American Mineralogist, Volume 72, pages 949–958, 1987

Positional disorder of A-site cations in *C*2/*M* amphiboles: Model energy calculations and probability studies

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ABSTRACT

Positional disorder of cations occupying the A sites of *C*2/*m* amphiboles has been modeled using structure-energy minimization techniques. Model energy calculations show that, relative to a tremolite end member, local charge deficiency on the T, M4, or O3 sites or charge excess on the M2 sites due to cation substitution will cause cations occupying the A site to assume positions significantly different from the 2*b* (2/*m*) special position. Calculations suggest that when a local charge configuration in the second-nearest neighbors of the A-site cation can be related by a symmetry element or combination of elements, the position of the A-site cation that results in minimum energy lies on that element or combination of elements, either 2*b* (2/*m*), 4*g* (2), or 4*i* (*m*), whereas a locally asymmetric charge configuration will favor the A-site cation to occupy a general position, 8*j*. Positional disorder may also be caused by different A-site cation species occupying distinctly different positions. K atoms need not be constrained to the mirror plane. Limiting-case probability calculations combined with the above conclusions suggest that for both richterite and edenite, the most probable position for the A-site cation is the general position, 8*j*, although in a significant fraction of cases, the A-site cation will occupy the 4*g* (2), 4*i* (*m*), or 2*b* (2/*m*) special positions.

INTRODUCTION

The position of the A-site cation in *C*2/*m* amphiboles, a major class of rock-forming minerals, has been a subject of debate. Because most naturally occurring *C*2/*m* amphiboles are chemically complex and simple end members are difficult to synthesize, the response of the A-site cation to various chemical substitutions remains poorly understood. Published structure refinements of *C*2/*m* amphiboles that constrain the A-site cations to the special position 2*b* (2/*m*) result in large *R* factors and an unreasonably large isotropic temperature factor for the A-site cation, on the order of 6 Å^2. Residual peaks displaced off the A-site special position (ASSP) on Fourier difference maps have been considered evidence for positional disorder (Papike et al., 1969; Hawthorne and Grundy, 1973a, 1973b; Cameron et al., 1983). This disorder has been interpreted as resulting from the nature of the O3 species (Gibbs and Prewitt, 1966), the nature of the A-site species (Papike et al., 1969; Hawthorne and Grundy, 1978), the fraction of Al substituting into either the T1 and/or the T2 sites (Hawthorne and Grundy, 1977), the fraction of 3+ and 4+ cations and their site preference in the octahedral strip (Hawthorne and Grundy, 1973a), and the fraction of Na on the M4 site (Cameron et al., 1983).

The contents of the A sites have been proposed to have direct effects on the stability of the mineral. Amphiboles with fully occupied A sites are stabilized at higher pressures and temperatures relative to those amphiboles with unoccupied A sites (Binns, 1965; Cooper and Lovering, 1970; Spear, 1976; Docka and Berg, 1980; Thompson, 1981). The extent of an A-site–filling substitution, ${}^{A}\mathrm{Na}\,{}^{VI}\mathrm{Al} = {}^{A}\square\,{}^{IV}\mathrm{Si}$, determines the proposed miscibility gap between tremolite-actinolite and hornblende-pargasite. Explaining and predicting such effects require an accurate description of A-site cation behavior in response to changes in that cation's immediate environment. For example, some thermodynamic calculations of amphibole energetics are dependent on approximations of A-site positional disorder (Westrich and Holloway, 1981; Wes-

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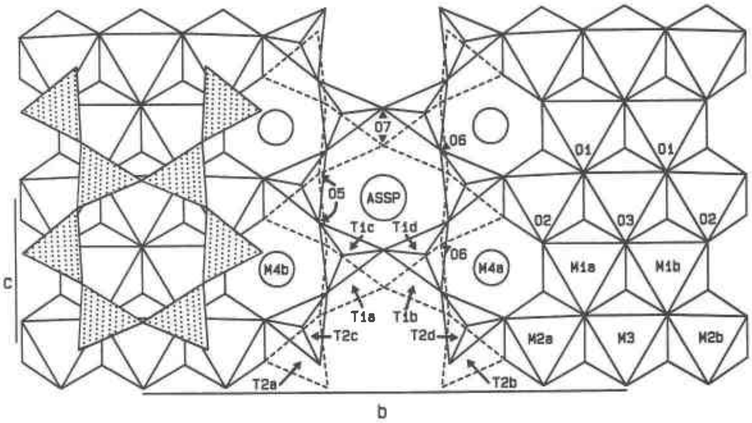

Fig. 1. *C2/m* amphibole structure projected down **a***. Cation positions are labeled for the 42-atom asymmetric unit (see text).

trich and Navrotsky, 1981; Graham and Navrotsky, 1986).

We have modeled the A-site cation position in different local environments using structure-energy minimization techniques. Results of structure-energy modeling are most readily interpreted when applied to ordered structures. We do not claim that our results are directly applicable to natural amphiboles. Rather we suggest that if the A-site cation position responds to chemical changes in second-nearest neighbors in our models, then the behavior of A-site cations in chemically complex and substitutionally disordered amphiboles may in part be predicted from our results. Structure refinements of these amphiboles may then be more accurately interpreted. The modeling is advantageous in that we can consider simple end-member compositions, thereby eliminating the problem of multiple substitutions.

A-SITE ENVIRONMENT

The A site lies within a large cavity formed by two opposing pseudohexagonal rings of six silicate tetrahedra (Fig. 1) and between two "I-beam" units. The A-site cation has 18 second-nearest neighbors: eight T1, four T2, four M4, and two M2 cations.

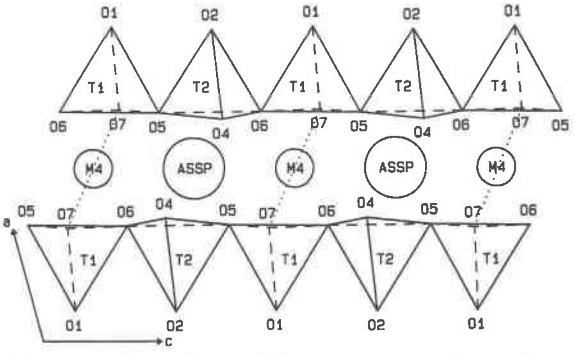

Fig. 2. *C2/m* clinoamphibole structure projected down **b** showing two A sites, their local configurations, and the offset of the tetrahedral chains due to the 2-fold axis.

The A-site cation is coordinated by three of the unique oxygens of the tetrahedral rings: O5, O6, and O7 (Fig. 2). The multiplicity of the ASSP symmetry (2/*m*) is four, and the coordination polyhedron is defined by a total of 12 oxygens. The O3 anion, either O, F, or Cl, is positioned at the coincident vertices of the two M1 and the M3 polyhedra of the octahedral strip, and is centered above and below each tetrahedral ring. In OH-bearing amphiboles, H^+ bonds to the O3 oxygen; the OH bond is approximately 0.9 Å long and orthogonal to the octahedral strip (Papike et al., 1969; Hawthorne and Grundy, 1976), extending into each tetrahedral ring.

The chemical environment of the A site is potentially dependent on any substitution that can alter the stoichiometry of the amphibole. Starting with the standard tremolite end member, substitutions that either add or subsequently change an A-site cation are of foremost interest. Substitutions that alter the nearest or second-nearest neighbors of the A-site cation are also important, i.e., a substitution involving the O3 anion or the T, M4, and the M2 cations. Substitutions that alter only the M1 or M3 sites of the octahedral strip are of substantially less interest. The simplest chemical substitutions important to the A-site cation are as follows: (1) ${}^{A}\mathrm{Na}{}^{IV}\mathrm{Al} = {}^{A}\square{}^{IV}\mathrm{Si}$ (edenite), (2) ${}^{A}\mathrm{Na}{}^{M4}\mathrm{Na} = {}^{A}\square{}^{M4}\mathrm{Ca}$ (richterite), (3) ${}^{A}\mathrm{K} = {}^{A}\mathrm{Na}$, (4) ${}^{O3}\mathrm{F}\square = {}^{O3}\mathrm{OH}$ (fluor-hydroxyl), (5) $\square = H^+$-($\mathrm{Fe}^{3+}\mathrm{O} = \mathrm{Fe}^{2+}\mathrm{OH}$) (oxy-hydroxyl), (6) ${}^{VI}R^{3+}\,{}^{IV}\mathrm{Al} = {}^{VI}R^{2+}$-${}^{IV}\mathrm{Si}$ (Tschermak, ferri-tk, Ti-tk, etc.).

These substitutions can be classified into three groups: cation-additive substitutions (1 and 2); cation-modifier substitutions (3); and environment-modifier substitutions (4, 5, and 6).

CALCULATIONS

Structure energy was calculated for a *C2/m* amphibole structure as a function of the A-site cation position. All of the energy calculations and minimizations were performed using the computer program WMIN (Busing, 1981). Short-range (repulsive) energies for anion-cation and anion-anion interactions were approximated using Born's

TABLE 1. Minimum-energy A-site positions and corresponding energies for *C* 2/*m* amphiboles

	Coordinates of minimum*			Coordinates of minimum**			Total displacement from ASSP	Energy
Composition of amphibole	*x*	*y*	*z*	*i*	*j*	*k*	(Å)	(kJ/mol)
				Hawthorne structure				
$NaCa_2Mg_5{}^{T1}AlSi_7O_{22}(OH)_2$	−0.022	0.533	−0.012	−0.210	0.601	−0.009	0.637	−107922
$NaCa_2Mg_5{}^{T1}AlSi_7O_{22}F_2$	−0.038	0.524	−0.058	−0.364	0.437	−0.210	0.606	−104060
$NaCa_2Mg_3Al_2{}^{T1}AlSi_7O_{22}O_2$	−0.052	0.519	−0.084	−0.500	0.336	−0.310	0.677	−110227
$NaCa_2Mg_5{}^{T2}AlSi_7O_{22}F_2$	−0.028	0.535	−0.063	−0.263	0.628	−0.266	0.731	−103981
$Na^{M4}NaCaMg_5Si_8O_{22}(OH)_2$	0.000	0.540	0.000	0.000	0.718	0.000	0.718	−110562
$Na^{M4}NaCaMg_5Si_8O_{22}F_2$	0.000	0.530	0.000	0.000	0.536	0.000	0.536	−106730
$Na^{M4}NaCaMg_3Al_2Si_8O_{22}O_2$	0.000	0.523	0.000	0.000	0.419	0.000	0.419	−113027
$KCa_2Mg_5{}^{T1}AlSi_7O_{22}(OH)_2$	−0.027	0.514	−0.050	−0.254	0.253	−0.200	0.410	−107809
$KCa_2Mg_5{}^{T1}AlSi_7O_{22}F_2$	−0.040	0.511	−0.075	−0.385	0.195	−0.297	0.524	−103964
$KCa_2Mg_3Al_2{}^{T1}AlSi_7O_{22}O_2$	−0.049	0.508	−0.090	−0.415	0.137	−0.354	0.607	−110127
$KCa_2Mg_5{}^{T2}AlSi_7O_{22}F_2$	−0.036	0.513	−0.071	−0.346	0.238	−0.285	0.508	−103876
$K^{M4}NaCaMg_5Si_8O_{22}(OH)_2$	0.000	0.516	0.000	0.000	0.282	0.000	0.282	−110449
$K^{M4}NaCaMg_5Si_8O_{22}F_2$	0.000	0.512	0.000	0.000	0.226	0.000	0.226	−106621
$K^{M4}NaCaMg_3Al_2Si_8O_{22}O_2$	0.000	0.519	0.000	0.000	0.195	0.000	0.195	−112926
				Double cells: $Na^{M4}NaCaMg_5Si_8O_{22}F_2$				
(Configuration 1—Site 1)	0.004	0.492	0.015	0.042	−0.145	0.069	0.165	−213455
(Configuration 1—Site 2)	0.000	0.504	0.003	0.003	0.065	0.013	0.064	
(Configuration 2—Site 1)	0.023	0.496	0.078	0.216	−0.070	0.013	0.422	−213397
(Configuration 2—Site 2)	−0.023	0.503	−0.078	−0.210	0.047	−0.358	0.417	
				Cameron structure				
$Na^{M4}NaCaMg_5Si_8O_{22}F_2$	0.000	0.522	0.000	0.000	0.394	0.000	0.394	−107612
$K^{M4}NaCaMg_5Si_8O_{22}F_2$	0.000	0.509	0.000	0.000	0.161	0.000	0.161	−107558

* *x, y, z* coordinates refer to actual unit-cell dimensions for each different structure; origin: M3. Hawthorne structure: $a = 9.863$, $b = 18.048$, $c = 5.285$ Å, $\beta = 104.79°$. Cameron structure: K-F-richterite—$a = 9.944$, $b = 17.972$, $c = 5.263$ Å, $\beta = 104.79°$; Na-F-richterite—$a = 9.824$, $b = 17.952$, $c = 5.258$ Å, $\beta = 104.22°$. See text for references.

** *i, j, k* are in ångströms using the ASSP as an origin. $i = \mathbf{a}^*$, $j = \mathbf{b}$, $k = \mathbf{c}$.

exponential form (Kittel, 1976, p. 88), and values for λ and ρ in the Born equation were taken from Post and Burnham (1986). Contributions of H^+ to short-range energies were neglected. Energy was minimized using Newton's method.

Input to the calculations included atomic positional parameters for the asymmetric unit of a *C*2/*m* amphibole base structure. We chose to use the structure reported by Hawthorne and Grundy (1976) primarily because they reported H^+ positions. Because of the problems inherent in modeling OH bonding, using this structure as input should provide the greatest insight regarding A-site cation positions for OH-bearing amphiboles. Only full integral charges were used in our calculations. To model the effect of chemical substitution on the position of the A-site cation, we reduced the symmetry of the structure to *C*1, resulting in a 42-atom asymmetric unit (40 in the case of fluor- or oxy-amphiboles). Reduction of symmetry permitted greater chemical variability in the local environment of the A-site cation and eliminated the point symmetry of the ASSP, thus permitting migration of the A-site cation position. *C*-centering was not removed because it does not operate on the local configuration of any given A site. Sites in Figure 1 are labeled to designate uniqueness in the 42-atom asymmetric unit cell. Reasonable end-member formulae consistent with these constraints were derived from a starting tremolite formula, by combination with the various substitutions discussed above, and used as input compositions (Table 1).

Base structures were chemically modified by changing only ion charges and short-range potentials. Since our energy-minimization procedure permits only A-site cation coordinates to vary, we have implicitly assumed that chemical substitutions at the T, M4, and O3 sites will not themselves alter the structure significantly to further affect minimum-energy A-site cation positions. Such an assumption is probably valid for O3 substitutions, less valid for A-site cation substitutions, and least valid for M4 and T substitutions. We have tested this assumption for end-member F-richterite, and our assessment is included with the results discussed in the following section.

MODELING THE A-SITE POSITION FOR AN ORDERED AMPHIBOLE: JOESMITHITE

We have tested our ability to model A-site positions for an ordered structure by determining the position of the A-site cation that results in minimum structure energy for the ordered clinoamphibole joesmithite. The structure of joesmithite can be considered topologically identical to a *C*2/*m* amphibole. In joesmithite, Be and Si are fully ordered on four T sites per asymmetric unit, with both Ca and Pb substituted on the A site. Be-Si ordering transforms the mirror to an *a* glide, the cell becomes primitive, and the space group is *P*2/*a*. The A-site cation in joesmithite is displaced along the 2-fold axis from ¼,¼,0 (the position equivalent to the ASSP in *C*2/*m* amphiboles) toward the Be T sites.

Calculation of the energy minimum was performed in

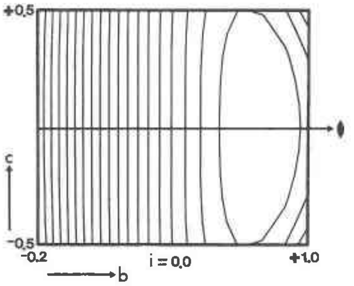

Fig. 3. Energy map of the plane ⊥**a*** at $x = 0$ through the A-site cavity for joesmithite. Axes and dimensions in Å as labeled. Contour interval: 21 kJ/mol.

the same manner as those for *C2/m* amphiboles. The input base structure was taken from Moore (1969) and Hawthorne (pers. comm., 1980). We calculated H^+ positions by assuming an OH bond length of 0.9 Å and orthogonality between the OH bond and the octahedral strip. The symmetry was reduced to *Pa* to remove the point symmetry of the ASSP and resulted in an 84-atom asymmetric unit. The idealized formula ${}^{A}CaCa_2Mg_3Al_2Si_6Be_2O_{22}(OH)_2$ was used as input. This formula met the constraints imposed by *Pa* symmetry and the lack of short-range pair potentials for transition metals (Post and Burnham, 1986), yet represented the real composition as closely as possible.

The structure refinement of joesmithite (Moore, 1969) places the A-site cation on the 2-fold axis at ¼,0.284,0, approximately 0.6 Å from the ASSP. Our calculations also place the minimum-energy cation position on the 2-fold axis, but at ¼,0.295,0, approximately 0.8 Å from the ASSP. An energy map (Fig. 3) shows the variation of structure energy with the A-site cation position. Our results do not exactly duplicate the position reported by Moore. We suggest that the results are quite reasonable, since we used Ca in place of Pb and, in this case, also assumed a H^+ position. Furthermore, results presented later in this paper suggest that there should be some degree of positional disorder present in joesmithite due to A-site occupation by two distinctly different species, Ca and Pb.

A-SITE POSITIONS FOR CHEMICALLY SUBSTITUTED TREMOLITE DERIVATIVES

Coordinates of the A-site cation positions that resulted in minimum structure energy and corresponding energies calculated for various compositions derived from the tremolite base structure are presented in Table 1. Energy maps of planes ⊥**a*** that intersect the cation position of minimum energy are given in Figures 4, 5, and 6. In the following discussion, most minimum-energy cation positions will be compared to the ASSP. The terms "right and left" and "above and below," when not specifically referred to any other site, are relative to the ASSP. References to the mirror plane and 2-fold axis through the ASSP are for spatial orientation only: because of chemical disorder, these elements do not rigorously exist in any of the model structures.

Cation-additive substitutions: T1-T2-M4

Results given in Table 1 and Figure 4 show the effect of A-site cation-additive substitutions. Models involving these substitutions include edenite, in which the charge-balancing cation, Al, can be substituted on either T1 or T2 sites, and richterite, in which the charge-balancing cation, Na, is substituted on M4. In all models, the site selected for the charge-balancing cation substitution was to the right of the ASSP in the direction of +**b.** In all cases, the positions given in Table 1 and Figure 4 show that the minimum-energy A-site cation position occurs between the local charge deficiency and the ASSP.

For T-site substitutions, Al was substituted in the lower ring, T1b or T2b in Figure 1. In these cases, minimum-energy cation positions occur below the plane ⊥**a*** at $x = 0$ (Figs. 4a and 4b). The minimum-energy A-site cation position for a T1 substitution is lower and to the left of the A-site cation position for a T2 substitution, reflecting the differences in location between T1 and T2 in the base structure, where T1b is to the left of, and approximately 0.1 Å lower than T2b. The distance between the ASSP and the minimum-energy A-site position in the **c** direction is nearly the same for a T1 substitution as for a T2 substitution (Figs. 4a and 4b, Table 1). This similarity in position can be explained when one considers that the

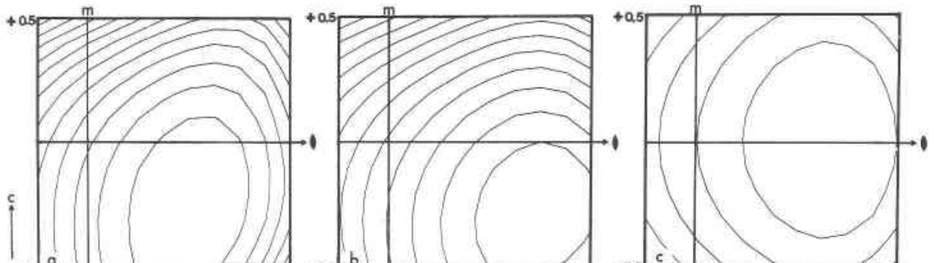

Fig. 4. Energy maps of planes ⊥**a*** through the A-site cavity illustrating changes in the minimum position due to varying cation-additive substitutions. (a) $NaCa_2Mg_5{}^{T1}AlSi_7O_{22}F_2$; (b) $NaCa_2Mg_5{}^{T2}AlSi_7O_{22}F_2$; (c) ${}^{A}Na^{M4}NaCaMg_5Si_8O_{22}F_2$. Axes, dimensions, and level as labeled in Å. Contour interval: 8.4 kJ/mol. *i* = position of plane along **a***.

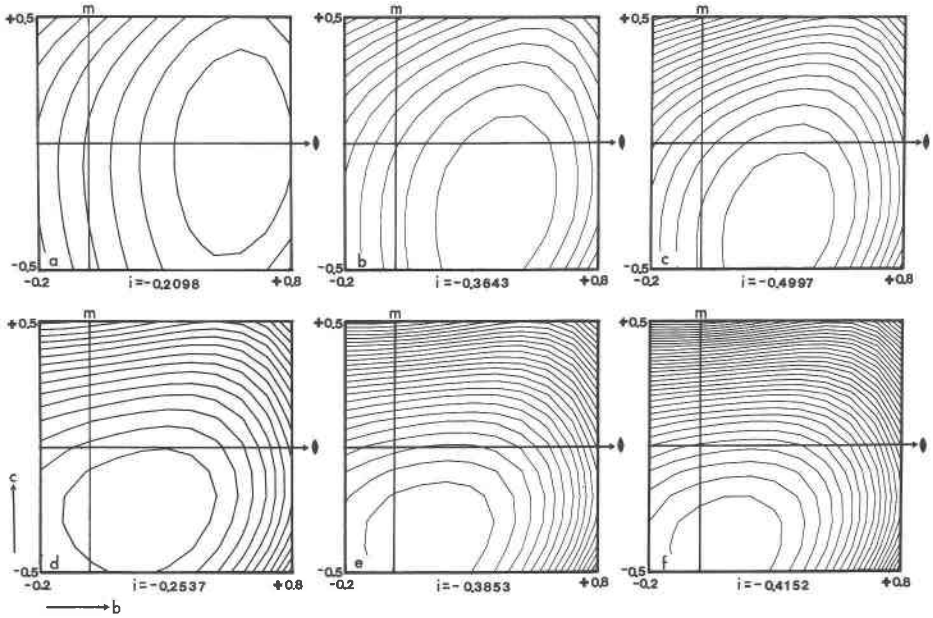

Fig. 5. Energy maps of planes ⊥**a*** through the A-site cavity illustrating changes in the minimum position due to varying cation-modifier and environment-modifier substitutions. (a) $NaCa_2Mg_5{}^{T1}AlSi_7O_{22}(OH)_2$; (b) $NaCa_2Mg_5{}^{T1}AlSi_7O_{22}F_2$; (c) $NaCa_2Mg_3Al_2{}^{T1}AlSi_7O_{22}O_2$; (d) $KCa_2Mg_5{}^{T1}AlSi_7O_{22}(OH)_2$; (e) $KCa_2Mg_5{}^{T1}AlSi_7O_{22}F_2$; (f) $KCa_2Mg_3Al_2{}^{T1}AlSi_7O_{22}O_2$. Axes, dimensions, and level as labeled in Å. Contour interval: Na in A site—8.4 kJ/mol; K in A site—21 kJ/mol. i = position of plane along **a***.

mean distance along **c** of the two nearest T1b cations is nearly the same as that of the nearest T2b cation (Fig. 1). Comparing the energy maps in Figure 4 to Figure 1, it is apparent that in response to the edenite substitution, the migration of the A-site cation is primarily limited by the O6 and less so by the O5 position in the lower ring. The energies presented in Table 1 are consistent with the observation that Al prefers to substitute into T1 relative to T2.

When considering the richterite substitution, note that the M4 sites lie on 2-fold axes in a plane ⊥**a*** at $x = 0$. The ASSP also lies in this plane, and the M4 sites are symmetrical about the ASSP (Fig. 1). In our models, Na was substituted on M4a (Fig. 1), such that Na and Ca alternate across the mirror plane but not along **c**. The minimum-energy cation position lies in the plane ⊥**a*** at $x = 0$ and is displaced along the 2-fold axis toward the mean charge deficiency on the M4 sites (Fig. 4c). In this case, migration of the cation position is limited by the two O5 oxygens in the upper and lower silicate rings, closest to the charge deficiency (Fig. 1).

Cation-modifier substitution: K-Na

Figure 5 depicts the effect of Na-K substitution on the A site. Comparison of Figures 5a and 5d, Figures 5b and 5e, Figures 5c and 5f, and results given in Table 1 shows that substitution of K for Na on the A site moves the minimum-energy cation position closer to the ASSP due to the inherently larger size of the K cation. Provided that the pair potentials used to describe K-O interactions are reasonable, our results show that the K atom prefers not to lie on the mirror plane, as opposed to suggestions of numerous authors. The calculations also suggest that if both Na and K partially occupy the A site, positional disorder will be evident in the refinement of such a structure.

Environment-modifier substitution: O3-M2

Comparison of Figures 5a, 5b, and 5c, and Figures 5d, 5e, and 5f shows the effect of the O3 anion, and for OH-amphibole, the associated H^+. For an edenite composition, positioning of F^- or O^{2-} on the O3 site allows the minimum-energy cation position to migrate closer to the charge deficiency on T1b, primarily by motion along **a***. Interaction with H^+ pushes the minimum-energy cation position up closer to the plane ⊥**a*** at $x = 0$, and, because of interaction with O6, farther to the right of the ASSP. The minimum-energy cation positions given in Table 1 for a richterite are also affected by O3 substitutions. The minimum-energy cation position remains constrained to the 2-fold axis because the substitutions occur on sites that are symmetrically related by the axis. For OH-bearing richterite, the minimum-energy cation position is closer to the substituted M4a sites and farther from the O3 sites and the ASSP than that of the F-richterite. The minimum-energy cation position of the F-richterite is in turn closer to the M4 sites and farther from the O3 sites and the ASSP than that of the oxy-richterite. Calculations on a richterite composition with a mixed O3 site ($NaNaCaMg_5Si_8O_{22}F(OH)$ or $NaNaCaMg_4AlSi_8O_{22}O(OH)$ would show a minimum-energy cation position either above or below the plane ⊥**a*** at $x = 0$, depending on

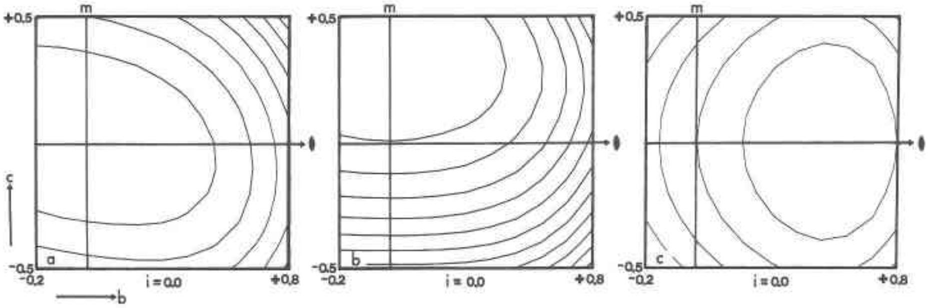

Fig. 6. Energy maps of planes ⊥**a*** through the A-site cavity for the 84-atom asymmetric unit calculations, Na^{M4}NaCaMg$_5$Si$_8$O$_{22}$F$_2$. (a) Na and Ca alternate across both the mirror plane and along **c** in the M4 sites. (b) Na and Ca alternate only along **c.** (c) Na and Ca alternate only across the mirror plane. Axes, dimensions, and level as labeled in Å. Contour interval: 8.4 kJ/mol. *i* = position of plane along **a***.

whether the O3 site with the absent H$^+$ or charge deficiency was above or below the ASSP.

The results of the richterite calculations suggest that substitutions on M2, which we have not modeled because of increased complexity, would have an effect on the A-site cation position. If Al substitutes on an M2 site, we would expect the minimum-energy A-site cation position to be driven away from that M2, with a displacement somewhat less than for M4 substitutions, since M2 is farther from the ASSP than is M4. This substitution is found in tschermakite, and presumably common Ca-amphiboles with both edenite and tschermakite components are likely to exhibit A-site positional disorder from combinations of these displacements.

84-atom asymmetric units

Because of the symmetry of the M4 sites about the ASSP, our richterite models constrain minimum-energy cation positions to lie on the 2-fold axis through the ASSP. Noting this bias, we have eliminated these constraints by doubling *c,* thereby generating an 84-atom asymmetric unit with two unique A sites. We modeled two configurations of M4 sites: (1) Na and Ca alternate along **c** and across the mirror; and (2) Na and Ca alternate only along **c**, but are equivalent across the mirror. Calculations required varying positional coordinates for both A sites in the asymmetric unit; two cation positions resulting in minimum energy for each configuration are given in Table 1. Energy maps in Figure 6 are for one site in each configuration.

For both configurations, the two minimum-energy A-site cation positions (Table 1) are displaced slightly along **b** in opposite directions. Because of the symmetry of the Na-Ca distributions, both cases ought to yield positions at *y* = ½, and these displacements along **b** must be due to electrostatic interactions between the two neighboring A-site cations themselves. The energy maps in Figure 6 show that the energy wells for the two configurations are shallow along **b** and imply that whereas exact positions may shift somewhat due to interaction between adjacent A-site cations, the differences in energy due to the shift are negligible.

Apart from the differences in *y* for the two positions, there are two important results to note from the double-cell models. For configuration 1, the energy well is very shallow and is centered on the ASSP (Fig. 6a). For configuration 2, the energy well is less shallow, is centered on the mirror plane, and is symmetrical across the mirror plane (Fig. 6b). Also for configuration 2, for both A-site cation positions, displacements along **a** and **c** relative to the ASSP are essentially equal, but opposite in sign. These displacements are due to the difference in configuration of the Na atoms for the two sites relative to the cant of the pseudohexagonal rings, not to interactions between adjacent A-site cations. For both sites, limits on the migration of the cation position are imposed by the O7 oxygens. For site 1, the minimum-energy cation position is pushed up in a direction ‖**a** by the O7 in the lower ring, whereas for site 2, the position is pushed down in a direction ‖**a** by the O7 in the upper ring (Fig. 2).

We have not modeled any double cells for edenite. Although these calculations would be of interest, doubling the cell results in 16 nonequivalent T sites and a prohibitively large number of configurational permutations. Constraining Al occupancy to the energetically favorable T1 site still allows eight possible configurations. We suggest that the very simple results we have presented thus far should permit reasonably certain prediction of the most energetically favorable A-site position for any local configuration of interest.

Effect of changing the input base structure

We have used a single base structure for all our models, excepting joesmithite. There is, however, no question that various chemical substitutions affect the atomic positional coordinates of the *C2/m* structure. Cameron and Gibbs (1973) compared the structures of the F- and OH-tremolites and have shown that a substitution of F for OH decreases *a* and *b,* as well as the T1–T1 distance across the mirror plane. From these trends one might assume that the space accessible to the A-site cation also decreases. However, the displacement of both O5 and O6 oxygens from the ASSP actually increases slightly with the F-OH substitution, whereas the O5–O6 distance between upper and lower silicate chains decreases slightly. We suggested previously that the O6 oxygens limit the migration of the A-site cation in edenite. Given this, changes in the structure due to substitution of F for OH should cause the minimum-energy cation position to migrate slightly out from the ASSP in a plane ⊥**a***.

Comparison of the F-tremolite structure (Cameron and Gibbs, 1973) with that of F-richterite (Cameron et al., 1983) shows that the effect of the richterite substitution is to greatly increase *a,* decrease *b,* and slightly decrease *c.* More importantly, the M4–O bonds increase in length, particularly M4–O5. The distance between O5 and the ASSP is significantly less in F-richterite than in F-tremolite. In the single-cell richterite calculations, the O5 oxygens limit the migration of the minimum-energy cation position. The structural changes produced by the richterite substitution should move the minimum-energy A-site cation position closer to the ASSP. Minimum-energy A-site cation positions calculated using the low-temperature structure refinements reported by Cameron et al. (1983) for ^{A}Na- and ^{A}K-richterite (Table 1) confirm the above. Energy maps for both the Hawthorne and Grundy (1976) and Cameron et al. (1983) ^{A}Na-F-richterite structures (Figs. 7a and 7b) depict the change in shape of the energy well due to the structural changes induced by the substitution. This change in shape is also due to changes in the positions of the O5 oxygens. In richterite, the O5 positions are not only closer to the ASSP relative to a tremolite structure, but the distance between the two O5 oxygens related by the 2-fold axis is less. The change in the minimum-energy cation position is sensitive to changes in O5 positions along **b,** whereas it appears that the steepening of the well along **c** is attributable to the change in distance between O5 positions across the 2-fold axis.

Cameron et al. (1983) compared structures of ^{A}Na-F- and ^{A}K-F-richterite and found that the structure is expanded for a ^{A}K-bearing structure. However, the effect on the minimum-energy cation position due to this expansion is small compared to the effect on the position due to the difference in size between Na and K, as can be seen from the results in Table 1 for the Cameron structures. Although the ^{A}K-F-richterite unit cell is larger than that of ^{A}Na-F-richterite, the minimum-energy cation position for ^{A}K-richterite is still much closer to the ASSP than that of ^{A}Na-richterite.

For both ^{A}Na-F- and ^{A}K-F-richterites, changing the input base structure to those reported by Cameron et al. (1983) affects the minimum-energy cation positions. More importantly, the difference between minimum-energy cation positions of different base structures but the same chemistry is significantly less than the displacement of the minimum-energy cation position from the ASSP.

As Ghose (1965) predicted, and Hawthorne and Grundy (1973b) and Papike et al. (1969) have subsequently shown, the tetrahedra rotate and the O5–O6–O5 angle decreases with increasing Al occupancy of T sites. Rotation of the tetrahedra causes the O5 position to move away from the ASSP, whereas the O6 position moves closer to the ASSP. The effect of this structural change on the minimum-energy cation position was not tested. Based on our previous results, we predict that as increased rotation occurs, the minimum-energy cation position will migrate in a direction approximately parallel to the direction of the change in the O5 position.

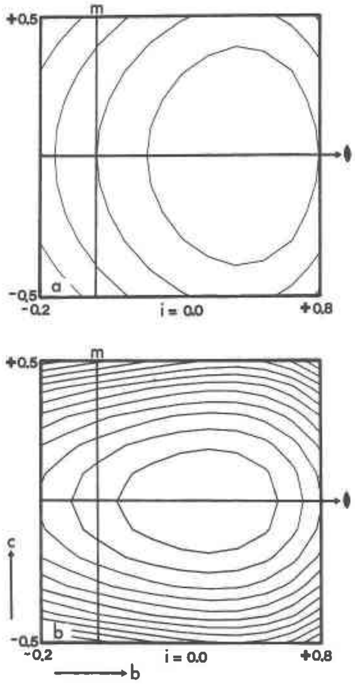

Fig. 7. Energy maps of planes ⊥**a*** through the A-site cavity for the composition $Na^{M4}NaCaMg_5Si_8O_{22}F_2$. (a) Hawthorne and Grundy (1976) structure; (b) Cameron et al. (1983) structure. Axes, dimensions, and level as labeled in Å. Contour interval: 8.4 kJ/mol. *i* = position of level along **a***.

APPLICATIONS TO REAL AMPHIBOLE STRUCTURES

Our results suggest that a locally symmetric charge configuration will cause the minimum-energy cation position to occur on a special position, and likewise an asymmetric charge configuration results in the minimum-energy cation position occurring on a general position. Thus, in the edenite model, where the charge configuration in the T sites is asymmetric, the minimum-energy cation position occurs on a general position. For the various richterite models, in which all configurations are symmetric, the minimum-energy cation position lies on one of the special positions, either 2*b* (2/*m*), 4*g* (2), or 4*i* (*m*). If our modeled minimum-energy cation position for an ordered structure gives a reasonable approximation of the position expected for the A-site cation in a similar locally ordered configuration in a disordered crystal, then our results should permit logical interpretation of structure refinements of natural and synthetic *C*2/*m* amphiboles.

To interpret results of structure analyses of real amphiboles properly, we must evaluate the frequency of oc-

TABLE 2. Probabilities of occurrence for A-site positions

	k	Total permutations	No. of $8j$ permutations	No. of $2b$ permutations	No. of $4g$ permutations	No. of $4i$ permutations	Total probability
Richterite, $n = 4$, $p(^{M4}Na) = 0.5$, k = no. of Na in M4							
	0	1	0	1	0	0	0.0625
	1	4	4	0	0	0	0.2500
	2	6	0	2	2	2	0.3750
	3	4	4	0	0	0	0.2500
	4	1	0	1	0	0	0.0625
Total		16	8	4	2	2	1.0000
			0.500*	0.250*	0.125*	0.125*	1.0000
Edenite, $n = 8$, $p(^{T1}Al) = 0.25$, k = no. of Al in T1							
	0	1	0	1	0	0	0.1001
	1	8	8	0	0	0	0.2670
	2	28	8	4	4	12	0.3115
	3	56	56	0	0	0	0.2076
	4	70	58	6	2	4	0.0865
	5	56	56	0	0	0	0.0231
	6	28	8	4	4	12	0.0038
	7	8	8	0	0	0	0.0004
	8	1	0	1	0	0	1.5×10^{-5}
Total		256	202	16	10	28	1.0000
			0.6598*	0.1526*	0.0475*	0.1401*	1.0000
Edenite, $n = 12$, $p(^{T}Al) = 0.125$, k = no. of Al in any T site							
	0	1	0	1	0	0	0.2014
	1	12	12	0	0	0	0.3453
	2	66	40	6	6	14	0.2713
	3	220	220	0	0	0	0.1292
	4	495	394	15	26	60	0.0415
	5	792	792	0	0	0	0.0095
	6	924	848	20	16	40	0.0016
	7	792	792	0	0	0	0.0002
	8	495	394	15	26	60	1.72×10^{-5}
	9	220	220	0	0	0	1.09×10^{-6}
	10	66	40	6	6	14	4×10^{-8}
	11	12	12	0	0	0	1.22×10^{-9}
	12	1	0	1	0	0	1.45×10^{-11}
Total		4096	3764	64	80	188	1.0000
			0.6831*	0.2274*	0.0269*	0.0626*	1.0000
Pargasite, $n = 8$, $p(^{T1}Al) = 0.5$, k = no. of Al in T1 site							
	0	1	0	1	0	0	0.0039
	1	8	8	0	0	0	0.0312
	2	28	8	4	4	12	0.1094
	3	56	56	0	0	0	0.2187
	4	70	58	6	2	4	0.2734
	5	56	56	0	0	0	0.2187
	6	28	8	4	4	12	0.1094
	7	8	8	0	0	0	0.0312
	8	1	0	1	0	0	0.0039
Total		256	202	16	10	28	1.0000
			0.7891*	0.0625*	0.0391*	0.1094*	1.0000
			0.8437†	0.0312†	0.0703†	0.0547†	1.0000
Pargasite, $n = 12$, $p(^{T}Al) = 0.25$, k = no. of Al in any T site							
	0	1	0	1	0	0	0.0317
	1	12	12	0	0	0	0.1267
	2	66	40	6	6	14	0.2323
	3	220	220	0	0	0	0.2581
	4	495	394	15	26	60	0.1936
	5	792	792	0	0	0	0.1032
	6	924	848	20	16	40	0.0410
	7	792	792	0	0	0	0.0115
	8	495	394	15	26	60	0.0024
	9	220	220	0	0	0	0.0003
	10	66	40	6	6	14	3.54×10^{-5}
	11	12	12	0	0	0	2.15×10^{-6}
	12	1	0	1	0	0	5×10^{-8}
Total		4096	3764	64	80	188	1.0000
			0.8335*	0.0596*	0.0321*	0.0748*	1.0000
			0.8709†	0.0298†	0.0619†	0.0374†	1.0000

* Total probability for site designated in column heading.

† Total probability for site designated in column heading as affected by the addition of M2 interaction.

currence of all local charge configurations. Although our richterite models have all had two out of four nearest M4 sites occupied by Na to maintain local charge balance, one could envision charge-imbalanced local configurations in which Na would occupy more or less than two of the four nearest M4 sites, so long as the total number of imbalanced configurations yields $^{M4}[\mathrm{Na}/(\mathrm{Ca}+\mathrm{Na})] = 0.5$ over the entire crystal. To a first approximation, the probability of occurrence of any configuration will equal $(n!/k!(n-k)!)p^k(1-p)^{n-k}$, where n is the total number of sites in the local configuration, p is the probability of selection of a substitution cation, and k is the number of substituted cations in the local configuration. The number of permutations of each configuration that yield a minimum-energy A site on the general position or any of the special positions is easily calculated. The total probability for occupancy of any of the kinds of A-site positions is calculated by summing probabilities over the total number of configurations. Three assumptions are implicit in this scheme: First, any degree of local charge imbalance is permitted. The probability that any charge-imbalanced configuration will occur is controlled solely by p and is not weighted in any way to account for the physically unfavorable highly imbalanced configurations. Second, p is assumed to be constant and not dependent on the selection made in other local configurations. Finally, all permutations of any configuration are presumed to be equally likely. Because none of these can be strictly true, we suggest that our calculations (Table 2) be considered to yield limiting probabilities, and our results analogous to those of thermodynamic calculations assuming equilibrium, or of petrologic calculations assuming perfect fractional crystallization: neither situation is likely to occur in reality, but nevertheless, both have provided valuable insights.

For richterite, using $p = 0.5$, $n = 4$, and $0 \leq k \leq 4$, we calculate a 50% probability for the minimum-energy A-site cation to occupy a general position, a 25% probability of occupancy of 2*b* (2/*m*), and 12.5% probability of occupancy of either 4*g* (2) or 4*i* (*m*). Structure refinements (Cameron et al., 1983) placed ^{A}Na on the general position, but ^{A}K on the mirror plane. It is clearly not necessary that ^{A}K be constrained to the mirror plane, and it could be that the most appropriate general position for ^{A}K would indeed lie close to the mirror plane; we have not modeled an asymmetric charge distribution for richterite because it would require a 168-atom asymmetric unit. It would be interesting to calculate Fourier difference maps for the refined structures reported by Cameron et al. (1983) and to look carefully for residual electron density in the vicinity of the A-site positions.

Probability analysis for edenite is substantially more complex. If Al is constrained to the energetically favorable T1 site, then calculations with $n = 8$, $p = 0.25$, and $0 \leq k \leq 8$ result in a 66% probability of the minimum-energy A-site occurring on the general position, 15% probability of occurring on 2*b* (2/*m*), 14% probability of occurring on 4*i* (*m*), and 5% probability of occurring on 4*g* (2). There is, however, a finite probability that Al will substitute on T2 even though it is the less-favorable site. Lacking a suitable weighting scheme, a limiting-case calculation can be performed for 12 sites ($n = 12$) with $p = 0.125$. Such a calculation is subject to certain ambiguities. It is possible that substitution on combinations of pairs of T1 and T2 sites, which separately result in symmetric minimum-energy cation positions, might result in a position of higher symmetry than either of the pairs separately. Likewise, asymmetric combinations of energetically unlike sites may fortuitously yield a minimum-energy A site in a symmetric position. Given such ambiguities, it is impossible to calculate with certainty the number of configurations that lead to symmetric minimum-energy A-site positions. Results of calculations for the 12-site case, assuming neither situation occurs, are listed in Table 2. Presumably, the real preference of Al for substitution on T1 rather than T2 will dictate that the actual situation lies between the 8- and 12-site calculations. Comparison of these cases suggests that as the preference for T1 substitutions increases, the probability of A-site occurrences on 4*g* (2) and 4*i* (*m*) increases at the expense of that for 2*b* (2/*m*) and the general position. The fact remains that the probability of the minimum-energy A-site cation occupying a general position never falls below 66%.

These results are at variance with the refinements of Hawthorne and Grundy (1973a, 1973b, 1976, 1977, 1978), where they typically found large electron densities on the 2-fold axis and lesser densities on the mirror plane. None of their refinements, however, were of edenite, and all of their amphiboles contained some tschermakite component (or some equivalent such as ferri-tschermakite) with significantly more than 1 Al per 8 T sites and a large amount of Al, Ti, or Fe^{3+} on M2 sites. If we calculate probabilities for a pargasite, similar in charge distribution to the composition of their refined amphiboles, two major changes occur: The probability of finding Al on T sites increases to 0.25 in the 12-site case and 0.5 in the 8-site case; in addition, half of the configurations that previously resulted in a 2*b* (2/*m*) A-site position will now result in a 4*g* (2) position, and half of the configurations that previously resulted in a 4*i* (*m*) position will now result in a general position, owing to interaction with the probabilities for the M2 configurations (Table 2). Again, the most probable position for the A-site cation is the general position (85%); among the special positions, the 4*g* (2) position is the most probable (7%). These results suggest that Fourier difference maps for Hawthorne and Grundy's various refinements might be expected to display residual electron density in the general position.

CONCLUSIONS

Modeling demonstrates that charge deficiency or excess in the local ionic configuration surrounding the A site results in minimum-energy A-site cation positions that are displaced from the nominal 2*b* (2/*m*) special position. When the distribution of charge deficiency or excess can be related by a symmetry element, the A-site position resulting in minimum structure energy lies on that symmetry element; when the distribution of charges is asymmetric, the A-site position resulting in minimum structure energy lies on a general position. Probability calculations suggest that for all compositions, the general position, 8*j*, is the most probable. However, a significant number of A-site cations must reside on special positions 2*b* (2/*m*), 4*g* (2), and 4*i* (*m*).

ACKNOWLEDGMENTS

This work was funded by NSF grants EAR79-20095 to Charles W. Burnham and EAR81-15686 to James B. Thompson. Early stages of this research benefited from discussions with F. C. Hawthorne and M. Cameron. The manuscript benefited from review by S. Ghose, F. C. Hawthorne, and G. D. Price.

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MANUSCRIPT RECEIVED JUNE 27, 1985
MANUSCRIPT ACCEPTED MAY 22, 1987