FIG. 51. Variation in length of the octahedral edges with the corresponding angles subtended at the central cation for the M1, M2 and M3 sites in the *Pnma* amphiboles.
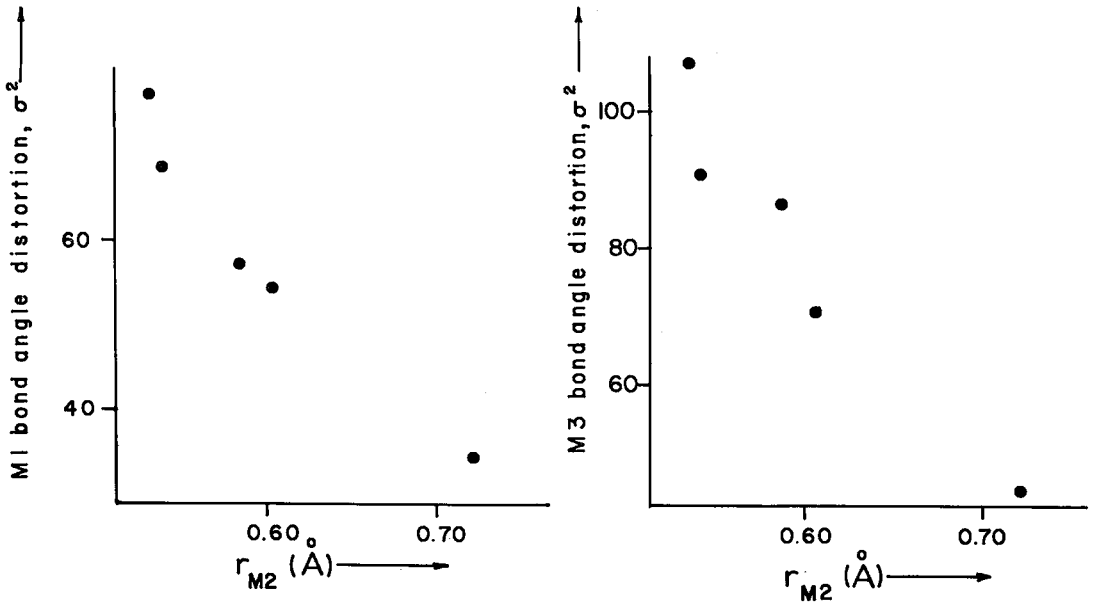

FIG. 52. Variation of the variance σ^2 in the octahedral angle for M1 and M3 with the mean ionic radius of the constituent M2 cations in the *Pnma* amphiboles.

the bond-length variations tend to minimize the deviations of the bond-valence sums from their ideal values. As is evident from Table 31, the M2 octahedron is far more distorted than the corresponding octahedra in tremolite(30) and fluor-tremolite(36), as expected for an amphibole with a high M4 occupancy of mono-valent cations. Polyhedral elements shared between adjacent polyhedra are generally shorter than the unshared elements, presumably as a result of cation–cation repulsion (Gibbs 1969), and the steric effects of the O4 bond-valence requirements significantly affect the interbond angles of the M2 octahedron, as shown in Table 31.

THE M(4) SITE

The M(4) site is situated at the junction of

TABLE 35. COMPARISON OF M-O BOND LENGTHS IN FOUR AMPHIBOLES WHERE THE OCTAHEDRAL SITES ARE OCCUPIED BY MAGNESIUM

	Proto-amphibole [20]	Tremolite (30)	Fluor-richterite (34)	Fluor-tremolite (36)
M(1)-O(1)	2.072(4)	2.064(2)	2.060(6)	2.059(3)
M(1)-O(2)	2.094(4)	2.078(2)	2.031(6)	2.054(4)
M(1)-O(3)	2.043(4)	2.083(2)	2.069(5)	2.057(3)
<M(1)-O,F>	2.070	2.075	2.053	2.057
M(2)-O(1)	2.179(4)	2.133(2)	2.186(6)	2.146(4)
M(2)-O(2)	2.084(4)	2.083(2)	2.059(6)	2.077(3)
M(2)-O(4)	1.986(4)	2.014(2)	2.011(6)	2.024(4)
<M(2)-O>	2.084	2.077	2.085	2.082
M(3)-O(1)	2.062(4)	2.070(2)	2.071(5)	2.055(3)
M(3)-O(3)	2.021(4)	2.057(3)	2.028(6)	2.011(4)
<M(3)-O,F>	2.048	2.066	2.057	2.040

the octahedral strip and the tetrahedral chain in all amphibole structure-types. The cation occupying this site bonds to nonbridging oxygen atoms of one I-beam module, cross-linking it to adjoining modules in the Y direction by bonding to the oxygen atoms that bridge along the length of the double chain. The importance of this site and its influence on the structure type of amphibole resulting from a given bulk-chemistry have long been known (Warren 1930, Whittaker 1960), and have been re-emphasized by recent studies (Papike et al. 1969, Ross et al. 1968a, 1969, Prewitt et al. 1970, Sueno et al. 1972a).

The C2/m amphiboles

The M(4) site has point-symmetry 2 and is *surrounded* by eight oxygen atoms, not all of which are necessarily bonded to the cation(s) occupying the M(4) site. The anion configurations are shown for tremolite(30), grunerite(22), potassian ferri-taramite(59) and potassium-arfvedsonite(67) in Figure 53. If the eight nearest-neighbor anions are included, the co-ordination polyhedron is a distorted cubic or tetragonal antiprism. The antiprism shares seven edges with adjacent polyhedra, four with the tetrahedra and three with the octahedra.

There has been some discussion as to the actual co-ordination number of the M(4) site in the ferromagnesian amphiboles, although for the calcic and sodic amphiboles the co-ordination number [8] is generally accepted. In his original description of the structure of grunerite(22), Finger (1969a) referred to the M(4)-site cation as six-co-ordinated on the basis of bond lengths. Subsequently, Donnay & Allmann (1970) proposed a one-sided fourfold co-ordination of the M(4) cation based on an analysis of

the bond valences. Brown & Gibbs (1969, 1970) and Mitchell et al. (1970a, 1971) implicitly assumed that the M(4) cation(s) is eight-co-ordinated in a series of nonaluminous clino-amphiboles; their treatment of Si-O distances was criticized by Baur (1971) because of this. Hawthorne & Grundy (1977b) examined this question of M(4)-cation co-ordination in four monoclinic Fe-Mg-Mn amphiboles. Essentially, this problem may be approached from a bond-valence viewpoint to see which model (co-ordination number) most closely approaches ideality. Table 36 shows the observed and calculated T-O bond lengths in the Fe-Mg-Mn amphiboles using the models of Baur (1970, 1971) for M(4) co-ordination numbers of [4], [6] and [8]. The results are rather ambiguous; for tirodite(28), a [6]- or [8]-fold co-ordination is suggested, whereas for grunerite(22), a [4]-fold co-ordination results; the cummingtonite (21) calculations show little or no preference for any of the three co-ordinations. A similar analysis using empirical bond-valences is shown in Table 37. In all cases, the deviations from an ideal value of 2.0 are least for [8]-fold co-ordination of M(4). Inspection of Tables 19 and 26 shows that the best anion-sums generally occur around O(5) and O(6); comparison of the deviations for the [4]- and [6]-fold co-ordinations with other anion deviations (where the nature of the co-ordination is not in question) shows them to be of the same magnitude. Hence it is questionable whether or not any significance can be attached to the result.

If the interaction between M(4) and the chain-bridging anions is so weak that a unique co-ordination number for M(4) cannot be defined in the cummingtonites, the question arises as to whether or not this interaction (if present) can be of any significance in the crystal chemistry of these minerals. There are several factors, unconnected with any theories of chemical bonding, that are pertinent to this question. Ross et al. (1968a, 1969) and Papike et al. (1969) have shown that where significant amounts of Mg occur in the M(4) site in cummingtonite, the structure assumes the space group $P2_1/m$ rather than the $C2/m$ symmetry that is characteristic of more Fe-rich cummingtonites, and this has since been confirmed by Kisch (1969) and Rice et al. (1974). Papike et al. (1969) showed that in the $P2_1/m$ structure, the tetrahedral chains distort independently, producing a change in the attitude of the chain-bridging anions adjacent to the M(4) site; they suggested that this change occurs "in order to provide the necessary co-ordination for the
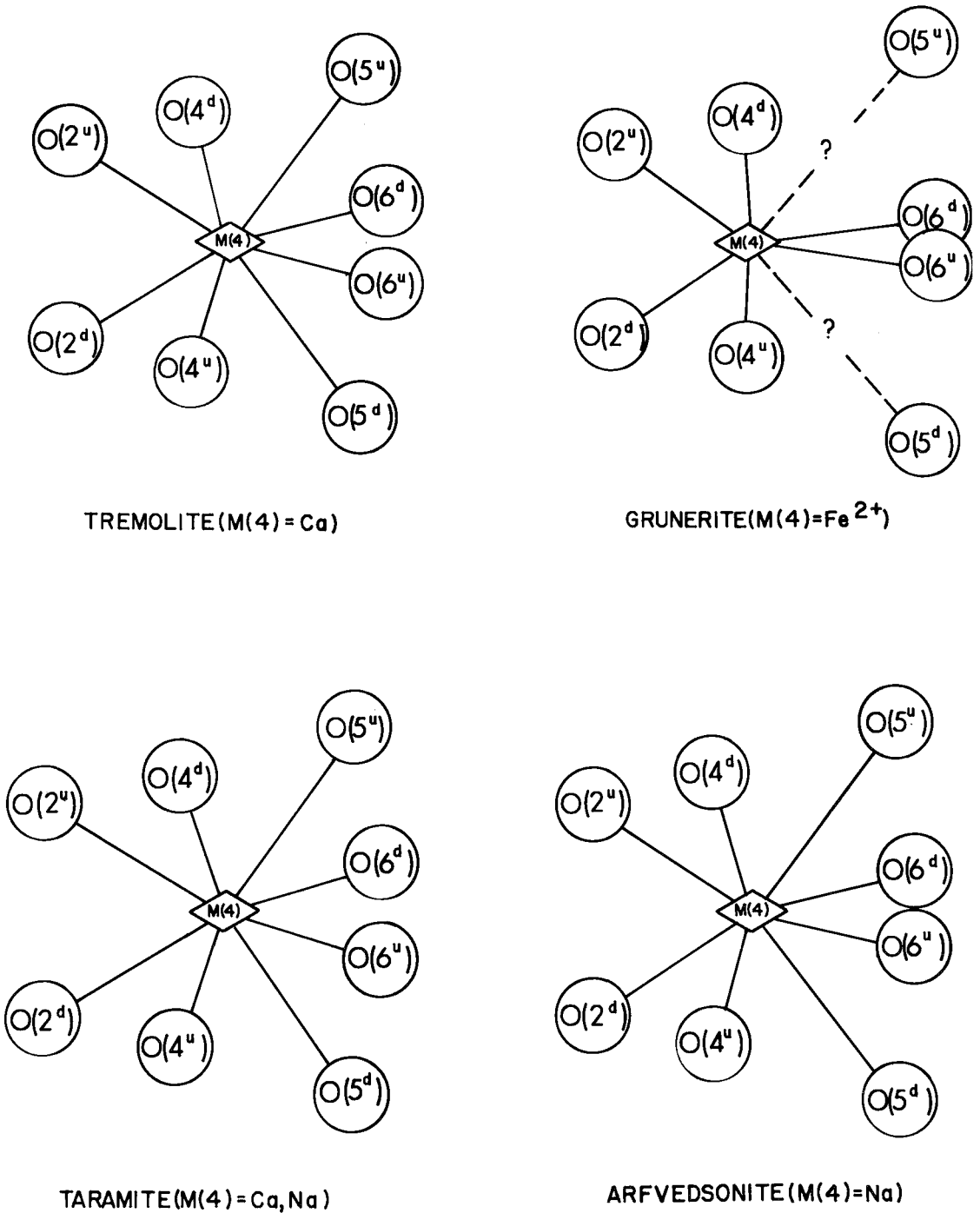
FIG. 53. The anion configurations about the M(4) site in $C2/m$ amphiboles with differing constituent M(4) cations; Y is horizontal, Z is vertical.

joint Ca/Mg occupancy" of M(4). If this inference is correct, it indicates an interaction between M(4) and the chain-bridging anions. At extremely magnesian compositions, the ferro-

TABLE 36. BOND LENGTH CALCULATIONS FOR Fe-Mg-Mn AMPHIBOLES CALCULATED USING THE METHODS OF BAUR (1971) FOR DIFFERENT M(4)-SITE COORDINATION NUMBERS

M(4) Coordination		[4]-Coordinate			[6]-Coordinate			[8]-Coordinate		
		(21)	(22)	(28)	(21)	(22)	(28)	(21)	(22)	(28)
T(1)-O(1)	OBS.	1.619	1.637(4)	1.610(3)	1.619	1.637(4)	1.610(3)	1.619	1.637(4)	1.610(3)
	METHOD 1*	1.616	1.616	1.616	1.611	1.611	1.611	1.611	1.611	1.611
	METHOD 2	1.619	1.627	1.620	1.611	1.619	1.612	1.608	1.616	1.609
T(1)-O(5)	OBS.	1.614	1.627(5)	1.622(4)	1.614	1.627(5)	1.622(4)	1.614	1.627(5)	1.622(4)
	METHOD 1	1.616	1.616	1.616	1.611	1.611	1.611	1.633	1.633	1.633
	METHOD 2	1.619	1.627	1.620	1.611	1.619	1.612	1.630	1.638	1.631
T(1)-O(6)	OBS.	1.628	1.630(4)	1.633(3)	1.628	1.630(4)	1.633(3)	1.628	1.630(4)	1.633(3)
	METHOD 1	1.616	1.616	1.616	1.641	1.641	1.641	1.633	1.633	1.633
	METHOD 2	1.619	1.627	1.620	1.641	1.649	1.642	1.630	1.638	1.631
T(1)-O(7)	OBS.	1.613	1.613(2)	1.616(2)	1.613	1.613(2)	1.616(2)	1.613	1.613(2)	1.616(2)
	METHOD 1	1.616	1.616	1.616	1.611	1.611	1.611	1.611	1.611	1.611
	METHOD 2	1.619	1.627	1.620	1.611	1.619	1.612	1.608	1.616	1.609
T(2)-O(2)	OBS.	1.625	1.633(4)	1.618(3)	1.625	1.633(4)	1.618(3)	1.625	1.633(4)	1.618(3)
	METHOD 1	1.634	1.634	1.634	1.622	1.622	1.622	1.623	1.623	1.623
	METHOD 2	1.644	1.637	1.640	1.629	1.622	1.625	1.627	1.620	1.623
T(2)-O(4)	OBS.	1.609	1.604(4)	1.595(3)	1.609	1.604(4)	1.595(3)	1.609	1.604(4)	1.595(3)
	METHOD 1	1.604	1.604	1.604	1.592	1.592	1.592	1.585	1.585	1.585
	METHOD 2	1.614	1.614	1.610	1.599	1.592	1.595	1.589	1.582	1.585
T(2)-O(5)	OBS.	1.639	1.611(5)	1.634(3)	1.639	1.611(5)	1.634(3)	1.639	1.611(5)	1.634(3)
	METHOD 1	1.619	1.619	1.619	1.622	1.622	1.622	1.646	1.646	1.646
	METHOD 2	1.629	1.622	1.625	1.629	1.622	1.625	1.650	1.643	1.646
T(2)-O(6)	OBS.	1.643	1.638(5)	1.655(4)	1.643	1.638(5)	1.655(4)	1.643	1.638(5)	1.655(4)
	METHOD 1	1.619	1.619	1.619	1.653	1.653	1.653	1.646	1.646	1.646
	METHOD 2	1.629	1.622	1.625	1.660	1.653	1.656	1.650	1.643	1.646
	$<\Delta>_1$	0.010	0.010	0.013	0.009	0.013	0.006	0.009	0.014	0.007
	$<\Delta>_2$	0.009	0.009	0.013	0.008	0.012	0.005	0.009	0.014	0.007

*Method 1 uses the value of $<d(Si-O)>$ calculated from the equation $<d(Si-O)>=1.584 + 0.0127<C.N.>$
Method 2 uses the observed mean bond-lengths.

TABLE 37. BOND-VALENCE SUMS(v.u.) AROUND O(5) AND O(6) IN SOME Fe-Mg-Mn AMPHIBOLES FOR DIFFERENT COORDINATION NUMBERS FOR M(4)

	M(4) Coordination	O(5)	O(6)
Cummingtonite(21)	[4]	1.980	1.894
	[6]	1.980	2.020
	[8]	2.030	2.020
Grunerite(22)	[4]	2.034	1.951
	[6]	2.034	2.038
	[8]	2.066	2.038
Tirodite(28)	[4]	1.984	1.899
	[6]	1.984	2.033
	[8]	2.033	2.033

TABLE 38. M(4)-O DISTANCES (Å) IN SOME Fe-Mg-Mn AMPHIBOLES

	Tirodite(28)	Tirodite P2₁/m(27)		Anthophyllite[23]	
M(4)-O(2)	2.204(3)	2.195(6)	2.208(6)	2.156(3)	2.128(3)
M(4)-O(4)	2.109(4)	2.139(8)	2.074(8)	2.044(3)	1.996(3)
M(4)-O(5)	3.101(3)	3.209(6)	2.932(6)	3.481(3)	2.865(3)
M(4)-O(6)	2.592(4)	2.511(8)	2.650(8)	2.387(3)	2.867(3)

rence of these three different structure-types with very similar chemical compositions if the M(4) site in cummingtonite $C2/m$ is considered as [4]-co-ordinate, as the major structural differences between these structures involve the configuration of the chain-bridging anions in the vicinity of the M(4) site. On the other hand, the relationships among these three structures may be adequately rationalized if M(4) is considered as bonding to the chain-bridging anion(s). The anion rearrangements about M(4) that accompany the changes in space group occur as a result of the different bonding requirements of the M(4) cation(s) as the amount of Mg at this site increases. Although this

magnesian amphiboles crystallize with the anthophyllite structure. The change in the double-chain configurations (Finger 1970b), when compared to that in cummingtonite $C2/m$, is accompanied by major changes in the anion arrangement around the M(4) site; a comparison of the relevant interatomic distances is given in Table 38. It is difficult to explain the occur-

suggests that the co-ordination of the M(4) site is not [4], it does not indicate whether [6]- or [8]-fold co-ordination is more realistic.

Another approach to this problem concerns the Mössbauer parameters for Fe^{2+} in the M(4) site. The isomer shift is sensitive to the co-ordination of the cation, and should give an indication of the M(4) co-ordination number. Comparison of the values obtained for Fe^{2+} in the M(4) sites of cummingtonite with those obtained for other ferromagnesian silicates suggests that the M(4) site should be considered as [6]-co-ordinate. The isomer shift is slightly less than that exhibited by Fe^{2+} in regular and slightly distorted octahedra; this could reflect the extremely distorted nature of the M(4) polyhedron when considered as an octahedron, as the bonding will become more covalent as the bond-length variation increases (see previous section). However, this does not negate the possibility of M(4) being [8]-co-ordinate. Although the observed isomer-shift of Fe^{2+} at M(4) in cummingtonite is much less than that normally encountered in [8]-fold co-ordination, the extreme bond-length distortion could lead to a considerable decrease in the isomer shift. As this effect is not very well characterized, this possibility cannot be dismissed.

Despite the fact that bond-valence arguments do not yield a decision among the co-ordinations [4], [6] and [8] for the M(4) site, the above discussion suggests that a [4]-fold co-ordination for M(4) is not valid, and that M(4) does bond to the chain-bridging anions. The evidence marginally favors [6]-fold over [8]-fold co-ordination, although it is certainly not conclusive. One additional factor that would indicate a co-ordination number of [6] to be more probable is the fact that the pair of O(5) oxygen atoms are further away from the M(4) cation than the

T(2), M(1) and M(2) cations in cummingtonite (21).

There has been no systematic attempt to examine mean bond-length variations at the M(4) site in amphiboles. Most studies of mean bond-length variations in minerals have concentrated on tetrahedrally and octahedrally co-ordinated cation sites. This is probably because bond-length variations in larger co-ordination polyhedra do not seem to correlate as well with the radius of the constituent cation as is the case for smaller co-ordination polyhedra (Hawthorne 1981c). It seems apparent that the lower bond-valences normally encountered in larger co-ordination polyhedra cause them to be more susceptible to inductive effects from the rest of the structure. This is the case for the M(4) site in amphiboles, where the radius of the constituent cation does not seem to be related to the mean bond-length, and large variations in mean bond-length occur from one structure to another without any change in the cation at the M(4) site. This is illustrated in Table 39, where it can be seen that variations of ~0.08 Å for M(4) = Na_2 and NaCa and ~0.04 Å for M(4) = Ca_2 occur, presumably as a result of effects in the rest of the structure. The average values of the mean bond-lengths are almost exactly in accord with the sum of the cation and anion radii (Table 39), showing that the size of the M(4) polyhedron is a function of the radius of the constituent cation. Note also the much greater dispersion of <M(4)–O> values in the alkali and sodic-calcic amphiboles than in the calcic amphiboles, as suggested above.

It is apparent from Table 39 that <M(4)–O> is strongly affected by what is going on in the rest of the structure. Consider the extended-chain model of the amphibole structure described earlier. An increase in the size of the octahedral

TABLE 39.   VARIATION IN M(4)-O DISTANCES (Å) FOR ALKALI, SODIC-CALCIC AND CALCIC AMPHIBOLES

	M(4)~Na_2			M(4)~NaCa			M(4)~Ca_2		
	(69)	(68)	(67)	G2*	(34)	(29)	(54)	(30)	(37)
M(4)-O(2)	2.403(3)	2.432(4)	2.419(4)	–	2.405(6)	2.431(4)	2.410(4)	2.397(2)	2.388(3)
M(4)-O(4)	2.332(3)	2.357(3)	2.374(4)	–	2.336(6)	2.414(5)	2.330(5)	2.321(2)	2.301(4)
M(4)-O(5)	2.828(3)	2.906(3)	2.937(4)	–	2.846(6)	2.822(4)	2.636(6)	2.767(2)	2.823(5)
M(4)-O(6)	2.457(3)	2.504(4)	2.614(4)	–	2.582(5)	2.604(4)	2.519(4)	2.539(2)	2.561(4)
<M(4)-O>	2.505	2.550	2.586	2.487	2.542	2.568	2.474	2.506	2.518
<M(4-O)>Av.		2.546			2.528			2.496	
$r_{cat}+r_{an}$		2.55			2.52			2.49	

*from Ungaretti et al. (1981)

strip may be accompanied by a straightening of the tetrahedral double-chain in order to maintain linkage. More importantly, as the strip is two octahedra wide along the M(4) . . . M(1) . . . M(1) . . . M(4) axis and three octahedra wide along the M(2) . . . M(3) . . . M(2) axis, there is increased expansion half-way between the M(4) sites (particularly as M(2) has a much wider range of possible values of the radius of the constituent cation), with the result that the tetrahedral double-chain to which the strip is linked in the Y direction moves further away from the M(4) position with increasing size of cation in the octahedral strip. This will produce much longer M(4)–O(br) bonds as the size of the M(1, 2, 3) cation increases. In this regard, it is instructive to examine the data for the alkali amphiboles, as the work of Ungaretti *et al.* (1978) provides a large data-set in which the compositional variables are not too complex. Figure 54 shows the <M(4)–O> distance as a function of the mean radius of the mean M(1,2,3) constituent cation-radius. A strong, possibly nonlinear positive
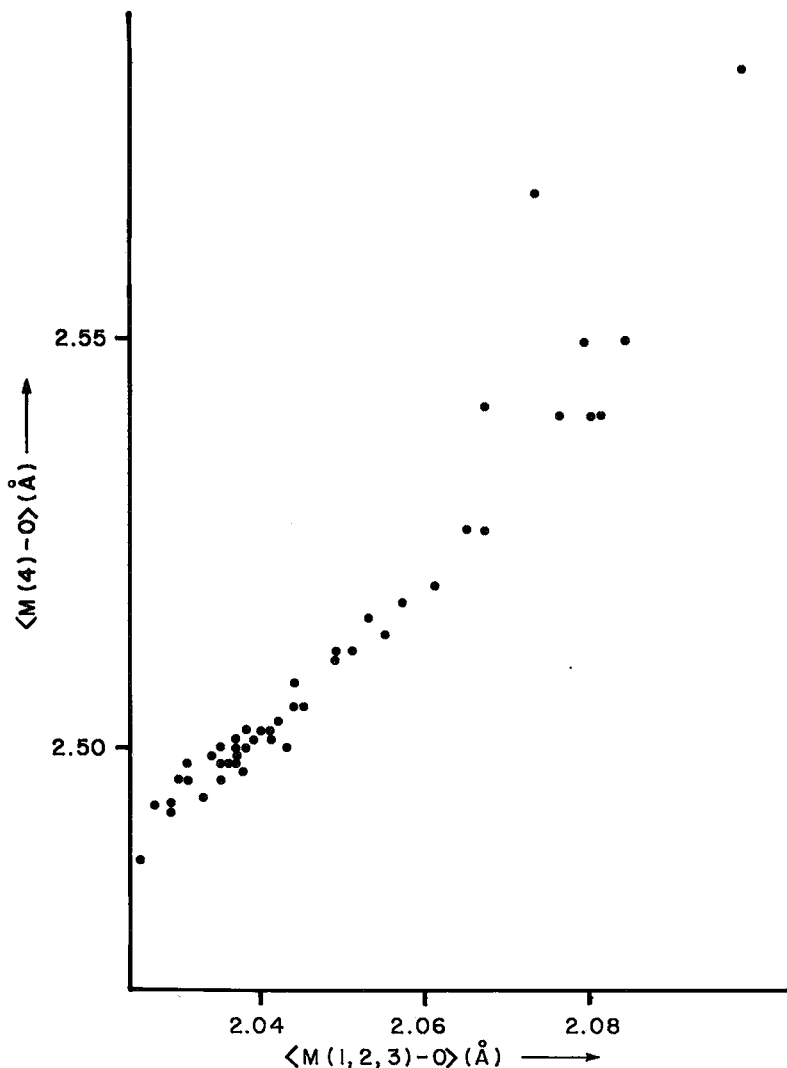

FIG. 54. Variation of <M(4)–O> as a function of <M(1, 2, 3)–O> in the alkali amphiboles.

correlation is exhibited; this is compatible with the mechanism suggested above and shows the strong inductive effect of the octahedral strip on the M(4) site. The size of the M(2) cation seems to be the dominant factor in this mechanism, and <M(4)–O> shows a strong correlation with the mean ionic radius of the constituent M(2) cation in the alkali amphiboles. If this is a significant effect and not merely a fortuitous correlation, similar relationships should be exhibited by the sodic-calcic and calcic amphiboles. This is examined in Figure 55, where it

is seen that this is the case. Although there are not as many data for these groups as for the alkali amphiboles, it can be seen that the data of Ungaretti *et al.* (1981) and the more reliable data from Appendices B2 and B3 fall on two parallel curves that are displaced to smaller <M(4)–O> values as expected; the approximate separation of the alkali and calcic amphibole curves is ~0.06 Å, as expected from the difference in [8]-co-ordinated radii for Na and Ca. Also seen in Figure 55 are the amphiboles of Ungaretti *et al.* (1981) that have M(4) site-
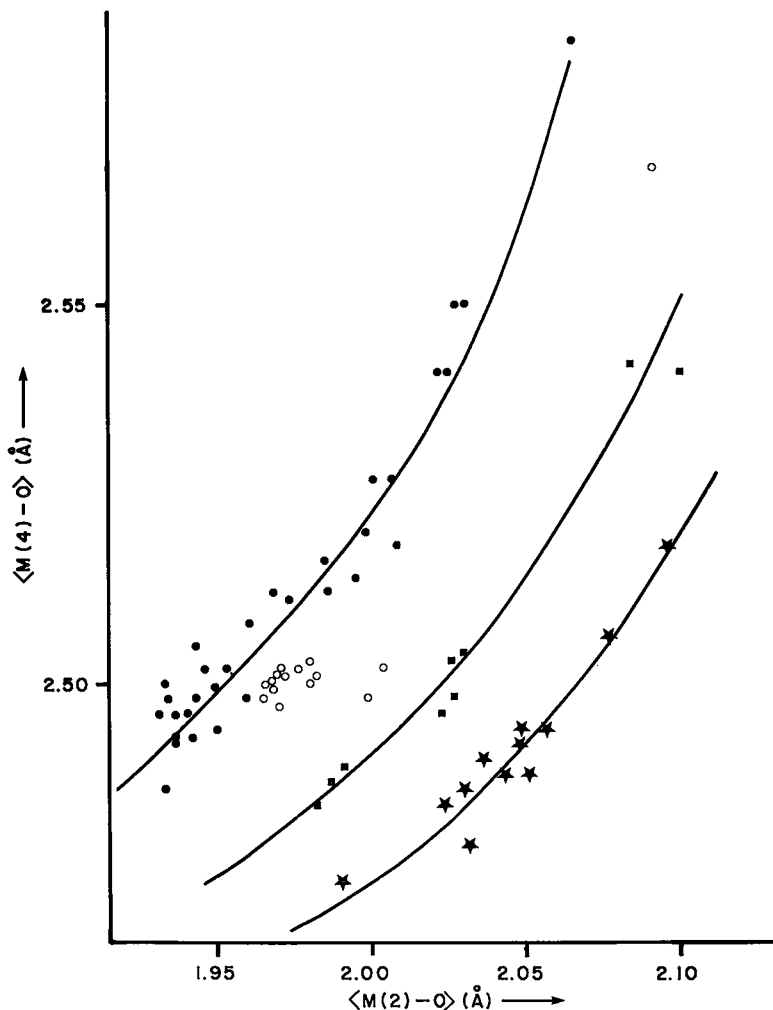

FIG. 55. Variation of <M(4)–O> as a function of <M(2)–O> in the *C2/m* amphiboles. Note the distinct trends for the alkali, sodic-calcic and calcic amphiboles (● alkali amphiboles, ■ sodic-calcic amphiboles, ★ calcic amphiboles; the symbol ○ denotes amphiboles of Ungaretti *et al.* (1981) that are intermediate between sodic-calcic and alkali amphiboles).
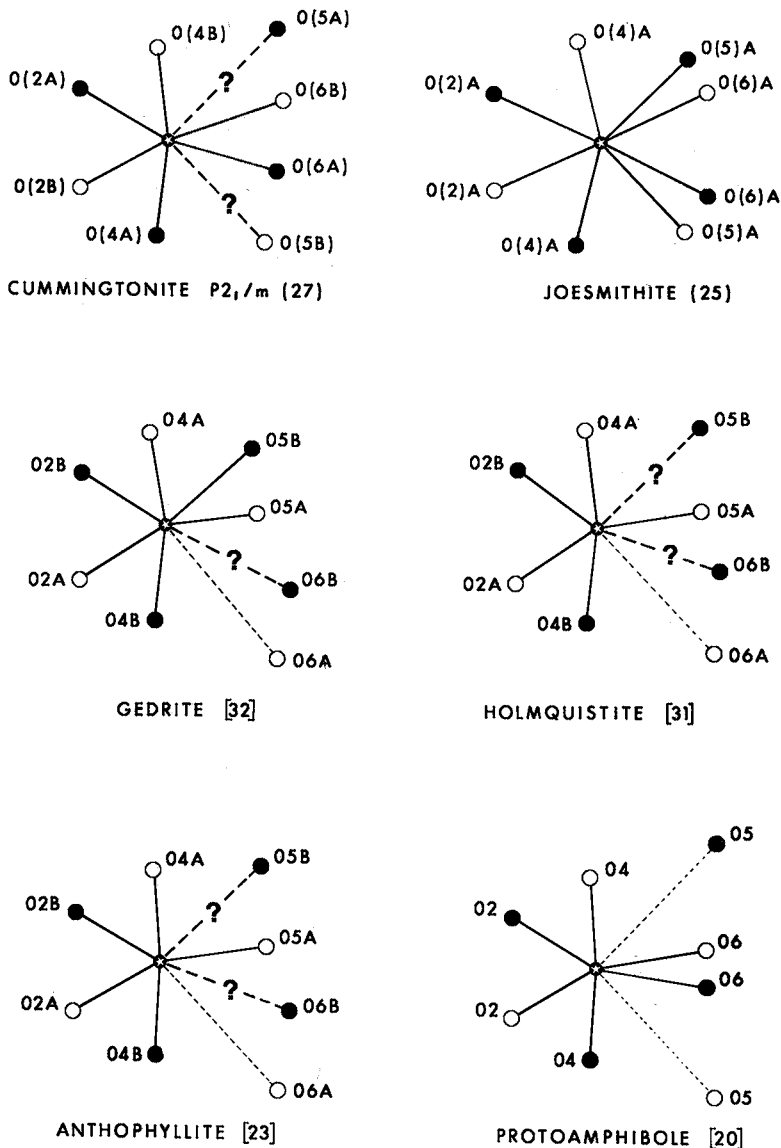
FIG. 56. The anion configurations around the M(4) site in assorted $P2_1/m$, $P2/a$, $Pnma$ and $Pnmn$ amphiboles. Only the M(4)A site of the $P2/a$ structure is shown, as the M(4)B site is indistinguishable (except for orientation) from the M(4)A site on the scale of the drawing.

occupancies between 1.0 Na and 0.5 Na+0.5 Ca; these lie between the alkali and sodic-calcic amphibole trends, as suggested by their inter-mediate compositions. Although other inductive effects are presumably present, the variation in radii of constituent M(2) and M(4) cations seems to account for the majority of the varia-tion exhibited by the <M(4)–O> distance in

$C2/m$ amphiboles.

The $P2_1/m$ amphiboles

The M(4) site has point-symmetry 1 and is *surrounded* by eight oxygen atoms, not all of which are necessarily bonded to the central cation(s). The anion configuration about M(4)

TABLE 40.   COMPARISON OF THE M(4) POLYHEDRA IN
TIRODITE P2₁/m(27) AND TIRODITE(28)

	Tirodite P2₁/m(27)		Mean($\overline{27}$)	Tirodite(28)
	A-set	B-set	<A+B>	-
M(4)-O(2)	2.195(6)	2.208(6)	2.202	2.204(3)
M(4)-O(4)	2.139(8)	2.074(8)	2.107	2.109(4)
M(4)-O(5)	3.209(6)	2.932(6)	3.071·	3.101(3)
M(4)-O(6)	2.511(8)	2.650(8)	2.581	2.592(4)
<M(4)-O>[8]	2.490		2.490	2.502
<M(4)-O>[6]	2.296		2.296	2.302

is shown for tirodite $P2_1/m$(27) in Figure 56. Comparisons of the individual bond-lengths with those in tirodite(28) (Table 40) show the effect of the relaxation in symmetry constraints. Three of the OB distances shorten and one, M(4)–O(6B), lengthens. The most noticeable differences involve the bridging oxygen atoms; differential kinking of the two symmetrically distinct chains in the $P2_1/m$ structure produces large changes in the bond lengths to the bridging oxygen atoms in both chains. The overall result is a slight contraction in all the average values for the $P2_1/m$ structure as compared with the $C2/m$ structure. The maximum changes are in distances to the O(5A) and O(5B) anions, which may not be bonded to M(4). However, the slight overall contraction [even when ignoring O(5A) and O(5B)] is in line with the argument that the $P2_1/m$ structure occurs in order to produce a tighter co-ordination around the Mg that enters the M(4) site in this structure-type.

The P2/a amphiboles

The M(4)A and M(4)B sites have point-symmetry 2 and are surrounded by eight oxygen atoms arranged in a distorted cubic antiprism. All eight oxygen atoms around each site bond to the central cation, and the overall arrangement around each site is very smilar to that in tremolite, as can be seen by comparing Figures 56 and 53. Each polyhedron shares three edges with adjacent octahedra, four edges with adjacent tetrahedra and two edges with the rather irregular A(2) polyhedron, and is entirely occupied by Ca in joesmithite(25). Whether this structure type is chemically restrictive or whether a whole family of amphibole species is possible is not yet known.

The Pnma amphiboles

The M4 site has point-symmetry 1 and is surrounded by eight oxygen atoms, not all of which bond to the central cation. The anion configurations for anthophyllite[20], holmquistite[31] and gedrite[32] are shown in Figure 56. The way in which the M4 polyhedra are linked to surrounding cation polyhedra depends on the assigned co-ordination-number, and because of the lower symmetry of the M4 site in the *Pnma* structure as compared with the $C2/m$ structure, there are significantly more possibilities. The M4 cation co-ordination may differ somewhat with change in amphibole type, as is suggested by the range of M4–O distances exhibited by this structure type (Appendix C4). Finger (1970b) suggested that the M4 cation has [7]-fold co-ordination in anthophyllite, Papike & Ross (1970) suggested [6]-fold coordination in gedrite, and Irusteta & Whittaker (1975) noted that the M4 site in holmquistite has five close neighbors. However, no quantitative justification was given for these assignments, and hence this aspect is examined here with the techniques used previously for the M(4) site in the $C2/m$ amphiboles. Of the orthorhombic amphiboles, only anthophyllite[23] may be examined using the techniques of Baur (1970, 1971), as there are no predictive curves for Li or [iv]Al in this scheme. The results are shown in Table 41 for the M4 co-ordination numbers [5] and [7]; as the sixth and seventh bonds to M4 are of equal length (see Appendix C4) in anthophyllite[23], the co-ordination number [6] is not possible. There is slightly better agreement for an M4 co-ordination of [5], but the difference is so small as to be of questionable significance. Table 42 shows selected bond-valence sums in the *Pnma* amphiboles for M4 co-ordina-

tion numbers of [5], [6], [7] and [8]; in general, the best agreement with ideal bond-valence sums occurs for a co-ordination number of [8]. However, the difference between the co-ordination numbers [8] and [7] is definitely not significant; this indicates that the eighth longest M4–O bond is of negligible valence (strength), and thus [7] is to be preferred to [8]. The bond-valence sums around M4 for a co-ordination number of [5] are significantly less than their ideal values, suggesting that the preferred M4 co-ordination number is greater than [5]. If this is the case, the M4 co-ordination number is [7] in anthophyllite and holmquistite, as the sixth and seventh strongest bonds (M4–O5B and M4–O6B) are of approximately equal strength. For the gedrites, bond-valence considerations indicate that an M4 co-ordination number of [7] is to be preferred, although geometrical considerations suggest a co-ordination number of [6]. As with the monoclinic amphiboles, the question of M4 co-ordination number is far from clearcut where this site is occupied by Fe^{2+} and Mg. The isomer shift of Fe^{2+} at the M4 site in Mössbauer spectra of

TABLE 42. BOND-VALENCE SUMS (v.u.) AROUND SELECTED ATOMS IN THE ORTHORHOMBIC AMPHIBOLES FOR DIFFERENT M4 COORDINATION NUMBERS

M4 Coordination number =		[5]	[6]	[7]	[8]
Anthophyllite[23]	M4	1.745	1.815	1.885	1.910
	O5A	2.056	2.056	1.056	2.056
	O5B	1.910	1.980	1.980	1.980
	O6A	2.033	2.033	2.033	2.058
	O6B	1.922	1.922	1.992	1.992
Holmquistite[31]	M4	0.881	0.946	0.998	1.022
	O5A	2.050	2.050	2.050	2.050
	O5B	1.983	1.983	2.035	2.035
	O6A	2.042	2.042	2.042	2.066
	O6B	1.978	2.043	2.043	2.043
Gedrite[32]	M4	1.680	1.861	1.934	1.954
	O5A	2.107	2.107	2.107	2.107
	O5B	1.792	1.973	1.973	1.973
	O6A	2.048	2.048	2.048	2.068
	O6B	1.912	1.912	1.985	1.985
Gedrite[33]	M4	1.669	1.859	1.925	1.941
	O5A	2.082	2.082	2.082	2.082
	O5B	1.729	1.919	1.919	1.919
	O6A	1.992	1.992	1.992	2.008
	O6B	1.856	1.856	1.922	1.922

orthorhombic amphiboles is not significantly different from values of isomer shift of Fe^{2+} at the M1, M2 and M3 sites; this could be interpreted as supporting the M4 co-ordination number [6] in all the *Pnma* amphiboles.

The Pnmn amphiboles

The M4 site has point-symmetry 2 and is surrounded by eight anions, only six of which appear to be bonded to the central cation. These six oxygen atoms are arranged in a very distorted octahedron, as shown in Figure 56. The M4 octahedron shares three edges with octahedra of the octahedral strip, one edge with the T2 tetrahedron and one corner with the T1 tetrahedron. Examination of the bond valences in the protoamphibole structure (Table 23) shows that the actual sum around the M4 cation (1.56 v.u.) is considerably less than the ideal value (1.75 v.u.); inclusion of the two next-nearest anions does not significantly improve the bond-valence sum (1.63 v.u.).

Structural and chemical aspects

The M(4) site is of major importance in the crystal chemistry of the amphiboles. This was recognized in early studies (Warren 1930, Kunitz 1930, Sundius 1946b) and in the work of Whittaker (1960), who emphasized the importance of the M(4) site to the structure and chemistry of the whole group. Whittaker (1960) treated the amphiboles as a packing of silicate

TABLE 41. BOND-LENGTH CALCULATIONS FOR THE TETRAHEDRAL DOUBLE-CHAIN IN ANTHOPHYLLITE[23] FOR M4 COORDINATION NUMBERS [5] AND [7], USING THE METHODS OF BAUR (1970, 1971).*

	M4=[5]		M4=[7]		
	1	2	1	2	obs.
T1A–O1A	1.622	1.612	1.622	1.614	1.618
T1A–O5A	1.657	1.648	1.647	1.640	1.640
T1A–O6A	1.622	1.612	1.622	1.615	1.611
T1A–O7A	1.622	1.612	1.622	1.615	1.615
<T1A–O>	1.631	1.621	1.628	1.621	1.621
T1B–O1B	1.622	1.623	1.622	1.611	1.618
T1B–O5B	1.621	1.623	1.647	1.637	1.636
T1B–O6B	1.622	1.623	1.648	1.637	1.622
T1B–O7B	1.622	1.623	1.622	1.611	1.617
<T1B–O>	1.622	1.623	1.635	1.623	1.623
T2A–O2A	1.628	1.626	1.617	1.622	1.619
T2A–O4A	1.597	1.595	1.587	1.592	1.601
T2A–O5A	1.657	1.655	1.647	1.652	1.655
T2A–O6A	1.622	1.620	1.622	1.626	1.621
<T2A–O>	1.626	1.624	1.618	1.624	1.624
T2B–O2B	1.628	1.645	1.617	1.626	1.630
T2B–O4B	1.598	1.614	1.587	1.596	1.608
T2B–O5B	1.621	1.638	1.647	1.656	1.643
T2B–O6B	1.622	1.639	1.648	1.657	1.653
<T2B–O>	1.617	1.634	1.625	1.634	1.634
|Δ|	0.009	0.006	0.009	0.005	

*
method 1. Si–O = $1.44 + 0.091 p_o$
method 2. Si–O = $<Si–O>obs + 0.091\Delta p_o$

double-chains, with the β angle of the unit cell controlled by the inter-chain contacts, the most important of which involve the M(4) polyhedron and the relative arrangement of the O(5) and O(6) anions in adjacent chains. Variation in β is strongly correlated with the mean ionic radius of the cations occupying the M(4) site (see also Gibbs 1966). Note that here we use the C-centred orientation, whereas Whittaker (1960) used the I-centred orientation. Decreasing β results in a closer packing of the tetrahedral chains because the increasing stagger in the arrangement of the O(5) and O(6) anions in adjacent chains allows closer approach without decreasing interchain anion–anion contacts. In the orthorhombic amphiboles, the staggering of adjacent silicate double-chains is almost complete, permitting a closer packing of the chains than does the monoclinic structure; according to the data of Finger (1967), the molar volume of pure anthophyllite and the extrapolated value for monoclinic $Mg_7Si_8O_{22}(OH)_2$ are equal, but with Fe^{2+} substitution in anthophyllite, the molar volume curve deviates strongly from the extrapolated curve of the monoclinic amphiboles. This argument is a persuasive one, but more recent data would suggest that other factors are also of importance. The importance of Mg occupancy of M4 in anthophyllite led Whittaker (1960) to suggest that Fe^{2+} should order preferentially at the M1 and M3 positions in order to avoid perturbing the "edge-wise" packing of the chains. X-ray and Mössbauer studies of anthophyllite show this not to be the case. Fe^{2+} is always strongly ordered at the M4 site, although the M4 site always contains significant Mg. Conversely, Whittaker (1960) indicated that a larger cation than Mg should not occur at M4 unless a smaller cation substitutes at M2; in line with this, the data of Seifert (1977) indicate an increase in ^{vi}Al (and ^{iv}Al) with increasing Fe/(Fe+Mg) and $X_{Fe^{2+}}{}^{M4}$ in anthophyllite.

Ross et al. (1968a, 1969) and Papike et al. (1969) emphasized the importance of the M(4) cation occupancy to the phase relations of the Fe–Mg–Mn and calcic amphiboles. At high temperatures, the divalent cations Ca, Mn, Fe and Mg can substitute readily at the M(4) site, and there is complete solid-solution, as suggested by both natural assemblages (e.g., Klein 1968) and phase-equilibrium studies (Cameron 1975). At lower temperatures, amphiboles intermediate between the Fe–Mg–Mn and calcic series are unstable because the difference in size (and bonding characteristics?) between Ca and (Mn, Fe^{2+}) is not compensated by large amplitudes

of thermal vibration as occurs at higher temperatures. The M(4) site of the $C2/m$ Fe–Mg–Mn amphiboles often contains up to ~0.40 Ca p.f.u., and the M(4) site of tremolite–actinolite can contain significant Fe^{2+} (Goldman & Rossman 1977a, Hawthorne et al. 1980). Whether these cations are distributed uniformly throughout the structure or are segregated to form Guinier–Preston (G.P.) zones or incipient exsolution lamallae must await transmission-electron-microscopy studies. Where the M(4) site of a monoclinic Fe–Mg–Mn amphibole is partly occupied by Mg, the symmetry may be $P2_1/m$ rather than $C2/m$. Papike et al. (1969) suggested that cummingtonite $P2_1/m$ occurs because the increase in positional degrees of freedom of the atoms at and around the M(4) site can allow the necessary co-ordination for the joint (Ca, Mg) occupancy of the M(4) site. This infers that the occurrence of Ca at M(4) is also a controlling factor in the existence of the $P2_1/m$ structure. As cummingtonite $P2_1/m$ can occur with down to ~0.06 Ca p.f.u. (Rice et al. 1974) and cummingtonite $C2/m$ frequently contains up to ~0.40 Ca p.f.u., the importance of Ca in this regard is somewhat questionable. In principle, this question may be examined using synthesis methods along the $Mg_7Si_8O_{22}(OH)_2 - Fe^{2+}{}_7Si_8O_{22}(OH)_2$ join. Popp (1975) and Popp et al. (1976) synthesized amphiboles along this join but these are orthorhombic and of unknown structure; whether or not this reflects the complete absence of Ca from the system is not clear. Using natural amphiboles, Yakovleva et al. (1978) have determined the transition composition between the $C2/m$ and $P2_1/m$ structures as 71% $Mg_7Si_8O_{22}(OH)_2$. This is approximately the boundary between cummingtonite and magnesio-cummingtonite and is exactly the composition $Fe_2Mg_5Si_8O_{22}(OH)_2$ at which Mg must begin to enter M(4) for the cummingtonite to be any more magnesian. This is not to say that the slightest amount of Mg at M(4) causes the $C2/m \rightarrow P2_1/m$ transition. Mössbauer experiments (Hafner & Ghose 1971, Ghose & Weidner 1972) have shown that Fe^{2+} occurs at the M(1, 2, 3) sites in the most magnesian cummingtonite known (Kisch 1969), from which we may draw the inference that Mg partly occupies M(4) at compositions less magnesian than $Fe_2Mg_5Si_8O_{22}(OH)_2$. If a K_d [$= X^{Fe}{}_{M(1,2,3)}$ $(1-X^{Fe}{}_{M(4)})/X^{Fe}{}_{M(4)}(1-X^{Fe}{}_{M(1,2,3)})$] value of 0.03 is assumed (cf., Ghose & Weidner 1972) as an average value for the composition $Fe_2Mg_5Si_8O_{22}(OH)_2$, the site occupancy $X^{Mg}{}_{M(4)} = 0.23$ is obtained. Although this value for the $P2_1/m \rightarrow$

TABLE 43. BOND LENGTHS (A) AND BOND VALENCES (v.u.) AROUND THE M(4) SITE IN TIRODITE(28), TIRODITE P2₁/m(27), AVERAGE TIRODITE P2₁/m($\overline{27}$), ANTHOPHYLLITE[23] AND GEDRITE[33]

	(28)	(27)	($\overline{27}$)	[23]	[33]
M(4)-O(2)A	2.204(3)	2.195(6)	2.202	2.156(3)	2.254(8)
M(4)-O(2)B		2.208(6)		2.128(3)	2.121(8)
M(4)-O(4)A	2.109(4)	2.139(8)	2.107	2.044(3)	2.129(8)
M(4)-O(4)B		2.074(8)		1.996(3)	2.019(8)
M(4)-O(5)A	3.101(3)	3.209(6)	3.071	2.387(3)	2.246(7)
M(4)-O(5)B		2.932(6)		2.867(3)	2.391(8)
M(4)-O(6)A	2.592(4)	2.511(8)	2.581	3.481(3)	3.911
M(4)-O(6)B		2.650(8)		2.865(3)	2.951
M(4)-O(2)A	0.322	0.324	0.320	0.321	0.256
M(4)-O(2)B		0.316		0.342	0.350
M(4)-O(4)A	0.401	0.366	0.395	0.418	0.343
M(4)-O(4)B		0.424		0.469	0.451
M(4)-O(5)A	0.058	0.054	.0.068	0.195	0.261
M(4)-O(5)B		0.082		0.080	0.190
M(4)-O(6)A	0.144	0.172	0.152	0.031	0.017
M(4)-O(6)B		0.132		0.081	0.065
Σ^{VIII}	1.850	1.870	1.870	1.937	1.933
Σ^{VI}	1.734	1.734	1.734	(1.745)^{V}	1.851

$C2/m$ transition is highly speculative and may vary with Mn, Fe^{2+} and Ca contents of the M(4) site, it is in accord with the few known values for $P2_1/m$ magnesio-cummingtonite and tirodite (Papike et al. 1969, Ghose & Weidner 1972), and values for $C2/m$ cummingtonite if allowance is made for Ca and Mn occupancies of M(4). It would seem probable that the transition composition (at room temperature) is a function of the distribution of Fe and Mg, and thus previous thermal history. However, whether or not this effect is significant is not yet known.

The $C2/m \rightarrow P2_1/m$ transition has been very well characterized experimentally, and the qualitative explanation that the transition occurs to provide the necessary co-ordination around Mg at M(4) appears satisfactory. However, attempts to provide a more quantitative rationalization in terms of bonding around the M(4) site are not as yet adequate. Bond lengths and bond valences around the M(4) cations in tirodite(28), tirodite $P2_1/m(27)$, anthophyllite[23] and gedrite[33] are shown in Table 43. Comparison of the bond valences in tirodite(28), tirodite $P2_1/m(\underline{27})$ and the average values for tirodite $P2_1/m(27)$ shows that there is no apparent significant difference between the three sets of values. Thus an empirical bond-valence analysis of the $C2/m \rightarrow P2_1/m$ transition does not seem to bear out the qualitative explanation given above. However, it should be noted that the bond-valence sums around M(4) are not satisfactory for co-ordination numbers of [6] or [8], except perhaps for [8]-co-ordination in anthophyllite[23] and gedrite[33], in which these co-ordination numbers do not appear to be reasonable. It should be noted that very irreg-

ular co-ordination polyhedra (such as M(4) in amphiboles and M2 in pyroxenes) are not amenable to close examination using bond-valence models. If the entry of Mg into the M(4) polyhedron requires a tighter co-ordination about the M(4) site, this could be achieved in the $C2/m$ structure by S rotation of the silicate double-chain element. The reasons why this could not occur are not clear, but may involve cation–cation repulsion between the M(4) and T(2) cations.

Klein (1968, 1969), Himmelberg & Papike (1969), Dobretsov et al. (1971), Miller (1977) and Raith et al. (1977) have documented the coexistence of calcic and alkali amphibole pairs, and the problem of miscibility between calcic and alkali amphiboles has been reviewed by Katagas (1974) and Ernst (1979). As with the Fe–Mg–Mn and calcic amphiboles, the stability of these amphiboles appears to hinge upon the occupancy of the M(4) site. However, unlike the Fe–Mg–Mn and calcic amphiboles, amphiboles intermediate to calcic and alkali amphiboles occur; in fact amphiboles of this type constitute the sodic-calcic group (Leake 1978). Inspection of the available compositions suggests that the immiscibility involves glaucophane only; there appear to be no well-documented accounts of amphiboles of the magnesio-riebeckite – riebeckite series coexisting with calcic amphiboles, whereas intermediate amphiboles of this composition do occur (Katagas 1974). This is in accord with the conclusions of Ernst (1979), who discussed the occurrence of alkali and calcic amphibole pairs in high-pressure metamorphic belts. Although the evidence is far from conclusive, coexisting amphibole pairs of this type are favored by low temperatures and relatively high pressures, consistent with the stability of glaucophane (Maresch 1977). The reason why a miscibility gap appears between glaucophane and the calcic amphiboles at high pressures is presumably connected with the different responses of the structures to pressure.

Studies have documented the coexistence of Fe–Mg–Mn, sodic-calcic and alkali amphibole pairs, but they are apparently nowhere near as common as the coexisting pairs discussed above. Klein (1966, 1968) documented coexisting tirodite and manganoan potassian ferri-winchite (named "magnesioriebeckite" in the original studies). Phakey & Ghose (1974) and Ghose et al. (1974) reported coexisting magnesio-riebeckite and sodian tirodite (named magnesio-richterite in the original studies). Again the key feature of the immiscibility seems to be the nature of the M(4) cation, although this is not

completely clear from the analyses of these coexisting pairs. The average composition of the tirodite–manganoan potassian ferri-winchite pair is almost the same as that of the sodian tirodite; there are some problems associated with the manganoan potassian ferri-winchite analysis (Klein 1966), and a new analysis is desirable. The amphibole $NaMgNaMg_5Si_8O_{22}(OH,F)_2$ is synthesized very easily, and the sodian tirodite of Ghose et al. (1974) is the Mn analogue of this composition. Possibly $Na(Mn,Mg)NaMg_5Si_8O_{22}(OH)_2$ is stable but immiscible with Fe–Mg–Mn amphiboles and alkali amphiboles. This situation is difficult to understand with regard to the M(4) occupancy unless $Na(Mn,Mg)NaMg_5Si_8O_{22}(OH)_2$ is a lower symmetry (subgroup of $C2/m$) structure-type, with two crystallographically distinct M(4) sites.

THE A SITE

The A site is a large cavity, situated between the back-to-back tetrahedral chains of the amphibole structures, and surrounded by an irregular array of twelve chain-bridging anions (Fig. 57). Warren (1929) noted that this site is empty in tremolite, but proposed (Warren 1930) that it is occupied by alkali cations in hornblende. This was later confirmed by a series of 2–D refinements of $C2/m$ amphiboles with $\Sigma(Ca+Na+K)>2$ (Heritsch et al. 1957, 1960, Heritsch & Kahler 1960, Heritsch & Riechert 1960).
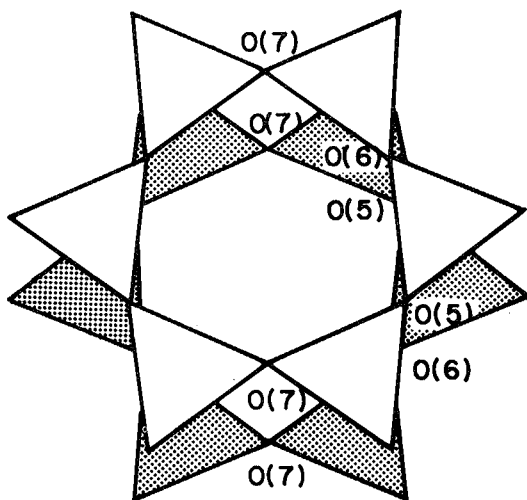

FIG. 57. The configuration of the tetrahedral chains around the A site in the $C2/m$ amphibole structure, projected down [100].

TABLE 44. A–SITE NOMENCLATURE IN C2/m AMPHIBOLES*

Site	Wyckoff symbol	Coordinates
A(2/m)	2b	0, 1/2, 0
A(2)	4g	0, y, 0
A(m)	4i	x, 1/2, z
A(1)	8j	x, y, z

*from Hawthorne & Grundy (1972)

The C2/m amphiboles

In order to simplify the following discussion, the site nomenclature of Hawthorne & Grundy (1972, 1978) is adopted; this nomenclature is summarized in Table 44. Early three-dimensional structure-refinements showed the presence of a highly anisotropic density of electrons at the A site in several $C2/m$ amphiboles. Heritsch (1955) was first to note this effect, with Na displaced along the 2-fold axis in edenitic hornblende(7). In Na–Co amphibole(15), the A-site Na was disordered along the 2-fold axis into special position 4g, the A(2) site. Conversely, in riebeckite(17) and $Na_2H_2Mg_5Si_8O_{22}F_2$(16), the A-site cation was disordered in the mirror plane into special position 4i, the A(m) site. Gibbs (1966) noted that the A-site cation occupies the A(2) position if O(3) corresponds to OH and the A(m) position if O(3) corresponds to F, and suggested that the A-site cation bonds to F occupying O(3) but is repelled by the proton if OH occupies O(3). Papike et al. (1969) observed A-site cation disorder in potassian titanian magnesio-hastingsite (24) and potassium-magnesio-katophorite(29); the disorder was considered to be primarily confined to the A(m) site although the occurrence of residual density at the A(2) site was noted. In a study of several calcic amphiboles, Hawthorne & Grundy (1972, 1973a, b) proposed a model wherein positional disorder of the A-site cations occurred both in the mirror plane and along the 2-fold axis. Cameron et al. (1973a, b) showed that in potassium-richterite (P3), the K is restricted to the mirror plane (4i) whereas in richterite(P2), the Na disorders at the 8j position. Hawthorne & Grundy (1978) examined numerous disorder models for the A site in potassian ferri-taramite(59), using the

site nomenclature shown in Table 44, and concluded that the best model involved disorder over the A(m) and A(2) positions, although they did not reject a model involving disorder over the A(m) and A(1) positions. Ungaretti (1980) and Ungaretti et al. (1981) have indicated that there is disorder over the A(m), A(2) and A(2/m) positions in a large series of natural amphiboles. It is important to note here that the site occupancies for these split positions derived from X-ray structure-refinements are not very reliable (Ungaretti et al. 1981), as the separation of the sites is commonly less than the wavelength of the X rays used in the diffraction experiment.

Various reasons have been suggested for the positional disorder of the A-site cations, including the type of O(3) anion, the type of A-site cation and the presence of tetrahedral Al. The A-site disorder patterns in potassium-magnesio-katophorite(29), potassium-arfvedsonite(67) and potassium-fluor-richterite(P3) suggest that the identity of the O(3) anion is not the major factor in the cation disorder. With all of the two-site disorder models, it is possible to obtain only the electron density at each site and not the actual site-populations in terms of the cation species, as there are generally three scattering species (Na, K and vacancy) to be distributed over the two sites. Hawthorne & Grundy (1978)

proposed that K disorders into the A(m) position and Na disorders into the A(2) or A(1) position. Figure 58 shows that the observed electron densities at the sites are compatible with such a model; it should be noted that Figure 58 does not confirm this model but is just compatible with it. Some scatter is apparent in Figure 58; Hawthorne & Grundy (1978) suggested that this may be due to cumulative errors in the chemical analyses. Even if this model is broadly correct, variable occupancy of the T(1), T(2) and M(4) sites could somewhat perturb this ordering scheme. Ungaretti (1980) has shown that positional disorder occurs over A(2/m), A(m) and A(2) in the absence of K, and this has been confirmed by Hawthorne et al. (1980). Ungaretti (1980) also confirmed that K avoids the A(2) site, as proposed by Hawthorne & Grundy (1978). Thus it appears that K occupies the A(m) and A(2/m) positions, and Na occupies the A(2), A(2/m) and A(m) positions but shows a preference for the A(m) position.

The question now arises as to why the positional disorder of the A-site cations occurs. Following Moore (1969), Papike et al. (1969) suggested that charge-balance considerations may cause Na to occupy the A(2) position in the presence of tetrahedral Al, whereas K is forced to occupy the A(m) position because
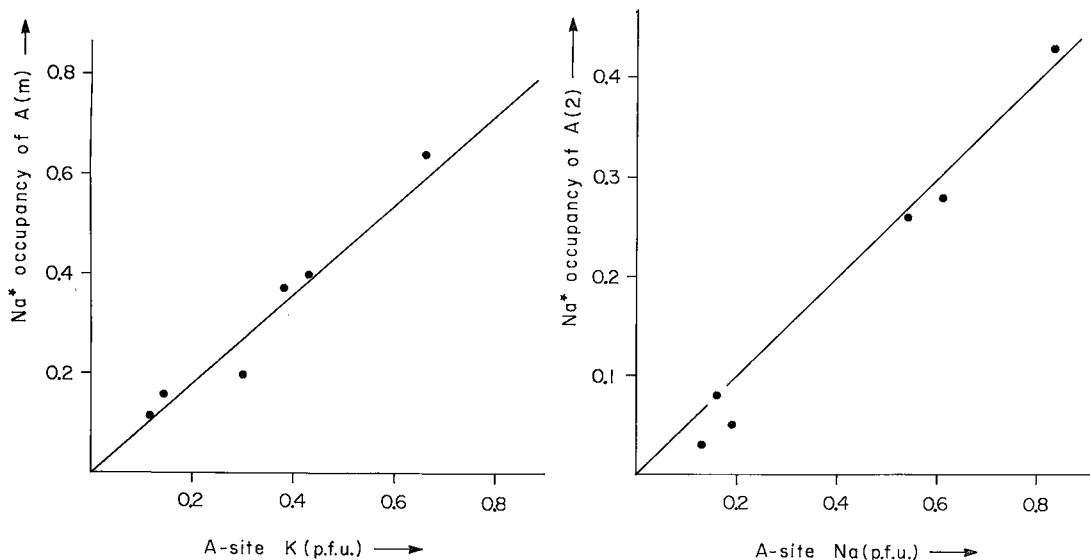

FIG. 58. The variation in refined A-site occupancies (Na* = Na+Na≡K) of some clinoamphiboles as a function of the amounts of K and Na at the A site as indicated by the cell contents derived from the chemical analysis [after Hawthorne & Grundy (1978)].

TABLE 45. A-SITE PARAMETERS FOR SEVERAL REFINED AMPHIBOLES

	(54)		(58)		(55)		(56)		(67)		(59)	
A-0(5)x4	3.056(4)Å		3.055(4)Å		3.068(9)Å		2.973(2)Å		2.755(3)Å		3.008(2)Å		
A-0(6)x4	3.159(3)		3.101(4)		3.079(5)		3.148(2)		3.212(3)		3.152(2)		
A-0(7)x2	2.518(4)		2.504(5)		2.456(7)		2.480(3)		2.629(2)		2.520(4)		
A-0(7)x2	3.735(4)		3.775(6)		3.700(7)		3.608(4)		3.720(2)		3.739(4)		
Mean [12]	3.114		3.099		3.075		3.055		3.047		3.097		
Mean [10]	2.990		2.963		2.950		2.944		2.913		2.968		
	K	Na	K	Na	K	Na	K	Na	K	Na	K	Na	
A-0(5)x4	0.093	0.066	0.093	0.066	0.091	0.065	0.105	0.075	0.148	0.103	0.100	0.071	
A-0(6)x4	0.080	0.057	0.087	0.062	0.090	0.064	0.081	0.058	0.074	0.053	0.081	0.058	
A-0(7)x2	0.221	0.151	0.227	0.155	0.248	0.169	0.237	0.162	0.183	0.126	0.221	0.151	
A-0(7)x2	0.038	0.028	0.036	0.027	0.039	0.029	0.044	0.032	0.039	0.028	0.038	0.028	
Mean [12]	1.210	0.850	1.246	0.876	1.298	0.912	1.306	0.920	1.332	0.932	1.242	0.874	
Mean [10]	1.134	0.794	1.174	0.822	1.220	0.854	1.218	0.856	1.254	0.876	1.166	0.818	
A(m)-0(5)x2*	3.042(4)	0.095	3.026(6)	0.097	3.057(9)	0.093	2.94(1)	0.111	2.846(5)	0.128	2.974(5)	0.105	
A(m)-0(5)x2	3.114(4)	0.085	3.210(7)	0.075	3.146(11)	0.082	3.10(1)	0.087	2.923(5)	0.113	3.145(5)	0.082	
A(m)-0(6)x2	2.095(5)	0.116	2.705(8)	0.161	2.737(19)	0.152	2.78(1)	0.142	3.037(5)	0.096	2.773(6)	0.153	
A(m)-0(6)x2	3.433(6)	0.055	3.507(11)	0.050	3.510(14)	0.050	3.56(1)	0.047	3.397(5)	0.058	3.580(7)	0.046	
A(m)-0(7)	2.504(7)	0.227	2.515(11)	0.223	2.501(15)	0.228	2.49(2)	0.233	2.616(8)	0.187	2.554(8)	0.208	
A(m)-0(7)	2.584(7)	0.197	2.527(11)	0.218	2.620(17)	0.185	2.58(2)	0.199	2.666(8)	0.171	2.609(8)	0.189	
A(m)-0(7)	3.391(8)	0.058	3.204(12)	0.075	3.273(19)	0.068	3.19(2)	0.077	3.491(8)	0.051	3.231(9)	0.072	
A(m)-0(7)	4.084(10)	0.025	4.104(12)	0.025	4.285(19)	0.020	4.10(2)	0.025	3.950(8)	0.029	4.261(9)	0.021	
Mean [12]	3.129	1.209	3.104	1.307	3.132	1.255	3.09	1.308	3.094	1.228	3.133	1.262	
Mean [8]	2.901	1.016	2.865	1.107	2.875	1.067	2.84	1.112	2.862	1.032	2.868	1.077	
A(2)-0(5)x2*	2.739(27)	0.106	2.945(11)	0.077	2.834(8)	0.091	2.83(3)	0.092	————		2.845(8)	0.090	
A(2)-0(5)x2	3.388(30)	0.042	3.192(12)	0.055	3.285(8)	0.048	3.12(3)	0.060	————		3.177(8)	0.056	
A(2)-0(6)x2	2.901(22)	0.083	2.978(11)	0.074	2.921(8)	0.080	3.03(2)	0.069	————		3.017(7)	0.070	
A(2)-0(6)x2	3.441(27)	0.040	3.185(12)	0.055	3.295(8)	0.048	3.27(2)	0.049	————		3.294(7)	0.048	
A(2)-0(7)x2	2.548(9)	0.144	2.460(7)	0.167	2.519(6)	0.151	2.486(4)	0.160	————		2.528(4)	0.149	
A(2)-0(7)x2	3.756(9)	0.027	3.703(9)	0.029	3.785(8)	0.026	3.684(3)	0.030	————		3.744(4)	0.028	
Mean [12]	3.129	0.884	3.077	0.914	3.107	0.888	3.07	0.920			3.101	0.882	
Mean [10]	3.003	0.830	2.952	0.856	2.971	0.836	2.95	0.860			2.972	0.826	

*bond valences calculated for K occupancy of A(m) and Na occupancy of A(2)

of its larger size. Conversely, Hawthorne & Grundy (1978) have examined this problem in terms of the cation bond-valence requirements. Table 45 lists bond lengths and corresponding bond valences for K and Na occupancy of the A(2/m) site for selected amphiboles. Irrespective of whether the cation co-ordination is taken as [12] or [10], K occupancy of the A(2/m) site would lead to an excess in bond valence around the cation, whereas Na occupancy of the A(2/m) site would lead to an overall deficiency in bond valence around the cation. This suggests that the observed positional disorder occurs as a result of the cation bond-valence requirements. In addition, the fact that K occupancy leads to a bond-valence excess whereas Na occupancy leads to a bond-valence deficiency suggests that K and Na will disorder differently, in agreement with the model outlined above. Table 45 also shows the bond lengths and corresponding bond-valences for the A(m) and A(2) sites assuming K and Na occupancy, respectively. For the A(m) site, a co-ordination number of [8] generally leads to

a fairly satisfactory bond-valence sum around the disordered K cation. However, for the A(2) site the bond-valence sums are significantly lower than ideal, although they are marginally higher than those calculated for Na occupancy of the A(2/m) site. This could be the result of partial occupancy of the site, giving bond lengths that appear longer than the actual bonds in the structure owing to the averaging effect of X rays. The same effect is not necessarily observed for the A(m) site, as it will depend on whether the site is in tension or under compression.

Docka et al. (1980) have examined this problem by calculating electrostatic structure energies as a function of A-site cation position, type and positions of charge-balancing substitutions and the O(3) anion species. Their results suggest energy minima when: (i) A(2) is occupied with [iv]Al ordered at T(1) in hydroxy-amphiboles, (ii) A(m) is occupied with [iv]Al ordered at T(1) in fluor- and oxy-amphiboles, and (iii) A(2) is occupied with [iv]Al ordered at T(2) for all O(3) anion species. Their calcula-

tions also showed an energy preference of ~20 kcal/mole for ordering of ^{iv}Al at T(1) over T(2); also, the positional disorder of the A-site cation seems to be affected by the nature of the M(2) and M(4) cations.

Hawthorne & Grundy (1978) have examined the possibility of interaction between the A-site cation and the H atom in hydroxy-amphiboles. Comparison of the principal stretching frequencies in the infrared in vacant A-site amphiboles and filled A-site amphiboles (Table 46) indicates that there is some interaction between the hydrogen atom and the alkali-metal cation at the A site. Table 46 shows the interatomic distances between hydrogen and the various A sites, taken from the neutron refinement of tremolite; most of the cation–H distances are shorter than most of the cation–O distances at the A site. In amphiboles with a fully occupied H position, some of the configurations of Table 46 must occur. Baur (1973) has considered possible interaction of H with alkali-metal cations in a series of Tutton's salts, $CuM^{+}_2(SO_4)_2 \cdot 6H_2O$ ($M^{+} = K$, NH_4,Cs). On the basis of the sums of the atomic radii (Slater 1965), he concluded that similar M^{+}–O and M^{+}–H distances do not necessarily imply bonding between M^{+} and H. However, it should be pointed out that the sum of the Slater radii are considerably less than the observed interatomic distances in the alkali-metal hydrides. For NaH and KH, the bond lengths are 2.44 and 2.85 Å, respectively. Comparison of these distances with those listed in Table 46 suggests that only one of the configurations, A(m) [x 0.445, y 0, z 0.897]–H = 2.35(4) Å, would lead to a hydride bond.

If the $C2/m$ symmetry of the bulk crystal is to be maintained, both A(m) positions must be occupied equally. This suggests that in a potassic hydroxy-amphibole, the H may be positionally disordered to avoid the formation of a hydride bond with half of the K atoms. In natural potassium amphiboles, this could be alleviated by a coupled association between occupancy of the one disordered configuration adjacent to O(3), with occupancy of O(3) by F or O^{2-}. This would account for the anomalously weak high-frequency principal OH band observed in natural clinoamphiboles (Rowbotham & Farmer 1973).

Huebner & Papike (1970) have synthesized compositions of richterite along the join $(K,Na)NaCaMg_5Si_8O_{22}(OH)_2$ and have discussed the effect of (Na,K) substitution at the A site on the cell dimensions and structure of the richterites. The cell dimensions of the two end-member compositions are shown in Table 47; the major changes are a and β (and V). Huebner & Papike (1970) noted that the total decrease in alkali-ion diameter is 0.70 Å, whereas the decrease in a is only 0.14 Å, and suggested that Na does not fit as tightly in the A site as does K. The b and c cell parameters change very little as Na substitutes for K, suggesting that this substitution does not significantly affect the geometry of the tetrahedral chains or the octahedral sheets.

The $P2_1/m$ amphiboles

As this structure-type is restricted to very magnesium-rich cummingtonite compositions, the A site is empty or perhaps has a very low

TABLE 46. HYDROGEN-A-SITE DISTANCES IN TREMOLITE, AND PRINCIPAL OH-STRETCHING FREQUENCIES FOR (MgMgMg)-OH-□/A CONFIGURATIONS IN AMPHIBOLES

Bond	A-site coordinates			Bond length
H–A(m)	0.4550	0	1.8973	2.35(4)Å
H–A(m)'	0.5450	0	1.1027	3.35(4)
H–A(2)	½	0.0103	1	2.833(7)
H–A(2/m)	½	0	1	2.827(6)

Vacant A-site amphiboles		
Tremolite	3685 cm^{-1}	Hawthorne & Grundy (1976)
Hornblende	3672	Wilkins et al. (1970)
Crocidolite	3668	Addison & White (1968)
Glaucophane	3665	Bancroft & Burns (1969)

Filled A-site amphiboles		
Richterite	3727	
Potassium-richterite	3734	Rowbotham & Farmer (1973)

TABLE 47. COMPARISON OF CELL DIMENSIONS FOR PURE RICHTERITE AND PURE POTASSIUM-RICHTERITE*

	Richterite	Potassium-richterite
a(Å)	9.907(2)	10.049(2)
b(Å)	17.979(4)	17.988(3)
c(Å)	5.269(1)	5.272(1)
β(°)	104.25(2)	104.80(1)
V(Å^3)	909.6(4)	921.4(5)

*from Cameron et al. (1973a,b)

cation occupancy. The A–O distances are very similar to those in cummingtonite $C2/m$, the major difference being the contraction and expansion of the A–O(5A) and A–O(5B) distances, respectively, relative to their values in cummingtonite $C2/m$ (see Appendix C4).

The P2/a amphiboles

In joesmithite(25), the A-site cations occupy the A(2) site, which is displaced ~0.6 Å along the 2-fold axis away from the central A(2/m) position; the A(2) site is analogous to the A(2) site in the $C2/m$ amphiboles. However, in joesmithite this displacement is ordered, with the A-site cation displaced toward the T(1)B site (Fig. 13) that is occupied by Be. It is probably this coupled ordered arrangement that results in the unusual space-group of this amphibole. Joesmithite is also unique in that it is the only amphibole to have the A site occupied by divalent cations, although Pb-bearing pargasite (Gillberg 1959) may have small amounts of Pb at the A site. Certainly the A-site content of $0.60Ca + 0.40Pb$ is unusual; the occurrence of Pb may be fortuitous (Moore 1969), although it should be noted that the off-centre configuration for Pb can also be rationalized on the basis of lone-pair stereochemistry.

There is little doubt that the coupled relationship between (Ca+Pb) and Be is the result of local bond-valence requirements. As Be contributes only about half the bond valence that Si does, the anions co-ordinating Be would be extremely undersaturated if the central A-site were occupied instead of the A(2) site (Moore 1969). This is illustrated in Table 48, which shows the bond valence contributed to the anions co-ordinating Be in the joesmithite structure. Although the bond-valence sums deviate considerably from their ideal value of 2.0, the values with the A(2)-site cation contribution are significantly closer to ideality than the values calculated assuming that the A-site cations occupy the central A-site position.

Although this bond-valence argument accounts for the coupled relationship between the A(2) site cations and Be, it does not explain why the structure adopts an ordered configuration. Moore (1969) offered several explanations for this: (i) the configuration adopted during incipient crystal-growth acted as a template for the rest of the crystal, (ii) ordered Be results in less violent distortions of the crystal than a disordered configuration, or (iii) the entropy of mixing for a disordered configuration may be too great for the stability of the crystal.

It is perhaps significant with respect to this problem that Be rarely substitutes directly for Si in crystal structures, but generally couples with a third element, thus avoiding joint (Be, Si) occupancy of a single site.

B TETRAHEDRAL CHAIN
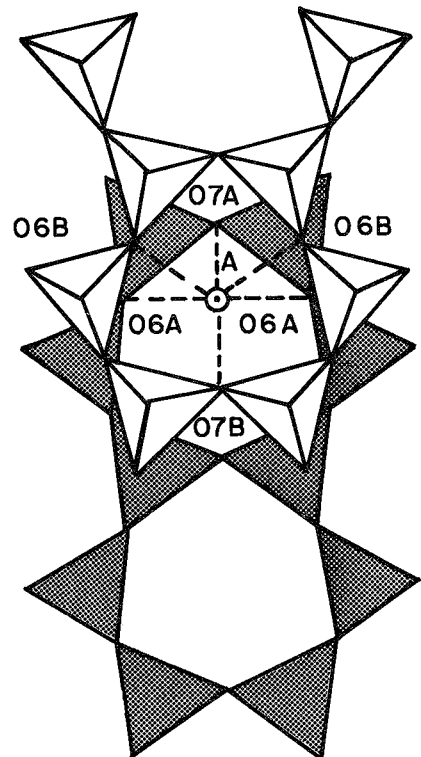
A TETRAHEDRAL CHAIN

FIG. 59. The configuration of the tetrahedral chains around the A site in the *Pnma* amphibole structure, projected down X.

TABLE 48.   BOND VALENCES (v.u.) AROUND SELECTED ANIONS
IN THE JOESMITHITE(25) STRUCTURE

	M(4)B	A(2)	T(1)B	T(2)B	T(1)A	Σ^1	Σ^2	Σ^3
O(5)B	0.23	0.26	0.45	0.94		1.62	1.73	1.88
O(6)B	0.21	0.24	0.44	0.97		1.62	1.73	1.86
O(7)		0.26	0.47		1.08	1.55	1.66	1.81

[1] Bond-valence sums without A-site cation contribution
[2] Sums with contribution from central A-site cation
[3] Sums with contribution from A(2) site cation

The Pnma amphiboles

The A-site cations in this structure type are much more tightly co-ordinated than the A-site atoms in the $C2/m$ amphiboles (Papike & Ross 1970). This is the result of the different configurations of the tetrahedral chains adjacent to the site in the two structures (Fig. 59). In the $C2/m$ amphiboles, the ditrigonal rings of the tetrahedral chains above and below the site are oppositely directed, and the nominal co-ordination-number of cations occupying the $A(2/m)$ site is [12] or [10], with no obvious cutoff in the cation–anion distances to signify a definite co-ordination-number. In the Pnma amphiboles, the tetrahedral chains above and below the A site are identically directed (Fig. 59). This results in six short A–O distances and six long A–O distances, suggesting that the A-site cations in gedrite are [6]-co-ordinate with the anions in a distorted octahedral arrangement. This contention is supported by the fact that the bond-valence sums around the A-site cation in gedrite[32] and [33] agree with those forecast from the cell contents (Appendix C3).

In the orthorhombic amphiboles, the A site may be empty as in anthophyllite and holmquistite, or may be partly occupied by Na as is the case for gedrite. Robinson et al. (1971) have shown that Na is an essential constituent of gedrite, and that gedrite can be represented by the general formula $Na_xR^{2+}_2(R^{2+}_{5-y}R^{3+}_y)$ $(Si_{8-x-y}Al_{x+y})O_{22}(OH,F)_2$, where $R^{2+} = Mg+Fe^{2+} +Mn$, $R^{3+}=Al+Fe^{3+}$ and $x\leq0.5$; thus the A site is rarely fully occupied in gedrite. With this in mind, it is of interest to examine the interatomic distances at the A site where it is partly and completely unoccupied. As the point symmetry of the A site in the Pnma amphiboles is m, the position is not completely fixed by symmetry, being free to move in the mirror plane; hence, where the site is unoccupied, a position and thus a mean site-size cannot be derived directly. However, the mean edge-length of the A octahedron can be derived in these circumstances. Drits (1970) proposed that the mean edge-length d of an anion pseudo-octahedron is related to the mean cation–anion distance l by the equation $d = l\sqrt{2}$. Although this equation is not strictly correct (Walsh et al. 1974, Ito & Matsui 1978), it is good enough for an approximate estimate of the "mean bond-length" of the A site when unoccupied. The values for anthophyllite[23] and holmquistite[31] have been averaged and are shown in Table 49. The values for gedrite[32] and [33] are shown as representing partly occupied sites.

TABLE 49. <A–O> DISTANCES AND A-SITE OCCUPANCY FACTORS IN THE Pnma AMPHIBOLE STRUCTURE

	Occupancy	$<^{vi}$A-O>
*	0.0	2.62Å
Gedrite[32]	0.34	2.55
Gedrite[33]	0.52	2.54
**	1.00	2.45

*calculated from <O-O> of A-octahedron in anthophyllite[21] and holmquistite[31]
**estimated from Na-O bond-valence curve of Brown & Shannon (1973)

To represent a completely occupied A site (octahedrally co-ordinated Na), the R_o value of the Na–O bond-strength curve of Brown & Shannon (1973) was used. Figure 60 shows the variation in <A–O> with the site occupancy of Na; the marked negative correlation exhibited is in accord with similar results for Li compounds presented by Shannon (1976). In structures with partly occupied sites, anions surrounding unoccupied sites will relax; if the polyhedron
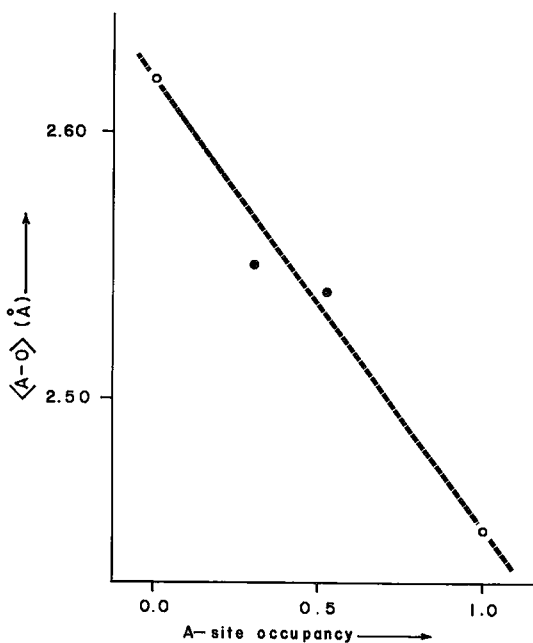

FIG. 60. Variation in <A–O> as a function of occupancy in the Pnma amphiboles. Closed circles are data for gedrite [32] and [33]; open circles are calculated values for full and empty A-sites in Pnma amphibole.

of the site is in tension, the anions will relax toward their bonded cation neighbors, and thus the mean cation–anion distance will be larger than if the site was completely occupied, as exhibited by the *Pnma* amphiboles.

Pnmn amphiboles

The A site in protoamphibole is occupied by Li according to the unit-cell contents derived from the results of the chemical analysis. However, Gibbs (1969) noted that difference maps of the A-site cavity did not show any significant concentration of electron density that could be attributed to Li, and suggested that Li was randomly distributed around the periphery of the cavity, being particularly close to the short O5–O7 edge of the T1 tetrahedron.

THE O(3) SITE

In what must have been one of its first applications, Warren (1929) used Pauling's second rule (Pauling 1929) to indicate that the O(3) position in tremolite is predominantly occupied by OH. In a general examination of the chemistry of the monoclinic amphiboles, Warren (1930) also assigned F to the O(3) position. Chemical analysis (Warren 1929) showed that O(3) could be completely occupied by OH. Fluor-amphibole was synthesized by Bowen & Schairer (1935), and chemical analysis of synthetic fluor-tremolite (Comeforo & Kohn 1954) showed that the O(3) position could be completely occupied by F. Chemical analysis of natural amphiboles (Geijer 1959, Leelanandam 1969a, b, Fominykh 1974) shows that Cl also occurs in amphiboles, apparently substituting for OH at the O(3) site; Leake (1968) recorded an amphibole (673) with O(3) completely occupied by Cl, although no end-member Cl amphiboles have yet been synthesized.

Details concerning the disposition of the OH^- anion were first obtained using infrared spec-

TABLE 50.   THE H ENVIRONMENT
IN TREMOLITE(56)

x	0.2088(6)
y	0
z	0.7628(14)
O(3)-H	0.960(6) Å
H-O(7)	2.764(7)
O(3)-O(7)	3.305(3)
O(3)-H-O(7)	116.4(2)°
O(3)'-O(3)-H	90.4(2)°

troscopy. Hanisch (1966) showed that the three-dimensional figure of absorption for the OH-stretching frequency in riebeckite is a lemniscate, rotated around its longer axis, which coincides with X^*; the O–H bond is thus parallel to X^*. A similar result was also found by Burns & Strens (1966); the absence of bands in the first overtone region of the polarized β spectrum shows the O–H bond to be confined to the (010) mirror plane, whereas from the relative overtone absorbances in the polarized α and γ spectra, calculations showed that the O–H bond makes an angle of 85(8)° with the Z axis. Papike *et al.* (1969) and Hawthorne & Grundy (1973a) approximately located the position of the hydrogen atom in tremolite(30) and ferro-tschermakite(54) using X-ray diffraction; these results were found to be in agreement with the infrared results concerning the orientation of the O–H bond. More precise data were provided by the neutron-diffraction study of tremolite(56b), pertinent results of which are summarized in Table 50. The O(3)–H bond length of 0.960(6) Å is fairly typical for a hydroxyl ion and shows that little or no hydrogen bonding with the chain-bridging anions occurs; the infrared absorption spectrum of this amphibole shows a single narrow band at 3684 cm^{-1}. The occurrence of the fundamental O–H band in amphiboles between 3600–3700 cm^{-1} is also indicative of little or no hydrogen bonding, in agreement with the crystal-structure results. Further support for this is found in the neutron inelastic scattering spectra of amphiboles reported by Naumann *et al.* (1966); bands around 650–610 cm^{-1} and 510–465 cm^{-1} that arise from torsional oscillations of OH groups are narrow and symmetrical, indicative of very weak or absent hydrogen bonding. However, arguments can be advanced for the presence of *weak* hydrogen bonding in amphiboles. In tremolite(30) and fluor-tremolite(36), <T(1)–O(7)> equals 1.616(1) and 1.606(2) Å, respectively, significantly different in each structure; if the bond-valence sum at O(7) in each structure is to be the same, O(7) in tremolite(30) must have an additional contribution of bond valence, the only possibility for which is from a (weak) hydrogen bond. Similarly, in tirodite $P2_1/m(27)$, <T(1A)–O(7A)> and <T(1B)–O(7B)> are 1.628(4) and 1.603(4) Å, respectively; applying the same aargument as above, there should be a weak hydrogen bond to O(7A) if the bond-valence sums are to be the same. If this is the case in tirodite $P2_1/m(27)$, the infrared absorption spectrum in the fundamental region should consist of two sharp peaks of approximately equal intensity, there being
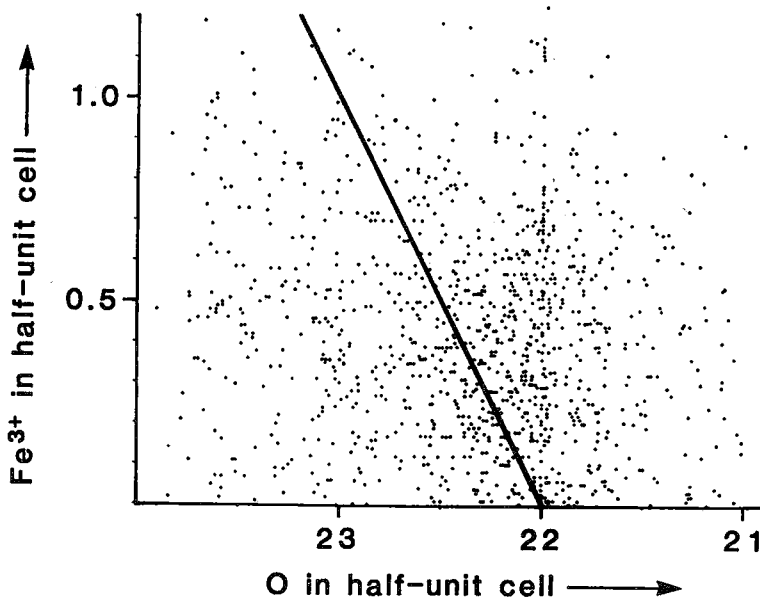
FIG. 61. Variation in Fe^{3+} p.f.u. as a function of oxygen content p.f.u. for all amphiboles in Leake (1968); after Leake (1968). The sloping line indicates the condition where the Fe^{3+} is sufficient to balance oxygen replacing the monovalent anion at the O(3) position. No correlation is apparent.

no fine structure due to cation disorder at M(1), M(2) and M(3), as these sites are occupied solely by Mg (Papike *et al.* 1969). Unfortunately, the necessary infrared absorption data for tirodite $P2_1/m(27)$ are not available.

The O(3) position may also be occupied by O^{2-} in oxy-amphiboles, but the origin and role of O^{2-} in this position are not well understood. Extensive studies on dehydroxylation and oxidation of both natural and synthetic amphiboles have shown that these are co-operative processes in iron-rich amphiboles, and hence the amount of O^{2-} at O(3) produced by dehydroxylation in the solid state should correlate with the amount of Fe^{3+} produced by the accompanying oxidation. No general correlation of this sort is apparent in natural amphiboles (Fig. 61), and the question arises as to whether this correlation is obscured by cation substitutions involving Fe^{3+}, or whether postcrystallization oxidation is not an important process in producing dehydroxylated amphiboles, except in certain high $f(O_2)$ environments. Certainly, an alternative possibility is that amphiboles may crystallize hydroxyl-deficient, with the $O^{2-} \rightleftharpoons OH^-$ substitution balanced by a polyvalent cation substitution (*e.g.*, Boettcher *et al.* 1978). This was suggested by Leake (1968), with Ti

being involved in the substitution; this possibility is supported by the data of Engel & Engel (1962), as indicated in Figure 62. Other results of good-quality analyses with fairly variable $(OH+F+Cl)$ contents give different correlations or no discernable correlations at all (*e.g.*, Binns 1965, Compton 1958, Appleyard 1975). However, intercation correlations from factor analysis of a large number of amphiboles (Saxena & Ekström 1970) show significant correlation between OH and Ti. Thus, it seems that O^{2-} substituting for monovalent anions at the O(3) position may be coupled with polyvalent cation substitutions as an integral part of amphibole chemistry that originates during the crystallization process.

Kitamura *et al.* (1975) have shown that Ti preferentially occupies the M(1) site in potassian oxy-kaersutite(40), a feature they interpreted as resulting from cation disorder accompanying oxidation–dehydroxylation. Presumably the strong ordering of Ti at M(1) occurs as a result of local bond-valence requirements upon loss of the hydrogen atom. This is certainly in line with the negative correlation between $(OH+F+Cl)$ and Ti shown in Figure 62, although the paragenesis of these amphiboles suggests that the hydroxyl deficiency may have
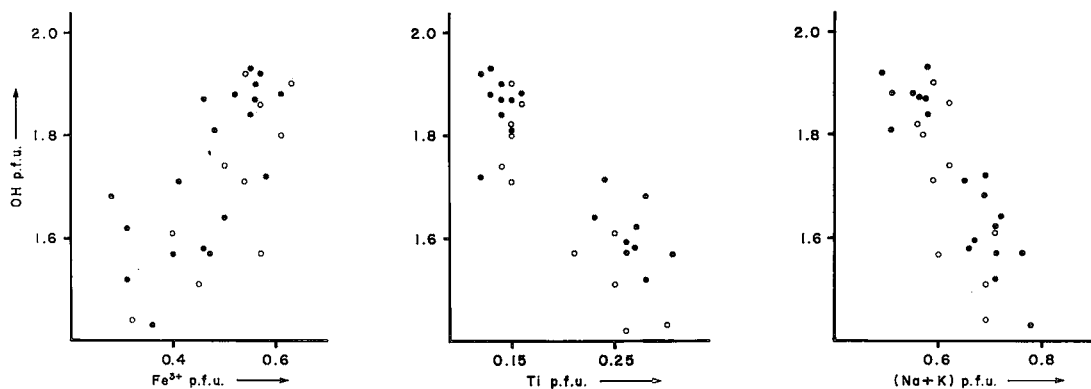
FIG. 62. Variation in (OH+F+Cl) p.f.u. as a function of Fe^{3+}, Ti and (Na+K) p.f.u. for the amphibole suite of Engel & Engel (1962) [after Leake (1968)]. Closed circles represent analyses with OH, F and Cl; open circles represent analyses with OH only.

originated during crystallization rather than by postcrystallization oxidation. Ungaretti (1980) has shown that dehydroxylation and oxidation of alkali amphiboles are accompanied by significant rearrangement of cations, with a concentration of higher valence cations at M(1) and M(3), around the O(3) site; this is to be expected on bond-valence considerations. Thus the amphibole structure is apparently stable with O^{2-} at O(3) and M^{3+} cations at M(1) and M(3), as the riebeckite examined by Ungaretti (1980) is presumably very low in Ti. An even more interesting factor shown by this elegant piece of work is the fact that upon oxidation, vacancies were produced at the M(4) site, with Na migrating to the previously empty A-site. It will be interesting to see if Na occupies a very off-centre position in the A-site cavity, enabling it to bond directly to O^{2-} at the O(3) position. This type of mechanism is certainly in line with the correlations of Figure 62; the possible role of Fe^{3+} in addition to Ti^{4+} in such substitutions may obscure the substitution mechanisms in some cases. There is a lot of interesting work still to be done in this area.

CRYSTAL-STRUCTURE REFINEMENT OF AMPHIBOLES

Crystal-structure refinement gives the relative locations and magnitudes of the electron-density centres in the amphiboles examined. Combined with a knowledge of the unit-cell contents, this allows the derivation of site occupancies and bond geometry. The derivation of bond geometry is quite straightforward and needs no discussion here; such information is

the basis of the entire discussion given above, and this information is given in detail in Appendices B4–6, C4–6 and D4–6 for published amphibole structure-refinements. The derivation of site-occupancy information is less straight-forward. A general discussion of the techniques involved is given by Hawthorne (1983); a summary of the methods applied to amphiboles is given here.

Where sufficient difference in scattering power occurs between cation species, site populations may be derived from single-crystal X-ray data. This procedure was first used for amphiboles by Ghose & Hellner (1959) and Ghose (1961) in the refinement of the structures of cummingtonite(9) and cummingtonite(21), where they assumed that the isotropic temperature-factors of the M-site atoms were equal, and manually adjusted the Mg–Fe site populations of these sites until this condition was satisfied. Fischer (1966) refined the structure of cummingtonite(21) using a procedure whereby the site populations were included as a variable in the least-squares refinement procedure. Site populations in several other amphiboles (Finger 1967, Papike & Clark 1968) were determined by including the total site scattering-powers as variables in the refinement procedure. However, Finger (1967, 1969a) and Burnham et al. (1971) showed that this procedure can result in significant deviations in the structure model from the cell contents indicated by the chemical analysis. They proposed that the movement off composition occurred as a result of the high correlations between the scale factor, site occupancies and temperature factors. It would appear more likely that both the movement off composition