

MÖSSBAUER SPECTRA OF OMPHACITES

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ABSTRACT

Mössbauer spectra of five omphacites are distinctive and can be used to characterize omphacites having $P2$ symmetry. The spectra have been fitted to Lorentzian line shapes, and consist of ten lines: eight due to four ferrous doublets, and two due to a ferric doublet. The center shift (C.S.) values for all the Fe^{2+} doublets are about 1.25 mm/sec, while the quadrupole splittings (Q.S.) vary from about 2.8 mm/sec for the outer peaks to about 1.7 mm/sec for the inner peaks. The C.S. and Q.S. for the ferric doublets are about 0.5 and 0.4 mm/sec respectively. We tentatively assign the four Fe^{2+} doublets to Fe^{2+} in the four $M1$ positions. The results indicate that appreciable amounts of Fe^{2+} occupy all four of these $M1$ positions; moreover the intensity of the one well-resolved ferrous peak indicates that the Fe^{2+} ordering varies markedly between these five omphacites. These differences in ordering may well reflect differences in temperature and pressure of formation. The ferrous/ferric ratios calculated from these spectra are not in good agreement with chemical analyses, which generally overestimate the Fe^{3+} content.

INTRODUCTION

Mössbauer spectroscopy has been found to be a useful method for characterizing the oxidation state, coordination number, and site symmetry of iron in silicate minerals (Bancroft and Burns, 1966; Bancroft, Burns and Maddock, 1967; Bancroft, Burns and Stone, 1968). For example, Fe^{2+} and Fe^{3+} in six-fold coordination give rise to absorptions having respective center shifts of about 1.25 mm/sec and 0.50 mm/sec (relative to stainless steel). For Fe^{2+} it is often possible to distinguish between six-coordinate sites having slightly different symmetry. Thus in orthopyroxenes, Fe^{2+} in the six-coordinate $M1$ and $M2$ sites give slightly different quadrupole splittings (Q.S.) and center shifts (C.S.). In addition, Mössbauer spectroscopy has been found to be a rapid method for detecting cation ordering, obtaining accurate ferrous/ferric ratios, and quantitatively estimating Fe^{2+} site populations in complex crystal structures (Bancroft *et al.*, 1968 and references; Virgo and Hafner, 1968 and references). For ferrous/ferric ratios, the agreement between chemical analyses and Mössbauer results is generally good (Bancroft, Burns and Stone, 1968; Bancroft, 1969). However, several errors in chemical analysis values have led us to believe that the Mössbauer method is more reliable and accurate than chemical analysis (Bancroft and Burns, 1969). The ferrous site populations for a cummingtonite and a glaucophane (Bancroft, 1969) are in good agreement with X-ray values. The assumptions and difficulties in obtaining site populations from Mössbauer areas have been discussed (Bancroft, 1969).

Omphacites and rocks containing omphacites have been the subject of considerable research (Clark and Papike, 1968 and references). Their recent X-ray work on an omphacite from the Tiburon Peninsula, California, has shown that this omphacite has space group $P2$, instead of the $C2/c$ space group for jadeite ($\text{NaAlSi}_2\text{O}_6$) and diopside ($\text{CaMgSi}_2\text{O}_6$). Whereas the $C2/c$

structure has one crystallographic site for each of Na^+ and Al^{3+} , Clark and Papike found that the omphacite structure has eight different sites for the cations. Four (the $M2$ positions) are occupied by Na^+ and Ca^{2+} , and the other four (the $M1$ positions) by Mg^{2+} , Fe^{2+} , Fe^{3+} , and Al^{3+} . On the basis of bond distances and charge balance considerations, they postulated that Mg^{2+} and Fe^{2+} occupied two of these $M1$ positions, and Fe^{3+} and Al^{3+} occupied the other two, thus giving an ordered cation distribution, with (Mg^{2+} , Fe^{2+}) octahedra alternating with (Fe^{3+} , Al^{3+}) octahedra.

In this paper, we report Mössbauer spectra of five omphacites, two of which have $P2$ symmetry (Clark and Papike, 1968) and are from the same locality as, and of similar composition to, the omphacite studied in detail by Clark and Papike. The omphacite spectra differ qualitatively from those of other pyroxenes, and can be used to characterize $P2$ omphacites. The Mössbauer areas suggest that four sites contain appreciable amounts of Fe^{2+} , and that the chemical analysis values for ferric to ferrous values are inaccurate. We comment on the differences in ferrous ordering for providing evidence of the history of pyroxene crystallization.

THE MINERALS AND EXPERIMENTAL TECHNIQUE

The analyses of the samples are reported in Table 1,¹ and Figure 1. The Mössbauer spectrometer and experimental methods have been described in previous papers (Bancroft, Maddock and Ward, 1965, Bancroft *et al.*, 1967). A 5 mCi ^{57}Co in Pd source was used for all spectra. Except for the Ca1059 and Cam958 samples, the absorber contained about 10 mg/cm² of natural iron. Better spectra for Ca1059 and Cam958 were obtained with only about 5 mg/cm² of natural iron. Close to 2×10^6 baseline counts were recorded at room temperature for Cam958, 113-RGC-58, and JD1059, while about 5×10^6 baseline counts were recorded for Ca1059, 102-RGC-58 and 88-SM-2. A preliminary spectrum of 113-RGC-58 at 80°K was also run.

It was heartening that such good spectra could be obtained

¹We are grateful to Dr. J. J. Papike and Dr. J. Dixon for providing samples for this study.

TABLE 1. CHEMICAL ANALYSES OF OMPHACITES

| Oxide | Weight Percent | | | | | | |
|--------------------------------|--|----------------------|----------------------|---------------------|---------------------|---------------------|----------------------|
| | 100-RGC ^a | 102-RGC ^a | 113-RGC ^a | Ca1059 ^b | Cam958 ^c | JD1059 ^d | 88-SM-2 ^e |
| SiO ₂ | 54.3 | 54.9 | 54.6 | 56.02 | 55.20 | 54.27 | 54.8 |
| TiO ₂ | 0.20 | 0.15 | 0.52 | 0.38 | 0.12 | 0.57 | 0.17 |
| Al ₂ O ₃ | 10.0 | 9.7 | 10.7 | 12.74 | 7.23 | 8.20 | 11.6 |
| Fe ₂ O ₃ | 3.5 | 4.3 | 2.0 | 0.88 | 0.18 | 4.65 | 17.3 |
| FeO | 3.2 | 3.1 | 3.8 | 1.64 | 1.34 | 3.69 | 0.8 |
| MnO | 0.02 | 0.05 | 0.04 | 0.00 | 0.01 | 0.37 | 0.22 |
| MgO | 8.2 | 7.7 | 7.7 | 8.01 | 13.24 | 7.35 | 0.91 |
| CaO | 13.3 | 13.1 | 15.0 | 12.45 | 19.52 | 13.52 | 1.24 |
| Na ₂ O | 6.8 | 6.8 | 5.9 | 7.05 | 3.30 | 7.20 | 13.3 |
| K ₂ O | 0.01 | 0.02 | 0.02 | 0.40 | 0.02 | — | 0.00 |
| Atom | Atomic Proportions Relative to Six Oxygens | | | | | | |
| Si | 1.96 | 1.98 | 1.97 | 1.98 | 1.97 | 1.99 | 1.98 |
| Ti | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.02 | 0.01 |
| Al | 0.43 | 0.41 | 0.45 | 0.53 | 0.30 | 0.35 | 0.49 |
| Fe ³⁺ | 0.10 | 0.12 | 0.05 | 0.02 | 0.01 | 0.13 | 0.47 |
| Fe ²⁺ | 0.10 | 0.10 | 0.11 | 0.05 | 0.04 | 0.11 | 0.02 |
| Mg | 0.44 | 0.41 | 0.41 | 0.42 | 0.70 | 0.40 | 0.05 |
| Ca+Na+K | 0.99 | 0.98 | 0.99 | 0.98 | 0.98 | 1.04 | 0.98 |

^a Coleman *et al.* (1965).

^b Morgan (1967).

^c Essene and Fyfe (1967).

^d Dixon (1968).

on samples with such a low percentage of iron. Close to 10 percent absorption was observed for the minerals containing relatively large percentages of Fe³⁺, while Cam958, with just over 1 percent by weight Fe²⁺ gave about 1 percent uncorrected absorption.

COMPUTER ANALYSIS OF THE RESULTS

The method used to fit the spectra (Stone, 1967) will be described briefly here because of its great importance to the

interpretation of these complex spectra. The observed spectrum consists of 400 numbers defining an envelope, and the problem thus consists of finding the shapes and positions of a number of lines which, when superimposed, give the best fit to the observed envelope. Fortunately, the Mössbauer line shapes, using our Co⁵⁷ in Pd source and mineral absorbers, have been found to be essentially ideal Lorentzians. Thus, the intensity of the transmitted gamma beam $y(x)$ as a function of its energy x has the following form:

$$y(x) = b - \frac{y(0)}{1 + \left(\frac{x - x(0)}{a/2}\right)^2}$$

where $y(0)$ is the intensity at the resonance energy (or velocity) $x(0)$, a is the width at half-height, and b is the baseline intensity. Thus the equation of the envelope for n lines becomes:

$$y(x) = b - \sum_i \frac{y(0)_i}{1 + \left(\frac{x - x(0)_i}{a/2}\right)^2} \quad (1)$$

Finally, a small baseline correction term $C \sin 2\pi(x - \phi)/400$ is added to correct for a very slight sinusoidal variation of the baseline due to source movement.

For an n -line spectrum, $y(x)$ is a function of $3n + 3$ parameters (position, width and intensity of each line, plus the baseline, baseline correction, and scan center), denoted q_i and written as a vector q .

One wishes to minimize the weighted sum of the squares:

$$\chi^2 = \sum_{r=1}^{400} w_r [y_r - y(x_r | q)]^2$$

where y_r is the observed count at channel r , $y(x_r | q)$ is the function (1) above, and w_r is the inverse of the variance for channel r .

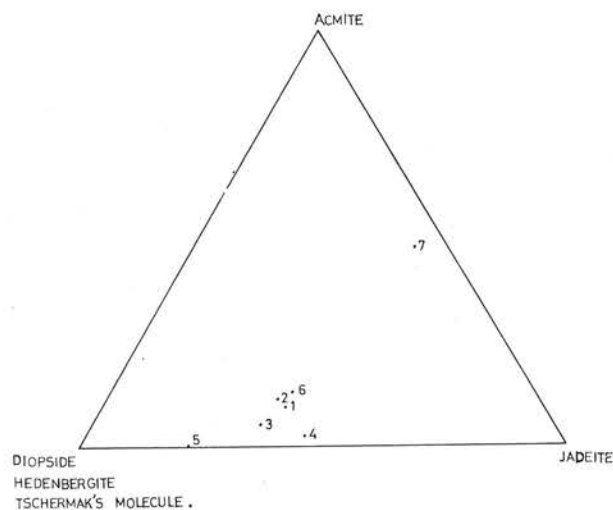


FIG. 1. Composition of the pyroxenes studied 1. 100-RGC-58; 2. 102-RGC-58; 3. 113-RGC-58; 4. Ca 1059; 5. Cam 958; 6. JD 1059; 7. 88-SM-2.

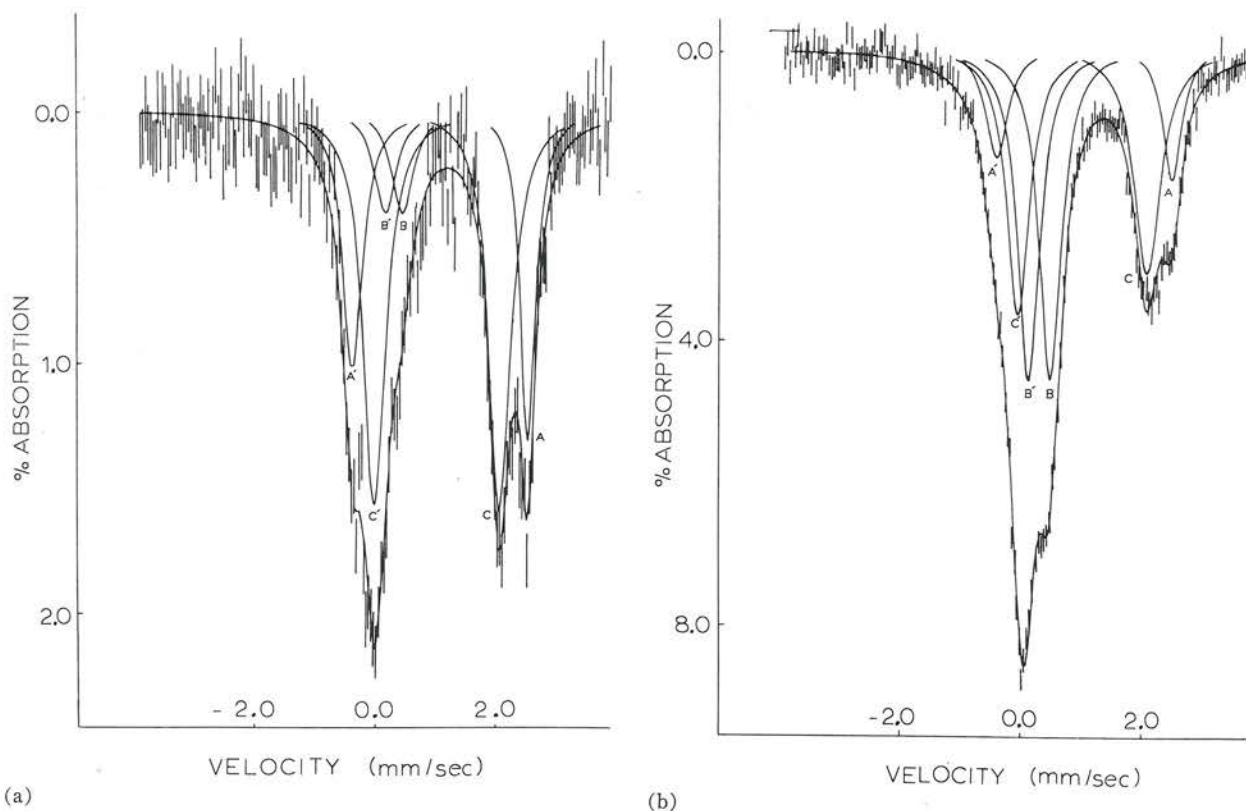


FIG. 2. Six-line computer fits to the Mössbauer spectra of: a) Ca 1059; b) 102-RGC-58. Letters A,A' and C,C' designate two ferrous doublets; B,B', a ferric doublet.

Initial estimates are chosen for the $3n + 3$ parameters q_i , and using:

$$\frac{d\chi^2}{dq_i} = 0$$

for each q_i , corrections are determined for each q_i such that χ^2 is minimized. This constitutes one iteration. The Cambridge University Atlas II computer is used to repeat the procedure using the corrected estimates from the previous iteration, until the values of χ^2 obtained in successive iterations differ by less than a suitable small quantity, chosen to be 10^{-6} . This normally takes from 5 to 10 iterations, depending upon the accuracy of the initial estimates. A statistically acceptable value of χ^2 (the 5% point) is about 450 for these spectra.

One of the advantages of this technique is that it enables any one parameter to be held constant, or any number of parameters to be held equal to each other, though not necessarily constant, throughout all, or any part of the fitting process. With complex spectra, it sometimes happens that χ^2 diverges instead of converging to a constant minimum value. The system of linear constraints mentioned above, together with experience of fitting many spectra, greatly assists in overcoming this difficulty. Thus, for the spectra in this study, the half-widths and intensities of the two components of a quadrupole doublet are held equal during the fitting process. These constraints have been justified in previous papers (Bancroft, Burns and Stone, 1968; Bancroft and Burns, 1969). Furthermore, as described later, it is considered reasonable, on the basis of previous experience, to constrain the half widths of the ferrous doublets in different crystallographic sites to be equal.

RESULTS AND THE VALIDITY OF THE FITS

Two six-line spectra are illustrated in Figure 2 and four ten-line fits, to 102-RGC-58, 113-RGC-58, JD1059, and Cam958 are shown in Figure 3, together with the spectrum of an aegerine-jadeite, 88-SM-2. The center shifts, quadrupole splittings, and half-widths are given in Table 2, together with predicted errors. The center shifts are quoted with respect to a stainless steel source. To convert these figures to values relative to sodium nitroprusside, 0.16 mm/sec should be added. The fractional amount of ferrous iron, and the ratio of ferric to total iron are quoted as percentages in Table 3. We assume that the areas are directly proportional to the amount of iron present (Bancroft, 1969). Standard deviations are quoted for the fractional amount of ferrous iron in site 1, and for the ratio of ferric to total iron, (except for Cam958) where the peaks are reasonably well resolved. Other percentages should be regarded as being only qualitatively correct.

The first stage of computing consists of fitting these spectra to six lines (fig. 2)—a ferric doublet (peaks B and B') and two ferrous doublets (peaks A and A', and C and C'). These fits look satisfactory to the uninitiated, but there are several pieces of evidence which suggest very strongly that these fits are incomplete:

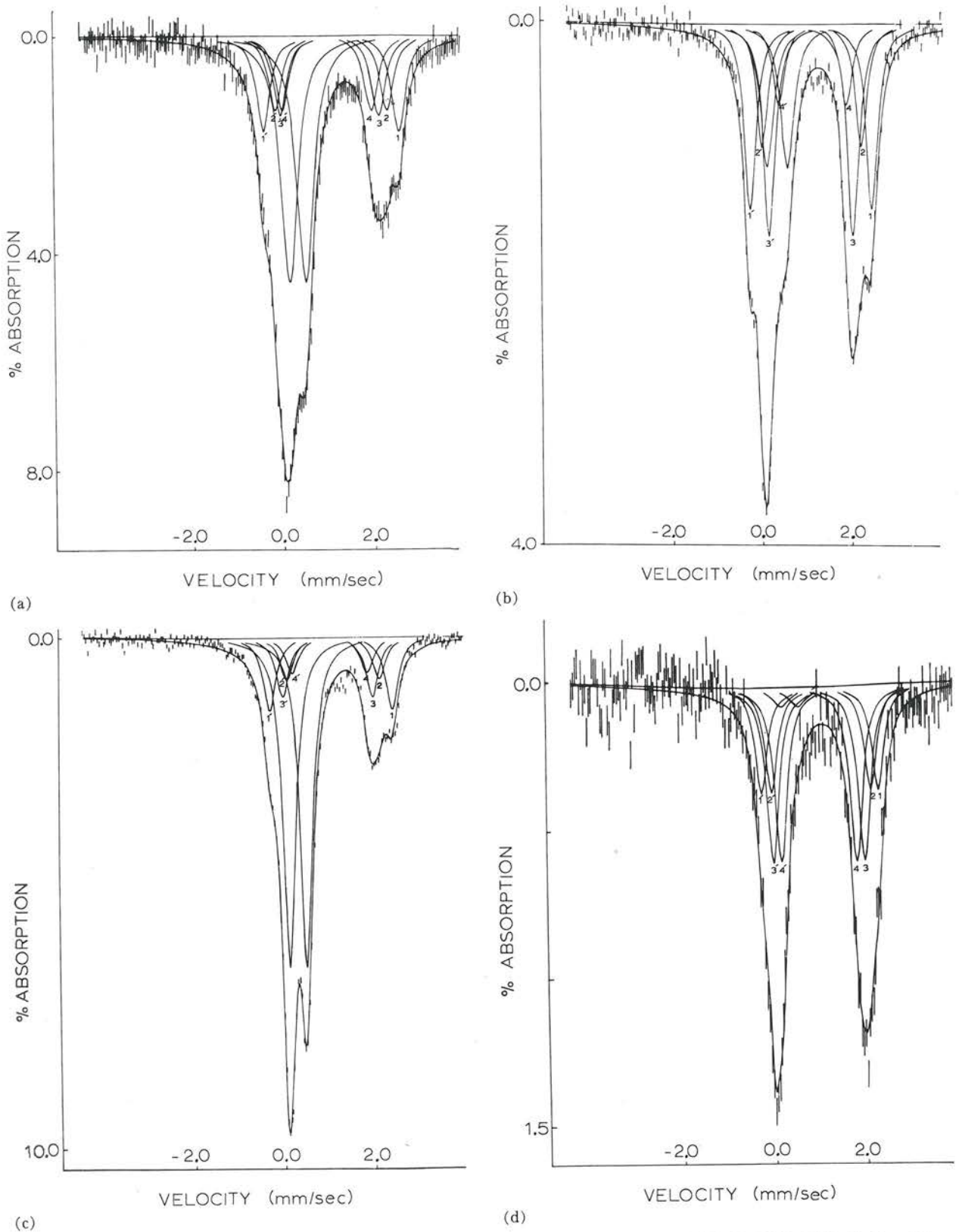


FIG. 3. Final ten-line computer fits to the Mössbauer spectra of: a) 102-RGC-58, b) 113-RGC-58, c) JD 1059, d) Cam 958. Numerals 1,1' to 4,4' designate the four ferrous doublets; the unlabelled doublet is due to ferric iron.

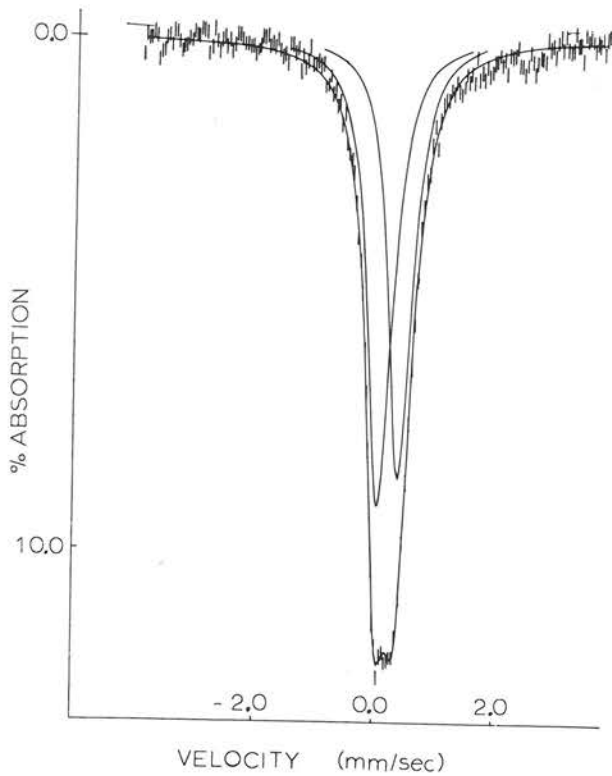


FIG. 4. Mössbauer spectra of sample 88-SM-2.

1. The half-widths of the Fe²⁺ peaks are very dissimilar. For example, the full width at half height of peaks A and A' in 113-RGC-58 is 0.33 mm/sec, while the width of peaks B and B' is 0.55 mm/sec. In all previous work, it has been found that if each of the ferrous peaks in a complex spectrum arises from one structural type of ferrous iron, the different peaks are very similar in width (± 0.03 mm/sec) (Bancroft, Burns and Maddock, 1967).
2. The χ^2 values are larger than usual.

TABLE 3. MÖSSBAUER SITE POPULATIONS^a

| Sample | Percent Fe ²⁺ /total Fe | | Percent Fe ²⁺ /total Fe ²⁺ | | | |
|------------|------------------------------------|-------------------|--|----------------|------|------|
| | Mössbauer | Chemical analysis | Mössbauer | | | |
| | | | i=1 | i=2 | i=3 | i=4 |
| 102-RGC-58 | 48.3±0.7 | 55.5 | 29.7±2.3 | 22.9 | 24.5 | 22.9 |
| 113-RGC-58 | 21.8±0.4 | 32.1 | 30.9±1.0 | 20.2 | 35.4 | 13.5 |
| Ca1059 | 14.1±1.4 | 32.6 | 36.8±2.5 | not determined | | |
| Cam958 | 4.5±1.7 | 11.0 | 18.6 | 18.6 | 31.4 | 31.4 |
| JD1059 | 60.1±0.2 | 53.1 | 34.5±1.3 | 20.3 | 28.1 | 17.1 |

^a Site populations for sites 2, 3 and 4 should be regarded as being only qualitatively accurate (see text). Errors quoted are standard deviations.

3. The preliminary spectrum of 113-RGC-58 at 80°K, gave a six-line fit totally inconsistent with the room-temperature spectrum. The liquid N₂ spectrum showed a distinct shoulder on the low velocity side of the ferrous envelope.

In several spectra, we then fit eight peaks, giving a marked decrease in χ^2 of approximately 50, and more reasonable half widths. However, the half widths were still markedly different from peak to peak, and it is highly unlikely, from the X-ray structure, that there is Fe²⁺ in three sites, as opposed to two or four.

At this stage, it appeared highly probable that there were indeed four ferrous doublets, but to fit four doublets to these spectra required many constraints in order that the fitting process did not diverge. We constrained all the low velocity peaks as in the six- or eight-line fits, and proceeded to fit four peaks (1, 2, 3, 4) in the high velocity region, constraining the half widths and intensities to be equal to each other, but not at any fixed value. Again, χ^2 decreased by about 20, usually to about 370. The intensity constraints were then released, usually giving only a marginal decrease in χ^2 . We then fit four corresponding peaks (1', 2', 3', 4') in the low velocity region, constraining the intensities in pairs, the half widths at the best value from the previous fit, and attempting to pair the peaks off so that the C.S. values

TABLE 2. MÖSSBAUER PARAMETERS (MM/SEC)^a

| Sample | Fe ²⁺ | | | | | | | | | Fe ³⁺ | | |
|--------------|------------------|------|------|------|------|------|------|------|------|------------------|------|------|
| | 1. | | 2. | | 3. | | 4. | | | C.S. | Q.S. | H.W. |
| | C.S. | Q.S. | C.S. | Q.S. | C.S. | Q.S. | C.S. | Q.S. | H.W. | | | |
| 102-RGC-58 | 1.26 | 2.88 | 1.27 | 2.35 | 1.22 | 2.09 | 1.20 | 1.89 | 0.36 | 0.53 | 0.34 | 0.44 |
| $\chi^2=400$ | 0.03 | 0.05 | 0.03 | 0.05 | 0.03 | 0.05 | 0.03 | 0.05 | .02 | .03 | .05 | .02 |
| 113-RGC-58 | 1.26 | 2.87 | 1.27 | 2.32 | 1.26 | 1.97 | 1.28 | 1.58 | .33 | .46 | .48 | .38 |
| $\chi^2=440$ | 0.03 | 0.05 | 0.03 | 0.05 | 0.03 | 0.05 | 0.03 | 0.05 | .02 | .03 | .05 | .02 |
| Cam958 | 1.26 | 2.72 | 1.29 | 2.32 | 1.23 | 2.13 | 1.23 | 1.76 | .34 | .55 | .40 | .50 |
| $\chi^2=393$ | 0.05 | 0.10 | 0.05 | 0.10 | 0.05 | 0.10 | 0.05 | 0.10 | .05 | .05 | .10 | .15 |
| JD1059 | 1.25 | 2.84 | 1.25 | 2.25 | 1.23 | 1.98 | 1.23 | 1.74 | .36 | .48 | .40 | .35 |
| $\chi^2=660$ | 0.05 | 0.08 | 0.05 | 0.08 | 0.05 | 0.08 | 0.05 | 0.08 | .03 | .05 | .08 | .02 |
| 88-SM-2 | | | | | | | | | | .49 | .33 | .48 |
| $\chi^2=492$ | | | | | | | | | | .01 | .01 | .02 |

^a The error in each number is quoted below the number. C.S. = center shift, Q.S. = quadrupole splitting, H.W. = half-width.

for all four doublets were approximately equal. At this stage the χ^2 value often increased markedly, but it should be realised that we are now really forcing the fit in order to obtain reasonable parameters. For example, the assumption of equal intensities is not perfect and the Fe^{3+} lines are due to a superposition of lines which may not be Lorentzian.

In the Cam958 spectrum, the positions of the small Fe^{3+} peaks were constrained at the six-line fit value, and the intensities of the ferrous lines were constrained in pairs. In 113-RGC-58 and JD1059, there appears to be a small absorption at about 1 mm/sec; the cause of this is unknown to us at the present, but it obviously results in a much larger χ^2 in JD1059.

The ten-line fits give parameters which are internally consistent for the four omphacites; also these parameters are what we would expect on the basis of previous experience. Thus the C.S. values are about 1.25 mm/sec for all sites in all spectra. Ferrous iron in the orthopyroxene spectra give very similar center shifts, as do other six-coordinate Fe^{2+} species. The ferrous half widths are identical (within error) for all spectra, and are similar to the half widths for other silicates. There is a little more variation in Q.S. values, from spectrum to spectrum, but they lie within the expected errors. Also, we would expect the Q.S. value to be more sensitive than the C.S. or half width to small structural changes. The ferric parameters are also very similar to those for the aegerine-jadeite. It is also gratifying that the pattern of ferrous intensities is very similar for 102-RGC-58, 113-RGC-58, and JD1059, especially since the former two come from the same locality.

DISCUSSION OF RESULTS

The five omphacite spectra reported in this paper contain four ferrous doublets and are distinctly different from the spectrum of a $C2/c$ hedenbergite reported earlier (Bancroft *et al.*, 1967). This spectrum (and most likely the spectrum of any $C2/c$ pyroxene) shows two ferrous doublets: one due to Fe^{2+} in the $M1$ position and the other due to Fe^{2+} filling the calcium deficiency in the $M2$ position. Clark and Papike have already shown that 113-RGC-58 and 102-RGC-58 have $P2$ symmetry. The similarity of all these omphacite spectra suggests that JD 1059, Ca 1059 and Cam 958 also have $P2$ symmetry. On the basis of composition it is surprising that Cam 958 has $P2$ symmetry. Because of the very low iron content of this sample and the resulting poor spectrum, this evidence should not be taken as conclusive. It is hoped that our prediction will be confirmed by X-ray methods. These spectra indicate, however, the Mössbauer spectroscopy should be useful in characterizing $P2$ omphacites and clinopyroxenes with space-group symmetry intermediate between $P2$ and $C2/c$.

Because the $M2$ -O bond distances are so large, and Fe^{2+} does not substitute for Ca^{2+} in other silicate structures such as actinolite, it is highly unlikely that Fe^{2+}

will occupy $M2$ positions in omphacites—unless this site is deficient in cations. As can be seen in Table 1, there is often an extremely small deficiency in the $M2$ sites which could be filled by Fe^{2+} . Assuming for the moment that Fe^{2+} does fill the very small Na+Ca discrepancy, we would then assign the outer two doublets to Fe^{2+} in either two or four $M2$ positions, and the inner two doublets to Fe^{2+} in either two or four $M1$ positions. This interpretation would be consistent with the hedenbergite spectrum, where the outer doublet is due to Fe^{2+} in the Ca ($M2$) position and the inner doublet is due to Fe^{2+} in the $M1$ position. This interpretation seems very unlikely for the following reasons:

1. The intensity of the outer two peaks in 113RGC, 102RGC and JD1059 suggest that at least half of the total Fe^{2+} (~ 0.05 atom per formula unit) along with some Mg^{2+} enters the $M2$ sites, implying either that the chemical analyses for Na+Ca are in large error (especially in JD1059), or that our samples do not reflect the chemical analyses quoted (*e.g.* due to zoning), or that Na and/or Ca enters the $M1$ sites.

2. We would expect that the amount of Fe^{2+} in the $M2$ sites would increase as the Na+Ca discrepancy increased. This does not occur. For example, our spectra indicate that there is more Fe^{2+} in $M2$ sites in JD1059 than in 113-RGC-58, yet the chemical analyses indicate a surplus of Na+Ca in JD1059.

Alternatively, we assign the four Fe^{2+} doublets to the four $M1$ positions. This interpretation does not conflict with the chemical analyses, and at this stage seems more likely than the other assignment. The rest of the discussion depends on this assignment being correct.

It is rather difficult to assign the four ferrous doublets to a particular $M1$ position. In a previous work (Bancroft *et al.*, 1967) there was a general correlation between the Q.S. and site distortion from octahedral symmetry. However, looking at the metal-oxygen bond distances, there is no obvious difference in distortion from one site to another, as there is, for example, in orthopyroxenes.

The ferric doublet is assigned to Fe^{3+} in any or all of the $M1$ positions. Ferric center shifts and quadrupole splittings are not sensitive to small differences in site distortion, and in no silicate spectra to date have we been able to resolve Fe^{3+} in different sites.

From the quoted average bond distances for these sites, it is rather surprising that appreciable amounts of Fe^{2+} enter the smaller $M1$ sites. However, the omphacite structure indicates a much larger than usual variation of bond distances (within each average), and also there is some difficulty in providing an explanation for charge balance on a simple ionic model (Clark and Papike, 1966). Our results may be useful in explaining these difficulties, and indicate the dangers of using bond length criteria for cation assignments in these complex structures.

The percentages of ferric iron (Table 3) from

Mössbauer areas are not in good agreement with chemical analysis values. As discussed in another paper (Bancroft and Burns, 1969), the Mössbauer method appears to be much more reliable and accurate than chemical analysis. As Essene and Fyfe (1967) have pointed out, an accurate knowledge of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio is essential in order to calculate the percent jadeite in these minerals. Using Mössbauer area ratios, it will now be possible to obtain this ratio accurately, and knowing the total iron from chemical analysis, a more precise percent jadeite may now be calculated (Table 4). From Table 4 it can be noted that there is little difference between the two values since the percent jadeite is determined principally by the Na content. The importance of this determination in potentially estimating the temperature and pressure of formation has been discussed (Essene and Fyfe, 1967).

Appreciable amounts of Fe^{2+} enter all four M1 sites; however, the three peaks (2, 3, and 4) all lie within about 0.35 mm/sec of each other, and any area estimates from such closely overlapping peaks must be regarded as being only of a qualitative nature. The results at 80°K should enable us to obtain accurate site populations for at least one more of these ferrous peaks. However, the percentage of ferrous iron in site 1 should be accurate to the values quoted in Table 3 because this peak is well resolved in each spectrum (except for Cam958). The percentage of Fe^{2+} in site 1 varies markedly from mineral to mineral *i.e.* in the order Com958 < 102-RGC-58 < 113-RGC-58 < JD1059 < Ca 1059. These site populations could be a useful indication

TABLE 4. COMPARISON OF JADEITE PERCENT OBTAINED FROM MÖSSBAUER RATIOS AND FROM CHEMICAL ANALYSIS

| Sample | Percent Jadeite | |
|------------|---------------------------------|--------------------------------|
| | Mössbauer ratios ^{a,b} | Chemical analysis ^b |
| 102-RGC-58 | 37.2 | 35.7 |
| 113-RGC-58 | 37.1 | 35.4 |
| Ca1059 | 47.4 | 46.1 |
| Cam958 | 22.6 | 22.3 |
| JD1059 | 36.3 | 38.0 |

^a Obtained by dividing the total iron from chemical analysis in the ratio given in Table 3.

^b Jadeite calculated as $\text{Jd} = \text{Na}^+ - \text{Fe}^{3+}$

of the *P-T* conditions of the minerals. The similarity of 102-RGC-58 and 113-RGC-58, which are from the same area, should be noted. One would expect that as the temperature increased and the pressure decreased, Fe^{2+} in these four sites would tend to disorder, *i.e.* Fe^{2+} in site 1 would tend to 25 percent of total. However, Dixon (pers. commun.) has estimated that his sample formed at 13 kbar and about 400°C, whereas Morgan (1967) estimated that Ca1059 formed at 540°C and 7 kbar. On this basis we would expect JD1059 to be much more ordered than Ca1059. It is hoped to resolve such discrepancies by studying a wide range of omphacites which, from mineralogical evidence, formed under a variety of temperature and pressure conditions.

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