



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 straightforward. 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

and the high correlations are due to the ill-conditioned normal equations that result from the incorrect expressions for the relevant derivatives, interacting with systematic error in the intensity data. This problem was circumvented (Finger 1969b) by the use of linear constraints in the least-squares process, whereby the sum of the site occupancies is constrained to be equal to the total site-group chemistry indicated by the chemical analysis, together with correctly modified derivatives. This procedure is generally used for the derivation of site occupancies in amphiboles from single-crystal diffraction data.

The most complex ordering in amphiboles generally occurs over the octahedral sites; there are often as many as six cation species occurring at these sites. These cations generally fall into two groups, those with scattering factors similar to Mg (Mg and Al) and those with scattering factors similar to Fe (Fe^{2+} , Fe^{3+} , Ti and Mn). Thus a normal site-occupancy refinement gives only the relative ordering of these two "compound species". Two additional methods have been used in attempts to derive site occupancies for three cation species at the octahedral sites, but these depend for a solution on the different relative rates of fall-off of scattering factors with $\sin\theta/\lambda$; even in the best of cases, the solution is only marginally defined. The first method involves successive cycles of refinement, varying the site populations of two of the chemical species with the third held constant. In the second method (Hawthorne & Grundy 1977b), each site is split into two half-occupied sites, each of which is occupied by two cation species; all site-populations may then be refined with the total site-chemistry constrained to the cell contents calculated from the chemical data. In a refinement of the structure of zincian tirodite(57), Hawthorne & Grundy (1977b) showed that the first method outlined above led to standard deviations that were too small by an order of magnitude (Table 51). Extremely large correlations are encountered between site-population parameters in the second method; this occurs because the solution is only marginally defined by the data, and suggests that the refinement of more than two scattering species over nonequivalent sites in a structure is not a practical proposition in the normal least-squares refinement of crystal structures.

Ungaretti *et al.* (1981) have developed a scheme for deriving both cation occupancies and cell contents from structure refinement using charge balance and the mean bond-length - cation-occupancy relationship at the M(2) site: (i) ^{10}Al is estimated from $\langle\text{T}(1)-\text{O}\rangle$, (ii) total

TABLE 51. STANDARD DEVIATIONS FOR THE SITE POPULATIONS IN ZINCIAN TIRODITE(57) CALCULATED BY FULL MATRIX AND PARTITIONED MATRIX METHODS

	Full matrix method			Partitioned matrix method		
	Zn	Mg	Mn	Zn	Mg	Mn
M(1)	0.042	0.080	0.065	0.004	0.004	0.004
M(2)	0.053	0.053	-	0.004	0.004	-
M(3)	0.083	0.098	0.091	0.007	0.007	0.008

charge at A+M(4) is estimated from site-occupancy refinements, Na (+K where available from chemical analysis) at the A site and Ca+Na+ Fe^{2+} at M(4) (Fe^{2+} being included only if indicated by difference Fourier maps), (iii) total charge of C-type cations is set equal to total charge of $(\text{Si,Al})_6\text{O}_{22}(\text{OH})_2$ minus total charge A+M(4), (iv) the M(2) site-populations are calculated from the refined electron-density at M(2) and the observed mean bond-length using the mean bond-lengths of Table 28. If the Ti content is available from chemical analysis, it can be incorporated into the procedure at this stage; otherwise, M(2) is assumed to be occupied by Al, Mg and Fe^{3+} only at this stage. (v) The residual charge (Q) to be neutralized by the M(1) and M(3) cations can now be calculated; in general, this will be equal to 6. If $Q < 6$, the sum M(1)+M(3) is assumed to be occupied by divalent cations only and sufficient Fe^{2+} is introduced into M(2) to make $Q = 6$ and to satisfy the corresponding electron-density and distance equations. If $Q > 6$, Fe^{3+} is introduced into M(1) or M(3) (or both), substituting for Fe^{2+} , and the relative amounts of Mg, Fe^{2+} and Fe^{3+} are estimated from the mean bond-lengths. (vi) If the total charge-imbalance ≤ 0.07 , ^{10}Al is modified to obtain a neutral chemical formula. If the total charge-imbalance > 0.07 , the A and M(4) compositions are adjusted by considering the occupancy of A by K, and then the occupancy of M(4) by Ca, Na and Fe^{2+} .

Ungaretti *et al.* (1981) found excellent agreement between amphibole compositions determined in this fashion and by electron-microprobe analysis of the crystals used to collect the X-ray data; in fact the X-ray compositions are closer to the WDS results than are the EDS results. This suggests that Ungaretti *et al.* (1981) have been successful in eliminating (or at least greatly reducing) systematic error in their data. It will be interesting to see how this method checks out for a wide variety of amphiboles; the fact that $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios can be derived, apparently with reasonable accuracy, on such

a small sample is a big step forward in analytical capability.

Crystal-structure refinement of amphiboles that have a completely ordered cation distribution at the octahedral sites [tremolite(30), fluorrichterite(34), fluor-tremolite(36), tremolite (56a, b)] indicates that the isotropic temperature-factors at the three octahedral sites are approximately equal. This also appears to be the case for amphiboles with cation disorder at the octahedral sites [grunerite(22), ferrotschermakite(54), potassium-arfvedsonite(67)]. This suggests that the isotropic temperature-factors at the octahedral sites provide an independent check on the refined site-populations. Two factors can give rise to incorrect site-populations: (i) systematic error in the diffraction data and (ii) incorrect linear constraints during site-population refinement. The effects of the second factor have not been investigated at all.

In summary, site populations may be derived directly from diffraction data where two cation species differ significantly in scattering power and are disordered over two or more sites. Any additional information must be derived from indirect methods, such as the mean bond-length – constituent-cation-radius relationships developed in the previous sections. Experimental results on published refinements of amphibole, together with a critical assessment of their probable accuracy, are given in Appendices A3, B3, C3 and D3.

MÖSSBAUER SPECTROSCOPY OF AMPHIBOLES

The Mössbauer effect is the recoil-free emission and resonant absorption of gamma rays by a specific atomic nucleus. Of the thirty or so isotopes sensitive to this effect, only ^{57}Fe is of use in amphibole studies; however, the almost ubiquitous occurrence of Fe^{2+} and Fe^{3+} has resulted in the application of this technique to a wide variety of amphiboles. Introductions to the theory and application of Mössbauer spectroscopy are given by Wertheim (1964), Frauenfelder (1962), Fluck (1964) and Bancroft (1973), and a general discussion of the problems inherent in the derivation of site populations is given by Hawthorne (1983).

The hyperfine parameters of amphiboles show significant variation with changes in coordination, site occupancy and compositional type. The systematics of these variations are of interest both with regard to peak assignment in Mössbauer spectra and the crystal-chemical

systematics of the amphiboles themselves. Some of the general conclusions of Ingalls (1964) concerning the behavior of the quadrupole splitting of high-spin Fe^{2+} with changes in ligand environment are pertinent. In particular, Fe^{2+} in a cubic field has no quadrupole splitting; slight distortion of the field from cubic symmetry produces a large quadrupole-splitting (~ 3.7 mm/s), with increasing distortion of the ligand environment producing a gradual decrease in the quadrupole splitting. The crystal-field contribution to the quadrupole splitting contains both distance and angular terms and hence is sensitive to distortion of the co-ordination polyhedron with regard to both bond lengths and bond angles. Consequently, the criterion by which distortion is measured should encompass both these factors; failure to do so has led to some confusion in discussions relating Mössbauer parameters to crystal structure. Next-nearest-neighbor cations will also have a significant effect on the quadrupole splitting. This is of particular importance in the amphiboles, where coupled polyvalent cation-substitutions at the M(2), M(4), T(1), T(2) and A sites are particularly common.

Perhaps the first applications of this method to amphiboles occurred in the oxidation studies of fibrous amphiboles by Gibb & Greenwood (1965). However, precise site-populations were not obtained until the introduction of least-squares refinement to the analysis of complex spectra (Stone 1967). This led to more quantitative estimates of site populations in amphiboles (Bancroft 1967), and systematic studies of amphiboles were soon appearing (Bancroft *et al.* 1966, 1967a, b, Bancroft & Burns 1968).

In most site-population studies of amphiboles, it is necessary to apply linear constraints during the least-squares-fitting procedure in order to attain convergence. These constraints are usually of two types: (i) equal-half-width constraints, and (ii) equal-area constraints.

The equal-half-width constraints are justified on the grounds that the component peaks of ferrous doublets representing iron in different sites have uniform half-widths in numerous minerals (Burns & Greaves 1971); hence this is justified empirically. This is perhaps overstating the case, as there are several reasons why unequal half-widths can be encountered in spectra from complex minerals. Variation in nearest-neighbor (anion) and next-nearest-neighbor (cation) site-occupancy can produce an increase in the half-width of the corresponding peak. Similarly, overlap of two or more peaks can lead to an apparent single peak with a slightly