Acta Cryst. (1960). **13**, 291

The Crystal Chemistry of the Amphiboles

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(*Received* 24 *June* 1959 *and in revised form* 18 *September* 1959)

The major differences in unit-cell shape of the different amphibole varieties, and the respective composition ranges of the orthorhombic and monoclinic amphiboles, are related to the effects of the ionic radius of the ions occupying two of the sets of ionic sites in the structure. These are the ions which serve to link together the talc-like strips from which the structure may be regarded as being built. The reason for the existence of both limited and unlimited isomorphous substitution ranges for the same ions in different parts of the composition field is shown to depend on the different effects on chain packing of the radius of the ions occupying these two sites as compared with each other and with the sites which are wholly inside the talc-like strips.

1. Introduction

The amphiboles are important rock-forming silicate minerals with a perfect prismatic cleavage, their cleavage angle being in the range 54°–56°. They occur in prismatic crystals and lamellae, and also in fibrous forms which are of commercial importance in the asbestos industry. They crystallize in either the monoclinic or orthorhombic system, and their range of composition, which is very wide indeed, may include substantial proportions of all the commonest mono-, di-, and tri-valent metals. The approximate structures of a typical monoclinic amphibole, tremolite, and a typical orthorhombic amphibole, anthophyllite, were determined by Warren (1930*a*) and Warren & Modell (1930) respectively. Warren (1930*b*) also showed that a number of other monoclinic amphiboles gave diffraction patterns so similar to that of tremolite that there could be no doubt that they had virtually identical structures. He also showed that the very variable compositions of the amphiboles could be largely covered by the general formula

$$(\mathrm{Ca,Na,Mn})_{2-3}(\mathrm{Mg,Fe,Ti,Al,Mn})_5(\mathrm{Si,Al})_8\mathrm{O}_{22}(\mathrm{OH,F})_2\,.$$

This formula does not cover all the substitutions which occur, however, nor does it indicate the various limitations of the ranges of substitution which are observed. It is frequently expressed more generally, and non-committally, as

$$X_{2-3}Y_5Z_8\mathrm{O}_{22}(\mathrm{OH,\,F})_2\,.$$

X may then represent any mono- or di-valent cation with an ionic radius from that of magnesium (0·78 Å) to that of potassium (1·33 Å), Y any di- or tri-valent ion of radius from that of aluminium (0·57 Å), to that of manganese (0·91 Å), and Z is mainly silicon but is replaceable up to about 25% by tri-valent ions with radius up to that of ferric iron (0·67 Å). Somewhat more, or less, hydrogen may also be present to balance otherwise unbalanced charges.

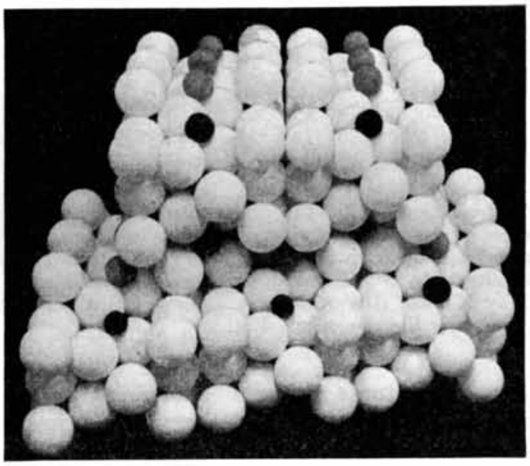

Fig. 1. A packing model of the clino-amphibole structure. The c-axis is directed away from the observer and the b-axis is vertical. The white spheres represent oxygen, the grey spheres represent X ions in M_4 positions, and the black spheres represent Y ions, but only those in M_2 positions are prominent. The silicon atoms also appear black in the photograph but are not very prominent.

The amphibole structure is based on infinite chain anions of composition $\mathrm{Si_4O_{11}}$. The structure of a monoclinic amphibole projected down the chain direction (c axis) is shown in Fig. 2. Two $\mathrm{Si_4O_{11}}$ chains sandwich between them, and co-ordinate octahedrally, the Y ions of the above formula, the co-ordination of which is completed by the hydroxyl ions. The Y ions occupy the positions marked M_1, M_2 and M_3 in Fig. 2, and together with the oxygen and hydroxyl groups in contact with them are arranged as in a strip of the brucite structure, the typical layer-lattice structure of the hydroxides of the Y metals. The whole complex of two $\mathrm{Si_4O_{11}}$ chains with the hydroxyl groups and Y ions sandwiched between them is equivalent to a narrow strip of the talc structure. The X ions up to two in number occupy the M_4 positions at the edges of these talc-like strips and serve to link them together in the crystal packing. The *Y* ions at M_2 lie near the edges of the talc-like strips and so also help to link them together, but to a less extent than the ions at M_4. *X* ions in excess of two lie in the so-called '*A*' position between the 'backs' of the chains when required to balance excess negative charge, rather like the interlayer ions in the micas. A model of this structure is shown in Fig. 1.

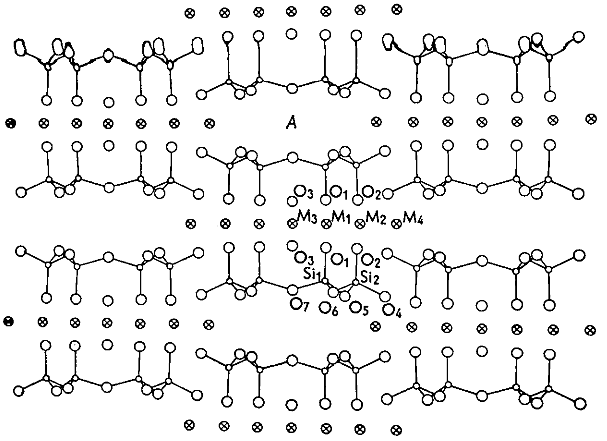

Fig. 2. Projection on (001) in crocidolite to show the nomenclature of the atomic sites and the way in which the structure is built up from talc-like strips, seen here in end-view. The sites M_1, M_2 and M_3 are occupied by *Y* ions and M_4 by *X* ions. Any *X* ions in excess of two per formula unit occupy the site marked *A*.

Refined structures of five monoclinic amphiboles of varied composition have been published in recent years, namely:

Bolivian crocidolite

$Na_{1.38}K_{0.13}Ca_{0.17}F''_{0.48}Mg_{3.06}Fe'''_{1.66}Al_{0.05}$
$(Si_{7.94}Al_{0.06})O_{22}(OH)_2$ (Whittaker, 1949).

Actinolite

$Ca_{1.47}Na_{0.11}K_{0.04}Mg_{3.78}Fe''_{1.07}Fe'''_{0.30}Cr$ etc. $_{0.05}$
$(Si_{7.13}Al_{0.76}Ti_{0.11})O_{21.09}(OH)_{2.84}F_{0.07}$
(Zussman, 1955).

Carinthine

$Ca_{1.75}Na_{0.88}K_{0.22}Mg_{3.31}Fe''_{0.59}Fe'''_{0.17}Al_{0.76}Ti_{0.17}$
$(Si_{6.37}Al_{1.63})O_{22.24}(OH)_{1.76}$
(Heritsch, Paulitsch & Walitzi, 1957).

Barroisitic hornblende

$Ca_{1.59}Na_{1.08}K_{0.03}Mg_{2.61}Fe''_{1.21}Fe'''_{0.10}Mn_{0\,03}Al_{0.90}Ti_{0.15}$
$(Si_{6.54}Al_{1.46})O_{22.13}(OH)_{1.87}$ (Heritsch *et al.*, 1957).

Tremolite

$Ca_{2.00}Na_{0.03}Mg_{4.92}Fe''_{0.04}Fe'''_{0.02}Al_{0.05}$
$(Si_{7.81}Al_{0.19})O_{21.99}(OH)_{2.01}$ (Zussman, 1959).

These refined structures have revealed some small errors in the atomic positions in Warren's approximate structure, but they have all been remarkably similar to one another. It has thus become clear that the main differences between monoclinic amphibole varieties do not reside in the internal geometry of the chains. A partial, but still qualitative, refinement of the anthophyllite structure has been published by Ito (1950). The structure of the chains given by Ito shows more difference from the monoclinic forms than they show among themselves, and, as will be seen later, this may be partly real. Ito does not give the composition of his specimen. The ideal formula of anthophyllite may vary from $Mg_7Si_8O_{22}(OH)_2$ to $Mg_4Fe''_3Si_8O_{22}(OH)_2$.

2. Composition relations in the amphiboles

The whole field of substitution relationships in the amphiboles is so complex that it is only possible to deal with limited parts of it at one time. Fig. 3 shows in somewhat idealized form three such parts which are the best established and which include some of the most important amphibole species. Figs. 3(*a*), and (*b*) are slightly simplified versions of those given by Sundius (1944) and 3(*c*) is an extension of that given by Frankel (1953*a*, *b*) to cover the probable range of riebeckite in the direction of magnesium if one assumes that the vertical extensions of riebeckite and of the low alkali series are constant throughout the

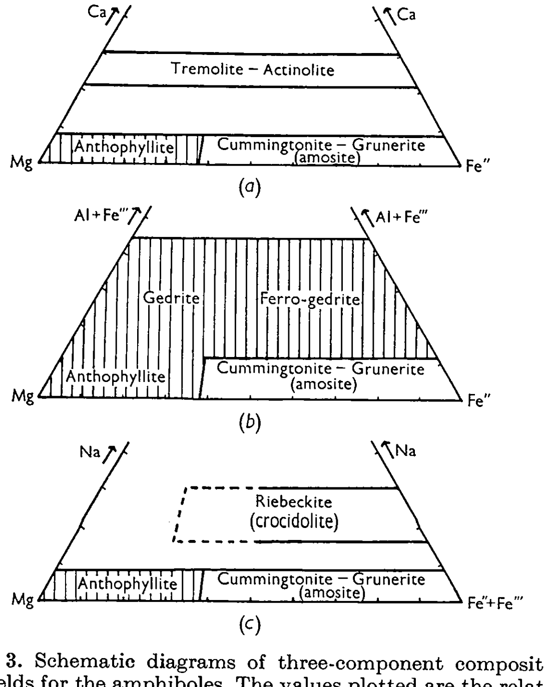

Fig. 3. Schematic diagrams of three-component composition fields for the amphiboles. The values plotted are the relative numbers of the ions specified, expressed as percentages of their sum. Orthorhombic phases are shaded. (*a*) The Mg–Fe''–Ca field in absence of alkali metals and tri-valent elements. (*b*) The Mg–Fe''–(Al, Fe''') field in absence of alkali metals and calcium. (*c*) The Mg–(Fe'', Fe''')–Na field in absence of aluminium and calcium.

range. Sufficient data do not appear to be available in the (Mg, Fe)–Ca–Na system to decide whether or not a continuous region of replacement exists connecting riebeckite, $Na_2 Fe_2''' (Mg Fe'')_3$, with soda-tremolite $Na_2Ca(Mg, Fe'')_5$ and tremolite. When both aluminium and alkali are present together, the number of named varieties and the number of different possible types of substitution become very large, so that the corresponding diagrams are complex and the distinctions are less well substantiated, but the varieties in this region which have been investigated will be shown to conform to the principles to be discussed. With one exception, the orthorhombic amphiboles are confined to the composition regions with low alkali and alkaline earth content. The exception is the aluminous lithium amphibole holmquistite, $Li_2Al_2Mg_3Si_8O_{22}(OH)_2$, which has recently been shown to be orthorhombic (Vogt, Bastiansen & Skancke, 1958).

The main problems with which we are faced by these data are as follows:

1. Why replacement of Mg, Fe by Ca or Na leads to a phase transition either from orthorhombic to monoclinic or from one monoclinic phase to another, in both cases with a broad 'forbidden region' between them.
2. Why complete mutual replacement of magnesium and ferrous iron is possible in the tremolite–actinolite and gedrite–ferrogedrite series whereas it leads to a phase transition from orthorhombic anthophyllite to monoclinic cummingtonite in the absence of Ca, Al, or Fe'''.
3. Why the orthorhombic amphiboles are so restricted in composition that their only established representatives outside the anthophyllite–gedrite region are holmquistite and a mangano–anthophyllite.

3. The angle β in the monoclinic amphiboles

Since the recent refinements of five monoclinic amphiboles have shown that the internal structure of the chains is very similar in all of them, it is clear that one must look for the differences between them at the inter-chain contacts.

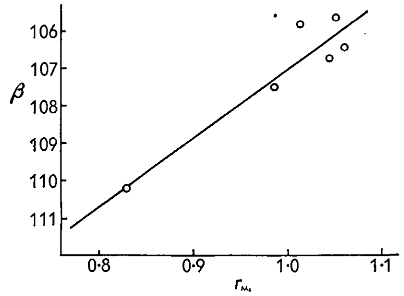

Fig. 4. Plot of β against the mean Goldschmidt radius of the ion at M_4 for the five clino-amphiboles whose structures have been published, and for amosite. The line is the regression line of β on r.

If the β angles of the different varieties are controlled by such inter-chain contacts they must be controlled by those that affect the relative translations of the chains parallel to the c-axis. These must occur on or close to the plane $y = 0{\cdot}25$, since in this region there is considerable interlocking of the edge atoms of the chains, whereas there is very little interlocking in the inter-chain contacts on the other plane of contact, $x = 0{\cdot}5$. The most promising contact to consider is that between the M_4 atom belonging to the chain which lies at a corner of the cell, with the O_4 of the chain which centres the cell (or vice-versa). Fig. 4 shows that there is in fact a close relationship between β and the mean Goldschmidt radius of the ions occupying M_4 for the five varieties whose structures have been studied, and for amosite. The value of β for amosite (a fibrous variety of grunerite) has been given as 70° (i.e. obtuse $\beta = 110°$) by Garrod & Rann (1952), and for the closely related cummingtonite as 102° 8′ by Johansson (1930). This disagreement is apparently due to the use of the convention of the C-centred cell by Johansson and the I-centred cell by Garrod & Rann (see Zussman, 1959, for the differences involved). The latter convention is used here and the value adopted (110° 10′) is a new determination by the author. The radius of M_4 in amosite is assumed to be that of ferrous iron, since the composition of grunerite shows that all the metal positions must be occupied by ferrous iron in the end-member, and it is usual for the largest ion present to occupy M_4 in the monoclinic structure.

In seeking to interpret this relationship more strictly in terms of the M_4–O_4 distance one must recognise that the published z coordinates for the oxygen atoms in crocidolite, actinolite, and the hornblendes are subject to considerable uncertainties; they are based not on diffraction data but on considerations of reasonable bond lengths compatible with the x and y coordinates. The relative weights given to different features of the structure by different investigators in arriving at the z coordinates have therefore probably been different. Valid comparisons of the M_4–O_4 distance in the different varieties are therefore not possible by simple calculation from the published coordinates; and in any case no z coordinates are available for tremolite and no coordinates at all are available for amosite. It has therefore been assumed that the relative positions of the oxygen atoms within the chain are constant as between varieties, and alternative calculations of the inter-chain M_4–O_4 distance have been made for each of the six varieties assuming in turn that each of the three published sets of coordinates is correct. The M_4–O_4 distance varies with β in a similar way on each assumption although the actual values found are different. The mean of the three sets of calculations gives the best agreement with expected values of the distance based on Goldschmidt radii, and in view of this, and of the fact that there are no strong grounds to prefer one set of coordinates to another, only the mean results are quoted here. The x and z coordinates of M_4 are fixed by symmetry. Its y coordinate varies slightly from one species to another and allowance was made for this, although the effect is very small since y_{M_4} and y_{O_4} are very nearly equal.

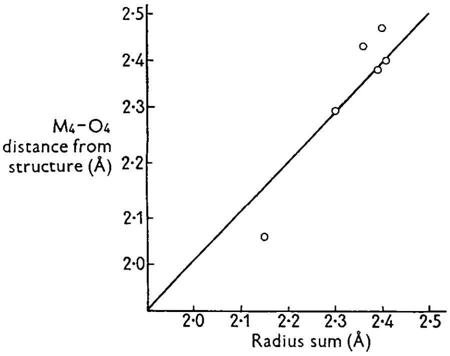

Fig. 5. The M_4–O_4 distance in the same six clino-amphiboles plotted against the radius sum for M_4 + oxygen. The line is the theoretical equality line at 45° to the axes.

The results of this calculation are shown in Fig. 5, where the M_4–O_4 distance is plotted against the sum of the oxygen radius and the mean radius of the ion at M_4. The latter was taken to be increased by 3% in the four varieties with the largest M_4 ion to allow for the fact that the coordination is there probably more nearly eight-fold than six-fold. The agreement is sufficiently good to confirm that the M_4–O_4 distance is the main factor determining the angle β. The discrepancies presumably arise from the second order differences which may be expected in the structure of the chains in different varieties and for which no allowance has been made, though the existence of minor effects from interactions other than between M_4 and O_4 are not excluded.

4. The value of *a* in the monoclinic amphiboles

Since both the M_4 and O_4 atoms lie close to the plane $y = 0{\cdot}25$, a section of the structure at this level reveals the way in which the M_4–O_4 distance controls the angle β. Such a section for crocidolite is shown in Fig. 6(*a*). If the perpendicular distance between the chains, in the direction perpendicular to the *bc* plane, were constant then the locus of the atomic positions would be parallel to *c*, and *a* would increase with increasing β in order to keep $a \sin \beta$ constant. If on the other hand it were the contacts between M_4 and O_4 which determined the closeness of packing perpendicular to the *bc* plane then this locus would be directed towards M_4 and $a \sin \beta$ would decrease sharply with increasing β. In fact the locus has an intermediate direction as shown in Fig. 6(*b*), since $a \sin \beta$ does decrease fairly markedly with increasing β as shown in Fig. 7. It follows that a closer packing of the chains is achieved when β increases, but the closeness of packing is not controlled directly by the M_4–O_4 distance. A section through the structure at $y = 0{\cdot}125$ shows that it is in fact controlled by the packing of O_5 and O_6 of adjacent chains (Fig. 8). At low values of β ($\sim 106°$) these atoms are almost exactly opposite one another, but as β increases a more and more staggered arrangement occurs so that a closer packing of the chains is achieved without any reduction in the minimum O_5–O_6 distance. The same thing is also true of the O_7–O_7' distance between adjacent chains.

It may be noted that for $\beta < 105° 30'$ the arrangement of O_5 and O_6 would begin to be staggered in the opposite direction so that it might be expected that $a \sin \beta$ would decrease with decreasing β in this region. In fact, however, such a reduction in $a \sin \beta$, coupled with the very large M_4–O_4 distance (large M_4 ion) which would be required to give such values of β, would lead to a rapid approach between O_4 atoms of adjacent chains. Such a reduction of $a \sin \beta$ at low values of β is therefore unlikely even if such values of β exist.

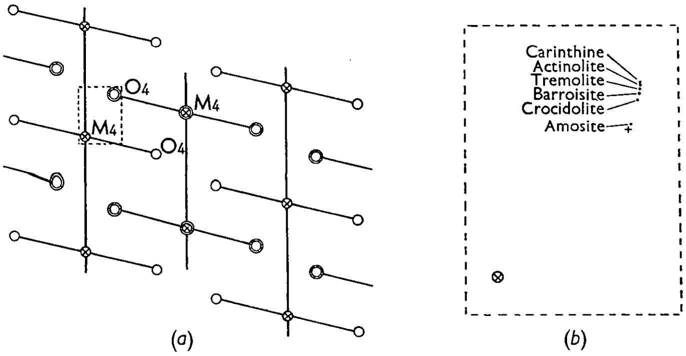

Fig. 6. Section of the clino-amphibole structure at $y = 0{\cdot}25$. In (*a*), the plain circles (single or double) denote O_4 and the crossed circles (single or double) denote M_4. The single circles denote atoms on the top of chains which lie below the section, and the double circles denote atoms at the bottom of chains which lie above the section. The lines connect together atoms belonging to a given chain; they do not correspond to direct chemical bonds. (*b*) Shows the area within the broken line on a larger scale in order to demonstrate the effect of the different values of β, for six varieties, on the position of O_4 (shown by dots).

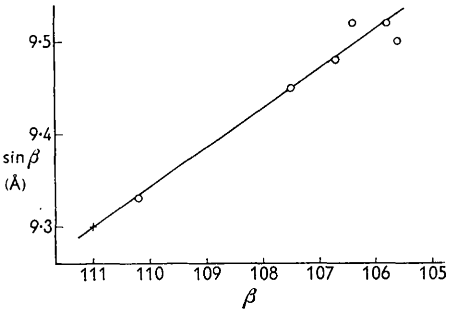

Fig. 7. Plot of $a \sin\beta$ against β for the same six clino-amphiboles. The line is the regression line of $a \sin\beta$ on β, and the cross shows the extrapolated value of $a \sin\beta$ for the hypothetical clino-amphibole $Mg_7Si_8O_{22}(OH)_2$.

It happens that the reduction in $a \sin\beta$ with increasing β is such that a is almost constant. Thus for the six varieties considered $a \sin\beta$ varies from 9·33 Å to 9·52 Å, whereas a varies only from 9·86 Å to 9·92 Å. This nearly constant translation period is denoted by a only in the I-centred convention. In the C-centred convention the quantities denoted by $a \sin\beta$ and $\sin\beta$ vary in opposite directions so that quite large changes occur in a. This fact can be of value in certain cases in revealing which convention has been adopted by a particular author, notably in the case of Johansson's results for cummingtonite (1930) mentioned in § 3 above.

5. Factors governing the existence of orthorhombic amphiboles

The purely magnesium amphibole $Mg_7Si_8O_{22}(OH)_2$ does not occur in the monoclinic form. However, one can extrapolate the line in Fig. 4 to give the angle β for such a hypothetical structure with magnesium at M_4, the value obtained being about 111°. Using this value one can then insert the positions in Figs. 6 and 8 which would be occupied by O_4, O_5 and O_6 in this hypothetical structure, and these positions are marked by crosses. One then finds that such a structure would not involve any abnormal interatomic distances. On the other hand, if the line in Fig. 7 is extrapolated to $\beta = 111°$ one obtains a value of $a \sin\beta = 9{\cdot}30$ Å for the hypothetical clino-magnesium-amphibole. This is slightly greater than the packing distance perpendicular to bc in anthophyllite, where this value is $\frac{1}{2}a$. The average value of $\frac{1}{2}a$ for the 10 anthophyllites studied by Rabbitt (1948) was 9·27 Å (with a total variation of $\pm 0{\cdot}02$ Å). It follows therefore that the orthorhombic structure permits a closer packing of the chains than does the monoclinic structure, and the reason for this is obvious from Fig. 9, which is a section of the anthophyllite structure corresponding to that given in Fig. 8 for the monoclinic amphiboles. The oxygen atoms are much more perfectly staggered in this structure.

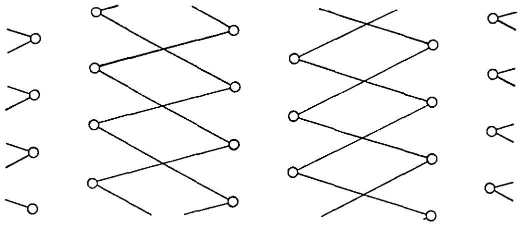

Fig. 9. Section of the anthophyllite structure, corresponding to that of the clino-amphibole structure shown in Fig. 8.

It must therefore be concluded that the problem presented by the orthorhombic amphiboles is not why they are not monoclinic. The problem is why all amphiboles are not orthorhombic, and this problem is solved by a consideration of Fig. 10, which is a section through the anthophyllite structure corresponding to Fig. 6. Consideration of interatomic distances in this structure is handicapped by the lack of a refined structure determination, and the position of O_4* is

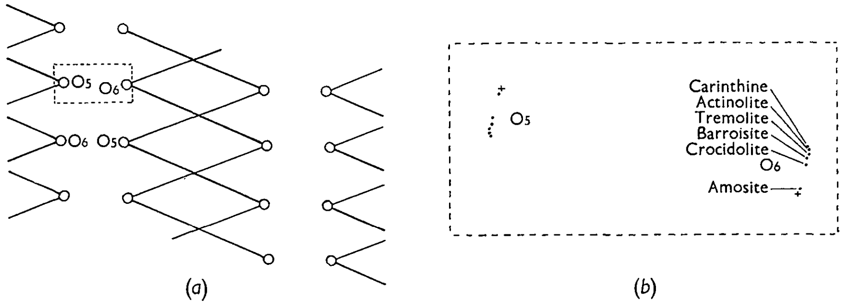

Fig. 8. Section of the clino-amphibole structure at $y = 0{\cdot}125$. In (a) the atoms which belong to any one chain are connected together by lines which do not represent direct chemical bonds. (b) Shows the area within the broken line on a larger scale to demonstrate the different extents of staggering of the O_5 and O_6 atoms in varieties with different values of β.

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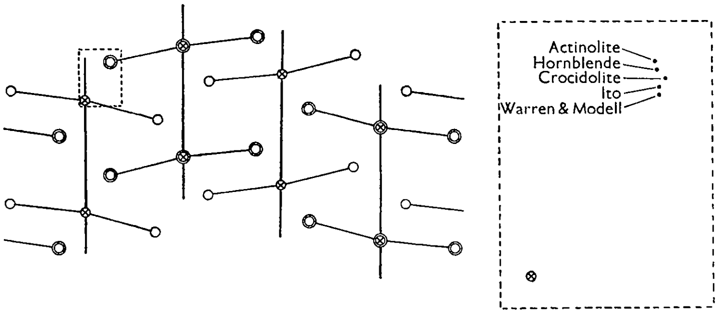
* The nomenclature of the atoms which is standard in the monoclinic amphiboles is here used to describe their counterparts in anthophyllite for the sake of continuity in the argument. Our M_4 corresponds to Warren & Modell's Mg_3 and our O_4 to both their O_5 and O_{10}. These two atoms are not related by symmetry. The distances of O_{10} from the metal ions cannot be varied by movements of the chains parallel to c whereas those of O_5 can. However, the two positions are chemically equivalent and no relaxation of the requirements for the radii of the metal ions can be achieved by adjusting the distances



(a) (b)

Fig. 10. (*a*) Section of the anthophyllite structure, corresponding to that of the clino-amphibole structure shown in Fig. 6. (*b*) Shows on a larger scale the relative positions of M_4 and O_4 according to the structure determinations of Warren & Modell, and of Ito, and also those which would occur if the individual chains had the same internal structure as in one or other of the clino-amphiboles.

therefore plotted in Fig. 10(*b*) on the basis of five different assumptions:

1. Warren & Modell's co-ordinates. These give a distance M_4–O_4 of 2·12 Å (radius sum = 2·10 Å), and M_2–O_4 slightly lower (2·09 Å). The distance O_4–O_4' between neighbouring chains (3·04 Å) is also in the expected range.
2. Ito's co-ordinates. These increase the discrepancy slightly between the M_4–O_4 and M_2–O_4 distances (2·20 and 2·07 Å respectively), and make O_4–O_4' smaller (2·94 Å) though still acceptable.

3, 4 and 5. The three published internal structures of the chain in actinolite, hornblende and crocidolite. These give excessively short M_2–O_4 distances (1·90, 1·94 and 2·02 Å respectively) and two of them give short O_4–O_4' distances (2·64, 2·74 and 2·96 Å respectively). They give excessively large M_4–O_4 distances (2·33, 2·28 and 2·26), which are large enough to admit a sodium atom, whereas sodium does not occur to an appreciable extent in orthorhombic amphiboles.

In view of the difficulties under 3–5 above it must be concluded that the internal structure of the chain in anthophyllite must be slightly different from that in the clino amphiboles. The most likely distortion to arise from environmental effects would be the rotation of silicon–oxygen tetrahedra about the Si_1–O_1 and Si_2–O_2 bonds, and this would affect the z coordinate of O_4 rather than its x coordinate, which agrees well with the fact that both Warren & Modell (1930), and Ito (1950), give an x coordinate for O_4 which is identical with the mean of the three values deduced under 3–5 above. Since $M_2 = M_4 = Mg$ it would presumably be best to assume that the two distances M_2–O_4 and M_4–O_4 should be equal. This would involve very little further movement and each would be about 2·10 Å.

On these assumptions we therefore reach a self-consistent structure for anthophyllite, and we see that it is impossible to put any atom larger than magnesium at M_4 unless we put a correspondingly smaller atom at M_2. If $M_4 = Fe''$ (radius 0·83 Å) then M_2 must not be larger than 0·74 Å. However, it is not possible to expand M_4 indefinitely even at the expense of M_2, since the O_4–O_4' distance would be unreasonably reduced. If we take 2·90 Å as a reasonable minimum for this distance, then the maximum radius of M_4 in anthophyllite will be 0·92 Å and this will require a corresponding reduction of M_2 radius to 0·70 Å.

6. Interpretation of the composition ranges of the amphiboles

(*a*) *Orthorhombic amphiboles*

In the absence of elements other than Mg and Fe'' it should be possible on the above theory to put Fe'' into three 'internal' positions ($2M_1 + M_3$) in anthophyllite without disturbing the 'edge-wise' packing of the chains. This would give a formula

$$Mg_2Mg_2Fe_3''Si_8O_{22}(OH)_2*$$

corresponding to 43% of the iron end-member. The boundary of the anthophyllite phase is given by Sundius as 38% which is in good agreement. One would expect the value to be lower than 43%, since the low entropy arising from the complete segregation of Mg and Fe must at some point offset the lower free-energy associated with the closer chain packing in anthophyllite as compared with cummingtonite. After the transition to cummingtonite it seems probable that the largest available atom (Fe'') will tend to occupy M_4 so that cummingtonite will have a formula close to

$$Fe_2''(Mg_{0{\cdot}8}Fe_{0{\cdot}2})_2(Mg_{0{\cdot}8}Fe_{0{\cdot}2})_3Si_8O_{22}(OH)_2\,.$$

Substitution in M_1, M_2, and M_3 can then proceed

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to one set of oxygen atoms and not to the other. We therefore assume with Warren & Modell that the two sets of distances will be equal and the discussion is based on the position of our O_4 where that is equivalent to their O_{10}.

* It is convenient to specify the cation sites in order of decreasing effect on packing, i.e. M_4, M_2, and $M_1 + M_3$ in that order. This convention is adopted consistently in what follows.

continuously right up to the grunerite end-member $Fe_2''Fe_2''Fe_3''Si_8O_{22}(OH)_2$ without a phase change, since M_1 and M_3 do not affect the packing and M_2 does so only to a minor degree in the clino-amphiboles.

If aluminium is introduced into the grunerite structure at M_2, then at an occupation of this site equivalent to $Fe''_{0\cdot66}Al_{0\cdot34}$ the mean radius will be reduced to 0·74 Å which is small enough to admit Fe'' to M_4 in the orthorhombic structure. If Fe''' replaces Fe'' the occupation of M_2 must be $Fe''_{0\cdot44}F'''_{0\cdot56}$ to achieve the same effect. The corresponding percentages

$$M'''/(M''+M''')$$

will depend on the way in which the extra charge is accommodated. This may occur either

(i) by leaving some vacant sites at M_4, (ii) by replacing some OH' by O'', or (iii) by replacing some Si by Al or Fe''', or by a combination of these processes.

Depending on which is adopted the above replacements correspond to between 10 and 18% (atomic) for aluminium and between 16 and 28% for Fe'''. At the magnesium-rich cummingtonite end the corresponding replacements of magnesium require 5–10% of Al and 10–18% of Fe'''. Sundius does not distinguish between the amounts of Al_2O_3 and Fe_2O_3 present at the boundary between the cummingtonite–grunerite series and the gedrite series, nor are the data sufficient to reveal the difference in the levels of the boundary at the cummingtonite and grunerite ends. The upper limit of $(Al_2O_3+Fe_2O_3)$ in cummingtonite–grunerite is given by Sundius as 5–6 mol.%, corresponding to 9·5–11·3 at.% (Al+Fe'''), but the lowest values he records in the gedrite region correspond to about 17 at.% (Al+Fe'''). The theoretical results are therefore in good agreement with the data.

The calcium atom (radius 1·06 Å) is of course much too big to enter the M_4 position in anthophyllite, and it would not be expected to enter the M_1, M_2 and M_3 positions in any of the amphiboles. It is therefore entirely understandable that the orthorhombic amphiboles should be confined to the low-calcium series. The amount of calcium (up to $Ca_{0\cdot6}$) which does occur in anthophyllite (Sundius, 1944; Rabbitt, 1948) can fairly certainly be assigned to the normally vacant '*A*' position, an appropriate number of balancing vacancies being left at M_4 or elsewhere. The sodium atom is also too large to enter M_4 in the orthorhombic structure so that there are no orthorhombic hornblendes of normal composition. Lithium, however, ($r=0\cdot78$ Å) can enter this position, and the lithium amphibole holmquistite (formula near $Li_2Al_2Mg_3Si_8O_{22}(OH)_2$) has recently been shown to be orthorhombic (Vogt, Bastiansen & Skancke, 1958). The formulation of holmquistite above with Al at M_2 is by analogy with crocidolite, in which the trivalent ion goes at M_2 for electrostatic reasons because of the deficiency of charge at M_4 when this is occupied by a monovalent ion (Whittaker, 1949). There is no clear necessity for Al to be at M_2 in holmquistite on grounds of ionic size, although its presence there will relieve any strain that is present in the distortion of the chains in anthophyllite as compared with the monoclinic amphiboles. There appears to be no other well-authenticated orthorhombic amphibole except a mangano–anthophyllite and in this the relatively small amount of manganese can be accommodated in M_1 and M_3.

The upper limit of replacement of Al+Fe''' in gedrite does not come within the scope of this discussion. It is clearly connected with the limit on the replacement of silicon by trivalent metals.

(*b*) *Monoclinic amphiboles*

The complete range of substitution of Mg by Fe'' in the tremolite-actinolite series is understandable, since this change, even at M_2, does not appreciably affect the packing of the chains in the monoclinic structure. The same is true within the riebeckite series, although here there is a minimum iron content because of the need for two Fe''' ions to preserve the charge balance.

The gap in composition between the cummingtonite–grunerite series on the one hand, and both actinolite and riebeckite on the other, must be due to the appreciably different chain packing which is evidenced by the markedly different values of β. Reference to Fig. 6(*b*) shows that this corresponds to a relative shift of interlocking chains by 0·38 and 0·24 Å respectively. The strain involved in making such adjustments locally to accommodate intermediate compositions would clearly be considerable. The possibility of intermediate compositions between actinolite and riebeckite is not covered by the phase diagrams shown and there does not seem to be sufficient evidence to decide it. The existence of such compositions as soda–tremolite $Na_2CaMg_5Si_8O_{22}(OH)_2$ does not prove that M_4 can accommodate substantial proportions of Na and Ca simultaneously, since the two elements might be segregated in M_4 and the '*A*' position. The minimum chain shift required to induce a discontinuity in composition is therefore unknown.

7. Conclusions

The theory proposed accounts satisfactorily for all the composition relationships of the known orthorhombic amphiboles and also for those of the commoner monoclinic ones for which sufficient analytical data are available. Its extension to others requires further analytical data, and in the case of the more complex substitutions will also require structural determinations to ascertain the occupancy of the M_4 position. Such work is also desirable to check the postulated positions of O_4 in anthophyllite and in a gedrite high in Fe'', and the predicted position of calcium in those anthophyllites which contain this element.

Further predictions from the theory may also be made of the possible existence of orthorhombic amphiboles of extreme compositions which are at present unknown, as follows:

nickel anthophyllite	$Ni_2Ni_2Ni_3Si_8O_{22}(OH)_2$
manganese gedrite	$Mn_2Al_2Mn_3Si_8O_{22}(OH)_2$
lithium riebeckite	$Li_2Fe_2^{\prime\prime\prime}(Mg, Fe^{\prime\prime})_3Si_8O_{22}(OH)_2$
lithium hornblendes	
such as	$Li_3Mg_2Mg_3Si_7AlO_{22}(OH)_2$
or even	$NaLi_2Mg_2Mg_3Si_7AlO_{22}(OH)_2$
and lithium tremolite	$CaLi_2Mg_2Mg_3Si_8O_{22}(OH)_2$

Of these the manganese gedrite is the most doubtful as it would have M_4 very close to the suggested maximum size.

It may also be predicted that it might be possible to bridge the 'forbidden' regions that exist between some of the monoclinic amphiboles by introduction of ions of intermediate size. Thus for example, there might be a continuous range of isomorphous replacement between grunerite and a mangano–grunerite $Mn_2Fe_2^{\prime\prime}Fe_3^{\prime\prime}Si_8O_{22}(OH)_2$ and also between such a mangano–grunerite and riebeckite

$$Na_2Fe_2^{\prime\prime\prime}Fe_3^{\prime\prime}Si_8O_{22}(OH)_2\ ,$$

because there would be no excessive strains in either series. If this is true then it would follow that all the monoclinic amphiboles could be regarded as belonging to one continuous system in a multi-dimensional phase space, but that this multi-dimensional continuum would be pierced by various channels corresponding to forbidden compositional transitions.

Further data on the composition and unit cells of 5 more monoclinic amphiboles have come to light from the literature since the completion of this work. Four of these, fluor–tremolite, fluor–richterite, fluor–edenite and fluor–boron–edenite (Comeforo & Kohn, 1955), agree well with the theory. The remaining one, tirodite (Bilgrami, 1955), agrees less well but has so complicated a composition that assignment of particular ions to the different sites is subject to a very large uncertainty. A redetermination of its unit cell (Zussman, private communication) is in good agreement with the relationship between $a \sin \beta$ and β of Fig. 7.

I wish to thank the Directors of Ferodo Ltd. for permission to publish this paper.

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