FIG. 100. Left: powder Raman spectrum of actinolite. Right: laser Raman spectrum of a crystal of tremolite [from White (1975) and Blaha & Rosasco (1978), respectively].

100). Tremolite is fairly well ordered and produces a detailed spectrum, whereas actinolite has significant cation disorder and gives a smeared weak spectrum; only a few weak bands are observed, the bridging oxygen mode at 670 cm⁻¹ being the only band of appreciable intensity, with weak bands observed at 1055, 1030, 387, 367 and 223 cm⁻¹. It should be noted, however, that the laser-Raman technique is useful for the characterization of fibrous or asbestiform amphiboles where these are highly ordered (as is often the case).

Neutron-inelastic scattering

Infrared absorption studies concerning the OH group in amphiboles have concentrated on the region of the principal stretching band around ~3650 cm⁻¹. There are other vibrations of the OH anion, considered as a rigid group bound in the structure, and these carry information concerning the bonding of the OH anion to other ions in the structure. However, these vibrations occur below 1000 cm⁻¹, where they are complicated by the extensive vibrational and lattice modes of the structure. Because of the differences in neutron-scattering cross-sections, the most intense peaks in neutron-inelastic-scattering spectra are those resulting from the motion of hydrogen-bearing groups. Consequently, oscillatory and translatory modes of the OH anion can be examined using this technique.

Naumann *et al.* (1966) have reported neutron-inelastic-scattering spectra for four amphiboles; the spectra are shown in Figure 101. The

principal features of each spectrum are the same. Each is characterized by a sharp primary maximum at ~650 cm⁻¹ and a sharp, secondary maximum at ~510 cm⁻¹, although the latter is much weaker in crocidolite than in the remaining three amphiboles. In addition, there are a number of less intense broader peaks at lower frequencies. The narrow symmetrical shape and high relative intensity of the 650 cm⁻¹ and 510 cm⁻¹ peaks characterize the motions involved as torsional oscillations of the OH groups. The narrow, symmetrical peak-shape is indicative of very weak hydrogen bonding or none at all. The remaining peaks (below 400 cm⁻¹) can be assigned to translatory vibrations of OH groups, optical (broader, less symmetrical and less intense than the oscillatory modes) and acoustic modes (the lowest frequency modes).

CATION DISTRIBUTIONS IN AMPHIBOLES

The wide variety of cation co-ordinations in the amphiboles, together with the large structural compliance of some of the sites, result in considerable chemical complexity in these minerals. A knowledge of the site occupancies and order–disorder relationships in the amphiboles is essential to a better understanding of their crystal chemistry, phase relations, optical and electrical properties and oxidation–dehydroxylation mechanisms. Consequently, the amphiboles, more than any other mineral group, have been studied from the viewpoint of site-population characterization.

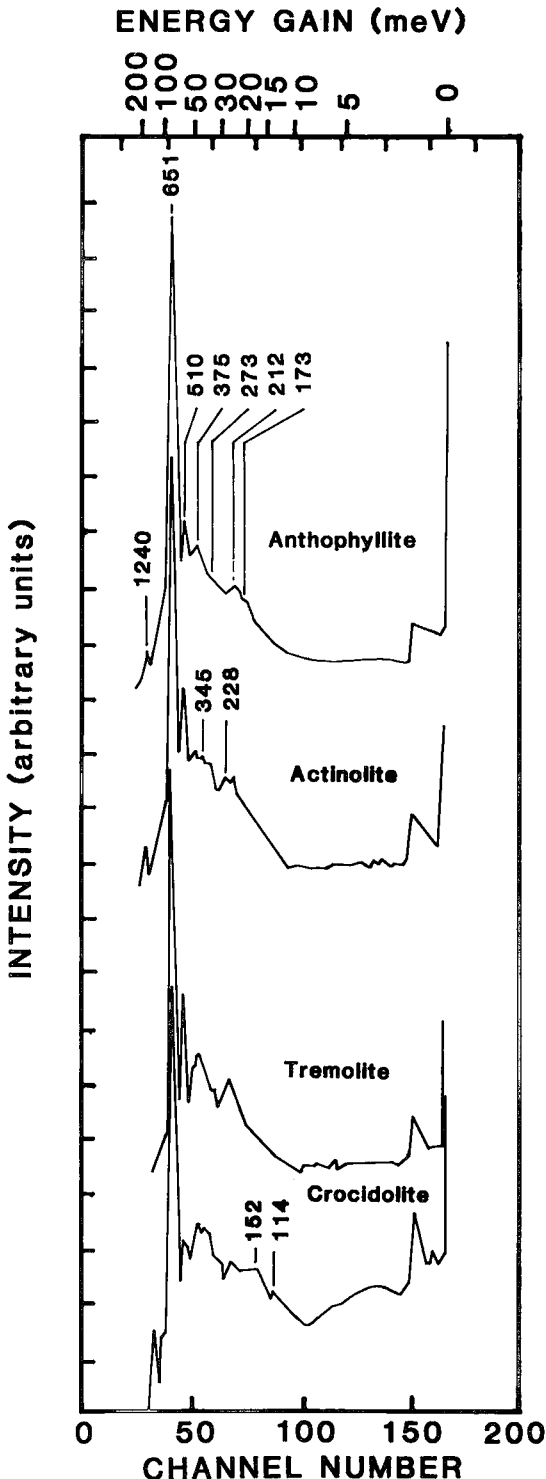Warren (1930) considered chemical varia-

FIG. 101. Neutron inelastic scattering spectra for miscellaneous amphiboles [from Naumann *et al.* (1966)].

TABLE 58.   NORMAL CATION SITE-ASSIGNMENTS IN AMPHIBOLES

Cation	A	M(4)	M(1),M(2),M(3)	T(1),T(2)
Si				————
Al			————————	————————
Fe^{3+}			————————	
Ti			————————	
Fe^{2+}		——	————————	
Mn		——	————————	
Mg		——	————————	
Li	—	——	————	
Ca		——		
Na	—	——		
K	—			

tions in the monoclinic amphiboles in terms of cation occupancies in the amphibole structure. He showed that the structures of several monoclinic amphiboles are very similar to that of tremolite with "certain replacements of structurally equivalent ions". Consideration of the amphibole structure, together with observed chemical variations in natural amphiboles and ionic radii of the substituting cations, led Warren (1930) to group certain elements together into four subgroups, similar to the general formula given in the previous section on nomenclature. He also showed that certain cations may occur in more than one subgroup, suggesting that this was a major factor frustrating previous attempts to systematize amphibole compositions. According to current usage, the Ca group of Warren (1930) is split up into the A and B groups (see Nomenclature section); apart from this, the general formula and cation groupings used today are virtually the same, as indicated in Table 58. Whittaker (1949) showed a nonrandom distribution of group-C cations over the M(1), M(2) and M(3) sites in magnesio-riebeckite(3), and Papike & Clark (1967) showed a nonrandom distribution of group-C cations over the T(1) and T(2) sites in potassian titanian magnesio-hastingsite(24). In the last fifteen years, considerable effort has gone into the characterization of cation ordering in amphiboles using the experimental techniques summarized above. What follows is a summary of the results from a wide variety of techniques; this gives a general view of cation site-occupancies in amphiboles.

Aluminum

As shown by Warren (1930), Al may be both a C-group and a T-group cation, *i.e.*, Al

may occur in both octahedral and tetrahedral co-ordination. When in tetrahedral co-ordination, Al shows considerable ordering; because of the similarity in X-ray scattering power of Si and Al, relative ordering of these cation species cannot be *directly* distinguished by X-ray diffraction. However, the considerable disparity in size between Si and ^{iv}Al (0.26 and 0.39 Å, respectively) allows ordering of Al over the tetrahedral sites in the amphibole structure to be examined by comparison of mean bond-lengths at the various sites (see previous section on ordering of tetrahedral Al). In monoclinic ($C2/m$) amphiboles, Al shows the site ordering T(1)>>T(2); subsilicic amphiboles definitely have Al at the T(2) site, but the presence of Al at T(2) in amphiboles where Si≥6.0 atoms p.f.u is somewhat questionable (Ungaretti 1980). In the orthorhombic (*Pnma*) amphiboles, Al shows the site ordering T1B≥T1A≥T2B>T2A; as indicated in Figure 41, the T2B site shows considerable Al occupancy in gedrite.

When Al is a C-group cation, very strong site-ordering occurs. However, because of the similarity in X-ray-scattering power of Mg and Al, relative ordering of these cation species cannot be *directly* distinguished by X-ray diffraction. Whittaker (1949) suggested that trivalent cations should be ordered at the M(2) site in magnesio-riebeckite(3). Refinement of the structure of glaucophane(26) (Papike & Clark 1968) showed that the mean bond-length at the M(2) site is much shorter than the mean bond-lengths at the M(1) and M(3) sites, suggesting that Al is very strongly or even completely ordered in the M(2) site in glaucophane. Later studies have confirmed that trivalent cations tend to be ordered at the M(2) site, the variation in size of the M(2) octahedron generally being compatible with this premise (Hawthorne 1978a). Results that are pertinent to this argument for ^{vi}Al-ordering are those for glaucophane(26), holmquistite[31], gedrite[32], gedrite[33], holmquistite[47], tschermakite[48] and ferro-tschermakite(54). However, these results are not sufficiently accurate to tell whether or not this ordering is complete. Bancroft & Burns (1969) have assigned weak peaks in the infrared absorption spectra of glaucophane to cation arrangements involving Al at the M(1) or M(3) sites. Because of the problems associated with the derivation of site occupancies from infrared absorption spectra (Hawthorne 1983), this cannot be considered as good evidence for occupancy of M(1) or M(3) sites. In support of this view, Strens (1974) reported that of fifteen samples of glaucophane examined by this

method, none show minor bands. In a detailed crystallographic analysis of twenty-six blue amphiboles, Ungaretti *et al.* (1978) used mean bond-length and charge-balance arguments to show complete order of Al at M(2). Thus there there is no direct evidence of Al occurring at the M(1) and M(3) sites, the current evidence favoring complete order at the M(2) site (except perhaps for oxy-amphiboles, in which drastic disordering of cations may accompany oxidation by dehydroxylation).

Ferric iron

Fe^{3+} is generally considered as a C-group cation; there is little evidence to prove otherwise (Phillips 1963), and Leake (1968) has shown that amphibole compositions deficient in Si+Al also tend to be classified as poor on grounds other than those connected with the summation of T-group and C-group cations. However, in the clinopyroxenes, the presence of Fe^{3+} in tetrahedral co-ordination has been shown (Huckenholz *et al.* 1969, Hafner & Huckenholz 1971, Virgo 1972b), and the similarity of the pyroxene and amphibole structure-types suggests that tetrahedrally co-ordinated Fe^{3+} could occur in amphiboles. Hawthorne & Grundy (1977b) provided some X-ray and Mössbauer evidence for Fe^{3+} occupancy of the T(2) site in zincian tirodite(57) but indicated that this evidence is of marginal significance.

Whittaker (1949) proposed that Fe^{3+} is strongly ordered at the M(2) site in magnesio-riebeckite(3). Later studies assumed that trivalent cations (including Fe^{3+}) were ordered at the M(2) site on the basis of the mean bond-length at M(2) being shorter than those at M(1) and M(3). Surprisingly enough, it is only recently that amphiboles sufficiently high in Fe^{3+} (potassian ferri-taramite(59) and potassium-arfvedsonite(67), see Appendix B3) have been examined to provide more definite size-evidence of this ordering. As ordering patterns based on mean bond-length are not very accurate, whether or not Fe^{3+} is generally completely ordered at M(2) is not certain. Subsilicic titanian magnesian hastingsite(58) apparently has Fe^{3+} at the M(1) or M(3) sites (or both; see Appendix B3), but the refinement results for this amphibole are somewhat peculiar. Detailed analysis of mean bond-lengths and charge requirements indicates complete Fe^{3+} order at M(2) in some cases (Ungaretti *et al.* 1978) and the occurrence of small amounts of Fe^{3+} at the M(1) or M(3) sites (or both) in other cases (Ungaretti *et al.* 1981). It is not clear whether this represents the

equilibrium-crystallization configuration or is the result of postequilibration oxidation by dehydroxylation.

Numerous amphiboles have been examined by Mössbauer spectroscopy, a technique that is sensitive to iron in its various valence-states. Burns & Greaves (1971) examined a series of actinolite samples and found that in some cases, the half-width of the doublet assigned to Fe^{3+} was significantly larger than the doublets assigned to Fe^{2+} at the various sites. They suggested that this was due to the presence of several closely overlapping doublets resulting from the presence of Fe^{3+} at the M(1) or M(3) sites (or both) in the structure. However, the larger half-widths of the Fe^{3+} doublet may be an artifact of the fitting procedure (Hawthorne 1983) or the results of variation in next-nearest-neighbor occupancies (Dowty & Lindsley 1973, Dollase & Gustafson 1978). Thus in normal amphiboles, this cannot be considered as definite proof of Fe^{3+} occupancy of the M(1) or M(3) sites. Mössbauer spectra of oxidized amphiboles (Ernst & Wai 1970) show a distinct increase in half-width of the Fe^{3+} doublet over the doublet in the corresponding unoxidized amphibole; in some cases, visible resolution of more than one Fe^{3+} doublet occurs (Ernst & Wai 1970, Fig. 6). Infrared absorption investigation of the same sample (C–4980) showed two minor peaks at 3625 cm^{-1} and 3654 cm^{-1}. As these were present in both natural and heat-treated material, they were assigned to configurations involving Fe^{3+}, suggesting the presence of Fe^{3+} at M(1) or M(3) (or both) in both unheated and heated material; however, note that a peak at 3654 cm^{-1} is not compatible with a configuration involving Fe^{3+}, according to Table 55. Several studies of natural amphiboles (Burns & Prentice 1968, Bancroft & Burns 1969, Burns & Greaves 1971) by infrared absorption spectroscopy have demonstrated that Fe^{3+} occurs at the M(1) and M(3) sites. Strens (7974) has suggested that these authors have overestimated the intensity of those peaks assigned to Fe^{3+}. Burns & Greaves (1971) have indicated that oxidation occurs during sample preparation for infrared absorption spectroscopy; thus the small amounts of Fe^{3+} possibly observed in these studies are due in some part to such sample preparation. This is supported by the results of Strens (1974) for numerous alkali amphiboles, where no peaks attributable to Fe^{3+} were observed in the infrared absorption spectra and where the samples were prepared by a method where no significant oxidation occurred.

Detailed crystal-structure refinements by

TABLE 59. K^d VALUES FOR FE^{2+} ORDERING AT M(1) AND M(3) FOR THE AMPHIBOLES OF BOCCHIO ET AL. (1978) AND UNGARETTI ET AL. (1981)

	including Fe^{3+}	without Fe^{3+}
A4	0.46	0.73
A5	0.48	0.89
B3	0.51	0.91
B6	0.46	0.91
C1	0.43	--
C3	0.45	--
D6	0.43	--
D7	0.40	--
D9	0.56	--
D18	0.48	--
E2	0.39	--
E9	0.58	--
E13	0.54	--
E14	0.52	--
F3	0.35	--
GH	0.37	--
H2	0.40	--
(70)	0.55	0.73
(71)	0.60	1.23
(72)	0.65	2.36

Values are calculated using both the observed Fe^{2+} site-occupancies, and including all Fe^{3+} at each site in the Fe^{2+} site-occupancy

Bocchio et al. (1978) and Ungaretti et al. (1981) show the presence of small amounts of Fe^{3+} at the M(1) and M(3) sites (see Appendix B3). Table 59 lists the K^d values (for Fe^{2+}) for M(1) – M(3) ordering. Each of these suites of amphiboles were taken from a small region over which the ambient conditions probably were fairly uniform. For the three amphiboles of Bocchio et al. (1978), the K^d values vary considerably. However, if K^d is calculated assigning all Fe at M(1) and M(3) as Fe^{2+}, the values are fairly similar. For the amphiboles of Ungaretti et al. (1981), K^d values are fairly similar for all amphiboles except those with Fe^{3+} at M(1) and M(3). Considering all Fe as Fe^{2+} at these sites, the calculated K^d values for the aberrant amphiboles now fall into the same fairly restricted range as the rest of the amphibole suite. Both of these results suggest that all the Fe at M(1) and M(3) in these amphiboles was Fe^{2+} at the time of cation equilibration, when the K^d values were set, and that those amphiboles with Fe^{3+} at M(1) or M(3) (or both) underwent postequilibration oxidation sufficiently mildly or at sufficiently low temperatures that there was no accompanying disorder among the cations.

Titanium

Titanium may have the valence states 3+

and 4+ in an oxide environment, but until recently was thought to be in the 4+ state in minerals (Deer *et al.* 1963, Hartman 1969). More recent work has shown the presence of considerable Ti^{3+} in lunar (Burns *et al.* 1976) and meteoritic (Dowty & Clark 1973a, b, Mao & Bell 1974, Mason 1974) pyroxenes, and in melanite–schorlomite garnets (Burns 1972, Huggins *et al.* 1977, Schwartz *et al.* 1980). Prewitt *et al.* (1972) synthesized $NaTi^{3+}Si_2O_6$, demonstrating that octahedrally co-ordinated Ti^{3+} does occur in pyroxenes. The similarity of the pyroxene and amphibole structure suggests the possibility of Ti^{3+} occurring in the amphibole structure. However, there is no convincing evidence concerning the valence state of Ti in amphiboles, although the wider range of structural environments in amphiboles suggests that mixed Ti valences are a distinct possibility. Even if Ti were always trivalent upon crystallization, subsequent partial oxidation–dehydroxylation could give rise to cation disorder and the formation of mixed valences of Ti.

Ti is generally considered as a C-group cation, although some authors do assign Ti^{4+} to the T group where Si+Al is less than 8.0. There is no evidence of tetrahedrally co-ordinated Ti in amphiboles. In most X-ray studies, Ti has been assigned to the M(2) site together with all the other trivalent cations in the formula unit. However, there is no direct evidence for this assignment of Ti. The only direct evidence for Ti ordering in amphiboles is the neutron refinement of potassian oxy-kaersutite(40) by Kitamura *et al.* (1975). They showed that Ti is strongly ordered at the M(1) site. Whether this is an equilibrium-crystallization feature or whether it is associated with postcrystallization disorder during oxidation–dehydroxylation is not known. However, the cation disordering that is known to occur on high-temperature oxidation–dehydroxylation (Ernst & Wai 1970) and the ordering behavior of trivalent cations such as Al and Fe^{3+} (see above) suggest that the ordering of Ti at M(1) in oxy-kaersutite is a postcrystallization phenomenon accompanying oxidation–dehydroxylation.

Schwartz & Irving (1978) have examined kaersutite using the general technique of Burns (1972); they derived $Ti^{3+}/(Ti^{3+}+Ti^{4+})$ ratios of 0.04, 0.04 and 0.09 for three samples of kaersutites with TiO_2 in the range 5.1–5.8 wt. %. As indicated by the authors, this is not convincing evidence for Ti^{3+} in amphiboles because of the low values and the uncertainty of the method; however, it seems to be the only way to examine this problem at the moment.

The possibility also exists that mixed valences of titanium may occur as a result of stereochemical criteria. For exxample, bond valence considerations suggest that local occupancy of T(2) by Al^{3+} might be coupled with the occupancy of M(2) by Ti^{4+}, whereas Si occupancy of T(2) might be associated with Ti^{3+} in M(2). In view of the numerous possibilities for mixed valences and site ordering of titanium in amphiboles, it is perhaps fortunate that titanium is generally a minor constituent in most varieties of amphibole.

Ferrous iron

Fe^{2+} is generally assigned to the B and C groups of the amphibole formula and can occupy the M(1), M(2), M(3) or M(4) sites. As the character of the ordering patterns exhibited by Fe^{2+} changes with the type of amphibole, it is convenient to consider each principal amphibole group separately.

The iron–magnesium–manganese amphibole group is characterized by considerable ordering of Fe^{2+}. It was first shown by Ghose & Hellner (1959) and Ghose (1961) using X-ray diffraction that in the structure of the cummingtonite – grunerite amphiboles, Fe^{2+} shows a nonrandom distribution over the four M sites, being preferentially ordered at the M(4) site. This ordering pattern has since been confirmed by additional X-ray diffraction (Finger 1969a) and extensive Mössbauer work (Bancroft *et al.* 1967a, b, 1968, Hafner & Ghose 1971, Buckley & Wilkins 1971); Ghose & Weidner (1972) have shown that the degree of ordering is to some extent a function of equilibration temperature. The Mössbauer spectra of cummingtonite – grunerite amphiboles show incomplete resolution (Appendix F), with the doublets from Fe^{2+} at M(1), M(2) and M(3) showing virtually exact overlap; thus Mössbauer spectroscopy provides no information concerning the ordering of Fe^{2+} over the M(1), M(2) and M(3) sites. However, the structure refinements of cummingtonite(21) and grunerite(22) both show the Fe^{2+} site-occupancy $M(3) \geq M(1) > M(2)$. The ordering of Fe^{2+} over the M(1), M(2) and M(3) sites has also been examined by Bancroft *et al.* (1967a) using a combination of Mössbauer and infrared absorption spectroscopy. Mössbauer spectroscopy gives the Fe^{2+} cation ratios at the M(1)+M(2)+M(3) sites and the M(4) site, whereas the infrared absorption method gives the Fe^{2+} cation ratios at the M(1)+M(3) and M(2)+M(4) sites; thus the relative ordering of Fe^{2+} between the M(1)+ M(3) and M(2) sites may be derived from the

combination of these two methods. The experimental results of Bancroft et al. (1967a) always indicate the Fe^{2+} site-occupancy M(1), M(3)> M(2); these authors stated that "in some grunerites, Fe^{2+} becomes enriched in the M(2) position", but provided no experimental evidence for this. Similar experiments by Buckley & Wilkins (1971) also showed Fe^{2+} to be preferentially ordered at the M(1)+M(3) sites relative to the M(2) site. The strong absorption band at ~ 1 μm in the β absorption spectrum of amphiboles of the cummingtonite—grunerite series (Fig. 88) is compatible with the high Fe^{2+} occupancy of the M(4) site throughout this series. As with most other amphiboles, Fe^{2+} ordering is affected by blocking of sites by other cations in the structure. Ca occupies the M(4) site in cummingtonite – grunerite amphiboles, thus affecting the *relative* ordering of Fe^{2+} between the M(4) and M(1)+M(2)+M(3) sites (Bancroft et al. 1967a); similar behavior has been recognized in clinopyroxenes (Hafner 1975). The preferential ordering of trivalent cations at the M(2) site may similarly affect Fe^{2+} ordering over the M(1), M(2) and M(3) sites.

The Fe^{2+} site-preference is completely different in the amphiboles of the tirodite – dannemorite series, although data are only available for the tirodite end of the series. Using a combination of Mössbauer and infrared absorption spectroscopy, Bancroft et al. (1967a)* found the Fe^{2+} site-occupancy M(1)+M(2)+ M(3)>M(4) for tirodite{7}. The Fe^{2+} cation ordering over the M(1), M(2) and M(3) sites is distinctly different from that exhibited by amphiboles of the cummingtonite – grunerite series; tirodite shows strong ordering of Fe^{2+} at the M(2) site, and the overall Fe^{2+} site-occupancy M(2)>M(4)$\geqq$M(1)+M(3). A combined X-ray-diffraction and Mössbauer-spectroscopy investigation of zincian tirodite(57) (Hawthorne & Grundy 1977b) showed the Fe^{2+} site-occupancy M(1) + M(2) + M(3) > M(4), in agreement with previous infrared absorption and Mössbauer results. On the basis of bond-length considerations and total scattering-powers at each site, Fe^{2+} seems to be strongly ordered in the M(2) site in zincian tirodite(57); although this conclusion is not as well established as the relative Fe^{2+} ordering pattern over the M(4) and M(1)+M(2)+M(3) sites, the overall pattern of ordering M(2)>M(4)>M(1), M(3) is com-

patible with the results of Bancroft et al. (1967a) on tirodite{7}. Papike et al. (1969) have refined the structure of tirodite(28) and found that (Fe+Mn) is strongly ordered at the M(4) site. On the basis of the results of Bancroft et al. (1967a), they assumed that Mn is strongly ordered in the M(4) site, and assigned cation site-populations at M(1), M(2) and M(3) on the basis of mean bond-lengths. Both the site populations given by Papike et al. (1969) and derived from the curves of Hawthorne (1978a) and given in Appendix B3 show the Fe^{2+} site-occupancy M(2)>M(4)>M(1), M(3) in agreement with Bancroft et al. (1967a) and Hawthorne & Grundy (1977b).

Fe^{2+} ordering patterns in the orthorhombic Fe–Mg–Mn amphiboles differ significantly from those of the monoclinic Fe–Mg–Mn amphiboles. Refinement of the structure of anthophyllite[23] (Finger 1970b) showed the Fe^{2+} site-occupancy M4$\gg$M1$\sim$M2$\sim$M3, in agreement with previous results by Mössbauer and infrared absorption spectroscopy (Bancroft et al. 1966). More recent Mössbauer results on anthophyllite[23] (Seifert & Virgo 1974, 1975, Seifert 1977) show excellent agreement with the X-ray results (Appendix C3). This distribution is also supported by the polarized absorption spectra of anthophyllite[23] (Fig. 87), where the barycentre energy of ~ 7000 cm^{-1} for the 1 μm(β) and 2.4 μm(α) bands is compatible with the <M4–O> distance in anthophyllite[23], according to the correlations of Faye (1972). There is as yet no information on the relative ordering of Fe^{2+} over the M1, M2 and M3 sites in anthophyllite with significant Fe^{2+} occupancy of these sites. Significant differences occur between Fe^{2+} site-ordering in anthophyllite and gedrite. Crystal-structure refinement of two samples of gedrite (Papike & Ross 1970) show an Fe^{2+} site-ordering M4>M1$\sim$M3>M2; however, the ordering is not as strongly developed as in anthophyllite. Gedrite samples have been examined by Mössbauer (Seifert 1977) and infrared absorption methods (Burns & Law 1970), but the peak overlap is such that the spectra cannot be adequately resolved; thus no information on cation ordering in gedrite has been derived using these methods. The polarized-absorption spectra of gedrite[32] (Fig. 87) supports the Fe^{2+} cation-ordering arrangement derived from the X-ray study of Papike & Ross (1970).

The Fe^{2+} distribution in holmquistite is very different from that exhibited by the other Fe–Mg–Mn amphiboles. Crystal-structure refinement (Irusteta & Whittaker 1975) shows the

*There is a misprint in Table 4, page 1021 of this reference; the quoted Fe^{2+} occupancy of M(2) in the unit formula of "Mn cummingtonite" should read 0.57. NOT 0.07.

TABLE 60. Fe^{2+} SITE-OCCUPANCIES FROM CRYSTAL-STRUCTURE REFINEMENTS

	M(1)	M(2)	M(3)	M(4)	Ordering pattern
Iron-magnesium-manganese group					
(21)	0.29	0.05	0.29	0.76	M(4) >>M(1) ~ M(3) > M(2)
(22)	0.85	0.77	0.89	0.99	M(4) > M(3) ~ M(1) > M(2)
(28)	0.03	0.16	-	0.09	M(2) > M(4) > M(1) > M(3)
(57)	-	0.17	-	0.05	M(2) > M(4) > M(1) ~ M(3)
(61)	0.25	-	0.30		M(3) > M(1) >>M(2) ~ M(4)
[23]	0.03	0.02	0.03	0.51	M(4) > M(1) ~ M(2) ~ M(3)
[31]	0.40	-	0.56	-	M(3) > M(1) >>M(2) ~ M(4)
[32]	0.12	(0.04)	0.10	0.42	M(4) > M(1) ~ M(3) > M(2)
[33]	0.33	(0.09)	0.39	0.65	M(4) > M(3) ≥ M(1) >>M(2)
Calcic group					
(24)	0.35	(0.11)	0.35	-	M(1) ~ M(3) > M(2) ≥ M(4)
(37)*	0.61	0.46	0.58	-	M(1) ≥ M(3) > M(2) >>M(4)
(38)	0.23	(0.20)	0.24	-	M(1) ~ M(3) > M(2) >>M(4)
(39)	0.32	(0.17)	0.32	-	M(1) ~ M(3) > M(2) ≥ M(4)
(42)	0.29	-	-	-	M(1) >>M(2) ~ M(3) ~ M(4)
(44)	1.00	0.59	0.59	-	M(1) > M(2) ~ M(3) >>M(4)
(45)	0.46	0.35	0.48	-	M(1) ~ M(3) > M(2) >>M(4)
(46)	0.49	0.42	0.27	-	M(1) > M(2) ~ M(3) >>M(4)
(48)	0.52	-	0.52	-	M(1) ~ M(3) >>M(2) ~ M(4)
(49)	0.7	-	0.6	-	M(1) > M(3) >>M(2) ~ M(4)
(50)	0.6	-	0.4	-	M(1) > M(3) >>M(2) ~ M(4)
(54)	0.61	0.05	0.78	-	M(3) > M(1) >>M(2) ≥ M(4)
(58)**	(0.69)	(0.31)	(0.84)	0.07	M(3) > M(1) > M(2) ≥ M(2)
(60)	0.36	0.18	0.45	-	M(3) > M(1) > M(2) >>M(4)
(61)	0.30	0.07	0.24	-	M(1) > M(3) >>M(2) ~ M(4)
(70)**	0.17	(0.15)	0.22	0.03	M(3) > M(1) >>M(4) ~ M(2)
(71)**	0.19	(0.15)	0.28	0.03	M(3) > M(1) >>M(4) ~ M(2)
(72)**	0.17	(0.16)	0.29	0.04	M(3) > M(1) >>M(4) ~ M(2)
(73)	0.32	(0.21)	0.45	0.17	M(3) > M(1) > M(4) >>M(2)
Sodic calcic group					
(35)	0.20	0.52	0.15	0.04	M(2) > M(1) > M(3) ~ M(4)
(51)	0.85	0.18	0.85	-	M(1) ~ M(3) >>M(2) ~ M(4)
(59)	0.73	0.13	0.71(0.85)	-	M(3) ≥ M(1) >>M(2) ~ M(4)
Alkali group					
(26)	0.16	-	0.29	-	M(3) > M(1) >>M(2) ~ M(4)
(64)	1.00	-	0.67	-	M(1) > M(3) >>M(2) ~ M(4)
(65)	0.93	0.34	0.88	-	M(1) ~ M(3) >>M(2) ~ M(4)
(66)	0.75	-	-	-	M(1) >>M(1) ~ M(2) ~ M(3)
(67)*	1.00	0.42	0.76(0.89)	-	M(1) > M(3) > M(2) >>M(4)
(68)*	0.93	-	0.48(0.64)	-	M(1) > M(3) >>M(2) ~ M(4)
(69)	0.59	-	0.80	-	M(3) > M(1) >>M(2) ~ M(4)

†values given in parentheses for the M(2) site are predominantly Fe^{3+}
*considerable Mn is included in the site-occupancies given; where an estimate of Mn site-occupancies has been made, individual Fe^{2+} site-occupancies are given with the combined Fe+Mn occupancy in parentheses
**results suggest significant Fe^{3+} at the M(1) and/or M(3) sites

Fe^{2+} site-ordering M3 > M1 ≫ M2 ~ M4 ~ 0.0, and this is confirmed by Mössbauer and infrared absorption spectroscopy (Wilkins et al. 1970, Law & Whittaker 1981) (see Appendices C3, F and G).

The calcic amphibole group shows an extremely complex variation in Fe^{2+} ordering. The results of crystal-structure refinements are summarized in Table 60, where it can be seen that no exact overall pattern is apparent. However, the predominant Fe^{2+} ordering pattern appears to be M(1)≥M(3)>M(2)≥M(4) although the Fe^{2+} content of the M(2) site is obviously strongly affected by the trivalent-cation content of the M(2) site. Ferro-tschermakite(54) shows M(3)>M(1)≫M(2)≥M(4), and this is compatible with the Mössbauer spectrum (Hawthorne 1973), although it should be noted that the other structure showing the Fe^{2+} site-occupancy M(3)>M(1), glaucophane(26), is also characterized by a particularly small mean size of the M(2) constituent cation. There has been some spectroscopic work on the derivation of site populations in calcic amphiboles, but this has tended to concentrate on the simpler chemical species. Amphiboles of the tremolite – ferro-actinolite series were first examined using Mössbauer spectroscopy by Bancroft et al. (1976b); the resolution achieved in this study was inadequate, but improved resolution in a later study (Greaves et al. 1971) led to the derivation of complete Fe^{2+} site-occupancies, with additional results being presented by Burns & Greaves (1971). Site populations for actinolite have also been derived by infrared absorption spectroscopy (Burns & Strens 1966, Wilkins 1970) and a comparison of results of both methods is given by Burns et al. (1970) and Burns & Greaves (1971). The results of Wilkins (1970) all show the site occupancy M(1)+M(3)>M(2), including an actinolite also examined by Burns & Strens (1966), who derived the Fe^{2+} site-preference M(2)> M(1)+M(3). The infrared absorption results of Burns & Greaves (1971) generally show the Fe^{2+} site-preference M(2)>M(1)+M(3), but this is at variance with their own Mössbauer data, which show the Fe^{2+} site-occupancy M(1)+M(3)>M(2)*; these authors concluded that the Mössbauer results are more reliable. Goldman & Rossman (1977a) have provided spectral evidence that Fe^{2+} does occur at the M(4) site in amphiboles of the tremolite – ferro-actinolite series. The polarized-absorption spectra of a tremolite and an actinolite show very strong bands at 1030 nm(β) and 2470 nm(α); the large band-intensity, together with the similarity of the spectra to others from Fe^{2+} in large, very distorted co-ordination polyhedra (Burns 1970a, Goldman & Rossman 1976, 1977b), suggests that these bands are due to the M(4) occupancy of Fe^{2+}. In addition, the observed energy of the barycentre is compatible with the correlations of Faye (1972). The behavior of the 1030 nm band in more iron-rich actinolite (Burns 1970a, Fig. 5.13) is also compatible with this assignment. The chemical analysis of this actinolite (Burns & Greaves 1971, Table 1, number 5) indicates significant C-group cation occupancy (Σ 5.15 atoms p.f.u.) of the M(4) site. Comparison of the average Fe^{2+} site-occupancies at the four M sites [M(1)~ M(2)~M(3)~0.48, M(4)~0.06] is in line with the more equal band-intensities of Fe^{2+} at M(4) and at M(1), M(2) and M(3) expected from

*There is an error in Table 5 of this reference; the Fe^{2+} populations for the M(2) and M(3) columns are interchanged. However, the site occupancies are given correctly in their Table 6.

two groups of co-ordination polyhedra with very different asymmetry. There is little spectral information on the more complex calcic amphiboles. Häggström et al. (1969) examined a series of calcic amphiboles but did not obtain adequate resolution of doublets to derive site populations. Burns & Greaves (1971) examined a pargasite using Mössbauer spectroscopy; the site populations indicate the Fe^{2+} site-occupancy $M(1) > M(3) > M(2) \gg M(4)$. The optical-absorption spectra of a pargasite (Goldman & Rossman 1977a) show the Fe^{2+} site-occupancy to be $M(1) + M(2) + M(3) \gg M(4)$. Semet (1973) showed, using incompletely resolved Mössbauer spectra, that Fe^{2+}-bearing synthetic magnesio-hastingsite has the Fe^{2+} site-occupancy $M(1) + M(3) > M(2)$. Khristoforov et al. (1973) have examined a series of calcic amphiboles of unspecified composition; their results, given in diagrammatic form, indicate the Fe^{2+} site-occupancy $M(3) \gg M(1)$. However, the spectra presented by them cannot be considered reliable (off-resonance counts from 16000 to 38000, maximum absorption up to 95%, half-widths up to ~1.0 mm/s).

The only published data on Fe^{2+} site-occupancies in sodic–calcic amphiboles are from crystal-structure refinements, the relevant data being summarized in Table 60. Fluor-richterite(35) shows the site preference $M(2) > M(1) > M(3) > M(4)$; as discussed later, the preference of Fe^{2+} for the M(2) site in fluor-richterite appears to result from the antipathy of Fe^{2+} for F-co-ordinated sites in silicate minerals. The remaining amphiboles show the Fe^{2+} site-occupancy $M(3) \gtrsim M(1) \gg M(2) > M(4)$; however, both contain considerable Mn at the M(1), M(2) and M(3) sites, and the exact site-populations are not known with certainty. For potassian ferri-taramite(59), mean bond-length criteria suggest Mn to be strongly ordered at M(3) with the resulting Fe^{2+} site-occupancy $M(1) \sim M(3)$, but this assignment is quite speculative. Virgo (1972a) reported the Mössbauer spectrum of synthetic ferro-richterite, synthesized by Charles (1972, 1974); the spectrum could not be adequately resolved, but indicated the presence of octahedrally co-ordinated Fe^{3+} in an amphibole nominally containing only Fe^{2+}. Ungaretti et al. (1981) have presented refinements of several samples of winchite, barroisite and magnesio-taramite. All these show the Fe^{2+} site-occupancy pattern $M(3) > M(1) \gtrsim M(4) \gtrsim M(2)$.

Considerable work has been done on Fe^{2+} site-occupancies in the alkali amphibole group; Table 60 summarizes some of the earlier results of crystal-structure refinements. Glaucophane

(26) shows the Fe^{2+} site-ordering pattern $M(3) > M(1) \gg M(2) \gg M(4)$; this pattern has been confirmed in several samples of glaucophane by Mössbauer spectroscopy (Bancroft & Burns 1969, Ernst & Wai 1970; see Appendix F) and in ferro-glaucophane(69) by X-ray and Mössbauer data. Structure refinement of fluor-riebeckite(68) shows the Fe^{2+} site-occupancy $M(1) > M(3) \gg M(2) \sim M(4)$; however, this seems to be caused by the ordering of Li at the M(3) site and is probably not representative of Fe^{2+} in Li-free riebeckite. Ernst & Wai (1970) examined several samples of riebeckite by Mössbauer spectroscopy and derived the Fe^{2+} ordering pattern $M(3) > M(1)$, as in glaucophane. Conversely, a riebeckite from Laytonville, California, {19}, examined by Bancroft & Burns (1969) by Mössbauer and infrared spectroscopic methods, shows the ordering pattern $M(1) > M(3)$. Ungaretti et al. (1978) examined a riebeckite of almost identical composition from the same locality and derived the Fe^{2+} ordering pattern $M(3) > M(1)$ from site-occupancy refinement of single-crystal X-ray data (see Fig. 102). Several samples of magnesio-riebeckite examined by Mössbauer and infrared spectroscopic methods (Bancroft & Burns 1969, Ernst & Wai 1970, Burns & Prentice 1968; see Appendix F) show the Fe^{2+} site-preference $M(1) > M(3)$, with
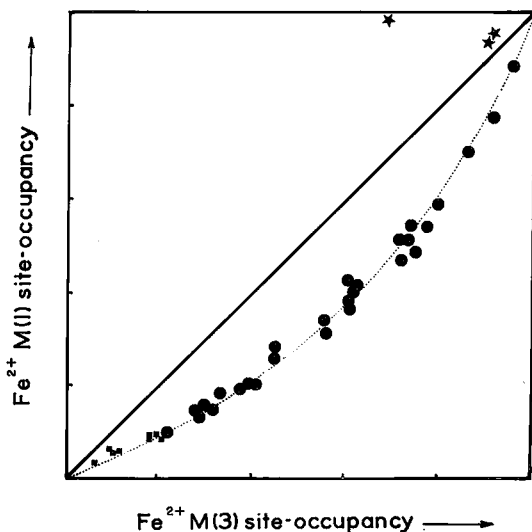

Fig. 102. The distribution of Fe^{2+} over the M(1) and M(3) sites in glaucophane – ferro-glaucophane – magnesio-riebeckite – riebeckite amphiboles (●) and nyboites (■) [from Ungaretti et al. (1978)]. The * indicates riebeckite of igneous origin that contains significant Li.

crossites showing Fe^{2+} enrichments into both M(1) (Ernst & Wai 1970) and M(3) (Bancroft & Burns 1969). An unusually extensive study by Ungaretti *et al.* (1978) showed that the Fe^{2+} site-ordering pattern in amphiboles of the glaucophane – ferro-glaucophane – magnesio-riebeckite – riebeckite series is extremely systematic (Fig. 102), with the pattern M(3)>M(1) throughout the whole compositional range examined, which *excluded* magnesio-riebeckite. The regularity of Figure 102 is so striking that it questions the previous spectral results on magnesio-riebeckite; additional work on magnesio-riebeckite is required.

Magnesium

The behavior of Mg in crystals is generally antipathetic to that of Fe^{2+}, and in thermodynamic treatments (Kretz 1959, 1963, Mueller 1962, 1967, 1969, Saxena 1968a, b, 1969a, b), ordering of these two species is usually considered as an exchange reaction. Thus the ordering and site occupancies of Mg will only be discussed where they are of particular crystal-chemical interest.

In C-centred amphiboles of the cummingtonite – grunerite series, Mg appears to be virtually excluded from the M(4) site. In studies where the derived Fe^{2+} occupancy of M(4) is less than 1.0, the balance may be assigned to the small amount of Ca generally present (see Appendix B3). Any significant M(4) occupancy by Mg occurs only in tirodite $P2_1/m$(27), and is thought to be the cause of this particular structural variant (Papike *et al.* 1968, 1969). The orthorhombic Fe–Mg–Mn amphiboles, anthophyllite[23] and gedrite[32] and [33] show considerable occupancy of M4 by Mg, and again it is this factor that is thought to be responsible for the existence of the orthorhombic structure-type. Other amphiboles with Mg at M(4) are the synthetic protoamphibole[20] and synthetic (Li,□) (Li,Mg)$_2$Mg$_5$Si$_8$O$_{21+x}$(OH)$_{3-x}$ grown by Maresch & Langer (1976). Both of these amphiboles have Mg and Li apparently miscible at the M(4) site; this is not surprising in terms of the ionic radii and single-charge difference between these two cations, particularly as protoamphibole is an orthorhombic structural variant with a small M4 site and the other amphibole is of unusual composition to say the least. Considerably more enigmatic is the existence of the synthetic monoclinic amphibole NaMgNaMg$_5$Si$_8$O$_{22}$(OH)$_2$ (*e.g.*, Witte *et al.* 1969), in which the M(4) site is presumably occupied by Mg and Na in equal proportions;

with regard to the normal crystal-chemical behavior of cations in crystals, this would seem less likely than miscibility between tremolite and magnesio-cummingtonite, unless its structure is not a $C2/m$ structure but a subgroup derivative of this.

Manganese

In principle, site occupancies of Mn in amphiboles should be difficult to derive. Mn and Fe have very similar X-ray-scattering factors and cannot be distinguished by this method; they have sufficiently similar electronegativity and mass that they cannot be distinguished by the infrared absorption method. However, Fe is sensitive to the Mössbauer effect and Mn is not; hence, the distribution of Mn in amphiboles can be derived by a combination of these methods. This was first done by Bancroft *et al.* (1967a) for tirodite{7}, using a combination of Mössbauer and infrared absorption spectroscopy; they showed that Mn is strongly ordered in the M(4) site, showing the site preference M(4)>M(1)+M(2)+M(3). A similar result was obtained for zincian tirodite(57) using a combination of crystal-structure refinement and Mössbauer spectroscopy; these authors also refined the Mn site-occupancies of the M(1), M(2) and M(3) sites, but the results were not statistically significant. Examination of mean bond-lengths in tirodite(28) suggests that Mn avoids the M(2) site, which is in accord with the results for zincian tirodite(57). In the calcic, sodic–calcic and alkali amphiboles, there is little or no information on the distribution of Mn. In principle, the problem is susceptible to a combination of X-ray and Mössbauer methods, but in practice the difficulties associated with deriving accurate Fe^{2+} site-occupancies from the incompletely resolved spectra have so far precluded the use of this method. When the sum of C-group cations exceeds 5.0, some studies have assigned the excess cations to the B group in the order Mn>(Fe, Mg); there is no direct proof of this, although it is in line with the behavior of Mn in the Fe–Mg–Mn amphiboles. Some studies (Hawthorne 1976, Hawthorne & Grundy 1978) have attempted to derive Mn site-preference in sodic–calcic and alkali amphiboles on the basis of mean bond-lengths at the M(1), M(2) and M(3) sites; the preference M(3)> M(1)~M(2) was observed in both studies, but these results are highly speculative. Bershov *et al.* (1966) and Manoogian (1968a, b) have shown by electron-spin-resonance studies that Mn in tremolite is (predominantly) divalent.

Both studies concluded that Mn^{2+} occupied "one site" [either M(4) or M(1, 2, 3) together] and assigned it to M(4); however, an argument can be put forward for reversing this assignment, so the situation is still not clear. Goldman (1977) examined a Mn-bearing tremolite using polarized electronic-absorption spectroscopy; he assigned bands to $d–d$ transitions in Mn^{3+} and perhaps Mn^{2+}. Thus the Mn situation is at present rather confused.

Lithium

Li occurs in significant quantities only in specific types of amphibole, although it is capable of occupying a wide variety of sites in amphiboles. In the Fe–Mg–Mn amphiboles, only holmquistite and clinoholmquistite show significant Li. Crystal-structure refinements (Whittaker 1969, Litvin *et al.* 1973a, Irusteta & Whittaker 1975) show Li to be virtually completely ordered at the M(4) site. These results agree with the infrared absorption results of Wilkins *et al.* (1970), which show that no significant Li occurs at the M1+M3 sites in holmquistite. Li also occurs in protoamphibole[20], where it occurs both at the M4 site (together with Mg) and at the A site. However, Gibbs (1969) did not observe any significant electron-density at the A site and suggested that Li was positionally disordered about the cavity surrounding the A site. A similar distribution of Li with significant occupancy of the M4 and A sites presumably occurs for the synthetic amphibole $(Li,\square)(Li,Mg)_2Mg_5Si_8O_{21+x}(OH)_{3-x}$ synthesized by Maresch & Langer (1976). Li is not a common constituent of calcic amphiboles. Calcic amphiboles coexisting with holmquistite (von Knorring & Hornung 1961, Wilkins *et al.* 1970) show only small amounts of Li (~0.16 atoms p.f.u.), and there is no evidence to show where the Li occurs in the structure. Conversely, Li can be an important constituent of alkali amphiboles, and stoichiometric considerations (Sundius 1946b, Borley 1963) suggest that Li is a C-group cation in these. On the basis of infrared absorption evidence, Addison & White (1968b) proposed that Li occurs at the M(1)+M(3) sites in riebeckite. Subsequent crystal-structure refinement of a fluor-riebeckite(68) containing significant Li (Hawthorne 1978b) showed Li to be almost completely ordered at the M(3) site. However, it should be stressed that this ordering pattern pertains to a fluor-amphibole [O(3) ~ 0.6F+0.4OH]; the ordering may be different in a hydroxy-amphibole, although high Li contents are generally associated

with high F contents in alkali amphiboles (Lyons 1976).

Calcium

Ca is virtually always assigned to the B group in the unit formula, and all X-ray studies of calcic and sodic–calcic amphiboles appear to be compatible with this assignment, Ca occupying the M(4) site in all structures so far examined. It is not certain whether Ca is ever significantly in excess of that required to fill the B group in the unit formula. Practically all compositions in which Ca exceeds 2.10 atoms p.f.u. are results of obviously poor analyses, as discussed by Leake (1968); even the composition with fairly well-documented high Ca (2.23 atoms p.f.u.) quoted by him (#801) is classified as inferior on the basis of the sum of C-group cations (4.58 atoms p.f.u.). Hawthorne (1976) has examined the sums of C-group cations in amphiboles of the eckermannite – arfvedsonite series, showing that only 10% of the analyses are satisfactory according to generally accepted criteria (Papike *et al.* 1974). There are several possibilities with regard to this situation: (i) minor occupancy of the M(1, 2, 3) sites by Ca does occur; if this is assumed, ~70% of the amphibole analyses will be classified as satisfactory. (ii) Significant amounts of minor components (*e.g.*, Li, Cr) were ignored during analysis, sufficient to bring the majority of the analytical results up to the satisfactory level. (iii) Vacancies can occur at the M(1,2,3) sites in amphiboles; in fact, vacancies at the M(3) site in amphiboles are not disadvantageous with regard to local bond-valence requirements.

In the Fe–Mg–Mn amphiboles, small amounts of Ca are assumed to occupy the M(4) site; whether this occupancy is real or whether these amphiboles contain incipiently developed lamellae of calcic amphibole must await detailed studies by transmission electron-microscopy. Certainly in coexisting Fe–Mg–Mn and calcic amphibole assemblages, exsolution of calcic amphibole by the Fe–Mg–Mn amphibole is widespread (Ross *et al.* 1968a, 1969, Jaffe *et al.* 1968, Robinson *et al.* 1969, Robinson & Jaffe 1969). In the rare amphibole joesmithite, Ca occupies the two M(4) sites and the A(2) site; this is the only recorded amphibole where the A cavity is occupied by a divalent cation.

Sodium

Na is assigned to the A and B groups of the unit formula. Warren (1929, 1930) proposed

that Na would occupy the M(4) and A sites in the amphibole structure, and this was confirmed experimentally by Whittaker (1949) and Heritsch et al. (1957). All subsequent crystal-structure work has confirmed these results.

Potassium

K is always assigned to the A group in the amphibole formula unit, and all experimental work so far published is in agreement with this (Papike et al. 1969, Cameron et al. 1973b, Hawthorne 1976). The positional disorder of Na and K is discussed in the section on the A site.

Beryllium

Joesmithite is a remarkable amphibole in which Be^{2+} occupies the T(1)B site, apparently showing no disorder with Si over the four distinct tetrahedral sites. The occupancy of a T(1)-type site by Be^{2+} is in accord with the criteria based on local charge-balance proposed by Hawthorne (1978c).

Boron

Kohn & Comeforo (1955) reported the synthesis of a calcic fluor-amphibole containing considerable B^{3+}. The chemical analysis indicates $1.12^{iv}B$ and $0.33^{vi}B$ p.f.u.; as B^{3+} has not been recorded in octahedral co-ordination in an oxide environment, additonal evidence is needed before this result can be accepted.

Cobalt

Co^{2+} occupies the M(1), M(2), M(3) and M(4) sites in the structure of "$Na_2H_2Co_5Si_8O_{22}(OH)_2$" (Prewitt 1963, Gibbs & Prewitt 1968), which apparently deviates somewhat from its ideal composition. Similar results are apparent from the chemical analysis of fibrous cobalt amphibole synthesized by Nesterchuk et al. (1968). On the basis of optical-absorption spectra, Chigareva et al. (1969) proposed that Co^{2+} occurs in both octahedral and [8]-fold co-ordination in synthetic cobalt fluor-richterite.

Nickel

Chemical analysis of synthetic nickel richterite (Fedoseev et al. 1968, 1970) shows Ni to occupy the M(1), M(2), M(3) and M(4) sites. Absorption spectra of a nickel fluor-richterite suggest the presence of Ni^{2+} in both octahedral and [8]-fold co-ordination (Chigareva et al. 1969).

Chromium

On the basis of optical-absorption spectra,

Chigavera et al. (1969) proposed that Cr^{3+} occurs in [8]-fold co-ordination in "chromium fluor-amphibole".

Zinc

Klein & Ito (1968) reported results of chemical analyses and physical data for several zinc-bearing amphiboles from Franklin, New Jersey. In zincian tirodite, the Zn content may attain 1.22 atoms p.f.u.; a combined X-ray structure refinement and Mössbauer-spectroscopy study (Hawthorne & Grundy 1977b) of zincian tirodite(57) showed the Zn site occupancy M(1) > M(3) ≫ M(2) > M(4). Chemical analyses of zinc-bearing amphiboles of the tremolite – ferro-actinolite series suggest that Zn is strongly ordered at the M(1), M(2) or M(3) sites (or all three) (Klein & Ito 1968); a similar preference appears to be exhibited by zincian magnesio-riebeckite.

Germanium

Sipovskii et al. (1972) and Grebenshchikov et al. (1974) reported synthesis and characterization of a fibrous amphibole, $Na_2Mg_6Ge_8O_{22}(OH)_2$, where Si is entirely replaced by Ge. As the ionic radius of Ge is slightly larger than that of Si, the cell parameters of the germanate amphibole are all slightly larger than those of the silicate analogue (Table 61).

FACTORS AFFECTING CATION ORDERING IN AMPHIBOLES

The amphibole structures have a wide variety of cation sites that can accept cations in the range 0.26–1.60 Å in size and 1+ to 4+ in formal charge. The extreme diversity of chemistry that this allows, together with the similarity of symmetrically distinct cation polyhedra, ensures that extensive solid-solution will occur

TABLE 61. COMPARISON OF CELL PARAMETERS FOR GERMANATE AND SILICATE AMPHIBOLES*

	$Na_2Mg_6Si_8O_{22}(OH)_2$	$Na_2Mg_6Ge_8O_{22}(OH)_2$
a(Å)	9.70(1)	9.98(1)
b(Å)	18.01(1)	18.31(1)
c(Å)	5.28(2)	5.35(5)
β(°)	103.0(1)	106.5(2)
V(Å³)	900(5)	935(10)
Space group	C2/m	C2/m
	2.98(2)	4.07(5)

*from Grebenshchikov et al. (1974)