling. However, we have elected to retain the original formulation of $\Delta z$ for the sake of comparison with other investigations.

3. Finally, it should be noted that $\Delta z$ and $\alpha$ are significantly more variable than any of the other parameters, both within and between the major dioctahedral and trioctahedral groupings.

Figure 2 is a plot of $\alpha$ and $\Delta z$ for the nonlithian micas from Bailey (1984) and Guggenheim (1984). The trioctahedral micas are plotted as solid symbols; the dioctahedral micas, as open symbols. The shape of the symbol indicates the polytype. Specific chemical traits are keyed by number to individual symbols wherever a coherent group, such as the paragonites, could not be encircled conveniently. The group marked Ge includes synthetic germanian micas in which Ge has been substituted for Si. The data points marked T&R (Takeda and Ross, 1975), R&R (Richardson and Richardson, 1982), talc, pyrophyllite, and 4 (anandite), are the bases for model structures used in our energy calculations. The following features should be noted: (1) Most of the trioctahedral micas are $1M$ polytypes. (2) Most of the dioctahedral micas are $2M_1$ polytypes. (3) With two exceptions (phengites), the $1M$ micas are restricted to low values of $\Delta z$ (less than approximately 0.10 Å). (4) With three exceptions, the $2M_1$ micas are restricted to high values of $\Delta z$ (greater than approximately 0.10 Å). (5) The trioctahedral mica celadonite, with a low $\Delta z$, is a $1M$ polytype. (6) The trioctahedral mica clintonite, with a high $\Delta z$, is a $2M_1$ polytype. But the structure (Akhundov et al., 1961) was very poorly refined (final $R \approx 19.5\%$) and may be discredited. Material from the same locality has since been shown to be disordered with only a statistical tendency toward $2M_1$ stacking (Bailey, pers. comm., 1987). (7) Except for andesite, the tetrahedral rotation (a) bears no obvious relationship to the polytype. (8) The combination of high $\Delta z$ and low $\alpha$ may be crucial in stabilizing the $2O$ polytype. (9) The brittle micas have extreme values for $\alpha$. The margarites and two of the clintonites have the highest $\alpha$ values, and the polytype, $2M_1$ and $1M$, respectively, depends on $\Delta z$ in a manner that is consistent with the potassium micas. At the other extreme, anandites have very low $\alpha$ values. (10) There are $1M$-trioctahedral Ba-rich micas with low $\Delta z$ values. Thus, the Ba in anandite is not necessarily responsible for the $2O$ stacking.

With regard to the relative stability of $1M$ and $2M_1$ polytypes, $\Delta z$ is the single most important parameter of those listed in Table 1 and in Bailey’s (1984) and Guggenheim’s (1984) more detailed tabulations. We recognize three kinds of corrugations:

1. **Pure corrugations.** This type of distortion complements a vacancy in the M1 site and, hence, is prominent in dioctahedral micas. Pure distortions may also occur in trioctahedral micas in conjunction with the ordering of very different cations on the M1 and M2 sites, such as in the trioctahedral lithian micas (Bailey, 1984). Pure corrugations, as defined here, have nothing to do with cation substitution on tetrahedral sites. Effects due to pure corrugations may, however, be difficult to separate from effects due to cation substitutions on the tetrahedral sites. Certainty that corrugations are pure, therefore, exists only in talc, pyrophyllite, celadonite, or other micas with no substitution on the tetrahedral sites.

2. **Ordered substitutional corrugations.** Individual and mean bond lengths for tetrahedrally coordinated Al are substantially longer than for tetrahedrally coordinated Si
were derived from well-refined structure determinations
and correspond essentially to those for the experimental
the exception of pyrophyllite and talc, the parameters
of the relevant parameters in the following model
structures on the basis of calculated cohesive enereies.

Margarite represents a special case. In margarite there
is a strict alternation of Al and Si tetrahedra (Guggenheim
and Bailey, 1975) in accordance with Loewenstein’s (1954)
principle of aluminum avoidance. Each basal oxygen is
shared equally between one Al and one Si such that the
position of each basal oxygen is influenced equally by the
two cations. Consequently, the corrugations, which are
significant (Fig. 2), must be regarded as pure.

3. Random (disordered) substitutional distortions. The
observed space group of muscovite-2M,, C2/c, permits
at least partial ordering of Al and Si on the tetrahedral
sites. Yet there is no evidence for long-range ordering of
any kind (Bailey, 1975, 1984). We will address this prob-
lem in more detail in subsequent sections. On the aver-
age, the two distinct tetrahedral sites in C2/c muscovites
are populated by the same 1/3 ratio of Al/Si. The reported
Δz values measure a pure distortion, but for an average
structure, possibly giving a false impression of the actual
shape of the surface defined by the basal oxygens. If there
is short-range ordering, the basal oxygens may be mod-
ulated in small domains, perhaps in a manner that is
contrary to that suggested by the measured Δz for the
average structure. On the other hand, if there is not even
short-range ordering, Δz for the average structure may
measure the only systematic disturbance of the surface
defined by the basal oxygens—a systematic disturbance
superimposed on random substitutional effects.

In this study, a great deal of effort was devoted to sort-
ing out the relative importance of pure corrugations ver-
sus substitutional effects. This end was achieved by vary-
ing the relevant parameters in the following model
structures and discriminating between the alternative
structures on the basis of calculated cohesive energies.

Test structures

Five unit-layer structures, and modifications thereof,
were tested in two or more of the four polytypic config-
urations: 1M, 2M,, 2M,, and 2O. The unit-layer models
were derived from well-refined structure determinations
on natural specimens: talc (Rayner and Brown, 1973),
pyrophyllite (Lee and Guggenheim, 1981), biotite (Takeda
and Ross, 1975), muscovite (Richardson and Rich-
ardson, 1982), and anandite (Filut et al., 1985). Table 2
lists unit-cell dimensions, mean bond lengths, and rele-
vant structural parameters for the model structures. With
the exception of pyrophyllite and talc, the parameters
correspond essentially to those for the experimental
structural determinations. The unit-layer structures for
both talc and pyrophyllite were idealized slightly to con-
form with 1M-C2/m symmetry. The actual structures are
triclinic in one-layer (10-Å) polytypes that defy descrip-
tion according to conventional stacking theories (Smith
and Yoder, 1956; Thompson, 1981). Unlike true micas,
in talc and pyrophyllite, the basal oxygens in the top of
one layer are juxtaposed with those in the bottom of the
next layer in such a way that the cations of the respective
tetrahedral sheets do not superimpose when projected
down c*. Nonetheless, the observed unit-layer structures
for both talc and pyrophyllite are very close to the slightly
modified C2/m structures for the parameters reported in
Table 2. In the hypothetical model structures, adjacent
sheets of basal oxygens were positioned as they are in
micas.

None of the structure determinations provided coor-
dinates for H. Initially, this problem was avoided by con-
sidering the OH to be replaced by F, thus neglecting in-
fluences of OH dipoles. Most of the models were tested
as F-micas. Later on, further work was deemed unwise
without taking into account the influences of OH bonds,
whose orientations are so very different in trioctahedral
and dioctahedral micas (Bassett, 1960; Giese, 1984). A
series of OH model structures was manufactured in ac-
cordance with the findings of Giese (1984) regarding the
length and orientation of the OH bond. For both triocta-
hedral and dioctahedral model structures, the OH bond
length was fixed at 0.9 Å. In the former, the bond was
oriented perpendicular to (001) and directed away from
the plane of the octahedral cations. In the latter, the OH
bond was oriented in the unit-layer mirror plane [i.e.,
(010) in 1M and 20, (110) in 2M,, and (1,1,0) in 2M] and
inclined 12° from (001).

The structure determinations by Takeda and Ross
(1975) are unique in providing the only direct compari-
son between naturally coexisting 1M and 2M, micas.
Among other observations, they showed that the two
polytypes have virtually the same composition and unit-
layer structure. In this case alone, there was no need to
construct one or more hypothetical polytypes from the
unit-layer structure of one real polytype. Energy calcula-
tions were performed on the actual structures.

For muscovite, a hypothetical 1M polytype was de-

erived by transformation of the unit-cell geometry and
atomic coordinates from the initial 2M, structure of Ta-
date and Ross, 1982), and anandite (Filut et al., 1985). Table 2
lists unit-cell dimensions, mean bond lengths, and rele-
vant structural parameters for the model structures. With
the exception of pyrophyllite and talc, the parameters
correspond essentially to those for the experimental
structure (Table 2).

Hypothetical 2O, 2M,, and 2M, polytypes were fash-
iioned using the initial C2/m unit-layer structures of both
talc and pyrophyllite (Table 2). Only the hypothetical 1M
polytype was constructed from the initial 2O anandite
structure (Table 2).

Table 3 reports the real and hypothetical models tested
in the investigation. Each row in Table 3 represents a

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(108)
model set, all of whose members have essentially the same unit-layer structure, at least within the limitations of (1) polytype-imposed symmetry differences and (2), where relevant, Al-Si ordering differences. Each entry in Table 3 under the different polytype headings is the number of distinct Al-Si (Fe-Si, in the case of anandite) ordered structures that were constructed for the corresponding polytype. The rationale for the limited choice of Al(Fe)-Si orderings (in contrast to Giese, 1984) is presented in the next section. For pyrophyllite and talc models, the tetrahedral sheets are pure SiO; hence one structure per polytype in each model set is sufficient. For the model sets labeled DLS in Table 3, Si-O and Al-O bond lengths were adjusted by distance-least-squares analysis (Baerlocher et al., 1977). The details of the DLS calculations are described in a later section. The Al(Fe)-Si orderings for the polytypes of the non-DLS model sets are distinguishable from one another only on the basis of charge distribution. For instance, in each 1M structure of the non-DLS OH-biotite model set, the atomic coordinates conform to C2/m, whereas the charge distribution (owing to the ordering of Al and Si) is in a lower-order space group (P21, P2, P1, and P1; see Abbott, 1984). For each structure in the DLS-adjusted OH-biotite model set, both the charge distribution and the atomic coordinates have the same reduced symmetry.

The corrugations were removed from some model sets by setting the z coordinate of each basal oxygen to the average of the z values in the actual corrugated structure. One model set for OH-pyrophyllite (α = 0) was constructed with the tetrahedral rotation (α) set to zero.

### Ordering of tetrahedral cations

The important observed space groups for biotite (C2/c in 2M, and C2/m in 1M), muscovite-2M, (C2/c), and anandite-2O (Pnmmn) permit partial (C2/c, Pnmmn) or no (C2/m) ordering of tetrahedral cations. In muscovite-2M, and biotite-2M, where limited ordering is possible, the structural determinations (Richardson and Richardson, 1982; Takeda and Ross, 1975) indicate that Al and Si are essentially completely disordered. The structure of anandite (Filut et al., 1985) indicates that Fe and one-third

### Table 2. Structural parameters and lattice geometries of model structures

<table>
<thead>
<tr>
<th></th>
<th>Ideal</th>
<th>Talc C2/m</th>
<th>Biotite C2/m</th>
<th>Biotite C2/c</th>
<th>Pyrophyllite C2/m</th>
<th>Muscovite C2/c</th>
<th>Anandite Pnmmn</th>
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<tr>
<td>a (Å)</td>
<td>-</td>
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<td>5.331</td>
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<td>5.160</td>
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<td>-</td>
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<td>95.09</td>
<td>100</td>
<td>95.78</td>
<td>90</td>
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<td>1.622</td>
<td>1.659</td>
<td>1.657</td>
<td>1.517</td>
<td>1.643</td>
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<tr>
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<td>1.622</td>
<td>1.659</td>
<td>1.657</td>
<td>1.517</td>
<td>1.643</td>
<td>1.560</td>
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<td>Δz (Å)</td>
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<td>-0.335</td>
<td>-0.334</td>
<td>-0.383</td>
<td>+0.378</td>
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<td>2.086</td>
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<td>59.2</td>
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<td>59.6</td>
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<tr>
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<td>2.086</td>
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<tr>
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<td>59.2</td>
<td>59.2</td>
<td>59.6</td>
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</table>

* M1-O and s(M1) relative to center of M1 (vacancy).

Note: Number of Al-Si (Fe-Si in the case of anandite) orderings. Boldface values indicate lowest-energy polytype.

* Results reported earlier (Abbott et al., 1986) and only summarized here.
of the Si are disordered on one of the two distinct sites (T2 = Fe\text{,}Si\text{,}) with the remainder of the Si on the other site (T1 = Si). As we already noted, Bailey (1975, 1984) has argued that there is no evidence for long-range ordering in either the 2M, or the 1M polytypes of muscovite or biotite, even when the structures are reconsidered in reduced-symmetry space groups. Recent nuclear magnetic resonance studies (Sanz and Serratosa, 1984; Sanz et al., 1986; Herrero et al., 1985; Herrero, 1987) indicate a somewhat ill-defined short-range ordering that does, however, comply with Loewenstein’s (1954) principle of aluminum avoidance. Other workers (Gatineau and Mering, 1966; Abbott, 1984) have postulated models for short-range ordering, based on X-ray or electron diffraction observations. Abbott et al. (1986) have considered the consequences and energetics of short-range ordering of tetrahedral cations. The problem of disordering versus short- or long-range ordering is crucial to the calculation of realistic cohesive energies.

The cohesive energy of a structure depends on nearest-neighbor forces (Burnham, 1985). In the ionic modeling approach, these forces make sense only in the context of individual sites in a structure being occupied by discrete atoms (i.e., T = Si or Al) and not by hybrid atoms (e.g., T = Al\text{,}Si\text{,}) (Giese, 1984; Burnham, 1985). Presumably, the real structure consists of a Boltzmann distribution of differently ordered unit cells. At present, the problem can be accommodated only crudely by three approaches:

1. Consider all possible ordering schemes. Even in seemingly simple cases, this can lead to an overwhelming number of structures. The problem becomes intractable, and for this reason alone, the approach has enjoyed little, if any, popularity.

2. Select, at random, a manageable subset of structures from the total number of possibilities. This approach has been used with some success by Giese (1984, 1986) who selected 100 Al-Si ordered muscovite structures from 1820 possibilities and 100 margarite structures from 12870 possibilities. The procedure has at least one serious flaw in cases where only one or two particularly favorable structures exist out of hundreds of possibilities, as in the case of margarite (Giese, 1984). In such cases, the one or more exceptional cases may be overlooked, if they cannot be anticipated a priori. In the case of margarite (Giese, 1984), the one favorable structure could be anticipated and was included in the set of structures tested. The approach does not discriminate between symmetrically equivalent structures, nor does it discriminate between crystal-chemically reasonable and unreasonable structures.

3. Use a set of ordered structures consisting of only symmetrically distinct arrangements that obey reasonable crystal-chemical principles. In their energy calculations concerning the relationship of Al-Si ordering to the position of Na in albite, by using symmetrically distinct Al-Si orderings that obey Loewenstein’s (1954) principle of aluminum avoidance, Post and Burnham (1987) limited the number of orderings from 1820 to 56. The approach is justified because symmetrically equivalent orderings have the same energy, hence are redundant, and because crystal-chemically unreasonable structures will have high energies, hence correspondingly low representations according to Boltzmann’s law.

We have adopted the third approach here, selecting only those Al-Si ordered structures that fulfill the following criteria:

1. For the muscovite and biotite model sets, each 2M, and 1M Al-Si ordered structure is symmetrically distinct under the space-group operations of C2/c and C2/m, respectively. For the anadite model sets, each 2O and 1M Fe-Si-ordered structure is symmetrically distinct under the operations of Pmn21 and P2/m, respectively.

2. All tetrahedral sheets in a given structure have the same ratio of Al to Si (Abbott, 1984; Abbott et al., 1986). This eliminates from consideration any subgroup of C2/m containing the mirror plane or the a-glide plane and any subgroup of Pmn21 containing the mirror plane. All model structures obey Loewenstein’s (1954) principle of aluminum avoidance (Sanz and Serratosa, 1984; Sanz et al., 1986; Herrero et al., 1985; Herrero, 1987).

After screening the possibilities (28 for 1M; 1820 for 2M; 1820 for 2O), there are only four symmetrically distinct and crystal-chemically reasonable 1M ordered structures (Abbott, 1984), twelve 2M, structures, and twelve 2O structures. Only one of the 2M, model subsets in Table 3 (dls-adjusted OH-muscovite) includes all 12 of the Al-Si orderings. Each of the other muscovite and biotite model sets—created for an earlier study (Abbott et al., 1986)—includes only 8 of the 12 possibilities, though we are confident, on the basis of the 2M, structure calculations on all 12, that our conclusions are unaffected by this earlier omission. Two of the 4 possible anadite-1M structures and 8 of the 12 possible anadite-2O structures were eliminated because they were not consistent with the observed (Filut et al., 1985) partial ordering of Fe and Si.

Each of the ordered structures can be characterized by a space group that is subordinate to the space group of the disordered or partially ordered structure. The space groups are reported in subsequent tables.

We have included tetrahedral-site orderings that violate what one of us (Abbott, 1984) has referred to as Güven’s rule. Güven (1971) argued that two apical oxygens of Al tetrahedra forming the same shared octahedral edge should be especially unfavorable with respect to the local balancing of electrostatic charge. The rule refers to the situation where both of the tetrahedra in Figure 1b are occupied by Al. The sum of the Pauling (1960) bond strengths reaching each apical oxygen is 1.75. Thus, two electrostatically undersaturated oxygens are juxtaposed.

**DLS analysis**

The tetrahedral bond lengths for the hypothetically Al-Si ordered muscovite and biotite models (and Fe-Si ordered anadite models) were adjusted by distance-least-squares analysis, using the program DLS-76 (Baerlocher et
Table 4. T-O bond lengths (Å) prescribed for DLS refinement

<table>
<thead>
<tr>
<th></th>
<th>Muscovite and biotite</th>
<th>Ananđite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-O$_{\text{basal}}$</td>
<td>1.612</td>
<td>1.623</td>
</tr>
<tr>
<td>Si-O$_{\text{apical}}$</td>
<td>1.633</td>
<td>1.613</td>
</tr>
<tr>
<td>O$<em>{\text{basal}}$-O$</em>{\text{apical}}$</td>
<td>2.648</td>
<td>2.689</td>
</tr>
<tr>
<td>O$<em>{\text{basal}}$-O$</em>{\text{basal}}$</td>
<td>2.628</td>
<td>2.594</td>
</tr>
<tr>
<td>O$<em>{\text{apical}}$-O$</em>{\text{apical}}$</td>
<td>2.566</td>
<td>2.564</td>
</tr>
</tbody>
</table>

Note: There are three distinct O$_{\text{basal}}$-O$_{\text{basal}}$ distances and three distinct O$_{\text{apical}}$-O$_{\text{apical}}$ distances for the Si tetrahedra.

The unit-cell dimensions of each polytype were not permitted to change during the course of DLS analysis. Changes in unit-cell geometry can be exaggerated in DLS analysis, leading to structures for which the calculated energies cannot be compared realistically. Unconstrained DLS analyses often lead to unrealistic changes in the articulation of the tetrahedral and octahedral coordination polyhedra. Even so, the conservative approach adopted here can lead to anomalous structures that are generally characterized by unrealistic A-site coordination polyhedra. Fortunately, the anomalous structures have correspondingly anomalous calculated energies and are therefore easily recognized. The DLS-adjusted J/M modifications of OH-muscovite afford a good example. The unusually low calculated energies for the P2$_{1}$, P1, and P1' structures—when compared with the energies for the various 2M$_{1}$ structures—are due to unrealistically short K-O distances. The K polyhedra are not comparable in the 1M and 2M$_{1}$ structures. By way of contrast, the K polyhedra are essentially the same in the 1M and 2M$_{1}$ structures of each biotite model set because Δz is close to zero.

Energy calculations

If meaningful results are taken as an indication, there is reasonable justification for treating many silicate structures as ionic (Burnham, 1985). The proof of this rests essentially on the generally favorable comparison between properties calculated on the basis of the ionic model and measured properties. In the ionic model, there are...
three important contributions to the cohesive energy, using
the terminology of Burnham (1985): a long-range, or
Coulomb, electrostatic term; a short-range repulsive term,
and a van der Waals term. Of the several computer pro-
grams now available for calculating the cohesive energy,
we used wMIN (Busing, 1981). In our calculations, we
have included neither the short-range repulsive energy
nor the van der Waals energy. We report only the Cou-
lomb electrostatic energy. This simplification is justified
in this study for the following reasons:
1. The models are based on the refined structures of
naturally occurring minerals. We have assumed, a priori,
that the structures represent equilibrium or, at the very
least, near-equilibrium configurations. Under these cir-
cumstances, the absolute magnitude of the short-range
repulsive energy is approximately 10% of the magnitude
of the long-range Coulomb electrostatic energy (Giese,
1984), and the van der Waals energy is small.
2. Our structures were fashioned in such a way that the
nearest-neighbor bonding relationships are, as nearly as
possible, identical in all members of a given model set.
This applies even to the DLS-adjusted structures. The es-
sential differences between any two members of a given
model set involve some combination of (a) the relative
position of the Al(Fe)-Si ordered tetrahedral sheets on
opposite sides of the octahedral sheet, (b) the manner of
stacking successive layers (the polytype), and (c) the geo-
metry of the interlayer-cation coordination polyhedron
(K, Ba, vacancy). Under these circumstances, the short-
range energy is essentially identical for all members of a
model set, at least according to the currently available
methods for evaluating the short-range energy (Burnham,
1985). It is therefore assumed that the differences in cal-
culated energies correspond to structural differences for
which the differences in short-range energy terms and van
der Waals terms are negligible.

Because of the way we have constructed our model sets,
the energy difference between two structures in the same
model set is directly related to the manner of articulation
of the different polyhedral units in the structures. The
structures of a given model set may be thought of as being
constructed from a fixed set of cation coordination poly-
hedra. In this sense, our calculations are a natural exten-
sion of the method especially effective in identifying an unusual
structure for which the energy deviates significantly from
the mean. (b) The formulation for the Coulomb electro-
static energy is exact, and in principle the energy can be
computed to any desired degree of precision. (c) The sig-
nificance of the results is directly proportional to the care
taken in the construction of the model structures. In the
end, we point to the consistency of our results when com-
pared with the natural states of micas and our expecta-
tions based on crystal-chemical principles.

Summary of previous results
Some of our results pertaining to biotite and muscovite
have been reported elsewhere (Abbott et al., 1986). For
the sake of comparison with the latest calculations, the
findings of this earlier work are briefly summarized here:
(1) For trioctahedral OH-micas (OH-biotite), the 1M
polytype is roughly 1.75 kJ/anion more stable than the
2M, polytype. (2) For trioctahedral F-micas (F-biotite),
the energy difference between the 1M and 2M, polytypes
is about 91 kJ/anion in favor of 1M. (3) For dioctahedral
OH- and F-micas (OH- and F-muscovite), the 2M, poly-
type is 1.2 to 2.1 kJ/anion more stable than 1M. (4) For
a given polytype and octahedral sheet structure, the vari-
ous Al-Si orderings (with or without DLS refinement) have
slightly different energies. (a) In 2M, and 1M polytypes
of biotite or muscovite, the lowest-energy Al-Si orderings
are consistently the ones with the most even distribution
of tetrahedral Al atoms. That is, the most favorable or-
derings maximize the closest Al-Al separations. (b) In 1M
and 2M, polytypes, Al-Si orderings consistent with a 2,
axis parallel to b are especially favorable. The lowest-
energy 2M, orderings are in subgroups P2,./n, P2,, and
P2;/c; the lowest-energy 1M ordering is in subgroup P2,,.
On the other end of the spectrum, Al-Si orderings with a
2 axis parallel to b have by far the highest energies. (5)
With the corrugations removed from the OH-muscovite
(Δz = 0), there is essentially no energy difference between
the lowest-energy Al-Si ordered 2M, and 1M polytypes.

New results and discussion
Pyrophyllite and talc. Table 5 reports the results of our
calculations for talc and pyrophyllite. These model sets
were prepared in order to examine the influence of pure
distortions on stacking, without complications due to Al-
Si substitutions.

The calculations on the various model sets for pyro-
phyllite indicate that 2M, is the most stable polytype when
Δz ≠ 0 and α ≠ 0. The range of calculated energies in
the unmodified OH model set spans a difference of 1.74
kJ/anion. Only the energies for the 2M, and 20 polytypes
differ by more than one standard deviation (σ = 0.7 kJ/
anion) from the mean energy (−7001.9 kJ/anion), such
that E2M1 < E1M < E2M0 < E2c. It should be noted that
the energy of the 2M, polytype is only 0.11 kJ/anion less
than that of the 1M polytype. For F-pyrophyllite, the
difference in the energies of the 1M and 2M, polytypes is
greater, approximately 0.56 kJ/anion, and still in favor of the latter polytype. When the structure is modified so that \( \Delta \zeta \) is zero, the relative stability of the 1M and 2M, polytypes reverses, and the difference in the energies of the two polytypes increases to 1.36 kJ/anion for OH-pyrophyllite and 0.9 kJ/anion for F-pyrophyllite. This reversal shows the influence of pure corrugations in stabilizing the 2M, polytype relative to the 1M polytype. When the structure is modified so that \( \alpha \) is zero, the relative stability of the various polytypes changes: \( E_{2M'} < E_{1M} < E_{2M} < E_{20} \), favoring the 2M, polytype. In the \( \alpha = 0 \) model set, only the 2M, and 20 polytypes have energies differing by more than 1 \( \sigma \) (0.7 kJ/anion) from the mean energy (–7052.0 kJ/anion). The high calculated energy for the 20 polytype in the pyrophyllite model sets is consistent with the extreme scarcity (Bailey, 1984) of this polytype in nature.

Calculations on talc show that the four hypothetical polytypes have nearly the same energy, regardless of the differences between the model sets. For the unmodified OH-talc model set, the difference between the highest (2M,) and lowest (1M,) energies is only 0.1 kJ/anion, and all of the calculated energies lie within 1 \( \sigma \) (0.04 kJ/anion) of the mean (–6680.76 kJ/anion). The calculated energies for the 1M, 2M, and 20 polytypes differ by less than 0.03 kJ/anion! The very small differences are obviously insignificant; the four polytypes are equally stable, hence equally likely. Alternatively, the layer-stacking scheme, if it obeys a Boltzmann distribution, would be random. It is interesting to note that when the structure is modified by setting \( \Delta \zeta \) to zero (from the already low initial value of 0.005 Å), the difference in the energies of the 2M, and 1M polytypes increases slightly, giving a correspondingly slight preference (0.24–0.28 kJ/anion) to the 1M polytype. This supports the observation (Fig. 2) that \( \Delta \zeta \) is the important parameter with regard to the relative stability of the 1M and 2M, polytypes.

For both the OH-pyrophyllite structures and OH-talc structures, the relative order of the four polytypes is consistent with Thompson’s (1981) suggestion that the geometry of the A-site coordination polyhedron (vacant in pyrophyllite and talc) is important in explaining the scarcity of the 20 polytype. For the 20 polytype under the conditions just stipulated, i.e., \( \alpha = 0 \) and \( \Delta \zeta > 0 \), the polyhedron is an orthorhombic parallelepiped with edges parallel to the 20 a, b, and c axes. Basal oxygens occupy the corners of the parallelepiped, and the A site is at the center. We shall refer to the O-O edge lengths as \( d_e \) (short), \( d_i \) (long), and \( d_r \). The short edge in the (001) face, \( d_e \), has a length equal to the shortest \( O_{basal}-O_{basal} \) distance. The edge length \( d_i \) equals \( \sqrt{3d_e} \); and \( d_r \), which is the shortest interlayer O-O separation, is approximately equal to \( d_i \) (\( d_i \approx d_r \)). The trace of the unit-layer mirror plane is shown on the (001) faces of the polyhedron. The four shortest interlayer O-O distances have the same length, \( d_r \). The next shortest interlayer distances are four in number, end-face diagonals each having length \( \sqrt{(d_i^2+d_r^2)} \). Other interlayer O-O distances are significantly longer. Figure 4b shows the A-site polyhedron for the 2M, polytype under the same conditions, \( \alpha = 0 \) and \( \Delta \zeta > 0 \). The polyhedron can be derived from the 20 A-site polyhedron by rotating one of the (001) faces 60° about the normal to (001). The (001) faces have the same dimensions as in the 20 polytype, \( d_r = (O- \text{polytypes. When } \alpha \text{ and } \Delta \zeta \text{ are both close to zero, as in talc, the coordination polyhedron for the A site (vacant) is essentially hexagonal prismatic—the coordination number is 12 and essentially the same in all four polytypes. It follows that if the geometry of the A polyhedron alone determines the polytype, two possibilities may sub- tend: (1) The different polytypes should have the same frequency, or (2) the stacking sequence in a given structure should be random. In fact, neither possibility gains much support from natural examples (Fig. 2). Even among the low-\( \alpha \) trioctahedral micas, the 1M polytype seems to dominate.

That 20 and 2M, micas are indeed scarce in nature can surely be ascribed to the fact that most trioctahedral and dioctahedral micas have \( \alpha \) values that differ significantly from zero (Fig. 2). Under these circumstances, the lowest-energy polytype is 2M, or 1M, depending on the presence or absence, respectively, of corrugations in the surface defined by the basal oxygens. It is interesting to note however that the three 2M, lithian micas reported by Bailey (1984) all have \( \alpha \) values around 5°, and the one phengite 2M, in Figure 2 has a value of \( \alpha \) of approximately 11°! At present, we can only speculate about the causes for these anomalies.

The difference in the calculated energies for 2M, and 20 pyrophyllites (Table 5) deserves additional comment. In both of the model sets that include these polytypes, the 2M, polytype has a significantly lower energy than the 20 polytype. In the unmodified model set, the energy difference is 1.04 kJ/anion, whereas in the modified model set (\( \alpha = 0 \)), the difference is approximately twice as great, 2.06 kJ/anion. This discrepancy might not otherwise command much attention if both polytypes had higher energies than either 2M, or 1M under all circumstances. But when \( \alpha = 0 \) and \( \Delta \zeta > 0 \), the very low energy of the 2M, polytype hints at a special structural problem. Figure 4a shows the A-site coordination polyhedron in the 20 polytype under the conditions just stipulated, i.e., \( \alpha = 0 \) and \( \Delta \zeta > 0 \). The polyhedron is an orthorhombic parallelepiped with edges parallel to the 20 a, b, and c axes. Basal oxygens occupy the corners of the parallelepiped, and the A site is at the center. We shall refer to the O-O edge lengths as \( d_e \) (short), \( d_i \) (long), and \( d_r \). The short edge in the (001) face, \( d_e \), has a length equal to the shortest \( O_{basal}-O_{basal} \) distance. The edge length \( d_i \) equals \( \sqrt{3d_e} \); and \( d_r \), which is the shortest interlayer O-O separation, is approximately equal to \( d_e \) (\( d_i \approx d_r \)). The trace of the unit-layer mirror plane is shown on the (001) faces of the polyhedron. The four shortest interlayer O-O distances have the same length, \( d_r \). The next shortest interlayer distances are four in number, end-face diagonals each having length \( \sqrt{(d_i^2+d_r^2)} \). Other interlayer O-O distances are significantly longer. Figure 4b shows the A-site polyhedron for the 2M, polytype under the same conditions, \( \alpha = 0 \) and \( \Delta \zeta > 0 \). The polyhedron can be derived from the 20 A-site polyhedron by rotating one of the (001) faces 60° about the normal to (001). The (001) faces have the same dimensions as in the 20 polytype, \( d_r = (O-
Fig. 4. A-site coordination polyhedron in (a) the 2O polytype and (b) the 2M₂ polytype, when Δz > 0, and α = 0.

O\textsubscript{base} distance, and \( d_i = \sqrt{3}d_c \). In the 2M₂ polytype, the two shortest interlayer O-O separations are of length \( d_c \). The next shortest interlayer O-O separations are six in number, each having length \( \sqrt{d_c^2 + d_z^2} \). Other interlayer O-O distances are substantially longer. The eight A-O bond lengths are the same (\( \approx \sqrt{5}d_z/2 \)) in both 2M₂ and 2O polytypes! Recalling that a Coulomb electrostatic repulsive force varies inversely with the square of the interatomic distance, the sum of the repulsions due to the eight shortest interlayer O-O distances would be approximately 20% more for the 2O polytype than it would be for the 2M₂ polytype. The 2M₂ polytype should thus be more stable than the 2O polytype. The argument is analogous to the one offered by Thompson (1981; Radoslovich, 1959, 1960, Güven, 1971) for the preference of trigonal antiprismatic (octahedral) coordination over trigonal prismatic coordination.

**Anandite.** Table 6 reports the results of our calculations on anandite. The first model set that we constructed was predicted on the basis that Fe and Si were disordered on one of the two crystallographically distinct tetrahedral sites, as indicated by the structure refinement (Filut et al., 1985). The average structure was treated as a fair representation of what would be, in this case, a special kind of substitutional distortion. The energies were calculated for different Fe\textsuperscript{3+}-Si charge-orderings in which the bond lengths were left unmodified by DLS. One of the 1M structures has a significantly lower energy than any other structure. This suggests that the distortions represented by the average structure are not responsible for the observed 2O polytype.

In the second model set, the Si-O and Fe-O bond lengths were adjusted by DLS. For these calculations, two of the 2O structures (Pn2₁n and P112₁n) gave significantly lower energies than the other structures. This suggests that the actual structure may have short-range ordering, possibly consisting of domains of the crystallographically equivalent complexions (Abbott, 1984) of one or both of the low-energy configurations. The observed 2O polytype appears to be stabilized by high Δz and low α in conjunction with distortions caused by Fe-Si ordering.

**Muscovite.** Table 7 and Figure 5 present our most recent calculations involving DLS-adjusted OH-muscovite structures. Of interest here are the very different characteristics of the results for the two polytypes, 1M and 2M₂. The anomalously low energies for three of the 1M structures are due to unrealistically short DLS-modeled K-O distances. The K polyhedra are simply not comparable in the 1M and 2M₂, DLS-adjusted structures; hence the

**Table 6. Coulomb electrostatic energies for anandite, Ba(Mg,Fe)₃(Si,Fe\textsuperscript{3+})O₄(OH)S**

<table>
<thead>
<tr>
<th>Polytype</th>
<th>Atomic coordinates</th>
<th>Charge distributions</th>
<th>Energy (kJ/anion)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1M P2/m</td>
<td></td>
<td>2O 1M P2/m</td>
<td>-6038.87</td>
</tr>
<tr>
<td>2M₂ Pn2₁n</td>
<td></td>
<td>2O 2M₂ Pn2₁n</td>
<td>-6038.04</td>
</tr>
<tr>
<td>2O Pn2₁n</td>
<td></td>
<td>2O 2O Pn2₁n</td>
<td>-6039.29</td>
</tr>
<tr>
<td>2O P112₁n</td>
<td></td>
<td>2O 2O P112₁n</td>
<td>-6035.00</td>
</tr>
</tbody>
</table>

**Table 5. Coulomb electrostatic energies for pyrophyllite and talc model structures**

<table>
<thead>
<tr>
<th>End member</th>
<th>Model characteristics</th>
<th>1M Polype energies (kJ/anion)</th>
<th>2O Polype energies (kJ/anion)</th>
<th>2M₁ Polype energies (kJ/anion)</th>
<th>2M₂ Polype energies (kJ/anion)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>Δz = 0</td>
<td>-6391.72</td>
<td>-6392.28</td>
<td>-6392.28</td>
<td>-6392.28</td>
</tr>
<tr>
<td>OH</td>
<td>Δz = 0</td>
<td>-7002.48</td>
<td>-7000.74</td>
<td>-7002.59</td>
<td>-7001.78</td>
</tr>
<tr>
<td>OH</td>
<td>α = 0</td>
<td>-7069.36</td>
<td>-7069.00</td>
<td>-7051.89</td>
<td>-7053.04</td>
</tr>
<tr>
<td>F</td>
<td>Δz = 0</td>
<td>-6094.76</td>
<td>-6094.69</td>
<td>-6094.69</td>
<td>-6094.69</td>
</tr>
<tr>
<td>F</td>
<td>Δz = 0</td>
<td>-6095.67</td>
<td>-6095.43</td>
<td>-6095.43</td>
<td>-6095.43</td>
</tr>
<tr>
<td>OH</td>
<td>Δz = 0</td>
<td>-6680.80</td>
<td>-6680.77</td>
<td>-6680.70</td>
<td>-6680.77</td>
</tr>
<tr>
<td>OH</td>
<td>Δz = 0</td>
<td>-6681.67</td>
<td>-6681.39</td>
<td>-6681.39</td>
<td>-6681.39</td>
</tr>
</tbody>
</table>

**Note:** Boldface values indicate lowest-energy polytype.
structures do not meet the criteria we have established for a valid comparison. The calculated energies cannot therefore be used as a reliable guide to the relative stability of the $1M$ versus the $2M_1$ polytype. However, the K-O distances are similar in the four $1M$ structures, so these structures constitute a valid set for comparing the effects of different Al-Si orderings. Likewise, the K-O distances are similar in the twelve $2M_1$ structures; hence they too constitute a valid set for comparison. Problems with the modeling of the A-site geometry were not encountered in the other model sets.

The energies for the four Al-Si ordered $1M$ structures are very different ($\sigma = 126.91 \text{ kJ/anion}$), with three structures ($P_{2_1}$, $P_{1}$, $P_{7}$) having the very lowest energies of all of the $2M_1$ and $1M$ structures and the remaining $P_2$ structure having the very highest energy. The Boltzmann distribution law would suggest that a hypothetical $1M$ muscovite should be dominated by the $P_{2_1}$, $P_{1}$, and $P_{7}$ arrangements. The hypothetical structure would probably consist of small domains of the different Al-Si orderings and symmetrically equivalent orderings (Abbott, 1984), or it may consist of a mosaic of individual, differently ordered unit cells.

In contrast, the twelve $2M_1$ structures have very nearly the same energy ($\sigma = 2.48 \text{ kJ/anion}$). The Boltzmann distribution law suggests that the different Al-Si orderings would be more or less equally represented. The actual energy would be close to the average, which just happens to be somewhat less than the average for the $1M$ structures. That there are so many (12 plus symmetrically equivalent complexions, making 48 altogether) more or less equally accessible low-energy states suggests that it should be disordered (Giese, 1984). As for the $1M$ polytype, a hypothetical, disordered muscovite-$2M_1$ may consist of small domains of the different Al-Si orderings (Abbott, 1984), or it may be a mosaic of individual, differently ordered unit cells.

On closer examination of Table 7, it becomes evident (Fig. 5) that there is a bimodal distribution of $2M_1$ energies. For this reason, it is instructive to sort the 12 structures into subsets, each being characterized by one or more common features. There are four distinct unit-layer structures, identified as $31$, $32$, $33$, and $34$. The designations refer to the Al-occupied sites as they are labeled in Figure 5a. Note that, within the limits of the standard deviation, the average energy is the same for each of the unit-layer groups. Evidently, the intralayer distribution of Al and Si (within the constraints set up earlier) has no bearing on the bimodal distribution of energies and, because the four unit-layer structures are very different (in terms of the relative positioning of the Al atoms), essentially no bearing on the preference for the $2M_1$ polytype. The 12 structures can be sorted in another way, according to elements of the space groups. In combinations or individually, the symmetry elements $2$, $2_1$, $c$, and $n$ relate one unit layer to another and, hence, relate to the structure of the interlayer region. When sorted in this way (Table 7), the average energy and standard deviation for the group characterized by the $2_1$ axis—space groups $P2_1/n$, $P2_1/c$, $P2_1$, $P1$—is $-6615.15(2.96) \text{ kJ/anion}$.

Fig. 5. (a) Labeling of tetrahedral sites in reference to Table 7. (b) Histogram of energies for 12 Al-Si orderings in muscovite-$2M_1$. Note: Values in parentheses represent one standard deviation. * Structures that obey Güven's rule.
† Structures that violate Güven's rule.
\[ \text{Intralayer relationships: muscovite-}2M_1, \]

\[ \begin{align*}
\text{Structures that obey Güven's rule} & : -6615.64(2.24) \\
\text{Structures that violate Güven's rule} & : -6616.26(2.41)
\end{align*} \]

\[ \text{Interlayer relationships: muscovite-}2M_1, \]

\[ \begin{align*}
\text{Structures with } c \text{ glide} & : -6615.57(2.30) \\
\text{Structures with } n \text{ glide} & : -6615.43(2.68) \\
\text{Structures with } 2 \text{ axis} & : -6613.96(2.13) \\
\text{Structures with } 2_1 \text{ axis} & : -6618.24(0.14)
\end{align*} \]

Table 7. Coulomb electrostatic energies for muscovite

<table>
<thead>
<tr>
<th>Structure</th>
<th>$T-T'$</th>
<th>Energy (kJ/anion)</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{2_1}$</td>
<td>$Al-Al'$*</td>
<td>-6689.73</td>
<td></td>
</tr>
<tr>
<td>$P_{1}$</td>
<td>$Al-Al'$*</td>
<td>-6664.35</td>
<td></td>
</tr>
<tr>
<td>$P_{2}$</td>
<td>$Al-Al'$*</td>
<td>-6682.20</td>
<td></td>
</tr>
<tr>
<td>$P_{2_1}$</td>
<td>$Al-Al'$*</td>
<td>-6382.20</td>
<td></td>
</tr>
<tr>
<td>$P_{c}$</td>
<td>$Al-Al'$</td>
<td>-6617.59</td>
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</table>

Muscovite-1M

Note: Values in parentheses represent one standard deviation.

Structures that obey Güven's rule.
† Structures that violate Güven's rule.
2. The calculations on pyrophyllite and talc support Thompson's (1981; Radoslovich, 1959, 1960; Güven, 1971) proposal regarding the scarcity of $2M_2$ and $2O$ polytypes for micas with rotated tetrahedra ($\alpha > 0$). This accounts for the vast majority of trioctahedral and dioctahedral micas (Fig. 2).

6. We suggest that the disordering of Al and Si in muscovite and biotite is subject to certain rules (Abbott, 1984; Abbott et al., 1986), chief among which are (a) the principle of aluminum avoidance (Sanz and Serratosa, 1984; Sanz et al., 1986; Herrero et al., 1985; Herrero, 1987) and (b) a constant ratio of Al to Si in all tetrahedral sheets (Abbott, 1984). On this basis, there are four crystallographically reasonable ordered unit-layer structures for $1M$ and $2O$ polytypes and four different ordered unit-layer structures for $2M_1$ and $2M_2$ polytypes. In a given biotite or muscovite model set, the lowest-energy Al-Si orderings are consistently the ones with the most evenly distributed tetrahedral Al. That is, the most favorable Al-Si orderings maximize the closest Al-Al separations. This is consistent with the findings of Sanz and Serratosa (1984), Sanz et al. (1986), Herrero et al. (1985), and Herrero (1987). In $1M$ and $2M_2$ polytypes, Al-Si orderings consistent with a $2_1$ axis parallel to $b$ are especially favorable. The relationships are not as clearcut for hypothetical $1M$-dioctahedral structures, though the tendency appears to be the same.
7. We support Giese's (1984, 1986) explanation for the disordering of Al and Si in muscovite. There are many Al-Si ordering schemes with very nearly the same low energy. According to the Boltzmann distribution law, the different Al-Si arrangements would be more or less equally represented in the real structure.

8. Güven's (1971) rule concerning the relative positioning of tetrahedral Al atoms on opposite sides of the octahedral sheet does not seem to be important in the energetics of micas. By all indications, the effect is minimal.

9. Energy calculations for the 2M, dls-adjusted OH-muscovite structures show that the ordering of Al and Si, subject to the constraints cited above, has little apparent influence on the energy attributable to the internal structure of the unit layer, but may have considerable influence on the energy attributable to the interlayer region. Hence, for 2M, structures, the interlayer Al-Al separations are more important than the intralayer Al-Al separations. By analogy, the interlayer relationships in 1M polytypes are probably more important than the intralayer relationships.

10. For the purpose of discriminating among the structures of a model set, as defined here, the use of the Coulomb electrostatic energy alone is justifiable. If a set of structures to be compared can be manufactured in such a way that the nearest-neighbor interatomic distances and bond angles are the same in all of the structures and hence the structures differ only in the articulation of a fixed set of polyhedral units, then the short-range repulsive energy and van der Waals energy will not vary significantly from one structure to another. Under these circumstances, differences in the cohesive energies will be due almost entirely to differences in the long-range Coulomb electrostatic interactions. The method is potentially very powerful in discriminating between structures that differ only in the ordering and articulation of a fixed set of polyhedral units. The effectiveness of the method depends on the strategy used in the design of the comparison and the skill in manufacturing the model sets. The approach is a natural extension of Hazen's (1985; Hazen and Finger, 1982) polyhedral approach to comparative crystal-chemistry.

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