

REVIEWS in MINERALOGY & GEOCHEMISTRY



## **Amphibole Spectroscopy**

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## Chapter 2 AMPHIBOLE SPECTROSCOPY

Frank C. Hawthorne

#### INTRODUCTION

The diversity of cation coordinations and chemical compositions in the amphiboles has encouraged the use of a wide variety of spectroscopic techniques on these minerals. Much of the early work was concerned with the oxidation and dehydroxylation characteristics of fibrous and asbestiform amphiboles; although this was only qualitative, it showed the potential of these techniques for amphiboles. A considerable amount of work has been done in the past 15 years, particularly in the area of site- $\check{\mathbf{o}}_{\mathbf{b}}$  population characterization. Most studies have used three types of Ospectroscopy: Mössbauer resonance, vibrational and electronic (optical) Sabsorption. Brief descriptions of each method are given here. More de-Stailed reviews with a bent towards mineralogy can be found as follows: dMössbauer spectroscopy -- Bancroft (1973); vibrational spectroscopy --Clazarev (1972), Farmer, (1974), Karr (1975); electronic absorption spectroscopy -- Burns (1970).

In what follows, we will concentrate on understanding the spectro-Scopic characteristics of amphiboles and determining what crystal-chemical  $\overline{\mathbf{L}}$ information we can or cannot derive from experiments. We will not dwell  $\hat{c}_{0}$  the use of such crystal-chemical information in a petrologic context, MÖSSBAUER SPECTROSCOPY The Mössbauer effect is the recoil-free emis

The Mössbauer effect is the recoil-free emission and absorption of  $\sigma \gamma$ -rays by a specific atomic nucleus. The emission of a  $\gamma$ -ray during a Enuclear transition causes a recoil of the emitting atom; this recoil energy dissipates by transfer to the phonon spectrum of the structure. As the phonon spectrum is quantized, this transfer must occur in integral multiples of the phonon energy and the probability exists that no energy is transferred. The effective line-width of the zero-phonon (recoil-free) process is that of the y-ray; this is extremely small (Wertheim, 1964) in relation to the characteristic energies of interaction between the nucleus and its surrounding electrons. If the zero-phonon  $\gamma$ -ray encounters

another nucleus, its energy may be absorbed by raising that nucleus to an excited state, provided that the transition energies of the emission and absorption events are equal to within the line-width of the  $\gamma$ -ray. As the line-width of the  $\gamma$ -ray is much smaller than the characteristic interaction energies between nuclei and electrons, a change in structural environment is generally sufficient to bring the two nuclei out of resonance. However, the energy of the  $\gamma$ -ray may be modulated by applying a doppler shift to bring the system into resonance. In this way, nuclear transition energies may be compared in different environments.

A change in the s-electron density at the nucleus of an atom will result in a shift in the nuclear energy levels. Where such a variation cicurs between emitter and absorber, the processes are separated in the expergy spectrum by an amount known as the Isomer Shift (I.S.) or Chemical  $\mathcal{B}$  ift (C.S.). This quantity is thus a measure of the relative s-electron Rensity at the nucleus. Two factors are principally responsible for variagions in isomer shift. Screening of s-electrons from the nucleus by  $\overset{\mathbf{0}}{\overset{\mathbf{0}}}{\overset{\mathbf{0}}{\overset{\mathbf{0}}{\overset{\mathbf{0}}{\overset{\mathbf{0}}{\overset{\mathbf{0}}}{\overset{\mathbf{0}}}{\overset{\mathbf{0}}{\overset{\mathbf{0}}{\overset{\mathbf{0}}}{\overset{\mathbf{0}}{$  $c_{\underline{o}}$ valent bonding. Thus isomer shift may be used to characterize valence state and coordination number. If the nucleus does not have a uniform charge density, a quadrupole moment arises which can interact with the edectric field gradient (E.F.G.) at the nucleus to lift the degeneracy of the nuclear state. This gives rise to a doublet in the energy spectown; the separation of the two components is known as the Quadrupole Splitting (Q.S.) and is thus a measure of the E.F.G. at the nucleus. Poincipal factors affecting the E.F.G. at the nucleus are the nonsoherical electron distribution in the atom itself, a function of velence state, and the non-spherical component of the crystal field. Thus quadrupole splitting may be used to characterize valence state and variations in structural environment.

There are 30 or isotopes that are sensitive to the Mössbauer effect; of these, only  $^{57}$ Fe is of use in amphibole studies. However, the almost ubiquitous occurrence of Fe<sup>2+</sup> and Fe<sup>3+</sup> has resulted in application of this technique to a wide variety of amphiboles. The hyperfine parameters of amphiboles show significant variation with changes in coordination, site-occupancy and compositional type of amphibole. The systematics of these variations are of interest both with regard to peak





zassignment in Mössbauer spectra and the crystal-chemical systematics of the amphiboles themselves. Some of the general conclusions of Ingalls  $\widehat{\alpha}$ (1964) concerning the behavior of the quadrupole splitting of high spin  $\sigma_{2}^{2+}$  with changes in ligand environment are pertinent. In particular,  $\ddot{e}_{Fe}^{2+}$ in a cubic field has no quadrupole splitting; slight distortion of The field from cubic symmetry produces a large quadrupole splitting ( ${\sim}3.7$  mm/sec), with increasing distortion of the ligand environment Producing a gradual decrease in the quadrupole splitting. The crystal and angular terms and hence is sensitive to distortion of the coordination polyhedron with regard to both bond lengths and bond angles. Consequently, the criterion by which distortion is measured should encompass both these factors, and failure to do so has led to some confusion in discussions relating Mössbauer parameters to crystal structure. Nextnearest-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.

## Site-occupancy characterization

In a typical experimental set-up, the  $\gamma$ -ray source is repeatedly swept through a range of velocities at constant acceleration. This energy-modulated Y-ray beam passes through a randomly-oriented powdered sample where absorption occurs. The resultant beam is recorded in a multi-channel analyzer, in which each channel accumulates the counts recorded while the Y-ray source was moving in a specific velocity interval. Two experimental Mössbauer spectra are shown in Figure 1. Each data point represents the number of counts recorded over that  $\hat{\mathbf{P}}$ articular source velocity interval. The counts at the margins of the Spectra represent the background counts and are approximately constant;  $\Xi$ he average background value is termed the off-resonance count. Towards the center of the spectra, the counts decrease. This is due to the resonant absorption of  $\gamma$ -rays of this specific energy by the sample. The deal shape of a single absorption peak (line) in a Mössbauer spectrum  ${\bf x}$ s Lorentzian. Thus, the observed spectra consist of a series of  $\underline{\sigma}$  $\stackrel{\checkmark}{\mathbf{c}}$ ion of the structural type and chemical composition of the amphibole. Deconvolution of an observed envelope into its component peaks is done  $\hat{\mathbf{a}}$ sing least-squares refinement techniques. This is a non-trivial process, ond the problems associated with it are discussed in detail by Hawthorne Bally 81). Ba

Bancroft *et al.* (1967a) have considered the assumptions inherent a using the Mössbauer effect for site-population characterization of for in silicates when two distinct quadrupole split doublets occur in the spectrum. We may generalize this to r quadrupole split doublets in the spectrum. The area under a peak is given by (Bancroft *et al.*, 1967a)

$$A_{i} = \frac{\Pi}{2} f_{i} f_{e} \sigma_{\sigma} \tau_{i} G(n_{i}, f_{i}, \sigma_{o}) n_{i}$$

where  $\boldsymbol{f}_i$  is the recoil-free fraction of the absorber

- $\mathbf{f}_{\rho}$  is the recoil-free fraction of the emitter
- $\sigma_{\rm o}$  is the maximum resonant absorption cross-section
- $\tau_i$  is the half-width of the peak (peak width at half-height)

 $G(n_i, f_i, \sigma_0)$  is the saturation correction,

n, is the number of atoms per formula unit.

Expressing the area of the jth doublet as a function of the total absorption,

$$A_j / \sum_{i=1}^r A_i = n_j / \sum_{i=1}^r C_i n_i ,$$

where  $C_i = \frac{f_i}{f_i} \frac{\tau_i}{\tau_i} \frac{G_i(n_i, f_i, \sigma_o)}{G_i(n_i, f_i, \sigma_o)}$ .

In most studies, C, is assumed to be unity. Considering the individual terms in the above expression for  $C_i$ , this generally seems to be a reaonable assumption. Saturation corrections approach unity for thin ab- $\check{\phi}$  orbers, and deviations from this value should be self-cancelling pro- $\overline{\mathbf{S}}$  iding that the n values are not radically different from each other.  ${ar{\mathfrak{P}}}$ xtensive experimental evidence has confirmed that half-widths of single  $\vec{B}$  are approximately equal; in principal, the recoil-free fractions Ban be determined, but this has rarely been done. Some studies have Berived C values different from unity but such results have often been  $\frac{\tilde{g}}{\underline{r}}$ omewhat controversial. Thus, site occupancies, n<sub>j</sub>, can be derived from  $\underline{A}_{i}$  ratios,  $A_{i}$   $\Sigma$   $A_{i}$ , in minerals.  $\underline{C}_{i}$   $\underline{C}_{i}$ 

The general appearance of amphibole Mössbauer spectra varies con-giderably with amphibole type, and the peak assignment in such spectra of frequently not straightforward. Consequently, we will look at a wariety of amphibole spectra and consider the systematics of the Möss-

**This** Fe-Mg-Mn amphiboles. Spectra for the orthorhombic Fe-Mg-Mn amphiboles are shown in Figure 1. The anthophyllite spectrum consists of two doublets; the outer doublet is attributable to  ${\rm Fe}^{2+}$  at the M1, M2 and M3 sites, with the inner doublet due to Fe<sup>2+</sup> at the M4 site. This contrasts with the gedrite spectrum, where only a single wide doublet occurs. The reason for this is apparent in the systematics of the quadrupole splittings for these amphiboles as shown in Figure 2. Extrapolation of the quadrupole splitting values for the M4 and M1+M2+M3 ( $\equiv$  M1,2,3) peaks in



Figure 2. Quadrupole splitting (at room temperature) as a function of Al p.f.u. in orthorhombic amphiboles. After Seifert (1977).

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the anthophyllite spectra to Al values typical of gedrite shows that the Q.S. values overlap, with a concommitant lack of resolution in the gedrite spectra.

The spectrum of holmquistite (Fig. 3) has three doublets that may be assigned to Fe<sup>3+</sup> at the M2 site (D1D2) and Fe<sup>2+</sup> at the M1(A1A2) and M3(C1C2) sites. It is unlike any other Fe-Mg-Mn amphibole spectra, because of the differences in next-nearestneighbor cation configurations. In holmquistite, these are

Guimilar to those in the glaucophane-riebeckite amphiboles, the spectra of which bear a strong similarity to that of holmquistite. Typical Mössbauer spectra for the monoclinic Fe-Mg-Mn amphiboles

 $\dot{\mathbf{F}}$ re shown in Figure 4; note the slightly greater resolution attained in gow-temperature spectra, a feature also exhibited by anthophyllite spec-<del>L</del>ra. The spectra are similar to the anthophyllite spectra, with the Guter and inner doublets assigned to  $Fe^{2+}$  at the M(1)+M(2)+M(3) and G(4) sites, respectively. Perhaps the most notable feature of the Fe-Mg-Mn amphibole spec

Perhaps the most notable feature of the Fe-Mg-Mn amphibole spectra the complete overlap of doublets due to  $Fe^{2+}$  at the M(1), M(2) and ₽s (3) sites. At first sight, this appears to be incompatible with the  $\mathbf{\widetilde{P}}_{ ext{act}}$  that these amphiboles show considerable differences in nearestand next-nearest-neighbor configurations among these three sites. However, closer examination shows an inverse relationship between the distance ( $\Delta$ ) and angle ( $\sigma^2$ ) distortion parameters (Fig. 5). One may thus surmise that the differences in angular distortion at the M(1), M(2), and M(3) sites are compensated for by the differences in bond length variations, with the result that the quadrupole splittings at the various sites are similar. This similarity is enhanced by the occupancy of the four M sites by Mg +  $Fe^{2+}$  + Mn only, leading to as similar



Figure 4. Room-temperature (upper) and liquid-nitrogen temperature (lower) Mössbauer spectra of magnesio-cummingtonite (left) and grunerite (right). From Hafner and Ghose (1971).



Figure 5. Left: octahedral angle variance as a function of polyhedral distortion for the M(1), M(2) and M(3) sites in the Fe-Mg-Mn amphiboles. Right: M(4) polyhedral distortion as a function of composition for the monoclinic Fe-Mg-Mn amphiboles.

The mean next-nearest-neighbor environment for the M(1), M(2) and M(3) sites the possible in the amphibole structure.

The quadrupole splitting of Fe<sup>-</sup> at M(4) is submatrix that of Fe<sup>2+</sup> at M(1), (2), (3). This is in agreement with Ingalls (1964) The quadrupole splitting of Fe $^{2+}$  at M(4) is significantly less than Formodel, the M(4) site having the more distorted environment. Further Esystematic variations of Mössbauer parameters have been characterized Ĝin several studies (Bancroft et al., 1967a,b; Barabanov and Tomilov, 21973; Seifert, 1977; Goldman, 1979). As shown in Figure 6, the quadru- $\tilde{\mathbf{x}}_{\text{pole splitting of Fe}}^{2+}$  at M(4) is negatively correlated with the Fe/ E(Fe+Mg) ratio of the amphibole, a slight non-linearity in the relation-Ship being apparent, particularly at low Fe/(Fe+Mg) ratios when the  $\breve{\mathbf{c}}$ orthorhombic amphiboles are included in the correlation. The correla- $\frac{9}{C}$ tion is perhaps improved slightly if the M(4) Fe<sup>2+</sup> quadrupole splitting is plotted against the mean Fe/(Fe+Mg) content of the M(1), M(2), and M(3) sites. This is in line with the suggestion of Hafner and Ghose (1971) that the octahedral distortions and thence the quadrupole splittings are dictated not by the site-occupancy of the specific site but by the linkage between the octahedral and tetrahedral parts of the structure. Certainly the geometry of the M(4) site in the monoclinic amphiboles is consonant with this suggestion. Figure 5 shows the variation in M(4) polyhedral distortion  $\triangle$  with the mean Fe/(Fe+Mg) content



Figure 6. Compositional systematics of the Mössbauer parameters in the Fe-Mg-Mn amphiboles.





Figure 8. Compositional systematics of the Mössbauer parameters in the alkali amphiboles.

the fact that the M4 polyhedron is far more regular in gedrite than in anthophyllite.

Alkali amphiboles. Spectra for alkali amphiboles are shown in Figure 7. The glaucophane spectrum consists of three doublets, one of which is assigned to Fe<sup>3+</sup> at M(2)(BB') and two of which are assigned to Fe<sup>2+</sup> at M(1)(AA') and M(3)(CC'), respectively. The magnesio-riebeckite spectrum is fairly similar, except the Fe<sup>3+</sup> doublet is stronger than in the glaucophane spectrum. Substitution of an actinolite and/or arfvedsonite component into riebeckite can give rise to a third Fe<sup>2+</sup> doublet due to a contribution from Fe<sup>2+</sup> at M(2). The arfvedsonite spectrum consists of four doublets, one due to Fe<sup>3+</sup> at M(2) and three due to Fe<sup>2+</sup> at  $\dot{\mathbf{T}}(1)$ , M(2) and M(3), respectively.

9 0 The systematics of the hyperfine parameters are shown in Figure 8.  $rac{d}{d}$  The quadrupole splitting of Fe<sup>2+</sup> at M(1) is fairly constant at  $\sim$ 2.80  $\infty$ m/sec, but has greater scatter at larger values of the M(2) cation  $\sigma$  adius; there does not seem to be any correlation with the M(4) site- $\overset{\mathbf{0}}{\mathbf{C}}$  ccupancy. The quadrupole splitting of Fe<sup>2+</sup> at M(3) shows a positive  $\overline{\mathcal{O}}_{\mathcal{A}}$  formed at the mean ionic radius of the M(2) cations. In this  $\overline{\mathcal{O}}_{\mathcal{A}}$  articular case, the effect of next-nearest-neighbor cation charge variztion is minimized, as the M(2) cations are mainly trivalent and the only  $\underline{C}$  variable at this site is cation size, and the M(3) site is remote from the  $\Delta(4)$  site, where some variation in cation charge does occur. Thus, the  $\sigma$  hange in quadrupole splitting of Fe<sup>2+</sup> at M(3) is due to a change in  ${\mathfrak{A}}(3)$  polyhedral distortion and/or a change in the next-nearest-neighbor ation distances. As was shown in the previous chapter, the angular  $\vec{\mathbf{a}}_{ ext{istortions}}$  of the M(1) and M(3) polyhedra are strongly dependent on The M(2) site-occupancy. Thus, increasing M(2) cation size causes de-Greased angular distortion of the M(3) octahedron, which results in  $f_{\text{ncreased quadrupole splitting of Fe}^{2+}$  at M(3), in agreement with the deductions of Ingalls (1964). The reason why the quadrupole splitting of Fe $^{2+}$  at M(1) does not exhibit analogous behavior is not clear. There seems to be no systematic variation of isomer shift with composition for  $Fe^{2+}$  at M(1) or M(3) in the alkali amphiboles.

Sodic-calcic amphiboles. Little has been done on the amphiboles of this group; the one available spectrum is shown in Figure 9. The spectrum



Figure 10. Room-temperature Mossbauer spectra of actinolite (left) and magnesio-normblend (right). From Burns and Greaves (1971) and Bancroft and Brown (1975), respectively. The doublets are assigned as follows:  $AA'-Fe^{2+}$  at M(1); BB'-Fe<sup>2+</sup> at M(3); CC'-Fe<sup>2+</sup> at M(2); DD'-Fe<sup>3+</sup> predominantly at M(2).



Figure 11. Room-temperature Mössbauer spectra of tremolite (left) and pargasite (right). From Goldman and Rossman (1977) and Goldman (1979), respectively. The doublets are assigned as follows: tremolite - outer doublet -  $Fe^{2+}$  at M(1,2,3); inner doublet -  $Fe^{2+}$  at M(4); plus a weak  $Fe^{2+}$  doublet. Pargasite -- the doublet quadrupole splitting parameters (mm/s) are shown and were assigned as follows: 2.59 -  $Fe^{2+}$  at M(1,3); 2.26 -  $Fe^{2+}$  at M(2); 1.88 -  $Fe^{2+}$  at M(4); 0.61 -  $Fe^{3+}$  predominantly at M(2).

of ferro-richterite consists of two resolvable doublets due to  ${\rm Fe}^{2+}$  and Fe<sup>3+</sup>; the Fe<sup>2+</sup> doublets consist of three closely overlapping quadrupole split doublets from Fe<sup>2+</sup> at M(1),(2),(3).

Calcic amphiboles. Interpretation of calcic amphibole spectra is not straightforward and peak assignments differ from study to study. Typical spectra are shown in Figures 10 and 11. Burns and Greaves (1971) have resolved actinolite spectra into four quadrupole-split doublets assigned to Fe<sup>3+</sup>(DD') and Fe<sup>2+</sup> at M(1)(AA'), M(2)(CC') and M(3)(BB'), respectively. Bancroft and Brown (1975) have resolved the spectra of a series of "hornblendes" in a similar fashion, except that the assignment of the C and D peaks was reversed. Goldman and Rossman (1977)  ${}^{\mathsf{V}}_{\mathsf{p}}$  resented the Mössbauer spectrum of a tremolite with one Fe  $^{3+}$  doublet  $\mathbf{q}^{(\text{CC'})}$  and two resolvable Fe<sup>2+</sup> doublets (Fig. 11); they advance per-Buasive evidence in the form of electron absorption spectra (see folowing sections) that the two Fe<sup>2+</sup> doublets represent Fe<sup>2+</sup> at M(4)(BB')and M(1), (2), (3)(AA'), respectively. As Fe<sup>2+</sup> contents of M(4) in Gremolite-actinolite amphiboles are low, any doublet due to Fe $^{2+}$  at (4) should be swamped out in ferro-actinolites by greatly increased  $\frac{\mathbf{\tilde{w}}}{\mathbf{r}}$ esponse from Fe<sup>2+</sup> at M(1),(2),(3); Goldman (1979) shows that this is Andeed the case.

Goldman (1979) proposed that the Fe<sup>2+</sup> peak assignments in previous tudies of actinolites be altered as follows: AA' = M(1)+M(3), BB' = Getails of actinofiles be aftered as follows: AA' = M(1)+M(3), BB' =
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- (iii) stoichiometric indications that C-type cations must occur at the M(4) site in the calcic amphiboles examined,

(iv) systematics of the hyperfine parameters in amphiboles.

Examination of Figure 8 shows that in the sodic amphiboles, the resolution of the M(1) and M(3)  ${
m Fe}^{2+}$  doublets decreases with increasing mean ionic radius of the M(2) cation. This would suggest that in amphiboles with large divalent cations at M(2), the resolution between the Fe $^{2+}$  M(1) and M(3) doublets is much less than in the sodic amphiboles.



Figure 12. Variation in quadrupole splitting of the outer Fe2+ doublet (AA' in Fig. 10 right) as a function of the Al203 contents in the calcic amphiboles of Bancroft and Brown (1975). From Goldman (1979).

Goldman (1979) has documented a similar systematic variation in Q.S.

values for a series of hornblendes (Fig. 12). Further complications may be illustrated by examining the spectro of pargasite (Fig. 11). This has been resolved into a doublet due to Further complications may be illustrated by examining the spectrum at M(2) and three doublets due to Fe<sup>2+</sup> at M(1)+M(3), M(2) and M(4),  $\mathbf{r}$ espectively. Comparison with the spectrum of magnesio-hornblende (Fig. d0) shows them to be very similar, suggesting that it will be difficult  $\mathbf{\Phi}$  recognize either an M(4) or an M(2) Fe<sup>2+</sup> doublet when *both* are present. Meneral considerations T

A general summary of the variation in  $Fe^{2+}$  quadrupole splitting with A general summary of the variation in Fe<sup>2+</sup> quadrupole splitting vmation site and amphibole type is given in Figure 13; this should aid



Figure 13. Ranges of quadrupole splitting for  $Fe^{2+}$  at the M(1), M(2), M(3) and M(4) sites in amphiboles.

peak assignment in the examination of as yet uncharacterized amphibole types. As is apparent from the above discussion, the refinement and assignment of calcic amphibole spectra is not always straightforward; however, some of the problems can be circumvented by use of a combination of experimental techniques.

The magnetic behavior of amphiboles has been investigated by Mössbauer spectroscopy, and low-temperature experiments have shown the presence of magnetic ordering (Buckley and Wilkins, 1971; Borg et al., 1974;

Borg and Borg, 1974, 1980; Eisenstein *et al.*, 1975). The ordering has an overall antiferromagnetic character, and the ordering temperature varies with the site occupied by Fe<sup>2+</sup> (Eisenstein *et al.*, 1975).

#### VIBRATIONAL SPECTROSCOPY

Vibrational spectroscopy involves the interaction between electromagnetic radiation and the vibrational modes of a crystal. A vibrational mode in a crystal will absorb electromagnetic radiation if the frequencies of the vibration and the radiation are coincident and if the excited vibration changes the dipole moment of the crystal; this effect gives rise to infrared absorption spectroscopy. Electromagnetic Sadiation may be elastically scattered by a crystal (Rayleigh scattergng). Scattering may also occur inelastically. In this case, the  $\dot{\mathbf{\varphi}}_{ ext{cattering episode is accompanied by a vibrational transition in the$  $\mathcal{R}$ rystal, where energy is absorbed from or imparted to the scattered  $\overline{oldsymbol{Q}}$ adiation; this is the Raman effect and gives rise to Ramam spectroscopy. Most vibrational spectroscopic work on the amphiboles has been concerned with infrared examination of the hydroxyl stretching region. dowever, some work has been done in the higher wavelength regions. Figure 14 summarizes infrared spectra for a variety of calcic amphiboles. There have been suggestions that such spectra be used for identification Surposes, but this has not met with general acceptance. However, corgelations of band frequency with chemical composition (Fig. 14) may be gef use. There has been little Raman spectroscopic work on amphiboles. The Raman effect requires exact translational symmetry over several unit

There has been little Raman spectroscopic work on amphiboles. The Graman effect requires exact translational symmetry over several unit of this symmetry by disorder to produce a sharp spectrum. Perturbation of this symmetry by disorder causes rapid peak broadening and loss of detail in the Raman spectrum. Experimental evidence to this effect can be seen by comparing the Raman spectra for actinolite and tremolite (Fig. 15). Tremolite is fairly well ordered and produces a detailed spectrum, whereas actinolite has significant cation disorder and gives a smeared weak spectrum. These features are independent of the different techniques used to record the spectra.



Figure 15. Left: powder Raman spectrum of actinolite. Right: laser Raman spectrum of a crystal of tremolite. From White (1975) and Blaha and Rosasco (1978).

### The hydroxyl stretching region

The fundamental band of the O-H stretching vibration occurs from 1500-3800  $\text{cm}^{-1}$ . The exact position of this band in the infrared region is a function of the strength of the hydrogen-oxygen bond. Strong bonds are associated with higher frequencies, the lower end of the range being characteristic of symmetrical hydrogen bonds. In the spectra of amphiboles, the fundamental band occurs from 3600-3700 cm<sup>-1</sup>, indicative of a strong hydroxyl bond and little or no hydrogen bonding; this is compatible with the O(3)-H distance of ∿1.0 Å found in crystallographic studies. End-member amphiboles show a single sharp hydroxyl stretching band in this region. However, the principal stretching band in inter-Rediate amphiboles shows considerable fine structure (Fig. 16) that has  $\dot{oldsymbol{ P}}$ een attributed to cation substitution effects at those cation sites  $\dot{\mathbf{Q}}$ oordinated by the hydroxyl ion. This is a result of the fact that the  $\widetilde{\mathbf{x}}$  requency of the stretching band varies with the actual cations bonded  $\overline{\mathbf{a}}$ o the hydroxyl ion. It is instructive to consider the case where the  $\Phi^{-}$ type cations are Mg and Fe<sup>2+</sup> only. There are eight possible ways of Of the second se mingle hydroxyl (Table 1). However, the three M sites coordinating the ydroxyl are in a pseudo-trigonal arrangement that introduces an acci- $\subseteq$   $\mathfrak{B}$ ental degeneracy to some bands, reducing the overall number of resolvable sands to four. The cation distribution can be partially derived from the  $\frac{1}{2}$  of these peaks. Using the nomenclature of Table 2, the total  $\frac{1}{2}$   $\frac{1}{2}$   $\frac{1}{2}$  content of the M(1) and M(3) sites in a binary (Mg,Fe<sup>2+</sup>) amphibole golid solution is given by

$$T_{f} = B_{0} + 2C_{0} + 3D_{0}$$

copy If the total Fe content of the amphibole is known from the chemical  $\mathfrak{A}$ nalysis, the Fe content of the M(2) and M(4) sites may be derived by difference. Where Mg and Fe are confined to the M(1) and M(3) sites, amphibole compositions may be derived. Strens (1966) proposed that the ratio  $\rho$  be used to indicate Mg/Fe ordering over the M(1) and M(3) sites, with  $\rho$  values greater than unity indicating preferential ordering of Fe  $^{2+}$ at the M(3) site.

Such band intensity considerations have been used to derive siteoccupancies in Fe-Mg-Mn amphiboles (Burns and Strens, 1966; Strens, 1966;

ctpa1 for	nt																			1	data taken mainiy irom Strens (1974) and Bancroft & Burns (1969): band	nomenclature slightly modified. Con-	figurations R,S and T of Bancroft & Burns (1969) not included. Bands E-Q	should not be considered as definitely	established. Each specific band con- figuration is permutable.			44
<ol> <li>Frequency shift of prin band relative to the A band various cation configurations</li> </ol>	Displaceme (cm <sup>-1</sup> )		0	į	-14	-29	-47	-22	-36	-44	-51	-58	-66	-9	-22	-38	ī	-38	ı	ı	-27	-34	-20	+24	+31	-75	-87, -99	+2n, 0<1
	Configuration		MgMgMg	2+	MgMgFe	MgFe <sup>2+</sup> Fe <sup>2+</sup>	$Fe^{2+}Fe^{2+}Fe^{2+}$	MgMgFe <sup>3+</sup>	MgFe <sup>2+Fe<sup>3+</sup></sup>	MgFe <sup>3+</sup> Fe <sup>3+</sup>	$Fe^{2+Fe^{2+Fe^{3+}}}$	Fe <sup>2+</sup> Fe <sup>3+</sup> Fe <sup>3+</sup>	Fe <sup>3+</sup> Fe <sup>3+</sup>	MgMgA1	$MgFe^{2+A1}$	$Fe^{2+}Fe^{2+}Al$	MgAlAl	Fe <sup>2+</sup> AlAl	MgFe <sup>3+</sup> Al	Fe <sup>2+</sup> Fe <sup>3+</sup> Al	Life <sup>2+re<sup>2+</sup></sup>	$LiFe^{2+Fe^{3+}}$	LiMgFe <sup>3+</sup>	Na at A	K at A	Al for S1	T1 at M(1,2,3)	Ca at M(4)
Table OH	Band		A		8	C	D	ы	н	Ċ	Н	Ι	Ţ	К	L	М	N	0	Ъ	δ	I	ī	I	I	ı	I	I	1
<ul> <li>Possible cation arrangements and hydroxyl ching band assignments in amphiboles<sub>2</sub><sup>4</sup>1th</li> <li>) completely occupied by Mg and Fe<sup>2</sup><sup>4</sup></li> </ul>	$M(1)$ $M(3)$ $M(1) \neq M(3)^{1}$ $M(1) = M(3)^{2}$	Mo Mr A A	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$						al band assignment for crystallographically inct configurations.		d assignments for configurations with dental degeneracy due to pseudo-trigonal ngement.				2. Nomenclature of Law (1976) used in the discussion of	n ordering and band intensities in infrared spectra	тί	total Fe <sup><math>t^+</math></sup> at M(1) and M(3) sites	site-occupancies of Mg and $Fe^{2+}$ at M(I)		normalized observed intensity of peak A	intensity of peak A for random distribution	calculated value of intensity of peak A	(B /B )/(C /C )		$(\mathbf{B}_{c}/\mathbf{B}_{r})/(\mathbf{C}_{c}/\mathbf{C}_{r})$		
Tabl stre M(1,	M(1)	Ma	Mg	Mg.	Fe.1	Fe <sup>21</sup>	Fe <sup>-</sup>	Fe <sup>2+</sup>		lide	dist	2 ban	acci				Table	Table cation		T_f	$\mu_{T}, \phi_{T}$		A 0	$\mathbf{A}_{\mathbf{r}}$	Ac	c	٩.	Pc

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Figure 16. Fine-structure in the fundamental OH stretching band in amphiboles of the magnesio-cummingtonite --- grunerite series (lower) and the tremolite --- ferro-actinolite series (upper); from Burns and Strens (1966). The band nomenclature is that of Table 3. The compositions of the samples, expressed as  $Fe^{2+}/(Mg+Fe^{2+})$ , is as follows: I - 0.00; II - 0.15; III - 0.30; IV - 0.48; V - 0.36; VI - 0.53; VII - 0.65; VIII - 0.89, IX - 0.98.



FREQUENCY (cm<sup>-1</sup>)

Figure 17. Re-plotted infrared spectrum (OH region) of manganoan ferro-actinolite showing the existence of minor bands when fitting normal gaussian peak shapes. From Burns and Greaves (1971).



Figure 18. Frequency shift of the principal OH band in C2/m amphiboles as a function of the mean electronegativity of the cations bonded to O(3).

Bancroft et al., 1966, 1967a,b; Buckley and Wilkins, 1971; Burns and Law, 1970; Wilkins et al., 1970), actinolites (Burns and Strens, 1966; Wilkins, 1970; Burns and Greaves, 1971), other calcic amphiboles (Wilkins et al., 1970; Semet, 1973; Nikitina et al., 1973) and alkali amphiboles (Burns and Prentice, 1968; Bancroft and Burns, 1969; Ernst and Wai, 1970; Strens, 1974; Maresch and Langer, 1976). Many of these studies involved amphiboles with other C-type cations present in

 $\overline{\mathfrak{S}}$ ddition to Mg and Fe<sup>2+</sup>. It is generally assumed than Mn<sup>2+</sup> can be grouped  $\underline{\underline{\theta}}$  ith Fe<sup>2+</sup>, but the presence of any other cations at the M(1) and M(3) sites o gill give rise to additional bands. Numerous minor bands have been recog-gized in these studies. Figure 17 gives an example of an actinolite spectrum where minor bands are apparently present; these were assigned  $\frac{c}{\mathbf{g}}$  cation configurations involving Fe<sup>3+</sup>. It is well known that the band requency is a function of the electronegativity of the cations bonded P¥ P To the hydroxyl, and this aids in the assignment of these minor bands. Bable 3 is a compilation of the bands assigned in previous work, and Gigure 18 shows the electronegativity dependence of the frequency shift  $oldsymbol{ ilde{o}}$ f these bands. The resolution of these bands in the hydroxyl spectrum as a function of both band width and frequency shift. The intrinsic width of the A and D bands in end-member monoclinic amphiboles is  ${}^{\sqrt{5}}$  $\mathbf{E}^{-1}$ , which may be broadened to  $\sqrt{6}$  cm<sup>-1</sup> by instrumental and/or minor substitutional effects. Generally, the frequency shift is considerably greater than the band width, ensuring resolution from the A band. Thus, the principal resolution problems arise from accidental overlap of configurations having similar frequency shifts.

Cation substitutions at other sites besides M(1) and M(3) also cause a frequency shift:

- (i) Each Ca present in the group of four M(4) positions around each A-site increases the stretching frequency by  $\sim 2 \text{ cm}^{-1}$ .
- Alkali cations entering the A-site increase the OH stretch-(ii)ing frequency considerably: +24 cm<sup>-1</sup> in riebeckite (Strens, 1974); 30-40 cm<sup>-1</sup> for hastingsite and pargasite (Semet, 1973), 56 cm<sup>-1</sup> and 62 cm<sup>-1</sup>, respectively, for sodium and potassium richterite (Rowbotham and Farmer, 1973).
- The substitution Fe<sup>3+</sup>  $\neq$  Al at the M(2) site in alkali amphi-(iii) boles (Bancroft and Burns, 1969) appears to increase the stretching frequency slightly. Possibly substitution at the tetrahedral sites could also have a slight inductive effect in Al<sup>IV</sup>-amphiboles.
- (iv) In orthorhombic amphiboles, the presence of two nonequivalent hydroxyl groups results in a slight broadening of the band width to  $\sim 7 \text{ cm}^{-1}$  in anthophyllite (Burns and Law, 1970).

on 2016-05-04 In the more complex amphiboles, such as the hornblendes and the Bedrites, the large number of bands together with the considerable band for oadening may result in spectra that are too complex to be resolved. There are several problems associated with the application of this technique to general site-population studies. Problems associated with

The curve-fitting procedure are discussed by Hawthorne (1981). One important point has been raised by Strens (1974). In principal, vibrational Fands are Lorentzian in form, but Strens (1974) has claimed that line-oroadening usually results in a band shape that approximates a skewed Gaussian. If this is the case, use of normal Gaussian curve shape in  $ar{\mathbf{a}}$ he spectrum refinement will give rise to spurious bands. Many of the Alinor bands in previous studies could be of this origin.

The derivation of ordering patterns from band intensities assumes S Hat the band intensity for a specific configuration is related to the frequency of occurrence of that configuration in the same way as all other bands are related to their corresponding configurations. Thus, the transition moment of the OH stretch is assumed to be independent of the type of configuration. Work on micas (Rouxhet, 1970) suggests that this is not the case; however, there is no evidence either way for the amphiboles. The occurrence of weak hydrogen bonding may significantly effect the transition moment of the OH band, whether or not the strength of the



The O(3) position may be occupied by F,  $0^{2-}$  and Cl in addition to Sopy. Thus, in order to derive site-occupancies in OH-deficient amphi- $\frac{9}{20}$  oles, it is necessary to assume random mixing of the O(3) anions, with no segregation at specific M(1), (2), (3) cation configurations. Unfortunately, the latter would not appear to be the case, either in F-rich amphiboles, where Fe $^{2+}$  tends to avoid F-coordinated sites (Cameron, 1970; Rosenburg and Foit, 1977), or in oxy-amphiboles where highervalence cations (Fe<sup>3+</sup>,Ti) are closely associated with 0<sup>2-</sup> at the 0(3) position (Kitamura et al., 1975).

Law (1976) has considered the criteria for ordering characterization and has shown them to be misleading. Consider the standard equations

relating peak intensity to mole fraction (see Table 2 for nomenclature):

$$\begin{aligned} A_{c} &= \mu_{1}^{2} \mu_{3} &= (1-\phi_{1})^{2}(1-\phi_{3}) \\ B_{c} &= \mu_{1}^{2} \phi_{3} + 2\mu_{1}\phi_{1}\mu_{3} = (1-\phi_{1})^{2}\phi_{3} + 2(1-\phi_{1})\phi_{1}(1-\phi_{3}) \\ C_{c} &= \phi_{1}^{2} \mu_{3} + 2\mu_{1}\phi_{1}\phi_{3} = \phi_{1}^{2}(1-\phi_{3}) + 2(1-\phi_{1})\phi_{1}\phi_{3} \\ D_{c} &= \phi_{1}^{2} \phi_{3} &= \phi_{1}^{2}\phi_{3} \end{aligned}$$

Inasmuch as  $\phi_1 = \frac{1}{2}(T_f - \phi_3)$ , each of the peak intensities can be related to the single variable  $\phi_3$ . The behavior of  $A_c, B_c, C_c, D_c$  and  $\rho_c$ with varying  $\phi_3$  is strongly a function of  $T_f$  (i.e., the chemical composition of the amphibole). This can be seen in Figure 19, which shows the pehavior of these parameters as a function of  $\phi_3$  (the site-occupancy variable) for amphiboles of different bulk compositions. Site-occupancies way be derived by setting  $A_c$ .... equal to  $A_o$ .... in the above equations and olving for  $\phi_3$ ; four values of  $\phi_3$  are obtained, and hence where the solugion is poorly defined by one or more equations, a fairly precise value as still obtainable from the remaining equations.

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#### ELECTRONIC ABSORPTION SPECTROSCOPY

The 3d orbitals of a transition metal ion are energetically degenerate in a spherically-symmetric potential field. Application of a potential field of lower symmetry removes this degeneracy, as the reducible representation spanned by these orbitals must contain the irreducible representation of the symmetry group. When light passes through a crystal containing a transition metal ion, certain wavelengths are absorbed by excitation of electrons between the nondegenerate 3d-orbital energy levels. As the character and amount of separation of the orbital energy levels is a function of the potential field applied by the crystal, occupancy of different sites in a crystal will produce absorption of dif- ${f Q}$  reent wavelengths of light. The spectra may also be complicated by  $\dot{\mathbf{Q}}_{\mathrm{inter-element}}$  electron transitions, i.e., charge transfer bands where the  $\omega$ Selectron transitions take place from cation to anion, anion to cation or cation to cation. These transitions are particularly common when adjacent  $\mathcal{G}_{\mathfrak{G}}$  ations have variable valence states (e.g., Fe<sup>2+</sup> and Fe<sup>3+</sup>, Ti<sup>3+</sup> and Ti<sup>4+</sup>,  $E^{2^+}$  and Ti<sup>4+</sup>) and are a major cause of color and pleochroism in amphizoles (Manning and Nickel, 1969; Faye and Nickel, 1970; Strens, 1970).  $\frac{\Omega}{II}$ he intensity of this type of band is about two orders of magnitude  $\overleftarrow{\mathbf{d}}$ arger than the intensity of normal d-d transitions. Thus, overlap of These two types of band in an absorption spectrum can obscure the d-d fransition bands. The occurrence of more than one type of transitionetal cation in the structure, as is common in most amphiboles, will  $\tilde{\mathbf{G}}$  urther complicate the interpretation of the absorption spectra.

The intensity of an absorption band depends on the probability of the transition. The transition probability is governed by the Laporte election rule (King, 1964) which forbids transitions between 3d orbitals. Shen a transition-metal cation occupies a site without a center of symmetry, mixing of the 3d and 4p orbitals allows a transition, the intensity of which is a function of the degree of 3d-4p mixing, which is, in turn, related to the deviation of the cation environment from centrosymmetry. Thus, when a transition-metal cation occurs in more than one site in a crystal, the intensities of the d-d bands are a function of both the cation occupancies *and* the deviation of the cation environment from centrosymmetry. In centrosymmetric sites, some 3d-4p orbital mixing







 $\hat{\mathbf{\sigma}}$ ations in these sites. Local disorder can also give rise to intensifivation of d-d bands in solid solutions. Robbins and Strens (1972) have 🖞oted this effect in micas and termed it "substitutional intensification."  $\overline{\mathbf{x}}$  his could lead to nonlinear relationships in Beer's law type plots.

September 2015 Sectra Sectra Sectra Sectra Sector S There is considerable variation in spectral appearance with amphi-Bole type, and as with Mössbauer spectra, the interpretation and assign-Bent of spectra is not a trivial matter.

Fe-Mg-Mn amphiboles. Spectra for these amphiboles are shown in S  $\dot{\mathbf{F}}$ igures 20 and 21. The anthophyllite spectra are dominated by an intense band at  $10,800 \text{ cm}^{-1}$  that is particularly intense in the  $\beta$  spectrum and a broad intense band at  $\sim 4200 \text{ cm}^{-1}$  that is particularly intense in the  $\alpha$ These are assigned to d-d transitions in Fe $^{2+}$  at the M4 site: spectrum. the predominance of these bands in the spectra is a result of the very noncentrosymmetric configuration about the M4 site that allows violation of the Laporte selection rule. The polarization characteristics of these bands are also compatible with this assignment. The remaining features

of the spectra are much less intense. The sharp spike on the  $\alpha$  spectrum at  $\sim$ 7300 cm<sup>-1</sup> is an overtone of the principal OH stretch. There are several minor bands in the region 17,000-23,000  $\text{cm}^{-1}$ ; these are assigned to spin-forbidden transitions in Fe<sup>2+</sup>. The gedrite spectra are fairly similar to those of anthophyllite. They are also dominated by intense bands at  $\sim 10,800 \text{ cm}^{-1}$  in  $\beta$  and  $\sim 4500 \text{ cm}^{-1}$  in  $\alpha$  that can be assigned to d-d transitions in Fe<sup>2+</sup> at M4; however, these bands are significantly weaker than in anthophyllite in response to the more regular M4 environment in gedrite. These bands are also broader than in anthophyllite, presumably the result of substitutional broadening. The strong sloping absorption in the gedrite spectra in the region >15,000 cm<sup>-1</sup> results  $\mathbf{A}^{\text{Erom}}$  the presence of Fe<sup>3+</sup> in the structure, causing the migration of the metal-ligand charge-transfer band into the visible region. The holmwuistite spectrum is shown in Figure 20; it is dominated by an intense Scharge-transfer band in the 12,000-20,000 cm<sup>-1</sup> region of the  $\beta$  and  $\gamma$ Spectra. There is also a spin-forbidden Fe<sup>3+</sup> band at  $\sim$ 22,800 cm<sup>-1</sup> and a  $\underline{\Phi}$  reak spin-allowed Fe<sup>2+</sup> d-d band at  $\sim 10,800 \text{ cm}^{-1}$  in the  $\gamma$  spectrum. Faye  $ar{\mathbf{Q}}$ and Nickel (1970) chose to deconvolute the major absorption into two ands; discussion of this is deferred until later.

Cummingtonite and grunerite spectra (Fig. 21) show prominent bands Cummingtonite and grunerite spectra (Fig. 21) show prominent bands get 1000 cm<sup>-1</sup> ( $\sim$ 1000 nm) in  $\beta$  and 4000 cm<sup>-1</sup> ( $\sim$ 2450 nm) in  $\alpha$ , assigned to  $\frac{\mu}{d}$ -d transitions in Fe<sup>2+</sup> at the M(4) site. Also common to both spectra  $\frac{1}{2}$  are the sharp but weak spin-forbidden Fe<sup>2+</sup> bands at 18,000-21,000 cm<sup>-1</sup>  $\check{g}_{3}$  500 nm) and the fine-structure overtones of the principal OH stretch  $\ddot{c}$  around 7100 cm<sup>-1</sup>. In the cummingtonite spectra, there is a very weak  $\overline{\mathbf{a}}$  and at  $\sim$ 8400 cm<sup>-1</sup> ( $\sim$ 1200 nm), becoming more prominent in the  $\alpha$  and  $\gamma$  $\mathbf{\widehat{G}}$ pectra of grunerite. Both the compositional dependence of the intensity and the position (by analogy with the orthopyroxene and pigeonite spectra) Esuggest that this may be assigned to a d-d transition in Fe<sup>2+</sup> at the M(1), M(2) and M(3) sites. Inasmuch as the environment of M(2) is much more noncentrosymmetric than those of the M(1) and M(3) sites, this should primarily be due to  ${\rm Fe}^{2+}$  at M(2). Comparison with the spectrum of hedenbergite (Rossman, 1980) suggests that other d-d bands due to  ${\rm Fe}^{2+}$ at M(1), M(2) and M(3) may be incorporated into the major absorption bands at ~10,200 cm<sup>-1</sup> (~1000 nm).

Calcic amphiboles. Spectra for these amphiboles are shown in Figure 22. The tremolite and actinolite spectra are dominated by an intense band at  $\sqrt{9800}$  cm<sup>-1</sup> in the  $\beta$  spectrum; also present is a broad absorption at  $\sim 4200 \text{ cm}^{-1}$ . Through examination of several amphiboles and heating experiments, Goldman and Rossman (1977) show that the intensity of the 9800  ${
m cm}^{-1}$  and 4200  ${
m cm}^{-1}$  bands are related, and thus the bands must arise from the same  ${\rm Fe}^{2+}$  cation. Comparison with the Mg-Fe-Mn amphiboles, stoichiometric arguments and band intensity considerations show that these two bands can be assigned to d-d transitions of  $Fe^{2+}$  at the M(4) site. Weak spin-forbidden  ${\rm Fe}^{2+}$  and  ${\rm Fe}^{3+}$  transitions occur from  ${\sim}18,000-$ 23,000  $\text{cm}^{-1}$ , and the overtone of the principal OH stretch is prominent at  $\frac{1}{2}$ 7300 cm<sup>-1</sup>. Bands at 15,200 cm<sup>-1</sup> in  $\beta$  and 13,800 cm<sup>-1</sup> in  $\gamma$  may be as $b_{\rm s}$  intervalence charge-transfer (IVCT) bands (in the  $\mathbf{G}$  because of Cr<sup>3+</sup>); there is no comparable band in the  $\alpha$  spectrum where Phere is no component of an  $VI_Fe^{2+}$  VI  $_{Fe}^{3+}$  separation parallel to the Electric vector. The broad weak bands between 8000 and 12,000 cm<sup>-1</sup> in The  $\gamma$  spectrum are probably d-d transitions of Fe<sup>2+</sup> at the M(1), M(2)  $\mathbf{Q}$ nd M(3) sites, particularly the M(2) site. The fine-structure in the  $\frac{1}{2}$  egion of  $\sim$ 4200 cm<sup>-1</sup> can be attributed to infrared combination modes. Ï The spectrum of pargasite (Fig. 22) lacks the prominent bands at The spectrum of pargasite (Fig. 22) lacks the prominent bands at  $\beta_{\alpha}$  0,200 cm in  $\beta$  and  $\sqrt{4}200$  cm<sup>-1</sup> in  $\alpha$  that are characteristic of Fe<sup>2+</sup> at  $\overline{\mathbf{U}}(4)$ ; this is in agreement with the stoichiometry of this particular  $\widehat{\mathbf{A}}$  $\overset{\bullet}{\mathbf{g}}_{\mathbf{g}}$ d Rossman, 1977). Weak bands in the 8000-13,000 cm<sup>-1</sup> region are most grobably d-d transitions of Fe<sup>2+</sup> at M(1),(2),(3), and weak spin-forbidden  $\bar{\mathbf{p}}^{2+}_{\mathbf{r}}$  and Fe<sup>3+</sup> bands occur above  $\sim 20,000 \text{ cm}^{-1}$ . In the  $\beta$  and  $\gamma$  spectra are  $\mathbf{k}$  oad bands at  $\sim 15,000 \text{ cm}^{-1}$ ; their position and polarization dependence  $\overset{\mathbf{O}}{\overset{\mathcal{O}}{\overset{\mathcal{$ weak compared with corresponding bands in other amphibole spectra. The wing of the ultraviolet charge-transfer band extends well into the visible region in the  $\beta$  and  $\gamma$  spectra, presumably the result of significant Fe  $^{3+}$ at the M(2) site.

Sodic-calcic amphiboles. Spectra are shown in Figure 23. The spectra of potassian ferri-taramite are dominated by broad assymetric bands centered on  $\sim 16,000 \text{ cm}^{-1}$  and  $\sim 15,000 \text{ cm}^{-1}$  in the  $\beta$  and  $\gamma$  spectra, respectively. The polarization dependence, position and intensity show





**Portugation Portugation Por**  $\frac{1}{2}$ engths, it would be premature to assign these to Fe<sup>2+</sup> at any specific site. Faye and Nickel (1970) deconvoluted the IVCT band into two moment bands at  $\sim 17,600$  cm<sup>-1</sup> and 14,300 cm<sup>-1</sup>, assigning these to Faye and Nickel (1970) deconvoluted the IVCT band into two com- $^{3+}_{M(3)}$  and  $Fe^{2+}_{M(1)} \rightarrow Fe^{3+}_{M(2)}$  interactions, respectively. This signment is rather unlikely considering the cation arrangement and 🖗 nfiguration in this amphibole (Hawthorne and Grundy, 1978). However,  $\check{\mathbf{M}}$ ese charge-transfer bands should be composite. The  $\beta$  spectrum should we two Fe<sup>2+</sup>/Fe<sup>3+</sup> IVCT bands of approximately equal intensity: and  $Fe_{M(1)}^{2+} \rightarrow Fe_{M(2)}^{3+}$ ; the  $\gamma$  spectrum should have a single Fe<sub>M(2)</sub>  ${\rm Fe}^{2+}/{\rm Fe}^{3+}$  IVCT band approximately equal in intensity to the resultant  $\operatorname{Fe}_{M(1)}^{2+} \rightarrow \operatorname{Fe}_{M(2)}^{3+}$ band in the  $\beta$  spectrum: This amphibole also contains significant Ti and Mn, giving rise to the possiblity of heteronuclear IVCT bands contributing to the major absorption.

Alkali amphiboles. Spectra for alkali amphiboles are shown in Figure 24. The spectra of glaucophane are dominated by intense charge-

transfer bands at  $\sim 18,500 \text{ cm}^{-1}$  and  $\sim 16,100 \text{ cm}^{-1}$  in  $\beta$  and  $\gamma$ , respectively. The  $\gamma$  band will contain only a component of the  $\operatorname{Fe}_{M(1)}^{2+} \rightarrow \operatorname{Fe}_{M(2)}^{3+}$  interaction, whereas the  $\beta$  band is due to both this and the  $\operatorname{Fe}_{M(1)}^{2+} \rightarrow \operatorname{Fe}_{M(2)}^{3+}$ interaction; the  $\beta$  band is slightly asymmetric, suggesting an  $\operatorname{Fe}_{M(1)}^{2+} \rightarrow \operatorname{Fe}_{M(2)}^{3+}$  component to its total intensity. The relative energies of the  $\operatorname{Fe}_{M(1)}^{2+} \rightarrow \operatorname{Fe}_{M(2)}^{3+}$  and  $\operatorname{Fe}_{M(3)}^{2+} \rightarrow \operatorname{Fe}_{M(2)}^{3+}$  interactions, as expected from their cation distances, are (M(1)-M(2) < M(2)-M(3)). The spin-forbidden  $\operatorname{Fe}^{3+}$  peak at  $\sim 22,300 \text{ cm}^{-1}$  and the OH stretch overtones at  $\sim 7100 \text{ cm}^{-1}$  are also present. The remaining weak bands between 8000 and 13,000 cm^{-1} are d-d transitions of  $\operatorname{Fe}^{2+}$  at M(1) and M(3).

The spectrum of riebeckite (Fig. 24) is similar to that of glauco-  $\beta$  hane in that it also is dominated by intense charge-transfer bands in  $\beta$  hand  $\gamma$  spectra. The reason for the much greater band width in rie- $\beta$  eckite as compared with glaucophane is not clear.

# other transition metals

Thus far we have only considered spectral contributions from Fe<sup>2+</sup> and Fe<sup>3+</sup>. Amphiboles are very gregarious and frequently associate with ther transition metals, particularly Mn and Ti. When present in significant amounts, these will contribute to the absorption spectrum, priharily through d-d transitions and heteronuclear IVCT transitions. It is necessary to characterize the spectra of these cations in chemically fimple amphiboles so that their presence in more complex amphibole pectra can be recognized.

Figure 25 shows the spectra of a tremolite containing significant The wide bands at 15,000-20,000 cm<sup>-1</sup> ( $\sim$ 550 nm) have been assigned do d-d transitions in Mn<sup>3+</sup>, with the sharp bands at  $\sim$ 22,000 cm<sup>-1</sup> ( $\sim$ 420 mm) being spin-forbidden Mn<sup>2+</sup> or Mn<sup>3+</sup> transitions. Many amphiboles have prominent Fe<sup>2+</sup>/Fe<sup>3+</sup> IVCT bands around  $\sim$ 15,000 cm<sup>-1</sup> ( $\sim$ 650 nm) in their  $\beta$  and  $\gamma$  spectra that will tend to obscure any Mn bands; however, the Mn bands should still be observable in the  $\alpha$  spectra.

Tremolite with significant  $Cr^{3+}$  (Fig. 26) shows broad bands at  $\sim 15,400 \text{ cm}^{-1}$  ( $\sim 650 \text{ nm}$ ) and  $\sim 22,200 \text{ cm}^{-1}$  ( $\sim 450 \text{ nm}$ ) that are (spin allowed) d-d transitions of  $Cr^{3+}$ , with sharp bands at  $\sim 14,400 \text{ cm}^{-1}$  ( $\sim 695 \text{ nm}$ ) and  $\sim 14,600 \text{ cm}^{-1}$  ( $\sim 685 \text{ nm}$ ) being spin-forbidden transitions. Figure 27 shows the spectrum of an actinolite with significant  $Cr^{3+}$ . The bands at



Figure 25 (top). Polarized electronic absorption spectra of Mm-containing tremolite.

Figure 26 (center). Polarized electronic absorption spectra of Cr-bearing tremolite.

Figure 27 (bottom). Polarized electronic absorption spectra of Cr-bearing actinolite.

All three figures from Goldman (1977).

 $\sim$ 15,400 cm<sup>-1</sup> ( $\sim$ 650 nm) are characteristic, particularly in the  $\alpha$  spectrum; without the  $\alpha$  spectrum, it is possible that these could be confused with an Fe<sup>2+</sup>/Fe<sup>3+</sup> IVCT band. This illustrates the importance of characterizing all transition-metal spectra in amphiboles so that transitions are not overlooked or wrongly assigned.

#### OTHER TYPES OF SPECTROSCOPIC INVESTIGATION

Other types of spectroscopy have not been extensively applied to the amphiboles, and any studies have been solely exploratory in nature. Kalinichenko et al. (1977) used proton magnetic resonance (PMR) to characterize the cation occupancies of the M(1) and M(3) sites; this method Gelectron spectra of anthophyllite and magnesio-riebeckite are reported By Adams et al. (1972); the occurrence of Fe<sup>2+</sup> and Fe<sup>3+</sup> in magnesio-2 Fiebeckite did not lead to any broadening of the Fe 2p or 3s lines. Bershov et al. (1966) and Manoogian (1968) have examined the electron Spin resonance (ESR) of Mn<sup>2+</sup> in tremolite; both studies concluded that  $\frac{c}{2}$ <sup>2+</sup> occupied "one site," and by analogy with the results of Vinokurov  $\frac{\mathbf{\tilde{g}}}{\mathbf{r}}t$  al. (1964) on diopside, Bershov et al. (1966) suggest that this is  $\overleftarrow{\mathbf{d}}$ he Mg site, i.e., M(1), M(2) and/or M(3). Ghose et al. (1968) and Ghose and Schindler (1969) advance a persuasive argument to reverse the Èite-assignment of the spin Hamiltonian parameters in diopside. Applying  $\mathbf{\Phi}_{\mathbf{w}}^{\mathsf{r}}$  he same argument to the results for tremolite indicates that  $\mathrm{Mn}^{2+}$  occu- $\tilde{\mathbf{g}}$  ies the M(4) site. Diffuse reflectance spectra of several amphiboles are presented by Hunt and Salisbury (1970), Adams (1975) and Smith and Strens (1976). These spectra exhibit far less resolution that corre- ${f g}$  ponding polarized transmission spectra. This

#### CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

In the decade of the 1970's there has been considerable advance in our understanding and interpretation of the spectroscopy of amphiboles. In many cases, this has involved the discovery of hitherto unrecognized problems in the application of these methods. However, this should be viewed as an important step forward as it leads to a more realistic use of each method. Particularly in minerals as complex as the amphiboles,

it is necessary to regard experimental techniques as complementary rather than competitive or mutually exclusive. The very specific sensitivity of many of the spectroscopic techniques make them a natural counterpart to both diffraction techniques and other spectroscopic methods. The difficulties and ambiguities involved in an experimental method can often be substantially reduced by using a combination of experimental techniques pertinent to the specific problem at hand.

Many of the problems of spectral interpretation could be alleviated by systematic examination of analyzed synthetic amphiboles:

- Mössbauer examination of Fe<sup>2+</sup> and Fe<sup>3+</sup> end-member compositions; because the relative peak intensities are fixed, the correct association of peaks and assignment of doublets will be apparent.
- (ii) polarized electronic absorption spectroscopy of synthetic (or possibly natural) amphiboles containing a single transition metal, particularly Ti and Mn.
- (iii) polarized electronic absorption spectroscopy of synthetic (or possibly natural) amphiboles containing pairs of transition metals in different valence states; this would allow evaluation of the different IVCT bands which must occur in the more complex natural amphiboles.
  - (iv) preparation of a series of synthetic amphiboles with M(2) = Al [or Sc] (pargasite/ferro-pargasite, glaucophane/ferroglaucophane) and their characterization by Mössbauer and infrared spectroscopy and crystal structure refinement. This would allow a practical evaluation of the infrared method under optimum conditions.

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