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CHARACTERIZATION OF THE AVERAGE STRUCTURE OF NATURAL AND SYNTHETIC AMPHIBOLES (**)

Abstract. – The average structure of natural and synthetic amphiboles may be characterized by a variety of techniques: electron microprobe analysis, single–crystal structure refinement, Mössbauer and infrared absorption spectroscopy. The use of these techniques for the characterization of natural amphiboles is discussed. Well–defined relationships exist between certain structural parameters and local site–chemistry, particularly with respect to mean bond–lengths and constituent cation radii at the tetrahedrally and octahedrally coordinated sites in the structure. Exploitation of these crystal–chemical relationships in conjunction with single–crystal structure refinement gives the most complete characterization of a natural amphibole attainable by a single technique. In regard to the application of this method to petrological problems, also of great importance is the change in outlook on the part of crystallographers that has recently promoted the use of crystallography on the large scale necessary in this context. This does not replace the electron microprobe in petrologic studies, but serves in a complementary manner both augmenting the microprobe results themselves and providing additional insight into mineral behaviour.

In most studies of synthetic amphiboles, characterization of run products has been by optical microscopy and X–ray powder diffraction. Those studies which have examined synthetic amphiboles by more sophisticated methods are reviewed; these suggest that many synthetic amphiboles are 'off–composition', and indicate that the standard characterization methods are inadequate. It is suggested that run products be characterized by scanning electron microscopy (preferably with EDS capability), infrared and Mössbauer spectroscopy where feasible, and the Rietveld structure refinement method where appropriate. Application of these techniques to synthetic amphiboles shows that many are 'off–composition' and that there are significant structural differences between analogous natural and synthetic amphiboles.

Riassunto. – La struttura mediata dagli anfiboli naturali e sintetici può essere caratterizzata tramite una serie di tecniche: analisi in microsonda elettronica, raffinamento strutturale a cristallo singolo, spettroscopia di assorbimento all'infrarosso e Mössbauer. L'uso di queste tecniche nella caratterizzazione di anfiboli naturali viene discusso. Esistono relazioni ben definite tra certi parametri strutturali e la composizione locale di certi siti, soprattutto per quanto concerne le lunghezze medie di legame e i raggi dei cationi presenti nei siti a coordinazione tetraedrica ed ottaedrica della struttura. Facendo uso di queste relazioni cristallochimiche in unione con un raffinamento strutturale a cristallo singolo si ottiene il massimo di

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caratterizzazione possibile con una sola metodologia per un anfibolo naturale. Circa l'applicazione di questo metodo a problemi petrologici, assume grande importanza il cambiamento di atteggiamento da parte dei cristallografi, che recentemente hanno cominciato a mettere a disposizione dati cristallografici su larga scala, nella misura necessaria al contesto geologico. Questo non sostituisce l'uso della microsonda negli studi petrologici, ma serve da contributo complementare, sia affinando gli stessi risultati analitici dovuti alla microsonda, sia fornendo schiarimenti supplementari sul comportamento dei minerali.

Nel caso di anfiboli sintetici, la caratterizzazione dei prodotti di sintesi è stata per lo più eseguita per via ottica e per diffrazione dei raggi X su polveri. Gli studi che hanno esaminato anfiboli con tecniche più elaborate sono qui riassunti. Questa revisione suggerisce che un buon numero di anfiboli sintetici sono «fuori composizione» e indica che il metodo usuale di caratterizzazione non è adeguato. Si suggerisce di caratterizzare i prodotti di sintesi combinando tecniche quali l'esame in microscopia elettronica a scansione (preferibilmente munito di spettrometro a dispersione di energia), la spettrometria di assorbimento in infrarosso e Mössbauer, dove possibile, e, dove è appropriato, il metodo di raffinamento strutturale di Rietveld. Applicando queste tecniche ad anfiboli sintetici, si scopre che molti di loro sono «fuori composizione» e che ci sono differenze significative di tipo strutturale tra anfiboli naturali ed i loro analoghi artificiali. (T.d.E.).

KEY WORDS. – Amphiboles, Natural, Synthetic, Characterization, Rietveld, Refinement (X-RAY).

INTRODUCTION

For many years, structural and chemical studies of minerals concentrated on the characterization of basic crystal structures and the rationalization of chemical composition and physical properties in terms of the basic atomic arrangement. With the general attainment of this goal, attention during the last decade has focussed on the detailed stereochemistry of major rock–forming mineral groups, with the investigative methods gradually being augmented by an increasing number of spectroscopic techniques. For the amphiboles, the rationale for this work lay in trying to unravel the relationships between the amphibole structure and the compositional variations exhibited by natural amphiboles, thus characterizing to what extent the amphibole structure itself exerts constraints on its own chemical composition during petrologic processes.

The methods that have evolved during this period for the characterization of (the average features of) natural amphiboles are of current interest for two reasons:

(i) these methods are now being used to investigate specific petrologic problems involving amphiboles, thus constituting the first geological applications of previous crystal–chemical studies

(ii) a resurgence of interest in the synthesis and phase relations of synthetic amphiboles has emphasized the need for improved techniques of run product examination.

Consequently, current techniques of amphibole characterization are reviewed here, and some further applications and improvements are suggested.

CRYSTAL CHEMISTRY OF C2/m AMPHIBOLES

There are at present five known structure–types of amphiboles. The C2/m structure is by far the most common, both with regard to chemistry and paragenesis, suggesting that it must be the most flexible or chemically compliant of the amphibole structures. The crystal chemistry of all structure types is covered in detail by Hawthorne (1981a, 1983a); consequently only those aspects that bear directly on amphibole characterization techniques will be covered here.

The C2/m Amphibole Structure

Schematic representations of the C2/m amphibole structure are shown in figs. 1 and 2. The essential feature of the structure

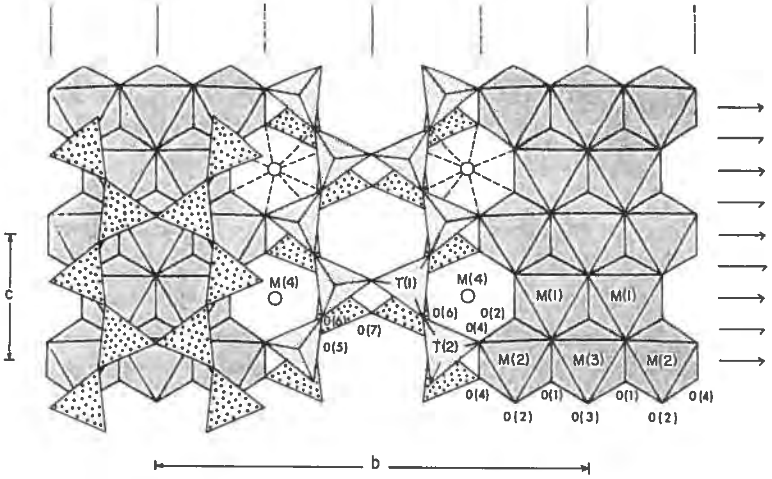

Fig. 1. – The C2/m amphibole structure projected on to (100); the space–group symmetry elements are shown; from Hawthorne (1983a).

is a double–chain of corner–linked tetrahedra that extends infinitely in the Z-direction and has a repeat distance of ~ 5.30Å. There are two distinct cation sites in this chain, the T(1) and T(2) sites, which alternate along the length of the double–chain. The T(1) site is coordinated by three bridging and one non–bridging anions and the T(2) site is coordinated by two bridging and two non–bridging anions. These steric distinctions are sufficient for the sites to respond quite differently to variations in amphibole bulk composition. As shown in fig. 1, the double–chain is not fully extended (0(5)–0(6)–0(5) ≠ 180°); this kinking of the double–chain is strongly correlated with amphibole compositions, and is one of the principal mechanisms whereby the double–chain maintains dimensions commensurate with the rest of the structure.

The double–chains are cross–linked into a three–dimensional framework by strips of edge–sharing octahedra that also extend parallel to the Z–axis. There are three distinct cation sites in this strip, the M(1), M(2) and M(3) sites with point symmetries 2,2 and 2/m respectively. The M(1) site is coordinated by four oxygens and two (usually) monovalent 0(3) anions, with the latter in a *cis* arrangement; the M(2) site is coordinated by six oxygens, and the M(3) site is coordinated by four oxygens and two 0(3) anions, with the latter in a *trans* arrangement. There are also significant differences in the next–nearest–neighbour arrangements (fig. 1). As with the T–sites, these steric distinctions are sufficient for the sites to respond quite differently to variations in amphibole chemistry. Apical oxygens from the tetrahedral double–chains link in the X–direction to an octahedral strip to form an I–beam (fig. 2), a tightly–bonded module in the structure. Adjacent I–beams are staggered in the X–direction, giving a compositional layering to the structure as a whole. The I–beams link in the Y–direction by corner–sharing between octahedra and tetrahedra (fig. 1), and intra–module linkage is much stronger than inter–module linkage.

At the margins of the octahedral strip is the M(4) site, with point symmetry 2. It is surrounded by eight anions, not all of which necessarily bond to the central cation. The M(4) cation has four short bonds to non–bridging oxygens of one I–beam, and four (or two) longer bonds to bridging oxygens of two adjacent I–beams. Consequently, it is the M(4) cation that provides most of the additional inter–module linkage in the structure. Between the back–to–back double–chains is a large cavity that is surrounded by twelve bridging oxygens. Within this cavity is the A–site; the position of the site and the configuration of the coordinating anions are a function of local stereochemical requirements, and vary with the chemistry of the amphibole. The A–site cations thus provide additional inter–module linkage in the X–direction.

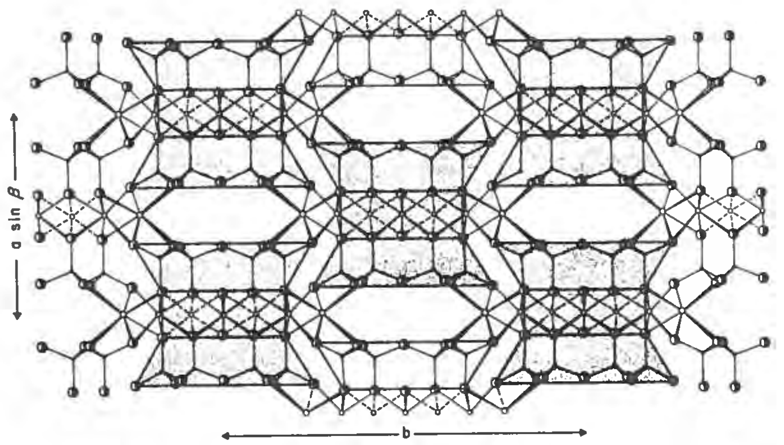

Fig. 2. – The C2/m amphibole structure projected down Z; the shaded areas show the I–beam modules of the structure.

Crystal Chemistry: A Qualitative Survey

A standard amphibole formula may be written as:

$$A_{0\text{-}1}B_2C_5T_8O_{22}W_2$$

where A = Na, K
B = Na , Li , Ca , Mn , Fe^{2+} , Mg
C = Mg , Fe^{2+} , Mn , Al , Fe^{3+} , Cr^{3+} , Ti , Li
T = Si , Al
W = OH , F , Cl , O^{2-}

The wide variety of cation coordinations together with the large structural compliance of some of the sites result in complex site–occupancy and order–disorder relationships. A brief general survey is given here, for more details see Hawthorne (1983a).

The T–group cations occupy the T(1) and T(2) sites of the tetrahedral double–chain. The Al content of the T–cations in amphiboles varies between 0.0 and ~ 3.5 atoms p.f.u., although amphiboles in which ^{IV}Al exceeds ~ 2.0 atoms p.f.u. are very uncommon. Extensive work has shown that ^{IV}Al is strongly ordered at the T(1) site in natural amphiboles, and that significant ^{IV}Al occupancy of the T(2) site occurs only for amphiboles in which ^{IV}Al > 2.0 atoms p.f.u.

The C–group cations occupy the M(1), M(2) and M(3) sites of the octahedral strip. In all of the natural amphiboles examined, trivalent cations are nearly completely or completely ordered at the M(2) site; one exception to this is oxy–kaersutite, in which Ti (probably quadrivalent) is strongly ordered at M(1), and Fe^{3+} and Al may be disordered or partly disordered over M(1), M(2) and M(3). Monovalent Li is almost completely ordered at M(3). The behaviour of Mg, Fe^{2+} and Mn is more complex, and much work still remains to be done in this area. However, the relative ordering of Fe^{2+} over the M(1) and M(3) sites does seem to be a function of the size and/or charge of the constituent M(2) cations (Ungaretti *et al.*, 1981a, 1984). The behaviour of Mn is still not well–characterized.

The B–group cations occupy the M(4) site, with coordination numbers of [8] for Na and Ca, and [8] or [6] for Li, Mn, Fe^{2+} and Mg. The cation occupancy of this site is the primary feature upon which the current nomenclature scheme (Leake, 1978) is based, and is a major factor in the crystal chemistry of the amphiboles, having a considerable influence on structure type.

The A–group cations occupy the A–site cavity, with coordination numbers of [12], [10] or [8], depending on the actual position assumed by the cation. The identity of the A-group cation is an important factor in controlling the local configuration, but chemical variation at next–nearest–neighbour sites also seems to be of importance.

Crystal Chemistry: Some Quantitative Aspects

Considerable effort has gone into putting stereochemical relationships in the amphiboles on to a quantitative basis, in order that they may be of direct use in deriving compositional and ordering data for amphiboles. The most precisely defined relationships focus on the most strongly bonded cation polyhedra, as these are least perturbed by what happens in the surrounding structure, and respond most directly and precisely to variations in their own constituent cations and anions.

Several authors have considered the relationship between mean tetrahedral bond–lengths and ^{IV}Al occupancy in C2/m amphiboles. Fig. 3a shows the variation in grand < T–O > distance as a function of ^{IV}Al content for selected C2/m structures. Most values are from Hawthorne (1983a), with the constraints that the individual standard deviations on the T–O bond–lengths be ≤ 0.005Å and the structural refinements not be considered deficient in any aspect; the remaining data are from Ungaretti *et al.* (1981b), with the constraint that the amphibole composition be derived by electron microprobe analysis. A linear relationship seems adequate; the results of a linear regression analysis are given in Table I.

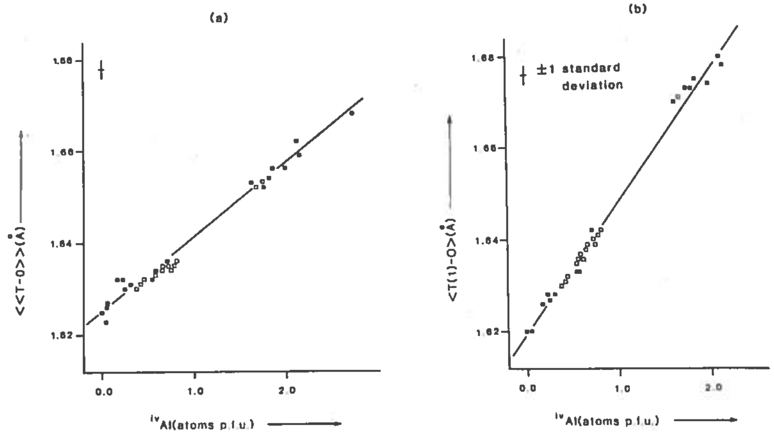

Fig. 3. – *a*) Variation in grand < T–O > distance with total ^{IV}Al (tetrahedrally coordinated aluminium) in the C2/m amphiboles for which external chemical analyses are available (■); □ denote values derived from a slightly different equation by Ungaretti et al. (1981b) and Ungaretti *et al.* (1983). *b*) variation in < T(1)–O > distance with total ^{IV}Al in the C2/m amphiboles; legend as for (*a*).

Examination of the stereochemistry of the tetrahedrally coordinated sites in non–^{IV}Al amphiboles (Hawthorne, 1983a) has shown that the < Si–O > bond–lengths are significantly affected by the behaviour of other parts of the structure. This is apparent in fig. 4, which shows the variation in individual < T–O > distances as a function of Δ, the polyhedral distortion parameter of Brown and Shannon (1973), for the non–^{IV}Al amphiboles. The variation in mean bond–length occurs primarily at T(2), which exhibits a total range of 0.014Å; conversely < T(1)–O > is fairly

TABLE I

Mean Bond–Length–Ionic Radius relationships for C2/m *Amphiboles.*

Dependent variable	Independent variable	*c*	*m*	R
^{IV}Al	$\langle\langle$ T–O $\rangle\rangle$	–100.767	62.004	0.992
^{IV}Al	$\langle$ T(1)–O $\rangle$	–55.782	34.448	0.996
$\langle$ M(1)–O $\rangle$	$r_{M(1)}$ $r_{O(3)}$	0.887	0.82 0.46	0.961
$\langle$ M(2)–O $\rangle$	$r_{M(2)}$	1.488	0.827	0.997
$\langle$ M(3)–O $\rangle$	$r_{M(3)}$ $r_{O(3)}$	0.387	0.73 0.87	0.925

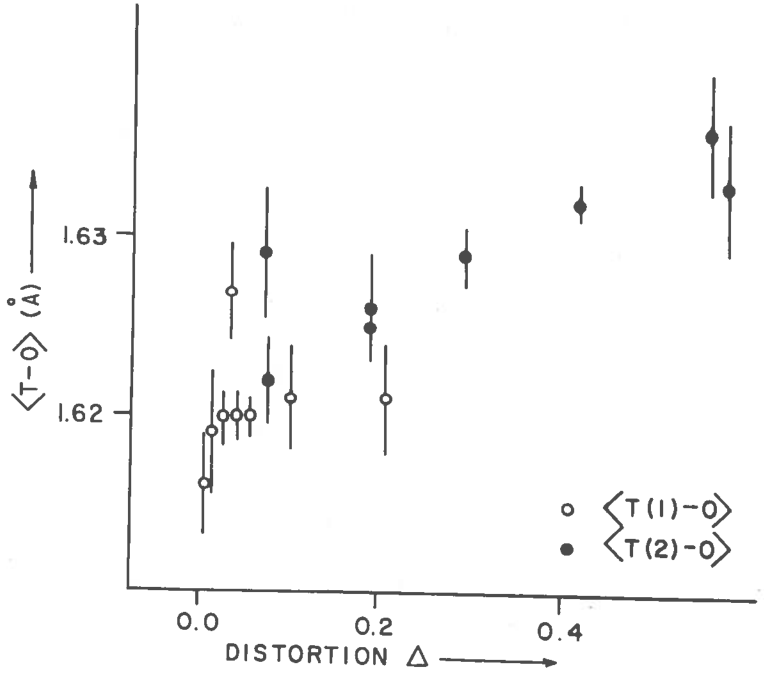

Fig. 4. – Variation in individual < T–O > distances as a function of polyhedral distortion Δ for the C2/m amphiboles with $^{IV}Al \leq 0.10$ a.p.f.u.; from Hawthorne (1983a).

constant at ~ 1.620Å, except for the single errant value for grunerite. This suggests that the T(2) tetrahedron is much more susceptible to inductive effects from the rest of the structure than the T(1) tetrahedron. In the ^{IV}Al–containing amphiboles, all < T(2)–O > distances (with the exception of subsilicic titanian magnesian hastingsite, Hawthorne and Grundy (1977a)) fall within the range of values shown in fig. 4. This suggest, but does not prove, that all ^{IV}Al orders at T(1), and that the minor variations in < T(2)–O > from structure to structure occur as a result of inductive effects from the rest of the structure rather than from small amounts of ^{IV}Al at T(2). Using this idea, Ungaretti (1980) produced a relationship between ^{IV}Al–content and < T(1)–O >; the statistical details are given in Table I. Fig. 3b shows the corresponding relationship using the same data set as for fig. 3a, and the linear–regression results are given in Table I. The relationships in Figures 3a and 3b are both extremely well–developed; the slightly higher correlation coefficient for the < T(1)–O > relationship does support the suggestion outlined above, that ^{IV}Al is completely ordered at T(1), but this is of marginal significance. Certainly either relationship would seem adequate for the extraction of compositional information from structural data.

Hawthorne (1983a) summarizes previous work on the stereochemistry of the octahedral strip in C2/m amphiboles; the relationships between mean bond–length and constituent cation radius are show graphically in fig. 5, and the statistical relationships are given in Table I. It is immediately apparent from fig. 5 that the relationship for the M(2) site is much better developed than those of the M(1) and M(3) sites. Much of this scatter for the M(1) and M(3) sites stems from the variable occupancy of the O(3) site by OH^-, F^-, Cl^- and O^{2-}.

Inclusion of the mean ionic radius of the O(3) anion as an independent variable in the relationships leads to significant improvement (Table I), but as shown by Hawthorne (1983a), there seem to be significant inductive effects from the rest of the structure affecting the M(3) and perhaps the M(1) sites. However, a linear relationship for the M(2) site is particularly well–developed (fig. 5); there may be small inductive effects due to variation in M(4) and/or A–site occupancy (Ungaretti *et al.*, 1981a; Ungaretti, 1980), but these seem to be of less significance at M(2) than at the M(1) or M(3) sites.

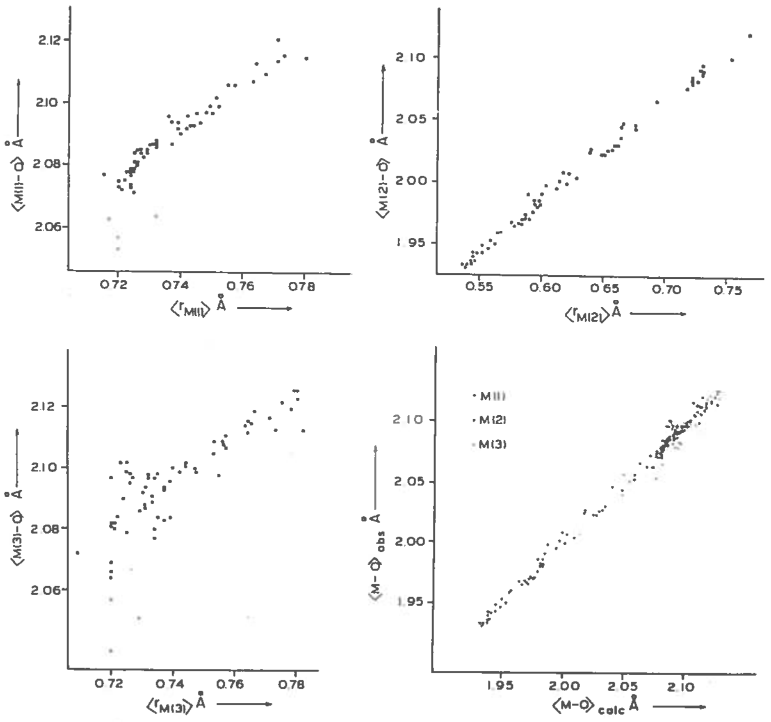

Fig. 5. – Variation in individual < M–O > distances with mean ionic radius of the constituent cations for the C2/m amphiboles (from Hawthorne, 1983a); also shown is a comparison of the observed mean–bond lengths with the corresponding values calculated from the regression equations of Table I.

TABLE II

Ideal < M–O > *distances* (Å) *for complete occupancy of* M (1, 2, 3) *sites by a single cation.*

	Ungaretti *et al.* (1981)			Hawthorne (1983a)		
Al	—	1.929	—	1.924	1.931	1.947
Fe^{3+}	—	2.031	—	2.014	2.022	2.027
Ti^{4+}	—	1.960	—	1.982	1.989	1.998
Ti^{3+}	—	—	—	2.035	2.043	2.045
Mg	2.078	2.078	2.083	2.075	2.084	2.082
Fe^{2+}	2.119	2.119	2.125	2.124	2.134	2.126
Mn^{2+}	—	—	—	2.165	2.175	2.163
Li	—	—	—	2.109	2.117	2.112

The relationship beteen < M–O > and cation occupancy has been treated in a slightly different fashion by Bocchio *et al.* (1978) and Ungaretti *et al.* (1981b). They proposed ideal mean bond–lengths for complete occupancy of the octahedrally coordinated M–sites by a specific cation; these value are shown in Table II, where they are compared with the analogous values calculated from the regression equations of Table I. There is generally reasonable agreement between these two sets, except for Fe^{2+} at M(2) and Ti^{4+} at M(2). The < Ti–O > value given here is very close to that given by Bocchio *et al.* (1978); the < M(2)–O > value observed in grunerite (Finger, 1969) suggests that the larger value is more nearly correct, but refinements of ferro–actinolite and/or ferro–richterite are needed to resolve this point.

CHARACTERIZATION OF NATURAL AMPHIBOLES

Several techniques have been used to examine various aspects of the average structure of natural amphiboles. All of these methods have inherent limitations that pertain to the experimental method; these are generally well–known and will not be covered here, except where they pertain specifically to amphiboles. When these techniques are used to quantitatively determine some feature or features of the average structure of a mineral, there are other inherent problems associated with the derivation of such results from the raw experimental data. Many of these have been reviewed recently by Hawthorne (1983b). What follows is a brief consideration of each technique, together with an evaluation of its strong and weak points specifically with regard to the characterization of natural amphiboles.

Electron Microprobe Analysis

This is by far the most common method for the chemical characterization of amphiboles and is of considerable importance, both because of its ease of use and because it can be used to characterize zoning and reasonably small–scale (> 1μ) structures. It can determine the proportions of most atoms with Z ≥ 9, exclusive of valence state, and it performs such analyses very rapidly. However, the disadvantages are considerable, particularly for amphibole studies; specifically, we cannot analyze for Li, H and the Fe^{3+}/Fe^{2+} ratio, constituents that are often crucial to the interpretation of amphibole chemistry. The lack of Li and H analyses (as Li_2O and H_2O) is generally of lesser importance, as the presence of Li or the absence of OH are generally characteristic of specific environments, and generally is of importance only in these particular instances. However, the lack of a Fe^{3+}/Fe^{2+} ratio is more important, as this parameter varies with paragenesis, and the role of Fe in the amphibole structure is strongly a function of its valence state. In many cases, this can be overcome by separation of a few milligrams of amphibole for wet–chemical analysis of FeO (Hey, 1974, 1982a,b); however, this method has not achieved popularity, and most effort has gone into attempts to calculate the Fe^{3+}/Fe^{2+} ratio during conversion of the chemical analyses to the unit formula.

The results of a chemical analysis are normally presented as the weight percentages of the oxides present; it thus provides the ratios of the chemical constituents in the structure (exclusive of oxygen), and calculation of the unit cell contents requires normalization to some standard basis that is characteristic of the structure (Hey, 1939). The schemes that have been used for this have recently been reviewed by Robinson *et al.* (1982) and Hawthorne (1983a), and will not be treated in detail here. However, it should be noted that all schemes based on normalization to specific numbers of anions or cations must lead to charge–balanced formulae, as the analysis start out with neutral oxides and constrains electroneutrality during renormalization. To calculate a Fe^{3+}/Fe^{2+} ratio, it is necessary to

(1) normalize the anions to a fixed number
(ii) normalize the cations to a fixed number
(iii) adjust the Fe^{3+}/Fe^{2+} to obtain electroneutrality.

This has been done by several authors (Stout, 1972, Papike *et al.*, 1974), using a total of 13 cations (Si + Al + Ti + Fe^{2+} + Fe^{3+} + Mn + Mg) to give a maximum value of the Fe^{3+}/Fe^{2+} ratio and a total of 15 cations (exclusive of Na + K) to give a minimum value of the Fe^{3+}/Fe^{2+} ratio. The maximum value thus calculated is not valid if there are significant vacancies at the M(1), M(2) and/or M(3) sites (cf. Leake *et al.*, 1981). However, these limits are generally reasonable, but frequently so wide as to be of little use.

Papike *et al.* (1974) suggested that the half–way point between the minimum and maximum be taken as an estimate of the actual Fe^{3+} content. This premise was tested for calcic and subcalcic amphiboles on the superior analyses from the compilation of Leake (1968); the results are shown in fig. 6, where it can be seen that there is no significant correlation between the observed and calculated values. A better interpolation between the minimum and maximum Fe^{3+}/Fe^{2+} ratios can probably be obtained by careful examination of the formula both with regard to crystal chemistry, bulk–rock composition and paragenesis. However, such estimation methods do not replace actual measurement.

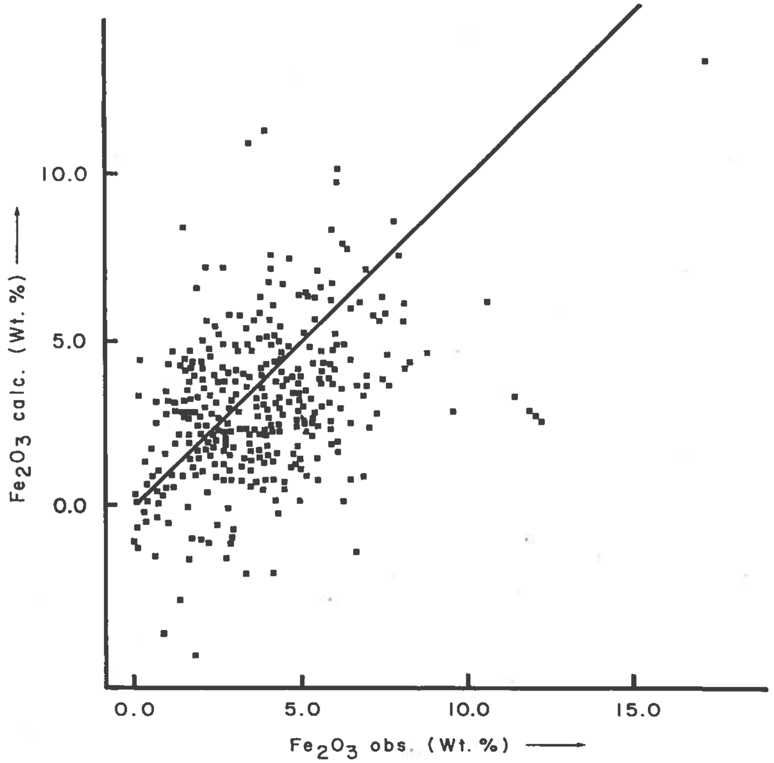

Fig. 6. – Fe^{3+} p.f.u. calculated by the method of Papike *et al.* (1974) compared with the observed values (based on a 24 (O,OH,F) calculation) for the superior analyses of Leake (1968).

Single–Crystal Structure Refinement

Single–crystal structure refinement gives the relative locations and magnitudes of the electron–density centres in the amphibole structure. An expert discussion on data collection and refinement techniques with regard to amphibole studies is given by Ungaretti (1980). A general discussion of site–occupancy refinement is given by Hawthorne (1983b), and a discussion of the development of these technqiues as applied to amphiboles is given by Hawthorne (1983a).

During the last decade or so, attention has focussed on the detailed stereochemistry of major–forming mineral groups. For the amphiboles, the rationale for this lay in trying to unravel the relationships between the amphibole structure and the compositional variations exhibited by natural amphiboles, thus characterizing to what extent the amphibole structure itself exerts constraints on its own chemical composition during petrologic processes. Most of these studies were done on amphiboles whose unit cell contents were derived by some other technique, and this information was used as a constraint on the site–occupancy refinement process. The details of this process are particularly interesting and will be discussed here, as they have conditioned our thinking with regard to structure refinement for some considerable time.

During Bragg diffraction, the amplitude F_{hkl} of the scattered wave is given by

$$F_{hkl} = \sum_{j=1}^{n} S_j \exp 2\pi i\, (hx_j + ky_j + lz_j) \exp\, (-B_j \sin^2 \theta/\lambda^2)$$

where S_j is the (total) scattering at the j^{th} site in the cell, x_j , y_j , z_j are the positional coordinates of the j^{th} site, and B_j is the isotropic temperature factor, a function of the vibrational displacement of the atom(s) at the j^{th} site. In this equation, S_j and $\exp\, (-B_j \sin^2 \theta/\lambda^2)$ are of similar form when expressed as functions of $\sin \theta/\lambda$. As F_{hkl} is the sum of products of these functions, they are highly correlated in least–squares refinement procedures derived from equation (1). Two important points stem from this:

(i) if $\sin \theta/\lambda$ dependent systematic error is present in the diffraction data, this will induce systematic error in both S_j and B_j. If the total ΣS_j (or some chemically specific component of it) is known, then this part of the refinement results can be constrained to be correct. However, this merely disperses the systematic error among the remaining parameters, all of which are still incorrect. Constraints of this sort were originally introduced to deal with the problem of unconstrained site–occupancy refinements converging to cell contents that did not agree with externally derived chemical analyses. However, as indicated above, this merely hides the error rather than removing it.

(ii) if there is no $\sin \theta/\lambda$ dependent systematic error in the diffraction data, then unconstrained site–occupancy refinement will converge to the correct answer, provided no model–dependent errors are introduced in the refinement process. Use of a correct bulk compositional constraint in the refinement procedure will lead to lowered correlations and a more *precise* solution, but both constrained and unconstrained refinements will lead to an accurate solution.

It is apparent from the above discussion that chemical compositions of amphiboles may be *determined* from structure refinement, provided significant systematic error can be eliminated from the diffraction data, and provided no errors in the model are introduced during the refinement procedure. Such unconstrained refinement determines the total scattering power at each site in the crystal, and for most amphiboles this is insufficient to determine the total bulk composition. However, this information may be combined with some of the quantitative crystal–chemical relationships outlined above to derive very complete bulk chemical compositions. The following procedure is due to Ungaretti *et al.* (1981b):

(i) Al^{IV} is estimated from $< T(1)–O >$;

(ii) total charge at A + M(4) is estimated from site–occupancy refinement, giving Na (+ K when available from chemical analysis) at the A–site and Ca + Na + Fe^{2+} at M(4) (Fe^{2+} being included only when indicated by difference Fourier maps);

(iii) total charge of C–type cations = total charge of $(Si , Al)_8O_{22} (OH)_2$ minus total charge at 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 II. 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 $Q < 6$, 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 satisfy the corresponding electron–density and distance equations. If $Q > 6$, trivalent cations are introduced into M(1) and/or M(3), substituting Fe^{3+} for Fe^{2+} and estimating the amount of Mg, Fe^{2+} and Fe^{3+} from mean bond lengths;

(vi) if the total charge imbalance ≤ 0.07, Al^{IV} 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.* (1981b) get excellent agreement between amphibole compositions determined in this fashion and by electron microprobe analysis of the crystals used to collect the X–ray data (Table III). Additional correlations between stereochemical parameters and chemical composition (Ungaretti *et al.*, 1981b) may then be used to confirm or reject the derived chemical composition.

TABLE III

Comparison of chemical compositions of single–crystals obtained by structure refinement (X), wavelength dispersive (W) and energy dispersive (E) electron microprobe analysis: From Ungaretti et al. (1981).

	A4			Cl			F3		
	X	W	E	X	W	E	X	W	E
Si	7.400	7.398	7.431	7.455	7.439	7.460	6.238	6.231	6.250
Al	1.300	1.294	1.292	1.535	1.578	1.575	2.882	2.978	3.035
Mg	3.821	3.693	3.656	3.435	3.340	3.324	2.929	2.696	2.649
Fe	0.618	0.674	0.706	0.681	0.648	0.680	0.911	0.990	0.976
Ti	0.026	0.025	0.025	0.024	0.022	0.015	0.040	0.039	0.040
Cr	—	0.004	—	—	0.002	—	—	—	—
Mn	—	0.004	0.012	—	0.003	—	—	0.016	—
Ni	—	0.012	0.015	—	0.012	0.012	—	0.005	—
Ca	1.105	1.103	1.127	0.750	0.752	0.767	1.062	1.060	1.075
Na	1.043	1.034	0.845	1.515	1.534	1.426	1.938	1.961	1.850
K	0.068	0.069	0.073	0.046	0.046	0.046	—	—	—
Σ	15.381	15.310	15.182	15.441	15.378	15.304	15.998	15.974	15.874

Obviously this is a macroscopic technique, in that it examines in bulk a single–crystal. Thus it cannot be used to characterize zoning, although it can be used to examine fairly small–scale microstructures (exsolution, inclusions) by virtue of their diffraction characteristics.

Mössbauer Spectroscopy

There are thirty or so isotopes sensitive to the Mössbauer effect, but only ^{57}Fe is of use in amphibole studies. Hawthorne (1983b) gives a general discussion of the method, and Hawthorne (1981b, 1983a) gives details of amphibole studies. Mössbauer spectroscopy can be used to characterize relative site–occupancies for Fe^{2+} and Fe^{3+}, provided the spectra are reasonably well–resolved. When combined with chemical analysis results, absolute occupancies can be obtained that are in good agreement with those derived from site–occupancy refinement (Hawthorne, 1983b). However, the results are of questionable accuracy in more complex amphiboles.

This is a macroscopic technique requiring a considerable amount (up to 0.1 g) of clean material. The experiment is quite slow, taking ~ 1 day to perform (about the same of time as for a crystal–structure data collection). Conversely, the very specific nature of its response can result in an answer when no other technique is adequate (Hawthorne and Grundy, 1977b).

Infrared Spectroscopy

The fine–structure in the fundamental band of the O–H stretching vibration in the infrared is sensitive to the cation occupancies of the M(1) and M(3) sites (Hawthorne, 1981b, 1983a,b). The relative intensities of the fine–structure bands can thus be used to derive quantitative site–occupancies at the M(1), M(2) and M(3) sites when used in conjunction with a chemical analysis of the amphibole. There are considerable technical problems associated with the use of this technique for fully–quantitative work, and it is of questionable accuracy in more complex amphiboles where the spectra are often irresolvably complicated.

As with Mössbauer spectroscopy, this is a macroscopic technique requiring a considerable amount (~ 5 mg) of clean material; however, the experiment is quite rapid. Also the technique does not characterize the average structure if some F, Cl or O^{2-} is present at the 0(3) site.

Summary and Application

The spectroscopic methods are very site–specific, and can be extremely useful in particular instances; however, in general they are only of use to augment the results of other techniques.

Electron microprobe analysis is currently the principal tool for amphibole characterization in petrologic studies. Numerous works show the power of this technique (see summary by Robinson *et al.*, 1982); as it is familiar to most people, no examples will be described here. However, it should be emphasized that the drawbacks of this method still remain to be overcome, and thus such studies still have significant deficiencies.

Current single–crystal structure refinement gives the most accurate characterization of an amphibole. However, this fact is not sufficient to make the technique a petrologic tool. The crucial step in this change of emphasis was the decision to use structure refinement on a large scale and directly apply the technique to specific petrologic problems. This step was taken by Giuseppe Rossi and Luciano Ungaretti in their pioneering studies of chain–silicates over the last five years. As an example of the effectiveness of this approach, some highly significant results from a recent study by Ungaretti *et al.* (1983) on the eclogitic rocks of the Sesia–Lanzo Zone, Western Alps, are described here.

The Eclogitic Micaschists of the Austroalpine Sesia–Lanzo unit are a sequence of high–grade paragneisses, amphibolites and marbles, intruded by gabbros and granitoids, which were re–metamorphosed under high pressures and intermediate temperatures during the Alpine orogeny. Clinoamphiboles are present in rocks of basic composition throughout the entire metamorphic sequence, and their composition seems to be closely related to the evolution of metamorphic conditions. Brown pre–Alpine hornblende gradually evolved to more sodic compositions, both by re–equilibration and by growth of new amphiboles. The sequence of amphiboles observed was characterized by X–ray structure refinement and electron microprobe analysis. As indicated in fig. 7, there is a narrow gap in evolving amphibole compositions. A similar gap has been reported in previous studies from other areas, using electron microprobe data, and several studies have documented the coexistence of calcic and alkali amphibole pairs (Klein, 1968, 1969; Dobretsov *et al.*, 1971; Miller, 1977; Raith *et al.*, 1977). However, the origin of this gap was not all that clear, as discussed by Katagas (1974) and Ernst (1979); were all the breaks in composition expression of the same complex miscibility gap in different regions of compositional space, or were some due to rapid compositional changes resulting from a hiatus in metamorphic conditions? Examination of the structural changes

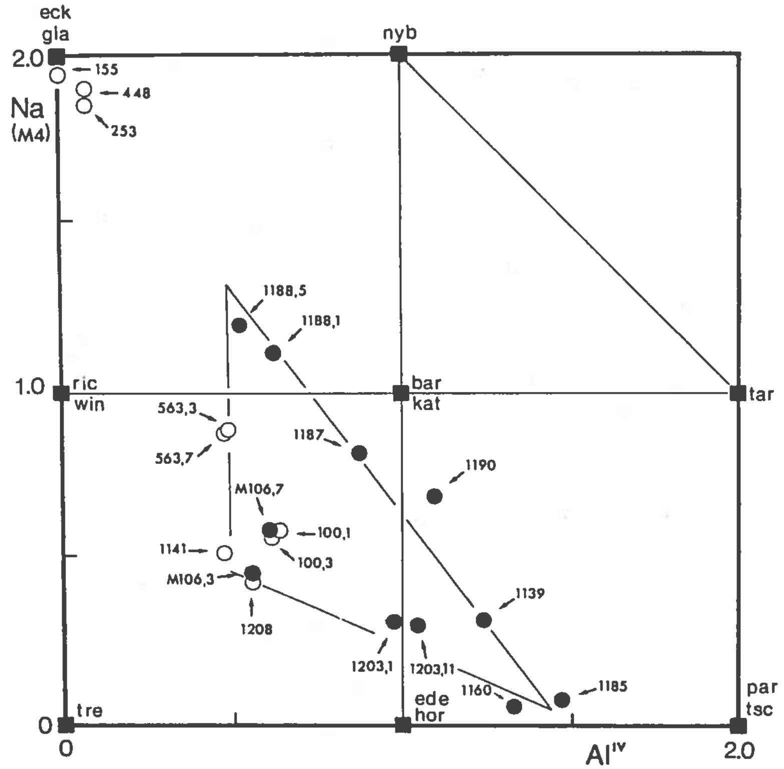

Fig. 7. – Variation in ^{IV}Al as a function of $Na^{M(4)}$ for the Sesia–Lanzo amphiboles; solid or open circles refer to amphiboles in rocks with or without pre–Alpine relics respectively; from Ungaretti *et al.* (1983).

around the M(4) site sheds light on this problem (Ungaretti *et al.*, 1983). Fig. 8 shows the variation in the 0(6)–0(5)–0(7) angle of the tetrahedral double chain as a function of the difference between the M(4)–0(5) and M(4)–0(6) bond lengths for 230 amphiboles refined at the Istituto di Mineralogia in Pavia by Luciano Ungaretti; an inset to the figure also shows the spatial relationships between these geometrical parameters and the configuration of the A, M(4) and T(1) sites. A distinct gap in the well–defined linear relationship is apparent for 0(6)–0(5)–0(7) angles between ~ 109½ and ~ 111°; without going into the rather involved crystal–chemical implications of this phenomenon, it seems that the amphibole structure cannot adopt a configuration within this region. Marked on fig. 8 are the amphiboles from the Eclogitic Michaschists of Sesia–Lanzo; the structural gap of Fig. 8 also corresponds to the compositional gap in the evolving sequence of amphiboles.

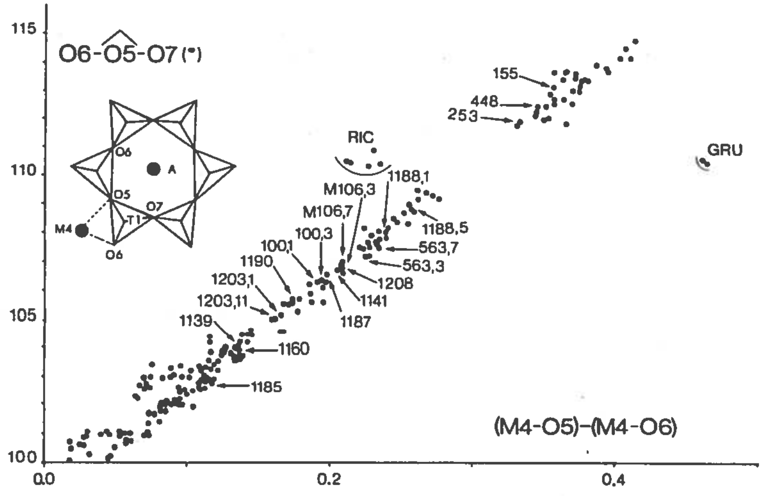

Fig. 8. – The difference in the bond lengths M(4)–0(5) and M(4)–0(6) as a function of the internal angle 0(6)–0(5)–0(7) of the tetrahedral chain (see inset sketch) for 230 refined amphiboles, with the Sesia–Lanzo amphiboles indicated by sample number; from Ungaretti *et al.* (1983).

The cation sites most closely involved in this effect are A, M(4) and T(1). Fig. 9 shows the sum of the charges at A + M(4) as a function of ^{IV}Al for 230 refined amphiboles, again with the Sesia–Lanzo amphiboles indicated by number. The evolution of amphibole compositions in these rocks can be characterized by a gradual loss of ^{IV}Al and a decrease in the net charge at A + M(4) in response to changing metamorphic conditions.

The compositional gap is seen to be due not to a limited miscibility of cations at a specific site, but to stereochemical restrictions on the combination of isomorphous substitutions occurring at two sites. Thus the compositional gap may be ascribed to crystal–chemical influences rather than to a hiatus in metamorphic conditions, a conclusion that would not be convincing without the crystallographic basis.

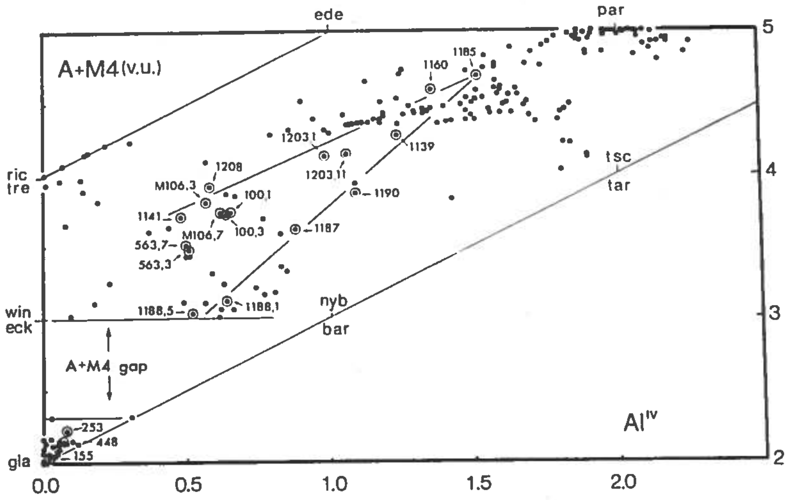

Fig. 9. – Variation in the sum of the formal cation charges at A+M(4) as a function of ^{IV}Al for 228 refined amphiboles, with the Sesia–Lanzo amphiboles indicated by sample number; from Ungaretti *et al.* (1983)

The Ideal Petrologic Study

The discussion given above shows the power of crystal–structure refinement when used in a petrologic context. However, it is important to stress that this technique should not be seen as an alternative to electron microprobe analysis. Crystallographic technique is extremely rapid nowadays, but is still two orders of magnitude slower than the microprobe as a producer of mineral analyses. In addition, the microprobe has certain innate characteristics that structure refinement does not (see previous discussion). Ideally these two techniques should be used to complement each other. The microprobe can produce a large number of analyses that can be related to small–scale textural features of their paragenesis; structure refinement can produce a smaller number of better–characterized analyses, together with the analogous stereochemical data that can be used to interpret chemical variations. The Fe^{3+}/Fe^{2+} ratio from the refined structures can be used to give realistic Fe^{3+}/Fe^{2+} ratios for the recalculation of the microprobe analyses; conversely, the microprobe analyses may be used to give certain element compositions (Cr, Mn and perhaps K and Ti) that cannot easily be derived by structure refinement. Hopefully this sort of study will develop in the future.

CHARACTERIZATION OF SYNTHETIC AMPHIBOLES

In the studies of the late 1950's and 1960's, the run products of amphibole synthesis studies were usually examined by optical microscopy and powder X–ray diffraction. Generally the amphiboles were assumed to be of nominal composition, and additional phases were ignored or considered metastable. Direct examination of many of these synthetic amphiboles by more sophisticated techniques during the 1970's showed many amphiboles to be 'off–composition'. These studies will be considered in some detail here, as they emphasize the need for better characterization methods in amphibole synthesis studies and indicate some of the more unexpected results of such studies, results that are frequently not widely appreciated. As with natural amphiboles, this section will be organized by technique.

Electron Microprobe Analysis

Run products are frequently too fine–grained to be characterized by electron microprobe analysis. However, some synthesis studies have used this technique. Cameron (1970) synthesized an iron–bearing fluor–richterite for crystal structure analysis; electron microprobe analysis showed it to have 0.08 Fe p.f.u. at the M(4) position (Table IV), corresponding to 8% cummingtonite–grunerite solid solution in the richterite. In his synthesis of ferro–glaucophane, Hoffman (1972) gave analyses of his amphibole products (Table IV); both analyses show considerable deviations from the ideal cell content, but the errors quoted are so large as to make the analyses of questionable significance. Oba (1978) synth-

TABLE IV

Electron–Microprobe Analyses of Synthetic Amphiboles.

	A	B	C	D	E	F	G	H	I	J	K	L
SiO_2	–	54.7(1.3)	54.0(0.7)	53.7	–	–	56.23	44.61	56.06	44.93	53.01	46.08
Al_2O_3	–	11.8(0.8)	13.9(5.4)	11.4	–	–	2.94	17.04	6.06	15.93	9.55	14.82
MgO	–	–	–	–	–	–	23.61	19.40	23.00	19.99	22.39	20.61
FeO	–	21.7(1.6)	23.6(3.7)	24.0	–	–	–	–	–	–	–	–
CaO	–	–	–	–	–	–	13.29	12.75	12.91	13.03	11.64	12.46
Na_2O	–	6.8(0.3)	6.9(0.6)	6.9	–	–	0.23	3.02	0.73	3.21	1.46	2.99
Σ	–	95.0	98.4	96.0	–	–	96.60	96.82	98.96	97.10	98.05	96.96
Si	7.97	8.12	7.81	–	6.1	5.9	7.72	6.22	7.50	6.26	7.17	6.41
Al	–	–	0.19	–	1.9	2.1	0.28	1.78	0.50	1.74	0.83	1.59
Σ	7.97	8.12	8.00	–	8.0	8.0	8.00	8.00	8.00	8.00	8.00	8.00
Al	–	2.06	2.18	–	1.5	1.7	0.19	1.03	0.48	0.87	0.69	0.84
Mg	3.45	–	–	–	3.5	3.3	4.81	3.97	4.52	4.13	4.31	4.16
Fe	1.60	2.69	2.82	–	–	–	–	–	–	–	–	–
Σ	5.05	4.75	5.00	–	5.0	5.0	5.00	5.00	5.00	5.00	5.00	5.00
Mg	–	–	–	–	0.3	0.6	0.02	0.06	0.07	0.02	0.20	0.11
Fe	0.08	–	0.04	–	–	–	–	–	–	–	–	–
Ca	0.90	–	–	–	1.7	1.4	1.95	1.91	1.85	1.94	1.69	1.86
Na	1.02	1.98	1.94	–	–	–	0.02	0.03	0.08	0.04	0.11	0.03
Σ	2.00	1.98	1.98	–	2.0	2.0	2.00	2.00	2.00	2.00	2.00	2.00
Ca		–	–	–	0.2	0.2	–	–	–	–	–	–
Na	[illegible]	–	–	–	–	–	0.12	0.78	0.11	0.83	0.27	0.78
Σ	[illegible]	–	–	–	0.2	0.2	0.12	0.78	0.11	0.83	0.27	0.78

A: fluor–richterite (Cameron, 1970); B: ferro–glaucophane, av. of 10 analyses; C: ferro–glaucophane, av. of 4 analyses; D: ideal ferro–glaucophane, B,C,D from Hoffman (1972); E: tschermakitic amphibole, grown at 15 kb; F: tschermakitic amphibole, grown at 20 kb, E and F coexist with garnet (Oba, 1978); (G,H), (I,J), (K,L); tremolite–pargasite pairs, grown at 800, 850 and 900°C respctively (Oba, 1980).

esized tschermakite and studied its stability at high pressure; he did not give analyses of amphibole when a single–phase run–product was produced, but gave cell–contents of amphiboles coexisting with other phases at higher pressures (Table IV). These analyses are peculiar, showing significant Ca at the A–site; it is a pity that analyses of the 'single–phase' amphibole were not presented. Oba (1980) studied phase relations on the tremolite–pargasite join; he showed the presence of a solvus at 1 kb and determined the miscibility limits by microprobe analysis. The analyses look quite respectable, but no 'single–phase' amphiboles were analyzed.

The results of Oba (1980) suggest that electron microprobe analysis may be a viable technique for synthetic amphibole characterization, provided the grain size of the run–product is sufficiently large to allow the excitation volume of the X–rays to lie within a single amphibole grain. Using substrates may be an alternative, but analyses derived by this method may not be of sufficient accuracy and precision to allow evaluation of the small compositional differences from an ideal formula that are suspected of occurring in some synthesis studies.

Mössbauer Spectroscopy

Burns and Greaves (1971) examined a ferro–actinolite synthesized by Ernst (1966); the spectrum is shown in fig. 10. If the composition of the amphibole is ideal, the spectrum should consist of three Fe^{2+} doublets with intensity rations 2 : 2 : 1, corresponding to Fe^{2+} at M(1), M(2) and M(3) respectively. This is obviously not the case. Burns and Greaves (1971) suggest that the doublet with the smallest quadrupole splitting is due to Fe^{2+} at M(4); this assignment is supported by the results of Goldman and Rossman (1977). The remaining doublets were assigned to Fe^{2+} at M(1) and at M(2) + M(3). The spectrum certainly indicates that the amphibole synthesized departs significantly from its nominal composition.

In a detailed study of synthetic magnesio–hastingsite, Semet (1973) showed directly that the Fe^{3+}/Fe^{2+} ratio in the synthesized amphibole is a function of oxygen fugacity. Spectra are shown in fig. 11; on the more oxidizing cuprite–tenorite (CT) buffer, only Fe^{3+} is present, but on the copper–cuprite (CCO) buffer, significant

Fe^{2+} is present. The percentage of Fe^{3+} varies from 13% on the IQF buffer to 100% on the CT buffer, indicating that at lower oxygen fugacities, the amphibole must be significantly 'off–composition'.

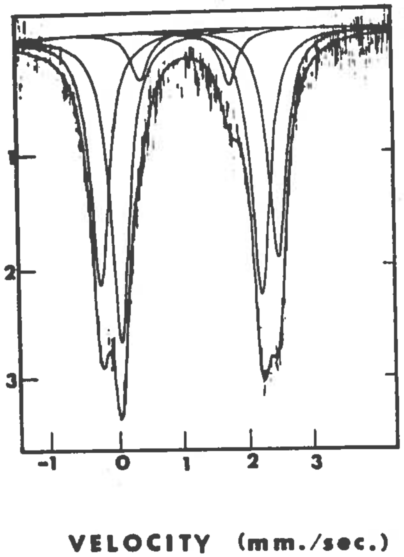

Fig. 10. – The Mössbauer spectrum of synthetic 'ferro–actinolie' ("ferrotremolite"); from Burns and Greaves (1971).

Virgo (1972) gives an unresolved Mössbauer spectrum of a ferro–richterite synthesized by Charles (1974); this is shown in fig. 12. It is immediately apparent from the spectrum that the ferro–richterite contains significant Fe^{3+} (~ 10%) as compared with the nominal value of zero. This result is quite surprising as the ferro–richterite was synthesized on the IW buffer.

Thomas (1982) gives a detailed examination of synthetic hastingsites; a typical spectrum is shown in fig. 12. Four doublets can be resolved (AA', BB', CC', DD') due to Fe^{2+} at M(1), M(3) and M(2), and Fe^{3+}. The observed Fe^{3+}/Fe^{2+} ratios are not compatible with the nominal composition, except for samples annealed on the QFM buffer. There are additional problems with these spectra (Thomas, 1982), but they do indicated departure from nominal composition.

All of the above studies show that the Fe^{3+}/Fe^{2+} ratios in the synthetic amphiboles departed significantly from their nominal values. For electroneutrality to be maintained, a futher charge–balancing substitution is required. Some studies have suggested that this involves additional or deficient hydrogen, but there are numerous other departures from compositional nominality that

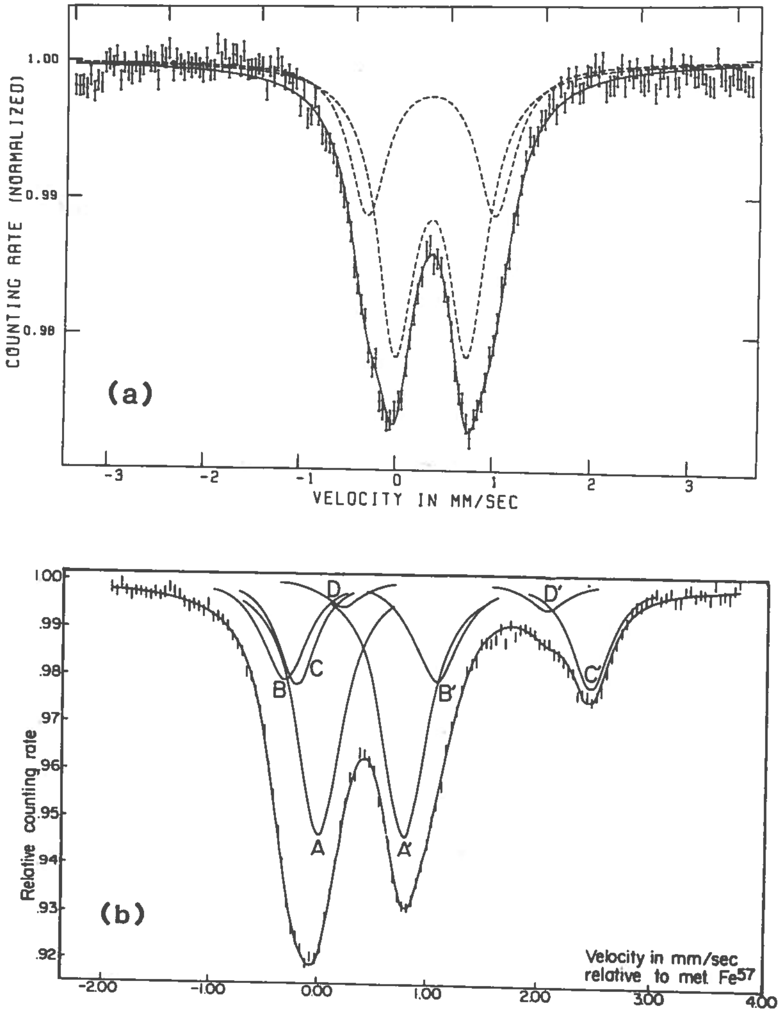

Fig. 11. – The Mössbauer spectra of synthetic 'magnesio–hastingsite'; *a*): grown on the CT buffer, no Fe^{2+} present; *b*) grown on the CCO buffer, considerable Fe^{2+} present; from Semet (1973).

could achieve the same result, and there is little direct evidence on this point.

Infrared Spectroscopy

Rowbotham and Farmer (1973) examined some synthetic richterites by infrared spectroscopy in the hydroxyl region (fig. 13). The spectrum of a solid solution amphibole of composition 75% tremolite – 25% richterite shows two bands with an intensity ratio on about 3 : 1, due to the richterite and tremolite configurations respectively. However, the spectra for nominal richterite and potassium–richterite (fig. 13), which should each show a single band, have an additional peak which corresponds to the tremolite position in the solid solution amphibole. Rowbotham and Farmer (1973) suggest that this shows the richterites to be deficient in A–site cations. Alternatively, it could also indicate the presence of talc in the run products.

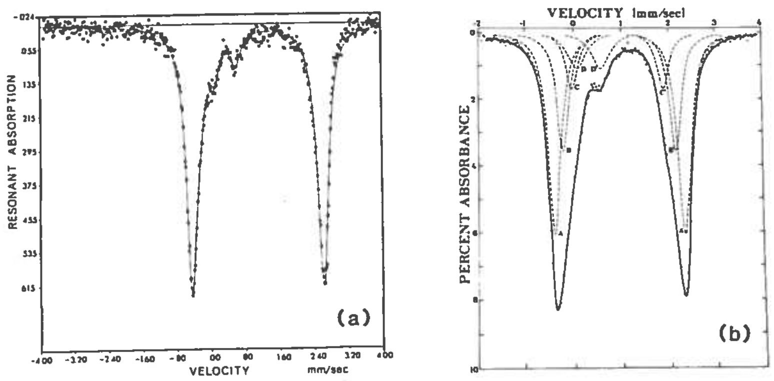

Fig. 12. – The Mössbauer spectra of: *a*) synthetic 'ferro–richterite' grown on the IW buffer, note the presence of significant Fe^{3+}; from Virgo (1972); *b*) synthetic 'hastingsite' grown on the WM buffer, note that the AA', BB', CC', DD' peak intensities depart from the ideal ratios 2 : 1 : 1 : 1; from Thomas (1982).

Semet (1973) also reports infrared spectra for magnesio–hastingsite. These show fine–structure, indicating the presence of Fe at the M(1) + M(3) sites in support of the Mössbauer spectral results; however, the valence states are not determined from the infrared study.

Indirect Methods

It must be admitted that the division of the methods into direct and indirect methods is rather arbitrary. However, the division is a pragmatic one, emphasizing that a direct method immediately indicates an 'off–composition' product, whereas an indirect method provides evidence from which an argument can be made for an 'off–composition' product. The best known example

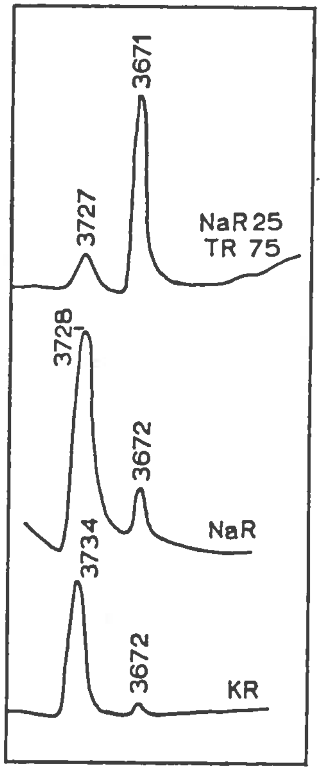

Fig. 13. – Infrared absorption spectra of a solid solution of 75% tremolite and 25% richterite (top), richterite (middle) and potassium-richterite (bottom); from Rowbotham and Farmer (1973). Note the weak peaks at 3672 cm^{-1} in the richterite spectra.

of this is glaucophane, the details of which were summarized by Maresch (1977); this will not be described here as it is dealt with elsewhere in this volume. Another well-documented example of this is the cell-dimension data for the richterite–ferro-richterite join (Charles, 1974). For a specific nominal composition ($Na_2CaMg_4Fe^{2+}Si_8O_{22}(OH)_2$), a sin β and V decrease significantly with increasing oxygen fugacity (fig. 14); this suggests the presence of Fe^{3+}, with the Fe^{3+}/Fe^{2+} ratio increasing with increasing oxygen fugacity. Fig. 14 also shows the variation in selected cell dimensions as a function of nominal composition for richterites synthesized on the IW (Iron–Wustite) buffer. The values for pure ferro-richterite are anomalously small when compared with the trend of the remaining values; again this suggests the presence of Fe^{3+} in nominal ferro-richterite, and this was actually confirmed directly by Mössbauer spectroscopy (fig. 12).

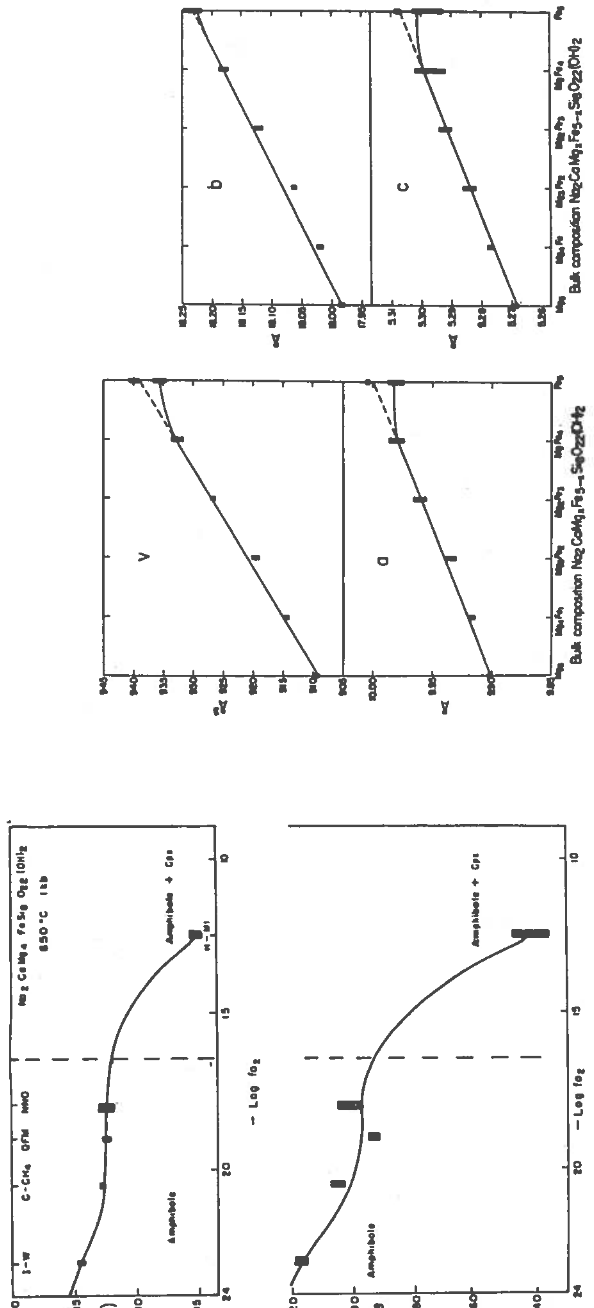

Fig. 14. – Selected cell dimensions as a function of oxygen fugacity during synthesis, and as a function of nominal amphibole composition; from Charles (1974).

Summary

In most cases where synthesized amphiboles have been examined carefully by spectroscopic, chemical analytical or crystallographic techniques, the amphibole has turned out to be 'off–composition'. It should be stressed that this is not the fault of the experiment; one does an experiment to find out what happens, and one cannot complain if the result does not agree with one's preconceptions. However, it does suggest that we should be taking a much closer look at our run products, as the literature on amphibole synthesis does not adequately reflect the situation as outlined here. In line with this, some additional techniques are suggested here that might be incorporated into a standard characterization procedure for run products.

Scanning Electron Microscopy

Scanning electron microscopy (SEM) is much superior to normal light microscopy for the optical examination of run products. The greater magnification and improved resolution make the recognition of different crystal morphologies much easier. This allows the recognition of additional phases that may either be present in amounts too small or be of inadequate crystallinity to register on an X–ray diffraction pattern. An EDS analytical capability also allows a qualitative assessment of the composition of any additional phases present. The amount of material required is small, and the technique is rapid. Some (non–amphibole) studies are now using this technique, but with the near–ubiquity of SEMs this should be a standard part of the experimental procedure.

Infrared Spectroscopy

This technique is extremely useful as a standard characterization method, because it is rapid and requires a fairly small amount of the run product. In addition, the chemical systems generally investigated do not contain the large number of minor components that often complicate the infrared spectra of natural amphiboles. Fig. 15 shows infrared absorption spectra for a series of pargasites with the octahedrally coordinated trivalent cations Al, Cr, Ga, Fe^{3+} and Sc.

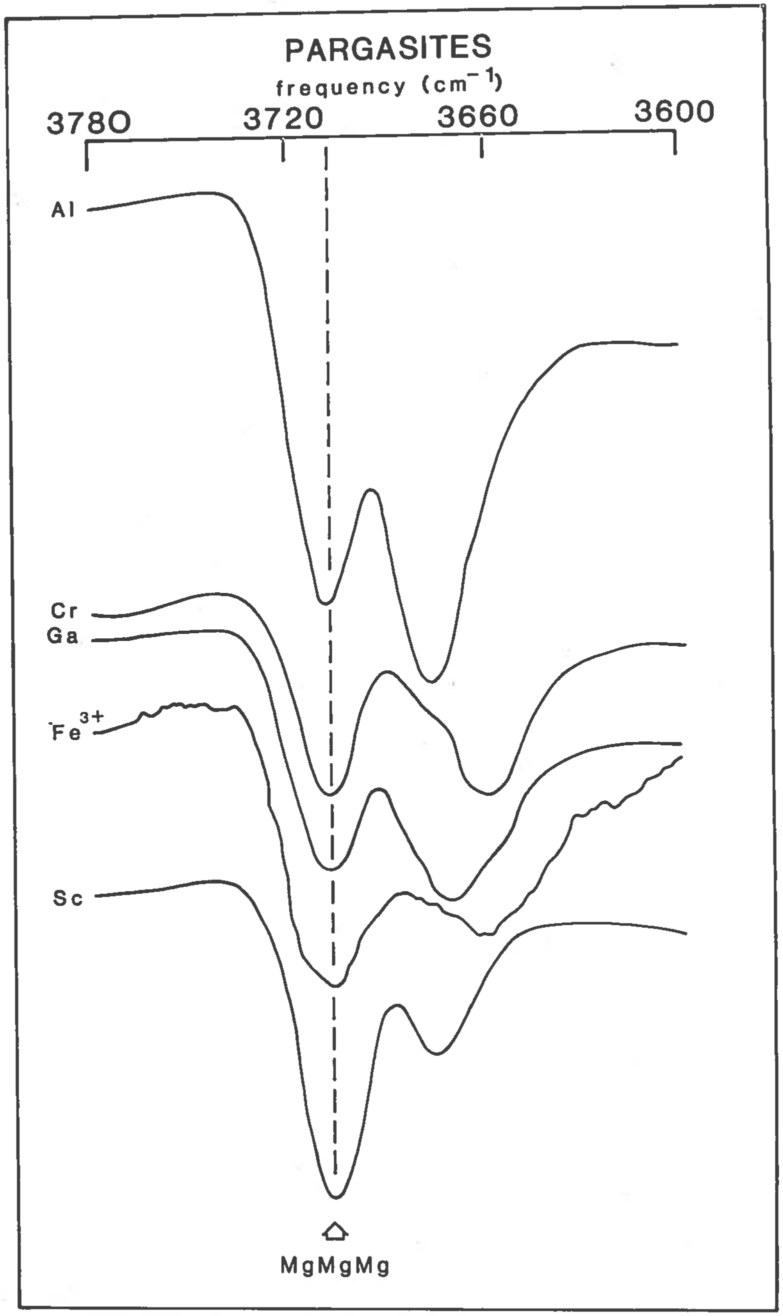

Fig. 15. – Infrared spectra of synthetic $NaCa_2Mg_4M^{3+}Si_6Al_2O_{22}(OH)_2$ (pargasite) run products with M^{3+} = Al, Cr^{3+}, Ga, Fe^{3+}, Sc; the band due to the MgMgMg–OH configuration is marked; from Raudsepp *et al.* (1982).

If the trivalent cations were completely ordered at the M(2) site, as is usually the case in natural amphiboles, each of these spectra would consist of a single band due to the configuration MgMgMg coordinated to O(3). Obviously this is not the case; there are two main absorptions in each spectrum. One is due to the MgMgMg configuration; the other is due to an $MgMgM^{3+}$ configuration, showing that the trivalent cations are disordered over the M(1), M(2) and M(3) sites in the structure. Here is a significant difference between natural and synthetic amphiboles. In natural amphiboles, octahedrally coordinated trivalent cations are highly or completely ordered at the M(2) site, whereas here they are almost completely disordered over the M(1), M(2) and M(3) sites in synthetic pargasite and magnesio–hastingsite (Semet, 1973).

Fig. 16 shows selected M^{3+} pargasite infrared absorption spectra. The lower Cr–pargasite spectrum shows a weak band that is not present in the upper spectrum. This weak band is at the position of the MgMgAl band in pargasite, indicating that the Cr–pargasite synthesized at 845°C and 2 kb contains some octahedrally–coordinated Al, and thus deviates slightly from its nominal composition. The spectrum of magnesio–hastingsite shows the same feature.

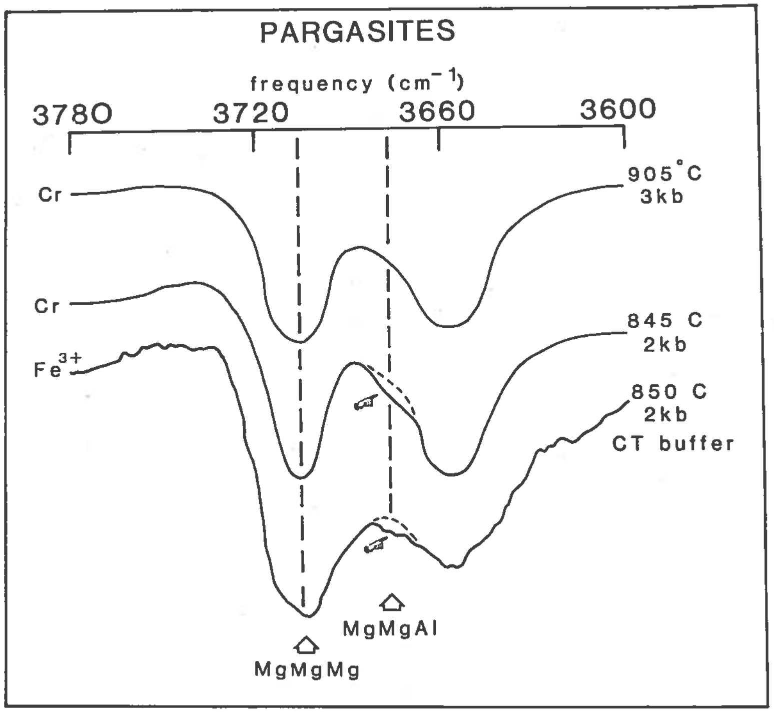

Fig. 16. – Infrared spectra of some synthetic $NaCa_2Mg_4M^{3+}Si_6Al_2O_{22}(OH)_2$ run products, with positions of the MgMgMg and MgMgAl bands marked; note the presence of weak MgMgAl bands in two of the spectra; from Raudsepp *et al.* (1982).

The Rietveld Method

The principal problem in characterizing synthetic amphiboles has been the fact that the crystals are not large enough to examine by conventional single–crystal techniques or electron microprobe methods. However, the importance of microcrystalline minerals in such diverse materials as nuclear waste, tooth enamel and industrial catalysts has promoted the development of a diffraction method to handle these materials. The Rietveld method (Rietveld, 1969) uses all of the information in a powder diffraction pattern (X–ray or neutron) to characterize the structure of the material examined. The structural parameters of the mineral, atomic coordinates, site–occupancies and thermal parameters, together with various experimental parameters affecting the pattern, are refined by least–squares procedures to minimize the difference between the entire calculated and observed powder patterns. The method is superior for neutron diffraction as compared with X–ray diffraction because neutron scattering does not fall off with scattering angle as does X–ray scattering, and because the diffraction intensity profile is more easily described mathematically in the neutron case. Nevertheless, extremely useful results on microcrystalline material have recently been obtained by X–ray diffraction (Young and Wiles, 1981).

There is obviously a lot less information contained in a powder diffraction pattern than in a complete single–crystal diffraction data set. In recognition of this, initial work with the Rietveld technique tended to concentrate on high–symmetry structures with small unit cells. However, this has gradually been extended to more complex lower symmetry structures in which order/disorder effects can be of importance (Nord, 1977; Nord and Stefanidis, 1980). In more complex cases, information from external sources can be incorporated into the refinement procedure, allowing the derivation of information that could not otherwise be determined. An obvious example of this is the incorporation of typical fixed temperature factors into a refinement when site–occupancy refinement is being carried out.

The Rietveld method has several advantages over normal powder X–ray diffraction methods for synthetic amphibole characterization. Firstly, it ensures that the X–ray pattern is correctly indexed; some published patterns show one or more peaks wrongly indexed, a feature that adversely affects the calculated cell dimensions.

TABLE V

Comparison of Cell dimensions for Synthetic Amphiboles by normal least–squares refinement and by powder profile refinement

	Fluor–pargasite		Sc–fluor–pargasite	
	Normal	Profile	Normal	Profile
a(Å)	9.827(4)	9.8279(6)	9.881(2)	9.8864(3)
b(Å)	17.928(7)	17.9308(11)	18.145(4)	18.1587(6)
c(Å)	5.296(2)	5.2938(3)	5.317(1)	5.3192(2)
$\beta^{(o)}$	105.17(3)	105.161(3)	105.17(2)	105.213(2)

Secondly, the method gives extremely precise cell dimensions (Table V), up to an order of magnitude more precise than normal powder methods. This occurs because the positions of the peaks are calculated from the whole peak profile, allowing for all the machine aberrations that affect the shape of the peak. The method can be used to characterize ordering when the cations involved have significantly different scattering power; this feature is particularly useful for fluor–amphiboles, in which the infrared method is not applicable. It can also be used to characterize deviations from nominal compositions, again if the scattering powers of the components involved are significantly different. Fig. 17 shows the observed and calculated X–ray powder pattern for scandium–fluor–pargasite; the structure is refined to an R–profile index of ~ 12% and an R–Bragg index of ~ 5%. The refined site–

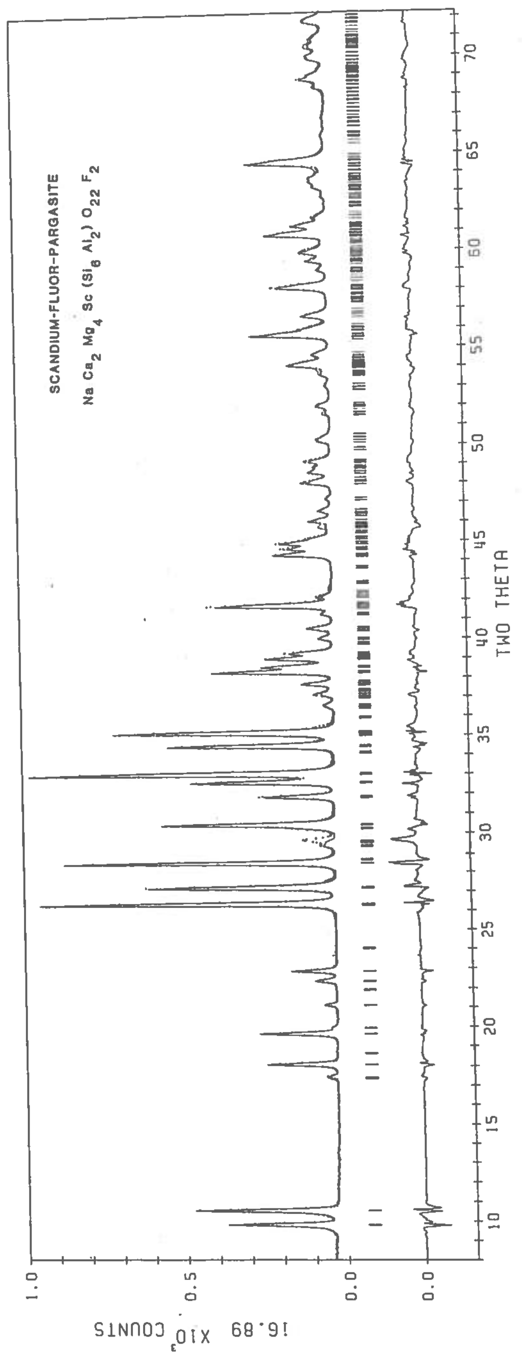

Fig. 17. – Observed and calculated X–ray powder patterns from the 'Rietveld' refinement of the structure of nominal scandium–fluor–pargasite; the position of each reflection is marked by a vertical line below the pattern and above the difference pattern.

occupancies show Sc to be fairly strongly ordered at the M(2) site, and also show the bulk composition to be Sc deficient when compared with the nominal composition. Also of value in this technique is the residual pattern that is left when the calculated amphibole pattern of any other phases in the run product, patterns that may have been partly or even completely obscured by the dominant amphibole pattern. For the scandium–fluor–pargasite of fig. 17, the residual pattern shows peaks of a pyroxene, intermediate in composition between diopside and $NaScSi_2O_6$, that were not very apparent in the complete pattern. Our initial experience suggests that this technique will prove to be useful, but more work is needed to give a realistic evaluation of its worth in this context.

Summary and Conclusions

Techniques for the characterization of both natural and synthetic amphiboles have undergone considerable development in the past ten years. Nevertheless, the optimum experimental approach is still rarely used in studies involving both natural and/or synthetic amphiboles. A general survey of these methods and their results indicates:

(i) large–scale crystal–structure refinement is a powerful tool for petrologic studies, particularly when used to complement and augment electron microprobe data;

(ii) many synthesized amphiboles are 'off–composition';

(iii) there are often significant structural differences between 'analogous' natural and synthetic amphiboles, particularly involving cation ordering; both (ii) and (iii) are of particular relevance to the determination and use of thermodynamic and physical properties of synthetic amphiboles;

(iv) we must be cautious both in applying the results of synthesis and stability studies to natural amphiboles, *and* in interpreting synthesis and stability data in terms of our crystal–chemical knowledge of natural amphiboles.

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