

A scheme of cation distribution in the amphiboles

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Summary. The four principles governing the cation distribution in various octahedral metal sites in the amphibole structure are: Ionic size—the M_4 position prefers large cations like Ca^{2+} , Na^+ ; charge balance—when the M_4 position is occupied by a monovalent ion, like Na^+ , Li^+ , the neighbouring M_2 position is occupied by a trivalent ion like Al^{3+} , Fe^{3+} ; role of the strongly polarizing cations—cations like Fe^{2+} prefer the M_4 site, since they tend to form covalent bonds with the O_4 oxygens; and the role of the (OH) ions—these form part of the brucite layer and repel large or strongly polarizing cations, which tend to distort the regularity of the sheet structure.

The Al-Si distribution in the two different tetrahedral sites are governed by three principles: relief of the Si-O-Si bond strain— Al^{3+} in the Si_1 site causes fewer Si^{4+} cations to share more than two anions with other Si^{4+} cations; charge balance—with the introduction of alkali ions in the 'A' position, Al^{3+} is introduced in the Si_1 position, since the coordinating oxygens around the A position mostly belong to Si_1 ; and steric considerations—occupation of the M_4 site by a large cation tends to rotate the Si_2 tetrahedron anticlockwise; Al^{3+} substitution in the Si_1 site rotates the Si_1 tetrahedron clockwise and thus the regularity and the constancy of the repeat distance of the silicate double chain is maintained.

Based on these principles, a scheme of cation distribution in the M_1 , M_2 , M_3 , M_4 , A, Si_1 , and Si_2 positions in the amphibole structure has been derived for most of the common amphibole varieties, except richterite, whose position is anomalous from a crystallochemical point of view.

AMPHIBOLES are important rock-forming minerals with the general formula $X_{2-3}Y_5Z_8\text{O}_{22}(\text{OH}, \text{F}, \text{O})_2$, where X is Na^+ , Li^+ , K^+ , Ca^{2+} , Mg^{2+} , Fe^{2+} , Mn^{2+} , etc., Y is Mg^{2+} , Fe^{2+} , Mn^{2+} , Al^{3+} , Fe^{3+} , Ti^{4+} , &c., and Z is Si^{4+} , Al^{3+} , Fe^{3+} , &c. The structure of an amphibole essentially consists of two silicate double chains having the formula Si_4O_{11} and a strip of Y type metal ions in octahedral coordination with oxygen and hydroxyl ions sandwiched between them. These silicate double chains are slightly curved away from the layer of metal atoms to effect a better fit between the octahedral metal layer and the tetrahedral silicate layer. The resulting talc-like strips are held together mostly by the X type cations. There are open channels in the structure running parallel to the extension of the silicate double chains, which are some-

times occupied by alkali or alkaline earth cations, like Na^+ , K^+ or Ca^{2+} . The structure of cummingtonite as an example of a typical amphibole is shown in fig. 1.

In this paper the possible cation ordering in the various octahedral and tetrahedral sites in the amphibole structure permitted by the symmetry of the known space-groups and cell-dimensions will be discussed

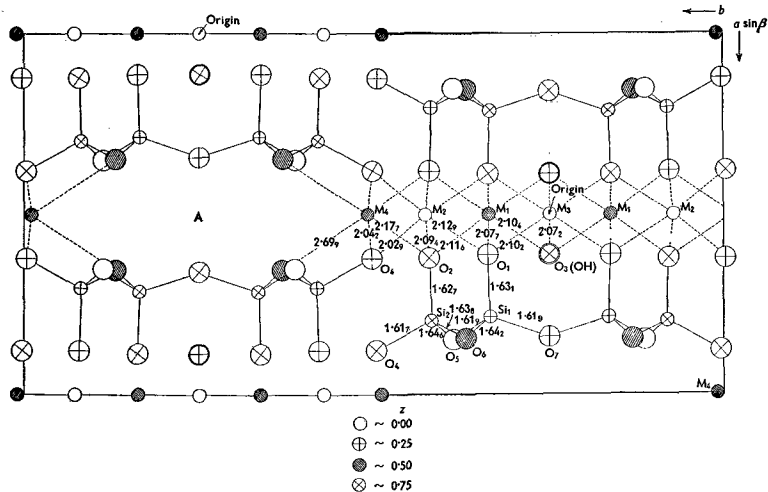


FIG. 1. Projection of the crystal structure of cummingtonite on (001). (After Ghose, 1961.)

for different varieties of naturally occurring amphiboles. The proposed scheme of cation ordering is expected to provide a working model for further experiments to determine the cation distribution in amphiboles more exactly.

Cation distribution in the octahedral sites

In contrast to pyroxenes there are usually four crystallographically different octahedral sites in amphiboles, M_1 , M_2 , M_3 , and M_4 . Of these the M_4 site is occupied by the X type cation and is similar to the M_{II} position in the pyroxene (see Ghose, 1962). This site has a highly distorted octahedral coordination when it is occupied by Fe^{2+} , Mg^{2+} or Mn^{2+} . The coordination increases to eight when it is occupied by Ca^{2+} or Na^+ . The neighbouring M_2 position has a regular octahedral coordination of oxygen ions only and is very similar to the M_1 position of the pyroxene. M_1 and M_3 sites have no parallel in the pyroxene

structure, since they have a very regular octahedral coordination consisting of four oxygen and two hydroxyl ions. These (OH) ions may sometimes be partially replaced by fluorine or chlorine, and in the oxidized or high temperature varieties by oxygen ions. In addition, there is the 'A' position $(0, \frac{1}{2}, 0)$ with a maximum of ten-fold coordination.

The following principles govern the cation distribution in the octahedral sites: M_1 , M_2 , M_3 , and M_4 of amphiboles, irrespective of their orthorhombic or monoclinic symmetry.

Ionic size. The M_4 site has a highly distorted six-fold or eight-fold coordination and can accommodate large cations like Ca^{2+} or Na^+ (not K^+ , however) in the monoclinic amphiboles. Alkali ions in excess of $4(\text{Ca} + \text{Na})$ ions per unit cell are accommodated in the 'A' site. In the orthorhombic amphiboles, the M_4 site has a six-fold coordination and can accommodate ions only with sizes equal to or smaller than those of Mg^{2+} , Fe^{2+} . Larger cations like Ca^{2+} in the M_4 site cause a distortion in the regularity of the silicate chain packing and the symmetry is lowered to monoclinic.

Charge balance. When the M_4 site is occupied by a monovalent ion like Na^+ , the neighbouring M_2 site is occupied by a trivalent ion like Al^{3+} or Fe^{3+} (Whittaker, 1949, 1960). In some high temperature amphiboles, where some (OH)⁻ ions have been replaced by O^{2-} , an M_3 site (likewise the M_1 site) can be occupied by a trivalent or even a tetravalent ion, like Fe^{3+} or Ti^{4+} (Mueller, 1962).

Role of the strongly polarizing cations. Strongly polarizing cations like Fe^{2+} tend to form covalent bonds with oxygens and prefer the M_4 site (Ghose, 1961, 1962). When two different types of strongly polarizing cations are present, they will tend to avoid each other.

Role of the (OH) ions. The (OH) ions form part of a brucite-type sheet structure with cations at the M_3 and M_1 sites, where the coordination is nearly ideally octahedral. Strongly polarizing cations like Fe^{2+} tend to distort this sheet and hence are repelled from the M_3 and M_1 sites. The fact that among coexisting orthopyroxenes and cummingtonites the latter are relatively richer in Mg^{2+} (Kranck, 1961) is explained by this principle.

Cation distribution in the tetrahedral sites

In amphiboles there are two crystallographically different tetrahedral sites, Si_1 and Si_2 . The following principles govern the cation distribution in the tetrahedral sites:

Relief of Si-O-Si bond strain. Si_1 shares three anions with other four-coordinated positions, while Si_2 shares only two. DeVore (1957) has pointed out that ordering of Al^{3+} in the Si_1 site is more likely, since 'Al³⁺ in this position causes fewer Si^{4+} cations to share more than two anions with other Si^{4+} cations' and hence helps to relieve the Si-O-Si bond strain.

Charge balance. With the introduction of alkali or alkaline earth ions in excess of $4(\text{Ca} + \text{Na})$ per unit cell, Al^{3+} or Fe^{3+} is simultaneously introduced in the tetrahedral sites to balance the charge (Warren, 1930). The 'A' site, where these excess alkali or alkaline earth cations are accommodated, has a maximum of ten-fold coordination. This maximum coordination is probably realized, when the 'A' site is occupied by K^+ ($r = 1.33 \text{ \AA}$). This site, however, is more commonly occupied by Na^+ ($r = 0.95 \text{ \AA}$), in which case it is likely that four of the O_5 or O_6 oxygens are drawn closer to the 'A' site and the coordination becomes essentially six-fold. These coordinating oxygens, including the two closest ones, O_7 , belong to the Si_1 tetrahedra. To balance the charge, Si_1 position must take some Al^{3+} (or Fe^{3+}). Typical $\text{Al}^{3+}:\text{Si}^{4+}$ ratios in hornblendes are 1:7 or 2:6. Hence, the Si_1 site will have $\text{Al} \frac{1}{4} \text{Si} \frac{3}{4}$ or $\text{Al} \frac{1}{2} \text{Si} \frac{1}{2}$. In muscovite the Al-Si ordering is similar, with $\text{Al} \frac{1}{2} \text{Si} \frac{1}{2}$ in the Si_1 site and Si in the Si_2 site (Radoslovich, 1960). When the Si_1 site in the amphibole is occupied by $\text{Si} \frac{1}{2} \text{Al} \frac{1}{2}$, O_7 gets a charge contribution of $\frac{7}{4}$ from two neighbouring Si_1 sites. The remaining charge must be balanced by Na^+ at the 'A' site. Assuming a regular octahedral coordination, the charge contribution from Na^+ will be only $\frac{1}{6}$. A closer bond between Na^+ and the O_7 oxygens is therefore likely than between Na and O_5 or O_6 oxygens. The resulting coordination-polyhedron around Na^+ will then be a squashed octahedron, as found in natrolite, $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$ (Meier, 1960) for example.

The steric consideration. In spite of the substitution of Si^{4+} by Al^{3+} in the tetrahedral sites in amphiboles, the repeat distance of the double chains remains remarkably constant, namely $5.30 \pm 0.03 \text{ \AA}$. (For a list of the cell dimensions of amphiboles, see Deer, Howie, and Zussman, 1963, p. 267). In view of the Al-Si substitution, as well as the occupation of the M_4 site by cations of various sizes, the Si_1 and Si_2 tetrahedra must rotate with $\text{Si}_1\text{-O}_1$ and $\text{Si}_2\text{-O}_2$ as axes to achieve this end (fig. 2). When the M_4 site is occupied by a large cation like Ca^{2+} or Na^+ , the O_4 oxygens are pushed away from the M_4 site and the Si_2 tetrahedron undergoes an anticlockwise rotation. If Al^{3+} is substituted in the Si_2 site, the (Al, Si)-O bond length increases and the Si_2 tetrahedron must

rotate further to keep the chain-length constant. On the other hand, if Al^{3+} is substituted for Si^{4+} in the Si_1 position, the Si_1 tetrahedron rotates clockwise. The latter seems more plausible sterically, since the resulting chain will be regular, with both Si_1 and Si_2 tetrahedra about equally rotated in opposite directions.

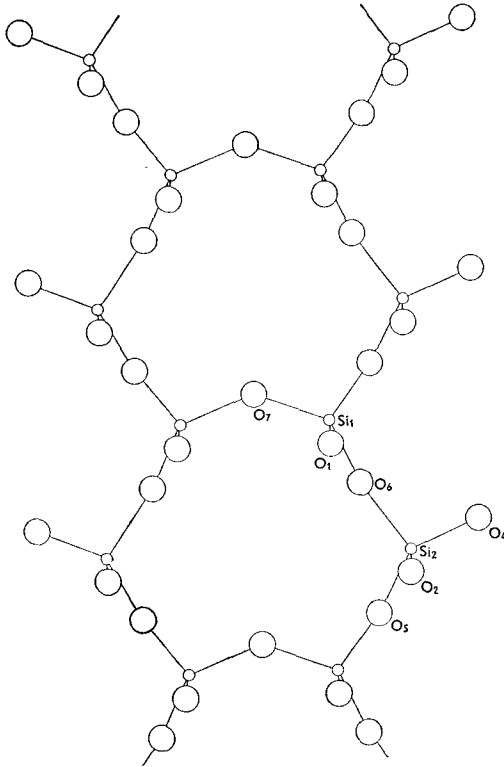


FIG. 2. Orthogonal projection of the silicate double chains in tremolite on (100) in $I 2/m$ orientation. (After Ghose, 1961.)

Discussion

The scheme of cation ordering in amphiboles presented in table I is essentially idealized and only attempts to show the trend. In nature the degree of order, as well as the metal content in various octahedral and tetrahedral sites in a particular variety of amphibole will be principally a function of temperature. However, the amphiboles formed in

TABLE I. A scheme of cation distribution in various octahedral and tetrahedral sites in amphiboles

	M_4	M_2	$M_1 + M_3$	A	Si_1	Si_2
Anthophyllite (Mg,Fe ²⁺) ₇ Si ₈ O ₂₂ (OH,F) ₂	Fe ³⁺	Mg ²⁺	Mg ²⁺ > Fe ²⁺	—	Si ₁	Si ₂
Cummingtonite (Mg,Fe ²⁺) ₇ Si ₈ O ₂₂ (OH,F) ₂	Fe ²⁺	Mg ²⁺	Mg ²⁺ > Fe ²⁺	—	Si ₁	Si ₁
Holmquistite Li ₂ (Mg,Fe ²⁺) ₈ (Al,Fe ³⁺) ₂ Si ₈ O ₂₂ (OH,F) ₂	Li ⁺	Al ³⁺ , Fe ³⁺	Mg ²⁺ > Fe ²⁺	—	Si ₁	Si ₁
Gedrite (Mg,Fe ²⁺) ₆₋₅ Al ₁₋₃ Si ₆ Al ₂ O ₂₂ (OH,F) ₂	Fe ²⁺	Mg ²⁺	Mg ²⁺ , Al ³⁺	—	Al _{1/2} Si _{1/2}	Si ₁
Tirodite (Mg,Mn ²⁺) ₇ Si ₈ O ₂₂ (OH,F) ₂	Mn ²⁺	Mg ²⁺	Mg ²⁺ > Mn ²⁺	—	Si ₁	Si ₁
Aëinolite Ca ₂ (Mg,Fe ²⁺) ₅ Si ₈ O ₂₂ (OH,F) ₂	Ca ²⁺	Fe ²⁺ > Mg ²⁺	Mg ²⁺ > Fe ²⁺	—	Si ₁	Si ₁
Common Hornblende (Ca,Na,K) ₂₋₃ (Mg,Fe ²⁺ ,Fe ³⁺ ,Al) ₃ Si ₆ (Si,Al) ₂ O ₂₂ (OH,F) ₂	Ca ²⁺	Fe ²⁺ > Mg ²⁺	{Mg ²⁺ > Fe ²⁺ {(Al ³⁺ ,Fe ³⁺)	Na,K	Al _{1/2} Si _{1/2}	Si ₁
Edenite NaCa ₃ (Mg,Fe ²⁺) ₅ Si ₇ AlO ₂₂ (OH,F) ₂	Ca ²⁺	Fe ²⁺ > Mg ²⁺	Mg ²⁺ > Fe ²⁺	Na	Al _{1/2} Si _{1/2}	Si ₁
Pargasite-Ferrohastingsite NaCa ₄ (Mg,Fe ²⁺) ₄ (Al,Fe ³⁺) ₁ Si ₆ Al ₂ O ₂₂ (OH,F) ₂	Ca ²⁺	Fe ²⁺ > Mg ²⁺	{(Mg ²⁺ > Fe ²⁺) [‡] {(Al ³⁺ ,Fe ³⁺) [‡]	Na	Al _{1/2} Si _{1/2}	Si ₁
Barkevikite (Na,K)Ca ₂ Fe ₂ ²⁺ (Mg,Fe ²⁺ ,Al ³⁺ ,Fe ³⁺) ₃ Si ₆ Al ₂ O ₂₂ (OH,F) ₂	Ca ²⁺	Fe ²⁺	{(Mg ²⁺ > Fe ²⁺) [‡] {(Al ³⁺ ,Fe ³⁺) [‡]	Na, K	Al _{1/2} Si _{1/2}	Si ₁
Glaucophanes Na ₂ Mg ₃ Al ₂ Si ₈ O ₂₂ (OH,F) ₂	Na ⁺	Al ³⁺	Mg ²⁺	—	Si ₁	Si ₁
Riebeckite Na ₃ (Mg,Fe ²⁺) ₃ Fe ₂ ²⁺ Si ₆ O ₂₁ (OH,F) ₂	Na ⁺	Fe ²⁺	Mg ²⁺ > Fe ²⁺	—	Si ₁	Si ₁
Catopharite Na ₂ Ca(Mg,Fe ²⁺) ₄ (Fe ³⁺ ,Al)Si ₇ AlO ₂₁ (OH,F) ₂	{Na ⁺ [‡] {Ca ²⁺ [‡]	{(Fe ³⁺ ,Al ³⁺) [‡] {(Fe ²⁺ > Mg ²⁺) [‡]	Mg ²⁺ > Fe ²⁺	Na	Al _{1/2} Si _{1/2}	Si ₁
Arfvedsonite-Eckermannite (Na,Li) ₃₋₅ Ca ₀₋₅ (Mg,Fe ²⁺ ,Fe ³⁺ ,Al) ₅ Si ₇ AlO ₂₂ (OH,F) ₂	{Na ⁺ ,Li ⁺ [‡] {Ca ²⁺ [‡]	{(Fe ³⁺ ,Al ³⁺) [‡] {(Fe ²⁺ > Mg ²⁺) [‡]	Mg ²⁺ > Fe ²⁺	Na	Al _{1/2} Si _{1/2}	Si ₁
Kaersutite (Na,K)Ca ₃ (Mg,Fe ²⁺ ,Fe ³⁺) ₄ TiSi ₆ Al ₂ O ₂₂ (OH,F,O) ₂	Ca ²⁺	Fe ²⁺ > Mg ²⁺	Ti ⁴⁺ ,Fe ²⁺ Mg ²⁺ ,Fe ²⁺	Na,K	Al _{1/2} Si _{1/2}	Si ₁

metamorphic rocks (amphibolite through to granulite facies) at least are expected to show pronounced degrees of cation ordering.

Detection of cation order by X-ray diffraction, particularly in the M_1 , M_2 , and M_3 sites is not always easy, since several of the ions involved, namely Na^+ , Mg^{2+} , Al^{3+} , Si^{4+} , have very similar X-ray scattering powers. Therefore, sole reliance on the peak heights in electron-density maps does not always lead to unambiguous results. Application of other methods, e.g. nuclear magnetic resonance, for studying the distribution of nuclei like ^{23}Na , ^{27}Al , ^7Li , &c., is complicated by the ubiquitous presence of strongly ferromagnetic nuclei like ^{57}Fe . Optical measurements, particularly infra-red absorption spectra of natural amphiboles unheated and heated (under proper water and oxygen pressures), as well as of amphiboles synthesized under various temperature and pressure conditions, may provide some indication of the degree of cation order-disorder.

From a detailed refinement of the structure of a cummingtonite based on three-dimensional X-ray data, it was found that M_4 site is occupied by 75 % Fe^{2+} , 25 % Mg^{2+} , the M_2 site by 85 % Mg^{2+} , 15 % Fe^{2+} , and the M_1 and M_3 sites by 67 % Mg^{2+} and 33 % Fe^{2+} (Ghose, 1961). A theoretical curve for the distribution of Mg^{2+} and Fe^{2+} among the lattice sites of cummingtonite has been derived by Mueller (1962) from the functions of heterogeneous ion-exchange equilibria for coexisting cummingtonite-actinolite. The derived distribution is in good agreement with that obtained by Ghose.

In Bolivian crocidolite the occupation of the M_4 site principally by Na^+ and the M_2 site principally by Fe^{3+} has been confirmed by Whittaker (1949) from an electron density projection on (001). In view of the Mg^{2+} - Fe^{2+} ordering found in cummingtonite, it is likely that in crocidolite also the M_4 site is occupied by some Fe^{2+} in addition to 0.69 Na^+ , and not all by Mg^{2+} as suggested by Whittaker. Recently, Ernst (1963) has detected two pressure polymorphs of glaucophane synthesized at 800° C, which differ only in cell volumes, but not in symmetry; the phase transition is second order. According to Ernst, in the high pressure phase Al is concentrated in the M_2 site and is more randomly distributed among all octahedral positions in the low pressure phase. However, for magnesio-riebeckite and riebeckite no change in cell-volumes could be detected under various temperature and pressure conditions, presumably because the cations Mg^{2+} and Fe^{3+} are similar in ionic size, as noted by Ernst.

The cation distribution scheme in holmquistite, as predicted by

Whittaker (1960), is essentially the same as is proposed here. From a consideration of the sizes of cations that are able to occupy M_1 and M_3 sites in orthorhombic amphiboles, Whittaker (1960) deduced that in the most iron-rich anthophyllites, M_1 and M_3 sites will be completely filled by Fe^{2+} and this is the compositional limit of orthorhombic Mg-Fe amphiboles. This is contrary to the cation distribution scheme in anthophyllite predicted already in the light of the cation distribution found in cummingtonite (Ghose, 1962). If the M_4 site is completely filled with Fe^{2+} , the composition becomes $\text{Fe}_2^{2+}\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$. Anthophyllites with about 25 mole % of the iron component occur most frequently in nature (Rabbitt, 1948), a fact which lends support to the cation distribution scheme proposed here. Except in gedrite, the presence of Al^{3+} in tetrahedral sites is always accompanied by Na^+ , K^+ , &c. at the 'A' site. Occupation of the 'A' site by excess alkali ions (Na^+ , K^+) in six hornblendes has been confirmed by Heritsch and his co-workers (1957, 1959) from electron density projections on (001). The failure to detect cation ordering in the M_1 , M_2 , and M_3 sites in the hornblendes and actinolite (Zussman, 1955) studied by electron density projection on (001) alone may be ascribed to the difficulty stated earlier.

Richterite, as represented by the conventional formula $\text{Na}_2\text{Ca}(\text{Mg}, \text{Fe}^{2+})\text{Si}_8\text{O}_{22}(\text{OH})_2$, does not fit into the scheme proposed here. In the absence of any Al^{3+} replacing Si^{4+} , it is difficult to understand how Na^+ can be held in the 'A' position, around which the coordinating oxygens are all charge satisfied. The anomalous richterite composition can be explained in two ways: either the published analyses may have been incorrect or carried out on impure materials or richterite may be a base-exchanged form of an original tremolite phase (Thompson, 1963). The second suggestion seems reasonable in view of the widespread occurrence of richterite in hydrothermally altered deposits (cf. Larsen, 1942).

In varieties like arfvedsonite, cataphorite, &c., where the M_4 site is simultaneously occupied by monovalent and divalent cations, and the neighbouring M_2 site by trivalent and divalent cations, it is expected that there are domains with short range order in which 'ionic couplings' of the type $\text{Na}^+-\text{Al}^{3+}$, $\text{Ca}^{2+}-\text{Mg}^{2+}$, &c. still persist.

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