

CORRELATIONS OF INFRARED AND MÖSSBAUER
SITE POPULATION MEASUREMENTS
OF ACTINOLITES¹

ROGER G. BURNS, *Department of Earth and Planetary Sciences,
Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139*

AND

COLIN GREAVES, *Department of Inorganic Chemistry,
University of Oxford, Oxford, England.*

ABSTRACT

Infrared spectra of the fundamental hydroxyl stretching frequencies of eight minerals of the actinolite series have been fitted by computer. Normalized intensities of peaks assigned to various distributions of the Mg^{2+} , Fe^{2+} , and Fe^{3+} ions in the $M(1)$ plus $M(3)$ positions coordinated to hydroxyl ions enabled site population estimates to be made. The Mössbauer spectra of each specimen were resolved by computer into three quadrupole-split ferrous doublets and assigned to Fe^{2+} ions in the $M(1)$, $M(2)$, and $M(3)$ positions. Such resolution has not been achieved before so that for the first time it was possible to calculate Fe^{2+} site occupancies for these three positions. Ferric doublets were also resolved for the first time in actinolite spectra, and values for the ratio $Fe^{3+}/total\ Fe$ calculated from the peak intensities were found to agree well with those from chemical analyses. The broad nature of the ferric peaks indicates that Fe^{3+} ions are distributed over several sites.

Although the infrared data for the $M(1)$ plus $M(3)$ positions are in reasonable agreement with those estimated by Wilkins (1970), they differ significantly from the site populations obtained by Mössbauer spectroscopy, particularly in iron-rich actinolites. The discrepancies are attributed to loss of OH groups and sample oxidation of Fe^{2+} during KBr disc preparation. The relative merits of the Mössbauer and infrared techniques are assessed, leading to the conclusion that Fe^{2+} site population data derived from Mössbauer spectroscopy are more accurate. The results support earlier deductions of relative enrichments of Fe^{2+} ions in actinolites of $M(1) > M(3) \geq M(2)$ and suggest that Mn^{2+} ions are enriched in $M(2)$ positions.

INTRODUCTION

Since its discovery in 1965 (Burns, 1965), the infrared technique for determining cation distributions in hydroxy-silicates has been used extensively in crystal chemical studies of amphiboles (Burns and Strens, 1966; Burns and Prentice, 1968; Burns and Law, 1970). In addition, Mössbauer spectroscopy has been used to obtain ferrous ion distributions in numerous iron-containing minerals (Burns, 1968, 1970). As a result the two techniques have complemented one another in site population studies of several amphibole series (Bancroft, Maddock, Burns, and

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Strens, 1966; Bancroft, Burns, and Maddock, 1967; Bancroft and Burns, 1969; Ernst and Wai, 1970).

Early studies of actinolites, ideally $\text{Ca}_2(\text{Mg}, \text{Fe}^{2+})_5 \text{Si}_8\text{O}_{22}(\text{OH})_2$, suggested that cation distributions in this series could be obtained independently by Mössbauer and infrared spectroscopy. Thus, Burns and Strens (1966) estimated the Mg and Fe^{2+} ion contents of the $M(1)$ plus $M(3)$ positions of three actinolites from a peak height analysis of the infrared spectra, and obtained $M(2)$ site populations by difference from the chemical formulae which had been derived from approximate refractive index and microprobe measurements. The Mössbauer spectra of two of these actinolites were later resolved by computer into two quadrupole split ferrous doublets, the outer peaks of which were attributed to Fe^{2+} ions in the $M(1)$ plus $M(3)$ positions and the inner doublet to Fe^{2+} ions in $M(2)$ positions (Bancroft, Maddock, and Burns, 1967). Certain anomalies were noted, however, in the Mössbauer spectra. There was distinct asymmetry in peak heights between the low velocity and high velocity components of each doublet, and the inner doublet attributed to $M(2)$ position- Fe^{2+} ions was broader than the outer composite doublet attributed to Fe^{2+} ions in the $M(1)$ plus $M(3)$ positions.

Therefore, it appeared that a more detailed investigation of several actinolite minerals on higher resolution spectrometers might provide a unique opportunity for correlating site populations by the two spectroscopic techniques and enable an assessment to be made of the reliability of each method in such studies. During the course of the investigation, advance information was received of a crystal structure refinement of the actinolite USNM 44973 from Rhode Island, in which cation occupancies of the $M(1)$, $M(2)$, and $M(3)$ positions were reported (Mitchell, Bloss, and Gibbs, 1970). This specimen was incorporated into the spectroscopic studies, thereby enabling site population estimates by X-ray, infrared, and Mössbauer measurements to be compared for one actinolite.

Recently, Wilkins (1970) reported iron-magnesium distributions from measurements of the hydroxyl stretching frequencies of sixteen actinolites, including four of the specimens assembled for the present study. Although complexities of band shape were noted, attempts were made to estimate $\text{Fe}^{2+}(+\text{Mn}^{2+})$ ion site populations semi-quantitatively from the two high frequency bands. These data thus enable a comparison to be made between the infrared measurements of two different research groups.

EXPERIMENTAL PROCEDURES

Specimens. Six actinolite minerals, including four specimens previously analysed, and a synthetic ferrotremolite (Ernst, 1966) were made available for this study. An analysed hornblende (hastingsite) was also used to assist in the assignment of ferric peaks in the

Mössbauer spectra. The compositions and sources of the specimens are summarized in Table 1. All specimens deviate from the ideal actinolite formula $\text{Ca}_2(\text{Mg}, \text{Fe}^{2+})_8\text{Si}_8\text{O}_{22}(\text{OH})_2$ in which Ca^{2+} ions fill $M(4)$ positions and Mg and Fe^{2+} ions are distributed over the two $M(1)$, two $M(2)$, and one $M(3)$ positions. Most of the specimens have been analysed for FeO and Fe_2O_3 contents, and contain significant amounts of Fe^{3+} ions as well as aluminium and sodium. Specimens 2 and 6 also contain appreciable amounts of manganese. Most of the specimens show a deficiency of $(\text{Ca} + \text{Na} + \text{K})$ from 2.0 per formula unit, while $(\text{Mn} + \text{Mg} + \text{Fe}^{2+} + \text{Fe}^{3+} + \text{Al}^{\text{VI}})$ exceed 5.0 p.f.u. after allocating some Al to silicon positions to give $(\text{Si} + \text{Al}^{\text{IV}}) = 8.0$ p.f.u. This indicated the possibility of some Mn, Fe^{2+} , and Mg ions filling vacancies in the $M(4)$ positions.

Infrared Spectroscopy. Measurements were made on a Perkin-Elmer model 225 double-beam recording infrared spectrophotometer on powdered amphibole samples in pressed KBr discs. About 10 mg of the oven dried mineral was ground under acetone to a particle size of 3 microns or less and blended with about 150 mg of oven-dried KBr. After the acetone had evaporated the mixture was dried at 131°C for 10 minutes and transferred to a 13 mm die also heated to 131°C . The die was evacuated for 10 minutes and then pressed under vacuum with a force of 9 tons. Evacuation and preheating of the die and sample were necessary to reduce water adsorption by the powder. To obtain a uniformly clear disc the pressure was applied for four periods of 30 seconds duration, the die being rotated through 90° after each pressing. In a further attempt to reduce water adsorption a dry-air purging unit attached to the spectrophotometer was used to keep the sample chamber free from water vapour.

Readings of absorbance on the spectrogram were corrected for baseline and converted to optical density units. Initial estimates were made of band heights, positions, and widths at half peak height, and these parameters were refined assuming Gaussian line shapes using a least-squares program written by Dr. B. D. Bird. The peak parameters obtained by each cycle of computation were used by the program to calculate the optical density at each point in the spectra and the deviation between observed and calculated values at each point was computed. Fitting was continued until the sum of the absolute values of these deviations fell below 10^{-4} . The values of the root mean squares and standard deviations were included in the output and gave a guide to the accuracy of a fit. The final peak parameters were given in terms of position, half-width, and oscillator strength. A curve plotting program was then used to plot the envelope produced by the refined parameters. Included in the plot were the experimentally observed optical densities. In this way the accuracy of a fit could be estimated visually. Unfortunately, the fitting program is unable to resolve two overlapping peaks if their separation is less than the sum of their half-widths at half peak height (Burns and Law, 1970). Many of the spectra obtained in this study were therefore resolved into component peaks using only the plotting program. The oscillator strengths of the peaks giving the best visual fit were then calculated using the fitting program, and were used in the site population calculations.

Mössbauer Spectroscopy. Measurements of the Mössbauer spectra were made on a Centronic Mössbauer spectrometer using a ^{57}Co source in palladium matrix. The spectra were accumulated in 512 channels of a Laben 4096 multichannel analyser using an asymmetric sawtooth waveform velocity distribution. Calibration was made against the spectrum of iron foil. Following earlier studies, absorbers were initially prepared by compacting the powdered mineral between cellotape in a perspex holder. It was found that this method induced preferred orientation of the crystallites which adversely affected the Mössbauer spectra of the actinolites. For some of the doublets, the ratio of the intensities of the low

velocity and high velocity peaks in the spectra was in excess of 2:1, which is far greater than that attributable to the Gol'danskii effect (Goldanskii *et al.*, 1963). That the effect observed was due to orientation was shown by varying the angle between the gamma-ray beam and the plane of the sample, during which the relative intensities of the two halves of spectrum varied as a function of the angle of incidence of the gamma-rays. It was in an attempt to reduce effects of preferred orientation that the method described by Bowen, Weed, and Stevens (1969) was adopted. The mineral sample and sucrose were ground together under acetone, and the mixture was then sprinkled into a lead holder between aluminium foil. The spectra of samples prepared in this way were found to exhibit substantially reduced asymmetry effects.

The Mössbauer spectra were fitted to component peaks using a program written by Stone (1967; personal communication). The observed spectrum consists of 512 numbers defining an envelope, and the problem is to find the shapes and positions of a number of peaks which, on superposition, give the best fit to the observed envelope. The Mössbauer line shapes for a source of ^{57}Co in Pd (as used in this study) and mineral absorbers, have been found to be essentially Lorentzian (Bancroft and Williams, 1969) so that the intensity of the transmitted gamma beam $y(x)$ as a function of its energy x has the form

$$y(x) = b - \frac{y(o)}{1 + \left(\frac{x - x(o)}{a/2}\right)^2} \quad (1)$$

where $y(o)$ is the intensity at the resonance velocity $x(o)$, a is the width at half-height, and b is the baseline intensity. Thus the equation of the envelope for n lines becomes

$$y(x) = b - \sum_i \frac{y(o)_i}{1 + \left(\frac{x - x(o)_i}{a/2}\right)^2} \quad (2)$$

A small baseline correction term $C \sin 2\pi(x-\phi)/512$ is added to correct for a slight sinusoidal variation of the baseline due to source movement.

For an n -line spectrum, $y(x)$ is a function of $3n+4$ parameters (position, width, and intensity of each line, plus the baseline, scan centre, fractional sine-wave component in the baseline, and fractional baseline drift per channel), denoted q_i and written as a vector \bar{q} .

One wishes to minimise the weighted sum of the squares:

$$\chi^2 = \sum_{r=1}^{512} W_r [y_r - y(x_r, \bar{q})]^2 \quad (3)$$

where y_r is the observed count at channel r , $y(x_r, \bar{q})$ is the function (2.), and W_r is the inverse of the variance for channel r .

The program requires the spectrum data and also some "steering data" which specify the way in which the spectrum data are presented and the way in which the fitting process is to be handled. Initial estimates are given for the $3n+4$ parameters q_i , widths and positions being expressed as channels, and intensities as areas (channels \times counts). Using

$$\frac{d\chi^2}{dq_i} = 0 \quad (4)$$

for each q_i , corrections are determined for each q_i such that χ^2 is minimised—this constitutes one iteration. The procedure is repeated by the computer, using the corrected estimates from the previous iteration; until the values of χ^2 for successive iterations differ by less than 10^{-6} . A statistically acceptable value of χ^2 is about 550 for the spectra studied.

The program enables any parameter to be held constant, or any number of parameters

to be held equal to each other, throughout all or any part of the fitting process. With complex spectra, χ^2 sometimes diverges instead of converging to a minimum value. The linear constraints mentioned above and specified in the "steering data," together with experience, assist in overcoming this problem. Thus, for many spectra in this study it is considered reasonable to constrain the half-widths of the ferrous doublets in different sites to be equal, since studies of several silicate minerals have indicated uniform half-widths.

RESULTS

Infrared Spectroscopy. In the series of actinolite compositions studied, four major peaks were observed (Figure 1). These occurred at 3671, 3657, 3641, and 3623 cm^{-1} . They correspond to the four peaks observed in the earlier study (Burns and Strens, 1966) for Mg and Fe^{2+} ions in the $M(1)$ and $M(3)$ positions, and are labelled accordingly. Thus, the highest energy peak *A* corresponds to three Mg ions in the $M(1)M(3)M(1)$ positions. In order of decreasing energy peak *B* corresponds to two Mg-one Fe^{2+} , peak *C* to one Mg-two Fe^{2+} , and peak *D* to three Fe^{2+} ions in the $M(1)$ plus $M(3)$ positions. The frequencies of the peak maxima show no compositional variations in the actinolite specimens studied. The iron-rich specimens 5, 6, and 7 all gave four-peak spectra typified by that of actinolite USNM 44973 in Figure 1a. For the other specimens peak *D* was not discernible as is illustrated by the spectra of specimens 3 and 1 in Figures 1b and 1c.

For all of the spectra recorded, except that of specimen 1, it proved difficult to estimate the baseline accurately. The major peaks appear to be superimposed upon a broad band presumably due to water adsorbed by the amphibole. This effect seems to be more serious for actinolites than other amphibole series studied previously (Bancroft *et al.*, 1966; 1967; Burns and Prentice, 1968; Bancroft and Burns, 1969; Ernst and Wai, 1970), and clearly limits the accuracy of quantitative site population estimates based on peak heights alone. In some of the spectra, particularly those of the iron-rich specimens, peaks *B*, *C*, and *D* were asymmetric and this was interpreted as being due to small peaks from Fe^{3+} ions in the $M(1)$ plus $M(3)$ positions occurring at slightly lower energy.¹ Thus, peak *B* due to MgMgFe^{2+} might be expected to have a small component due to MgMgFe^{3+} at slightly lower frequency as a consequence of the greater polarizing power of trivalent iron (Burns and Prentice, 1968). When the spectra were corrected for the baseline, the peaks due to Fe^{3+} ions in the $M(1)$ plus $M(3)$ positions became more apparent and appeared as shoulders on the low frequency side of the major peaks. This is demonstrated by the spectrum of specimen USNM 44973 shown in Figure 2a. The points were plotted by computer which gives a reversed frequency

¹ Similar asymmetrical features are also apparent in Wilkins' (1970) infrared spectra. Note, in particular, his figure 1d for specimen 7 (Klein 11B).

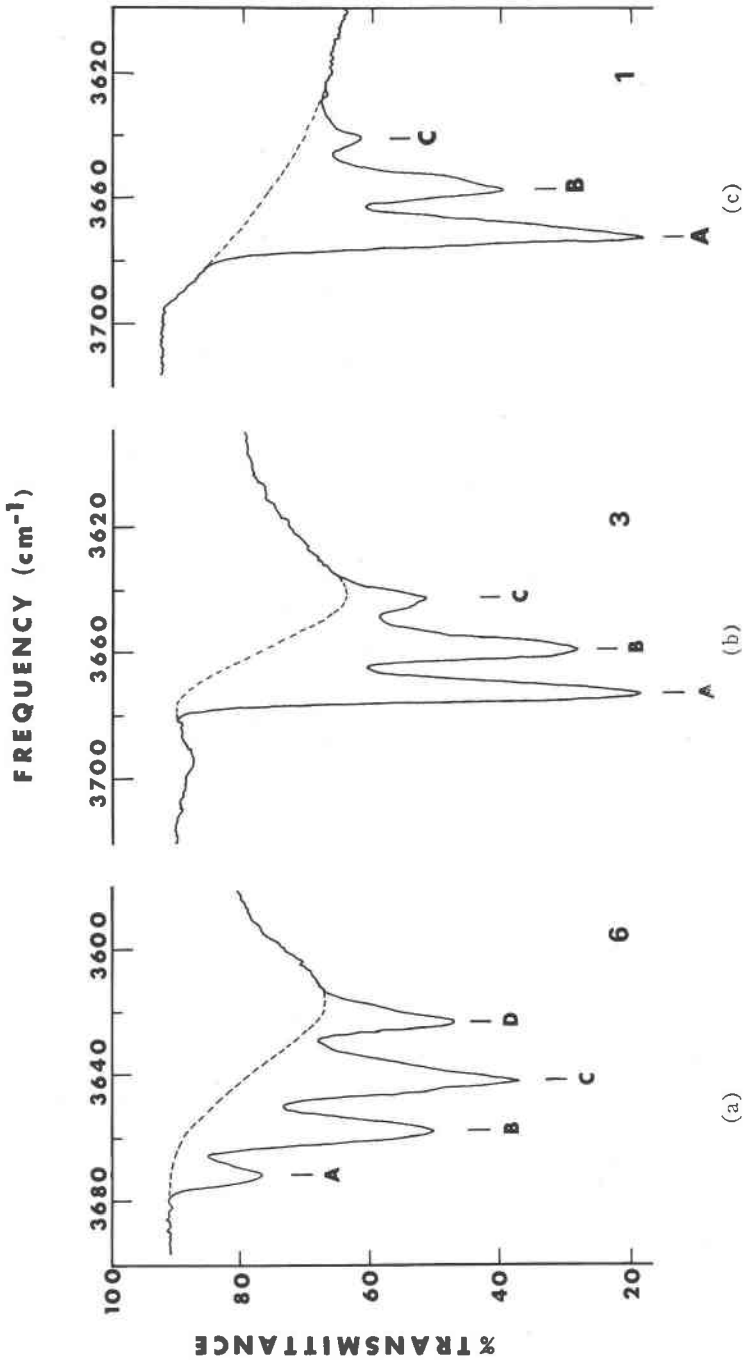


FIG. 1. Infrared spectra of actinolites in the region of fundamental hydroxyl stretching frequencies. (a) Specimen 6; (b) Specimen 3; (c) Specimen 1.

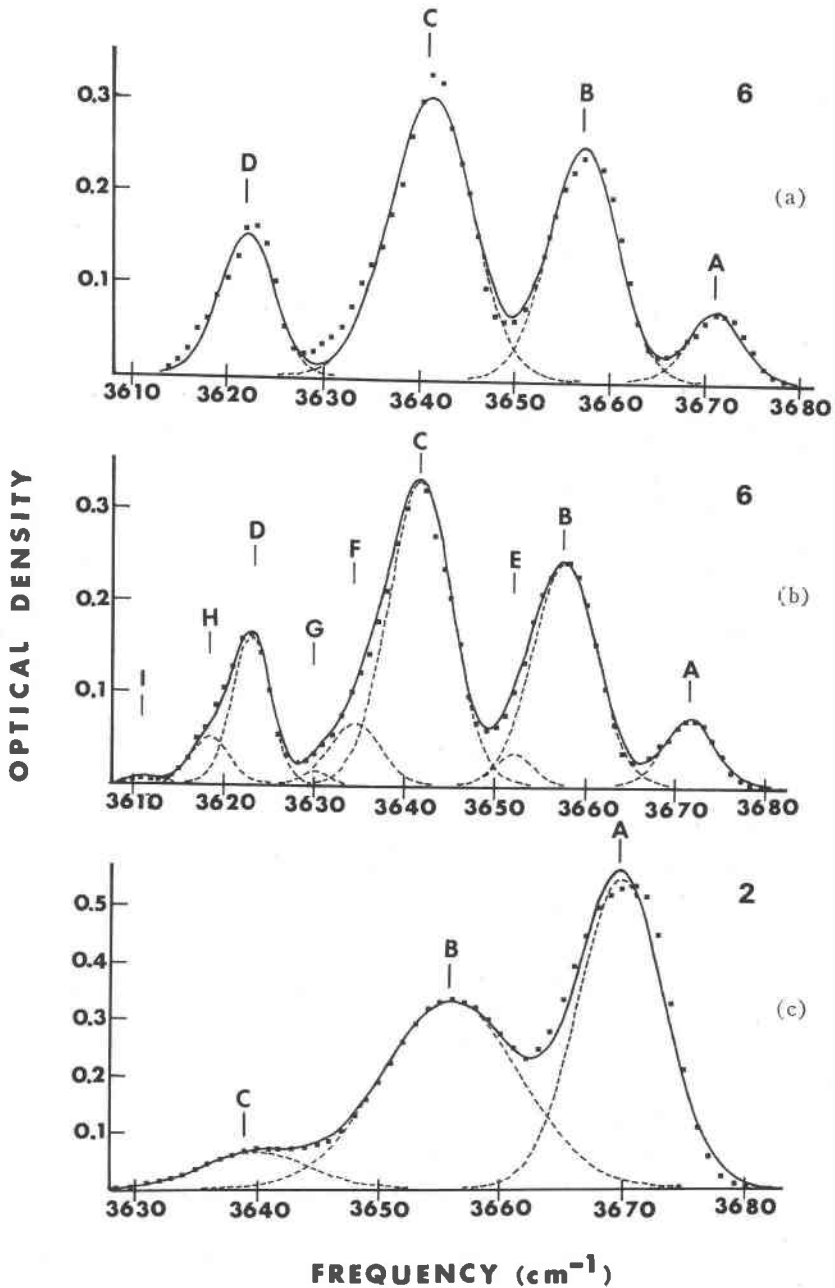


FIG. 2. Computer plotted infrared spectra of actinolites. (a) Specimen 6—four-peak fit; (b) Specimen 6—nine-peak fit; (c) Specimen 2.

Table 2. Parameters for the Computer-fitted Infrared Spectrum of Actinolite USNM 44973.

Peak	Assignment	Frequency (cm ⁻¹)	Optical Density	Half-Width (cm ⁻¹)	Oscillator Strength	Normalised Oscillator Strength
A	MgMgMg	3671	0.072	4	0.221	A ₀ = 0.069
B	MgMgFe ²⁺	3657	0.242	5	0.927	B ₀ = 0.290
E	MgMgFe ³⁺	3652	0.033	3	0.076	E ₀ = 0.024
C	MgFe ²⁺ Fe ²⁺	3641	0.329	5	1.260	C ₀ = 0.395
F	MgFe ²⁺ Fe ³⁺	3634	0.065	4	0.199	F ₀ = 0.062
G	MgFe ³⁺ Fe ³⁺	3630	0.014	2	0.021	G ₀ = 0.007
D	Fe ²⁺ Fe ²⁺ Fe ²⁺	3623	0.160	3	0.368	D ₀ = 0.115
H	Fe ²⁺ Fe ²⁺ Fe ³⁺	3618	0.050	3	0.115	H ₀ = 0.036
I	Fe ²⁺ Fe ³⁺ Fe ³⁺	3611	0.005	2	0.008	I ₀ = 0.002

and absorption scale from that of the originally measured spectra (Figure 1a). Thus, peak *A* is now on the upper right of Figure 2a as indicated. The envelope was first fitted by computer to four peaks but the fit shown in Figure 2a was not very satisfactory and clearly indicated the presence of Fe³⁺ ions in the *M*(1) plus *M*(3) positions. An attempt was made to introduce extra peaks into the fitting program but no useful results were obtained due to the close proximity of neighboring peaks. Estimates were therefore made of the positions, half-widths and optical densities of peaks due to Fe³⁺ ions in the *M*(1) plus *M*(3) positions and these were fed into the plotting program to obtain the plot shown in Figure 2b. The fitted spectrum shown in Figure 2b incorporates nine component peaks and appears to be a visually satisfactory fit. The parameters of these peaks are summarized in Table 2, together with the oscillator strengths computed using the curve-fitting program. Site occupancies of the *M*(1) plus *M*(3) positions were calculated from the normalized oscillator strengths as follows:

$$\text{Fe}^{2+} \text{ in } M(1)M(3)M(1) = B_0 + 2C_0 + 3D_0 + F_0 + 2H_0 + I_0$$

$$\text{Fe}^{3+} \text{ in } M(1)M(3)M(1) = E_0 + F_0 + 2G_0 + H_0 + 2I_0$$

$$\text{Mg}^{2+} \text{ in } M(3)M(3)M(1) = 3A_0 + 2B_0 + 2E_0 + C_0 + F_0 + G_0$$

Inherent in these calculations are the assumptions that (i) Fe²⁺ estimates

may include some Mn^{2+} , since vibrational energies of O-H bonds of hydroxyl ions coordinated to these divalent transition metal ions should be almost identical; (ii) the sum of ($\text{Mg}^{2+} + \text{Fe}^{2+} + \text{Mn}^{2+} + \text{Fe}^{3+}$) ions in the $M(1)$ plus $M(3)$ positions is 3.0 p.f.u.; (iii) any nonstoichiometry of OH groups in $O(3)$ positions is random; (iv) the presence of Al and Ti in the $M(1)$ plus $M(3)$ positions is ignored.

The computer-fitted spectra of the other iron-rich actinolites (specimens 5 and 7) are almost identical to that of specimen 6 shown in Figure 2b. Similarly, the spectra of the magnesian actinolites were similar and are typified by the three peak fit for specimen 2 shown in Figure 2c. The inclusion of extra peaks due to Fe^{3+} ions in the $M(1)$ plus $M(3)$ positions did not lead to significantly improved fits. Note, however, the larger width of peak *B* compared to peak *A* (except in specimen 3), indicating small contributions to peak *B* by the distribution MgMgFe^{3+} . In contrast to the iron-rich actinolites, duplicate spectra on second KBr discs of the more magnesian actinolites were identical indicating that, in the present study, the iron-rich actinolites are more prone to sample oxidation during KBr disc preparation than magnesian actinolites. However, all four spectra illustrated by Wilkins (1970) for actinolite compositions spanning the Fe^{2+} mole fraction range 0.17–0.55 display asymmetry features, suggesting that iron oxidation may also occur in magnesian actinolites. Site populations calculated for each of the actinolites from the infrared spectra are summarized in Table 3. The figures for the magnesian actinolites are expressed in terms of total iron (+manganese) since there is some evidence of peaks due to small amounts of Fe^{3+} ions in the spectra.

Mössbauer Spectroscopy. The Mössbauer spectra of the actinolites are shown in Figure 3. Each experimentally determined, unfitted spectrum (represented by vertical dashed lines) usually showed two well resolved doublets with isomer shifts and quadrupole splittings characteristic of paramagnetic octahedrally coordinated, high-spin Fe^{2+} ions. However, an additional shoulder or inflexion in the high velocity region indicated contributions from a third Fe^{2+} ion. The spectra were further complicated by another peak or inflexion centered around 0.6 mm/sec, which was attributed to Fe^{3+} ions and had a quadrupole split component at lower velocity. Thus, the low velocity region of the Mössbauer spectra generally consisted of up to five overlapping peaks (*A*, *B*, *C*, *D*, and *D'*).

The fitting process is illustrated by reference to the spectrum of specimen 1 (Figure 3.1). There are clearly two Fe^{2+} peaks in the high velocity region, 2–3 mm/sec, and three peaks are suggested in the low velocity region of the spectrum. Of these three peaks, two correspond to the two Fe^{2+} peaks at high velocity and the third, a broad shoulder at about 0.6

TABLE 3. CATION SITE POPULATIONS IN ACTINOLITES FROM INFRARED SPECTROSCOPY

Specimen	Cation	Number (p.f.u.)	Position of Cation			
			In M(1)+M(3)	Per M(1)+M(3)	In M(2)+M(4)	Per M(2)+M(4)
1	Mg ²⁺	4.18	2.48	0.83	1.70	0.85
	Fe ²⁺ +Mn ²⁺	0.49	0.52	0.17	0.14	0.07
	Fe ³⁺	0.15				
2	Mg ²⁺	4.18	2.42	0.81	1.76	0.88
	Fe ²⁺ +Mn ²⁺	1.02	0.58	0.19	0.63	0.32
	Fe ³⁺	0.19				
3	Mg	3.83	2.40	0.80	1.43	0.72
	Fe ²⁺ +Mn ²⁺	0.74	0.60	0.20	0.45	0.23
	Fe ³⁺	0.31				
5	Mg	2.40	1.41	0.47	0.99	0.50
	Fe ²⁺ +Mn ²⁺	2.44	1.46	0.49	0.98	0.49
	Fe ³⁺	0.20	0.13	0.04	0.07	0.04
6	Mg	1.86	1.29	0.43	0.57	0.29
	Fe ²⁺ +Mn ²⁺	2.85	1.56	0.52	1.29	0.65
	Fe ³⁺	0.32	0.14	0.05	0.18	0.09
7	Mg	2.38	1.35	0.45	1.03	0.52
	Fe ²⁺ +Mn ²⁺	2.91	1.46	0.49	1.25	0.63
	Fe ²⁺	0	0.20	0.07		

mm/sec was assigned to Fe³⁺. Thus, at first the spectrum was fitted to six peaks, two quadrupole split doublets due to Fe²⁺ and one Fe³⁺ doublet. The position of the hidden Fe³⁺ peak at low velocity was estimated using evidence from three sources: (i) the fact that both Fe²⁺ peaks at low velocity appear more intense than their complimentary peaks at high velocity implies that the Fe³⁺ peak lies somewhere between them; (ii) the appearance of other spectra in the present study, particularly specimens 3 and 4 (Figures 3.3 and 4) containing high ratios of Fe³⁺/total iron (Table 1); and (iii) the Fe³⁺ parameters reported for alkali amphiboles (Bancroft *et al.*, 1968; Bancroft and Burns, 1969; Ernst and Wai, 1970).

The half-widths and intensities of the components of each doublet were constrained to be equal and the fitting process converged to a χ^2 of 557. Although this value is indicative of a good fit, the fit did not appear to be satisfactory between the two Fe²⁺ peaks in the high velocity region of the spectrum. For this reason, a third Fe²⁺ doublet was introduced into the fitting process, the positions of the extra peaks being estimated such that the isomer shifts for each of the Fe²⁺ doublets were approximately equal. The half-widths of the six Fe²⁺ peaks were kept equal and the halfwidths of the two Fe³⁺ peaks were constrained to be

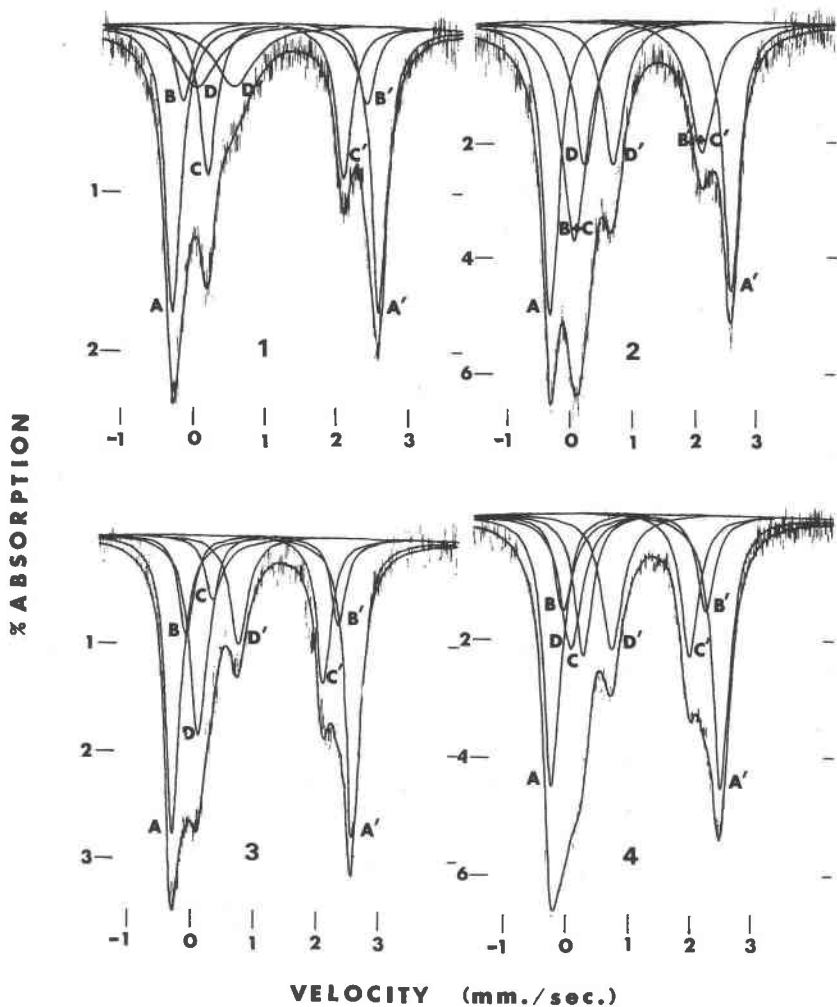


FIG. 3. Computer plotted Mössbauer spectra of actinolites for specimens 1-4, respectively.

equal; the intensities of the two peaks of each doublet were also kept equal. The fitting process again converged but to a reduced χ^2 value of 508, which justified the introduction of the third Fe^{2+} doublet. Although the intensity constraints were later removed, attempts to remove some of the halfwidth constraints usually led to unacceptable halfwidths for one or more of the ferrous doublets. Thus, the spectra illustrated in Figure 3 all have the constraints of equal halfwidths for peaks A , A' , B , B' , C , and C' and for peaks D and D' . The assumption for the ferrous peaks is

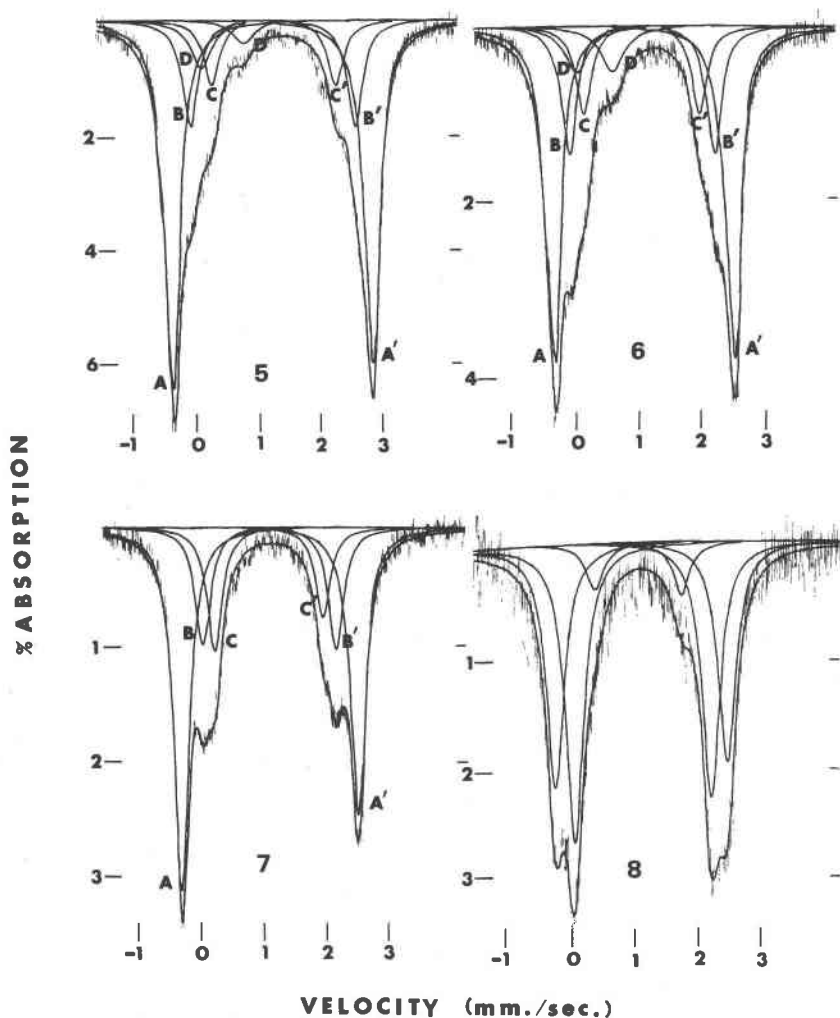


FIG. 3 (cont'd). Specimens 5-8.

justified by the observation that in the Mössbauer spectra of other iron silicate minerals, the Fe^{2+} halfwidths are remarkably uniform (Bancroft *et al.*, 1967, 1968; Virgo and Hafner, 1970).

The assignment of the peaks was made as follows. Assuming that Ca^{2+} , Na^{+} , and K^{+} occupy most of the $M(4)$ positions, the Mössbauer spectra show that ferrous ions in each of the three remaining positions $M(1)$, $M(2)$, and $M(3)$ are being resolved. The doublet with the largest quadrupole splitting, peaks AA' , was assigned to Fe^{2+} in the least dis-

torted $M(1)$ sites (Ingalls, 1964; Bancroft *et al.*, 1967). This assignment is supported by the facts that (i) in all of the actinolite spectra peaks AA' are more intense than either peaks BB' or CC' , and there are two $M(1)$ positions to one $M(3)$ position per formula unit; and (ii) crystal chemical arguments suggest that Fe^{2+} ions are concentrated in the two $M(1)$ and one $M(3)$ sites relative to the slightly smaller $M(2)$ sites, particularly in Fe^{3+} -rich specimens in which Fe^{3+} ions are predicted to favor $M(2)$ positions by analogy with other amphibole series. The assignment of the remaining ferrous doublets is less definite. Peaks BB' and CC' may represent Fe^{2+} ions in either the $M(2)$ and $M(3)$ positions, respectively, or the reverse. The latter alternative is preferred here, however, on the basis of correlations with the Mössbauer spectra of alkali amphiboles. Bancroft and Burns (1969) and Burns and Tew (unpublished) have resolved the Mössbauer spectra of pegmatitic riebeckites and arfvedsonites into three ferrous doublets having parameters similar to those summarized for actinolites in Table 4. The doublet attributed to Fe^{2+} in $M(2)$ positions of alkali amphiboles, not only has the smallest quadrupole splitting, but also is the least intense because Fe^{3+} ions are concentrated in the $M(2)$ positions. Therefore, in this study the assignment adopted is: peaks BB' to Fe^{2+} in $M(3)$ positions, and peaks CC' to Fe^{2+} in $M(2)$ positions. This assignment differs from that chosen earlier to interpret actinolite site populations data (Burns, Greaves, Law, Tew, and Prentice, 1970). The parameters derived from the Mössbauer spectra of actinolites are summarized in Table 4 and the site population data are shown in Table 5.

A noteworthy feature of the computer-fitted spectrum of specimen 1 (Figure 3.1) is the large half-width of the ferric peaks. Although it proved

TABLE 4. MÖSSBAUER PARAMETERS FOR CALCIC AMPHIBOLES

Specimen	Isomer Shift (mm/sec)				Quadrupole Splitting (mm/sec)				Halfwidths (mm/sec)		χ^2
	$M(1)$	$M(3)$	$M(2)$	Fe^{3+}	$M(1)$	$M(3)$	$M(2)$	Fe^{3+}	Fe^{2+}	Fe^{3+}	
1	1.14	1.12	1.14	0.28	2.89	2.57	1.91	0.53	0.26	0.68	508
2	1.13	1.07 ¹		0.44	2.89	2.04 ¹		0.45	0.31	0.40	614
3	1.13	1.11	1.20	0.41	2.38	2.44	1.80	0.63	0.28	0.35	536
4	1.11	1.07	1.10	0.38	2.71	2.30	1.72	0.65	0.32	0.41	634
5	1.13	1.14	1.12	—	2.86	2.19	1.77	—	0.28	—	773
5a ²	1.25	1.27	1.29	0.48	3.18	2.64	1.99	0.67	0.30	0.41	740
6	1.15	1.14	1.14	0.40	2.89	2.32	1.85	0.57	0.29	0.46	555
6a ²	1.23	1.20	1.11	0.52	3.10	2.65	2.10	0.53	0.20	0.45	595
7	1.11	1.12	1.11	—	2.81	2.13	1.73	—	0.29	—	587
8	1.12	1.14 ¹		1.08 ³	2.72	2.16 ¹¹		1.37 ³	0.34	—	727

¹ Average for the $M(2)$ plus $M(3)$ positions.

² Spectra obtained at 77°K.

³ Parameters for assumed $M(4)$ position.

TABLE 5. DISTRIBUTIONS OF IRON CATIONS IN ACTINOLITES FROM MÖSSBAUER SPECTROSCOPY

Specimen	Amount of Fe ²⁺ (p.f.u.)			Ratio Fe ³⁺ /total iron	
	In M(1)	In M(2)	In M(3)	Mössbauer Spectra	Analytical
1	0.27	0.07	0.14	0.236	0.233
2	0.38	0.37 ^a		0.253	0.204
3	0.44	0.14	0.15	0.277	0.295
4	0.72	0.26	0.38	0.246	0.211
5	1.48	0.46	0.46	— ^b	0.077
5a ^c	1.58	0.50	0.31	0.086	0.077
6	1.53	0.58	0.40	0.116	0.113
6a ^c	1.66	0.50	0.34	0.126	0.113
7	1.68	0.62	0.56	— ^b	0

^a estimated (M(2)+M(3))

^b Fe³⁺ peaks not resolved

^c Spectra obtained at 77° K (the remainder are room-temperature spectra).

impossible to resolve closely overlapping ferric peaks, their breadth is indicative of Fe³⁺ ions being located in more than one site of the actinolite structure. The fluctuating Mössbauer parameters for Fe³⁺ doublets in the other actinolite spectra (Table 4) is partly the result of different relative enrichments in the *M*(1), *M*(2), and *M*(3) positions of the specimens and partly the result of the high degree of overlap with neighboring peaks.

Only two ferrous and one ferric doublets could be resolved in the spectrum of specimen 2 (Figure 3.2). The close proximity of peaks *BB'* and *CC'*, together with the similar Fe²⁺ site occupancies of the *M*(3) and *M*(2) positions in this actinolite as indicated also by the infrared data (Wilkins, 1970 and Table 3), results in a broad envelope closely approximating Lorentzian line shape (compare Burns and Law, 1970, Figure 3.1). The poor agreement between the chemical and Mössbauer determined ratios Fe³⁺/total Fe may be due to the incomplete resolution of ferrous peaks in the Mössbauer spectrum, although some doubt is cast on the chemical analysis. The fitted spectrum for specimen 3 (Figure 3.3) shows asymmetry in peaks *CC'* and *DD'*, which may result from preferred orientation in this sample. There is a small discrepancy between the Fe³⁺/total Fe ratios, which might again be due to poor resolution of overlapping peaks. The halfwidths of the ferric doublet is the smallest in specimen 3, suggesting that Fe³⁺ ions are concentrated in one site in this actinolite. This is also in accord with the infrared spectrum. The Möss-

bauer spectrum of a hornblende, included in the present study of clarify Fe^{3+} peak positions, is shown in Figure 3.4. The fitted spectrum is similar to those of the magnesian actinolites, indicating that Fe^{2+} and Fe^{3+} peaks may be resolved even in a chemically complex mineral such as hornblende, but the $\text{Fe}^{3+}/\text{total Fe}$ ratio is only in fair agreement with the analysis figure.

The room temperature spectrum of specimen 5 gave a very poor fit and it proved impossible to resolve the ferric doublets even though the chemical analysis indicated about 7.7 percent ferric iron. However, a ferric doublet was fitted to the low temperature spectrum, obtained at 77°K (Figure 3.5), by applying additional constraints in the fitting process. Thus, in addition to the equal halfwidth constraints for the six ferrous peaks, the halfwidths of the ferric peaks were held constant at the value 0.41 mm/sec, and the intensities of peaks BB' and CC' were held equal in pairs. The fitted spectrum displays some asymmetry of the intensity-free peaks AA' and DD' , but the ratio $\text{Fe}^{3+}/\text{total Fe}$ is in good agreement with the analysis value. The high velocity region of the spectrum is not fitted satisfactorily, and there are indications of a fourth ferrous peak. This possibility is also suggested by analogies with the spectrum of synthetic ferrotremolite (Figure 3.8) and by the substantial deficiency of $(\text{Ca}+\text{Na}+\text{K})$ from 2.0 per formula unit, indicating that about 18 percent of the $M(4)$ positions are available to occupancy by divalent cations. The spectrum of USNM 44973 (specimen 6) gave an excellent fit (Figure 3.6). Not only are preferred orientation effects absent, but the $\text{Fe}^{3+}/\text{total Fe}$ ratio is in good agreement with the analysis figure. The Mössbauer spectrum of specimen 7 could be fitted to only three ferrous doublets (Figure 3.7). Although the fit is not very good in the region where peak D' is expected, no satisfactory fit could be obtained when a ferric doublet was included even in the 77°K spectrum, suggesting that there is very little Fe^{3+} present in the specimen.

The Mössbauer spectrum of synthetic ferrotremolite would be expected to consist of three ferrous doublets whose intensity ratios would approach 2:1:2, corresponding to Fe^{2+} in the $M(1)$, $M(3)$, and $M(2)$ positions. The spectrum obtained is shown in Figure 3.8. It is of poor quality owing to large background scatter. Convergence in the fitting process could only be obtained for a six-peak fit by constraining all the halfwidths to be equal. The fitted spectrum is unsatisfactory, as indicated by the high χ^2 value. However, the spectrum is of interest for several reasons. First, the position of the innermost doublet does not compare with that of peaks CC' in the actinolite spectra: the quadrupole splitting is much too low and the isomer shift is also slightly low. Second, the intensities are not in the ratio 2:1:2 as expected for resolution of the $M(1)$, $M(3)$, and

$M(2)$ positions, respectively. The spectrum may be explained tentatively by invoking the occupation of the very distorted, eight-coordinated $M(4)$ site by some Fe^{2+} ions, giving rise to the innermost doublet with smallest quadrupole splitting. The outer doublet could then be assigned to $M(1)$ and the central doublet to $M(3)$ plus $M(2)$. This would partly explain the high χ^2 value, since the halfwidth constraints are not valid: the central doublet would be expected to be broader than the other two. If this assignment of the doublets is correct and some Fe^{2+} ions displace calcium in $M(4)$ positions, the deficiencies in the $M(1)$, $M(2)$, and $M(3)$ positions must be compensated for by calcium occupying these sites. Clearly this raises some crystal chemical problems and calls for further investigation of ferrotremolite.

DISCUSSION

Comparison of Site Population Data. This study was initiated to measure and compare cation site populations obtained independently by Mössbauer and infrared spectroscopy. However, as the investigation proceeded new complexities were encountered in addition to those known from previous work, which made it difficult to compare accurately determined site population data. Nevertheless, stemming from this and earlier studies certain assessments can be made of the relative merits of each spectroscopic technique.

The Fe^{2+} site population data obtained in the present study are summarized in Table 6, together with the infrared results of Wilkins (1970) for duplicate actinolite specimens. There is reasonable agreement between the two sets of infrared data for the $M(1)$ plus $M(3)$ positions, particularly when the Fe^{3+} ion contents are included in the estimates.

TABLE 6. COMPARISON OF Fe^{2+} SITE POPULATION DATA FOR ACTINOLITES

Specimen Number	In $M(1)+M(3)$ Positions (p.f.u.)			In $M(2)+M(4)$ Positions (p.f.u.)		
	Mössbauer	Infrared (this study)	Infrared (Wilkins, 1970)	Mössbauer	Infrared (this study)	Infrared (Wilkins, 1970)
1	0.34	0.52 ^a	—	0.14	0.14 ^a	—
2	0.57 ^b	0.58 ^{ac}	0.63 ^c	0.36 ^b	0.63 ^{ac}	0.32 ^c
3	0.58	0.60 ^a	0.72	0.15	0.45 ^a	0.24
5	1.94	{ 1.46 ^d 1.59 ^a 1.63 ^d	1.62	0.46	{ 1.05 ^a 1.29 ^d	0.88
6	2.11	{ 1.70 ^a 1.46 ^d	—	0.40	1.47 ^a	—
7	2.30	{ 1.66 ^a	1.71	0.56	1.25	1.04

^a Includes Fe^{3+} .

^b Estimated.

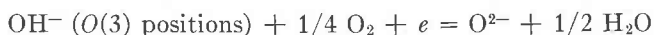
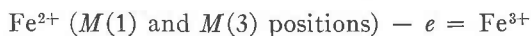
^c Probably includes Mn^{2+} .

^d Excluding Fe^{3+} .

Thus, Wilkins' method of ignoring Fe^{3+} peaks and calculating Fe^{2+} site populations from the areas under the two high intensity peaks (*A* and *B*) appears to be invalid, since the present study shows that peak *B* consists of overlapping components due to both MgMgFe^{2+} and MgMgFe^{3+} assemblages. However, there are large discrepancies between the two sets of $M(2)$ data. This might be expected since the $M(2)$ estimates contain accumulative errors resulting from subtraction of the $M(1)$ plus $M(3)$ data from chemical formulae.

The agreement between the infrared and Mössbauer site populations is not good. Although the $M(1)$ plus $M(3)$ data are similar for the magnesian actinolites, the infrared results for iron-rich specimens are consistently lower than the values obtained by Mössbauer spectroscopy. As a result there is poor agreement between the sets of $M(2)$ site populations. The lack of agreement for the $M(1)$ plus $M(3)$ positions may be explained by the loss of hydroxyl groups resulting from oxidation of Fe^{2+} ions. This is discussed below.

Assessment of the Spectroscopic Methods. The discrepancies between the sets of site population data in Table 6 led us to examine critically the relative merits of the two spectroscopic techniques. Some of the problems and assumptions encountered in Mössbauer and infrared spectroscopy are summarized in Table 7. Perhaps the most serious difficulty experienced in the infrared measurements is sample oxidation during KBr disc preparation, which is indicated by poor reproducibility of duplicate infrared spectra and contrasting results with Mössbauer spectroscopy. This is perhaps best illustrated by specimen 7 for which both chemical analysis and Mössbauer spectra showed that very little Fe^{3+} was present, but the ferric peaks in the infrared spectra were the most intense observed. This highlights the dilemma encountered in infrared measurements. In order to increase the percentage absorption relative to internal reflexion and scattering and to reduce asymmetry in the spectra arising from the Christiansen effect, particle sizes must be less than the wavelength of incident radiation (*i.e.*, 3 microns in the present study). This renders the powdered specimen prone to water adsorption, and since H_2O also experiences vibrations along O-H bonds in the 3700 cm^{-1} region of the infrared spectrum, it must be eliminated. If this is attempted by drying the powdered specimen above 100°C oxidation of Fe^{2+} ions in iron-rich actinolites occurs, presumably through the mechanism (Addison and Sharp, 1962):



Loss of OH^- ions from $O(3)$ positions affects the relative intensities of peaks A , B , C , and D in the infrared spectra (Ernst and Wai, 1970) and renders Fe^{2+} and Mg^{2+} estimates of $M(1)$ plus $M(3)$ positions inaccurate.

Other assumptions inherent in the infrared technique which are summarized in Table 7 are self explanatory or have been discussed earlier. Note, however, that Fe^{2+} and Mn^{2+} ions cannot be discriminated and non-stoichiometry in the $M(1)$ plus $M(3)$ positions cannot be detected at present. Thus, the Fe^{2+} site populations from infrared spectroscopy summarized in Table 3 and in Table 6 have errors associated with these effects.

The most serious problem with the Mössbauer spectra encountered in this study was the influence of preferred orientation of the actinolite crystallites on the relative intensities of the peaks of quadrupole-split doublets. Once this effect had been reduced or eliminated by mixing the powdered sample with sucrose, success was obtained in resolving the Mössbauer spectra into three ferrous doublets, together with a ferric doublet in most spectra. However, several constraints had to be imposed in order to attain convergence in the fitting process. The results of this study not only represent an advance over earlier measurements (Bancroft, Maddock, and Burns, 1967), but also resolve the dilemma encountered in the previous study. At that time only two quadrupole split Fe^{2+} doublets were resolved, the inner doublet of which (assigned to the $M(2)$ positions) was broader than the outer doublet (assigned to the $M(1)$ and $M(3)$ positions). The increased resolution achieved in the present study, together with the attempts to eliminate asymmetry effects and also to allocate absorption to a Fe^{3+} doublet, enabled a third Fe^{2+} doublet to be resolved (Greaves, Burns, and Bancroft, 1971). However, there is considerable overlap of neighboring peaks which limits the accuracy of site population estimates. Bancroft (1970) stated that if two peaks are closer than their half-widths at half peak-height, they cannot be resolved by computer (Burns and Law, 1970) and accurate areas are undeterminable. Bancroft based his arguments on a peak-width at half height of 0.30 mm/sec. He estimated that if peaks are about 0.20 mm/sec apart, the standard deviations in the site populations can be large (≈ 15 percent) since the computer is just able to resolve the peaks. If the peak separation is greater than 0.30 mm/sec, the statistical errors become more reasonable (*i.e.*, ≈ 10 percent). In the present study using a source with line-width 0.24 mm/sec, the Fe^{2+} peaks have half-widths of 0.26–0.29 mm/sec. In the high velocity region of most of the actinolite spectra component peaks are about 0.25 mm/sec apart. Thus, the Fe^{2+} site populations summarized in Table 5 are considered to be accurate to within ± 10 percent of the figures quoted.

TABLE 7. ASSUMPTIONS AND DIFFICULTIES OF THE INFRARED AND MÖSSBAUER METHODS IN SITE POPULATIONS STUDIES OF ACTINOLITIC AMPHIBOLES

Infrared	Mössbauer
baseline affected by water adsorption by sample	baseline unaffected by water; smoothed in high resolution spectrometers by accumulating in excess of 10^6 counts
particle size must not exceed 3 microns	probably no restriction on particle size, although colloidal materials become superparamagnetic
preferred orientation of crystallites unimportant	preferred orientation must be eliminated
sub-three micron particles prone to sample oxidation, affecting $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios and OH^- stoichiometry	sample oxidation probably unimportant
either stoichiometry of OH^- assumed (2.0 p.f.u.) or random distribution of OH^- in $O(3)$ positions assumed; O^{2-} (oxidation) and F^- (substitution) do not absorb in region of hydroxyl stretching	stoichiometry of OH^- unimportant, although type of anion may affect positions of peaks
stoichiometry in $M(1)$ plus $M(3)$ positions assumed (3.0 p.f.u.)	no assumptions made on $M(1)$ and $M(3)$ stoichiometry
Gaussian shaped bands assumed	Lorentzian line shapes assumed
assume transition moments of O-H bonds independent of cation occupancy of $M(1)$ and $M(3)$ positions	assume recoilless fractions equal for Fe^{3+} and all types of Fe^{2+}
component peaks resolved by computer provided separation exceeds $10\text{--}12\text{ cm}^{-1}$; otherwise, curve-fitting by hand or computer plotter may be used	component peaks resolved by computer provided separation exceeds $0.12\text{--}0.13\text{ mm/sec}$
cannot discriminate between cations in $M(1)$ and $M(3)$ positions	can resolve Fe^{2+} ions (only) in $M(1)$, $M(3)$ and $M(2)$ positions
cannot discriminate between Fe^{2+} and Mn^{2+}	Mn^{2+} does not give a Mössbauer spectrum
can obtain Mg^{2+} , Fe^{2+} and Fe^{3+} occupancies of $M(1)$ plus $M(3)$ positions directly	Fe^{2+} site populations only obtained; sometimes, Fe^{3+} distributions deduced qualitatively

TABLE 7.—(Continued)

Infrared	Mössbauer
each cation must exceed 5–10 percent occupancy of $M(1)$ plus $M(3)$ positions	iron concentration of specimen should exceed 1%; species resolvable if it exceeds about 5% of the amount (Fe^{3+}) or position
best suited to simple two-cation ($Mg-Fe^{2+}$) amphiboles; quantitative site populations impossible when appreciable amounts of Mn, Al, Li, etc. occur in $M(1)$ plus $M(3)$ positions and excess alkali metal ions present in A-sites	Fe^{3+} and component Fe^{2+} peaks resolved even in complex amphiboles such as hornblende and pegmatitic riebeckites and arfvedsonites
technique applicable to hydroxysilicates	technique applicable to most iron-containing minerals
measurements require only 1–2 mg. mineral	sufficient sample required to give total iron concentration of about 5 mg/cm ²

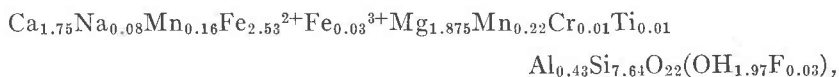
In most of the spectra where Fe^{3+} peaks were resolved, they are broader than peaks arising from Fe^{2+} ions. The narrowest Fe^{3+} peaks were found for specimens 3 and 2, the specimens for which infrared spectroscopy suggests little Fe^{3+} in the $M(1)$ plus $M(3)$ positions. Therefore, most of the broadening of the Fe^{3+} peaks is due to the presence of Fe^{3+} ions in more than one site of the actinolite structure. The half-widths of the Fe^{3+} doublet in specimen 1 are by far the largest encountered in this study, suggesting a wide distribution of Fe^{3+} ions over several sites. Such information is unattainable from X-ray crystallography (Mitchell *et al.*, 1970).

Two other features relating to the Mössbauer site population data concern assumptions for recoil-free fractions and peak assignments in the Mössbauer spectra. The site population data in Table 5 have been calculated on the assumption of identical recoilless fractions for Fe^{2+} ions in each site which are independent of actinolite composition. The spectrum of synthetic ferrotremolite should clarify these points. However, as stated earlier when describing Figure 3.8 there appear to be complications over the Fe^{2+} and Ca^{2+} ion distributions in this specimen. The site populations obtained from the liquid nitrogen spectra of iron-rich actinolites disagree with those obtained at 300°K which, may indicate a differential temperature variation of the recoil-free fractions of each site. However, it may also be a reflection of the high degree of overlap of component peaks.

The peak assignments chosen in this study were based on correlations with those deduced from the Mössbauer spectra of alkali amphiboles. However, as noted earlier, there may be some ambiguity over the peak assignments for the $M(2)$ and $M(3)$ positions. Again, the spectra of synthetic ferrotremolite should have clarified the assignment had other complications been absent. Clearly, correct peak assignment affects the site populations derived from Mössbauer spectroscopy. As a result the figures quoted in Table 5 of this study differ from those cited earlier for actinolites (Burns, Greaves, Law, Tew, and Prentice, 1970).

In summary, because of its specificity for Fe^{2+} ions and because it is possible to resolve all three positions ($M(1)$, $M(2)$, and $M(3)$), the Mössbauer site population data of actinolites are considered to be significantly more accurate than those determined by infrared spectroscopy.

Comparison with Crystal Structure Refinement Data. Specimen 6 (USNM 44973) was included in the present investigation after it was learned that Mitchell *et al.* (1970) had performed on it a crystal structure refinement by least squares and Fourier methods. The site populations for this actinolite, the formula of which was expressed (on the basis of 24 O plus F) as



obtained by X-ray crystallography, were (Mitchell *et al.*, 1971; G. V. Gibbs, personal communication):

$M(1)$: 0.78Mg + 1.22 Fe^{2+}	(for 2 positions)
$M(2)$: 0.68Mg + 0.92 Fe^{2+} + 0.32 Fe^{3+}	(for 2 positions)
$M(3)$: 0.42Mg + 0.58 Fe^{2+}	(for 1 position)
$M(4)$: 1.76Ca + 0.16Mn + 0.08Na	(for 2 positions)

These data may be compared with the iron distributions for this specimen obtained from Mössbauer spectroscopy (Table 5):

$M(1)$: 1.53 Fe^{2+}
$M(2)$: 0.40 Fe^{2+}
$M(3)$: 0.58 Fe^{2+}

Note that the large halfwidth of the ferric peaks (0.46 mm/sec) indicates that the Fe^{3+} ions are located in more than one site.

Although there is exact agreement for the $M(3)$ position, the Fe^{2+} estimates of the $M(1)$ and $M(2)$ positions differ between the two techniques.

The accuracy of the Mössbauer data has been discussed earlier. The maximum error of ± 10 percent assessed for the Mössbauer Fe^{2+} site populations is insufficient to bring the two sets of data into good agreement.

However, the following points about the X-ray data should be noted. First, the total Fe^{2+} occupancy of the $M(1)$ plus $M(2)$ plus $M(3)$ positions (2.72 p.f.u.) exceeds the chemical formula (2.53 p.f.u.). However, there are 0.22 Mn^{2+} ions to be allocated to these three positions. Thus, the X-ray determined Fe^{2+} estimates must include some manganese. Second, all of the Fe^{3+} ions are allocated to only the $M(2)$ positions. This is contrary to the ferric ion distribution deduced from Mössbauer spectroscopy. These two features highlight the dilemma encountered in X-ray crystallography of differentiating between Fe^{2+} , Fe^{3+} , and Mn.

Nevertheless, in spite of the difficulties and assumptions of the two techniques, there is fair agreement between the X-ray and Mössbauer data when manganese is taken into account. One may conclude from the two sets of data that Mn^{2+} and Fe^{3+} ions are enriched in $M(2)$ positions, while each technique indicates the relative enrichment (per position) of Fe^{2+} ions is $M(1) > M(2) > M(3)$.

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