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Omphacite studies, II. Mössbauer spectra of *C2/c* and *P2/n* omphacites

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Abstract

Mössbauer spectra of two *C2/c*, seven *P2/n*, and three *P2/n* omphacites annealed at 300° to 1000°C and 15 to 18 kbar, have been recorded at 295 K and in some cases at 110 K. The Mössbauer spectra of both *C2/c* and *P2/n* omphacites contain three ferrous doublets which have been assigned, on the basis of Mössbauer and compositional evidence, to Fe^{2+} in the *M1* position. The three *M1* doublets arise from next-nearest-neighbor effects caused by different combinations of Ca^{2+},Na^{+} cations in the *M2*, *M2(1)* positions. The doublets are characterized by Q.S. values of ~2.8 mm/sec, ~2.2 mm/sec and ~1.8 mm/sec, and arise respectively from the Ca^{2+}, Na^{+} combinations: 1Ca 2Na, 2Ca 1Na, and 3Ca. The trend in the relative ferrous peak areas with Ca/(Na+Ca) ratios is in agreement with theoretical predictions, and the observed and theoretical relative ferrous peak areas are in good agreement, particularly for *C2/c* samples. The Mössbauer spectra of samples of *P2/n* omphacites annealed below and above the *P2/n* ⇄ *C2/c* transition temperature are very similar. Thus, the nearest-neighbor environment of Fe^{2+} in omphacite is independent of (Mg,Fe^{2+}), Al^{3+} and Ca^{2+},Na^{+} long-range order. The *M1* quadrupole splittings in pyroxenes appear to increase greatly with increasing distortion of the *M1* site from octahedral symmetry.

Introduction

The crystal chemistry of omphacite clinopyroxenes was thoroughly studied and reviewed almost ten years ago (Clark and Papike, 1968; Clark *et al.*, 1969). Clark and Papike found that omphacites in a restricted composition range in the system Jd–Ac–Di–He–Tsch had the *P2* space group rather than the *C2/c* space group of jadeite and diopside. The *P2* structure has eight cation sites (four *M1* and four *M2*) rather than the two cation sites of the end members.

In an attempt to elucidate further the crystal chemistry of ferrous iron in omphacites, Bancroft *et al.* (1969) examined the Mössbauer spectra of a number of omphacites, mostly having the *P2* space group. The complex spectra definitely contained more than two ferrous doublets. Mainly to be consistent with the *P2* crystal structure, four ferrous doublets were fitted, and they were tentatively assigned to the four *M1* positions. Further Mössbauer work by Williams (1970) showed that the four-doublet fit was probably not correct for a Bavarian omphacite of probable *C2/c* space group.

Recent X-ray and Mössbauer studies strongly indicate that the above interpretation of the *P2* omphacite spectra is incorrect. Matsumoto *et al.* (1975) have determined the structure of a Japanese omphacite and found the space group to be *P2/n* rather than *P2*. It was also found that the true space group of the Californian omphacite studied by Clark and Papike (1968) was *P2/n*, and it is likely that all *P2* omphacites have the *P2/n* space group. The extra reflections satisfying the relation $h + l \neq 2n$ in *h0l* reflections are multiple reflections which disappeared when the precession angle was changed from 30° to 25°. In the *P2/n* space group, there are only four cation sites [*M1*, *M1(1)*, *M2* and *M2(1)*] rather than the eight sites in the *P2* space group. However, it does not seem likely that any of the four ferrous doublets can be assigned to the *M2* positions, mainly because of

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the large temperature-dependence of the four doublets (Williams, 1970; Bancroft *et al.*, 1971).

Dowty and Lindsley (1973) suggested that next-nearest-neighbor effects probably give rise to extra peaks in the omphacite Mössbauer spectra. Prior to 1971, it was always assumed that ferrous iron in one structural site in a silicate mineral would give rise to one doublet, with perhaps some broadening from next-nearest-neighbor effects (Bancroft *et al.*, 1967). Williams *et al.* (1971), Matsui *et al.* (1972), and Dowty and Lindsley (1973) noted that this assumption was not satisfactory for Ca,Fe^{2+} pyroxenes, and at least two *M1* doublets had to be present to interpret their spectra. Dowty and Lindsley showed that a distinct Fe^{2+} doublet arises from each of the four different combinations of Ca, Fe cations (3Ca, 2Ca 1Fe, 2Fe 1Ca, 3Fe) in the three next-nearest-neighbor *M2* sites surrounding Fe^{2+} in *M1*. They postulated that the next-nearest-neighbor effect was caused by slight positional adjustments of the oxygen atoms coordinating *M1*, in response to the differing occupancies of the three adjacent sites. Consistent with this postulate, Ohashi *et al.* (1975) determined the crystal structures of some minerals from the hedenbergite–ferrosilite suite studied by Dowty and Lindsley (1973), and found that there was positional disorder among the oxygen atoms surrounding the *M2* cations.

In this paper, we reinvestigate the Mössbauer spectra of a variety of natural and heat-treated omphacites, considering the ordered omphacites to have the *P2/n* space group. Of particular importance in this investigation are the spectra of *C2/c* omphacites (both natural and inverted *P2/n*) and a titanium ferro-omphacite which show the same features as the other *P2/n* samples investigated earlier. The Mössbauer spectra of both *P2/n* and *C2/c* samples are then readily interpreted by considering Ca,Na next-nearest-neighbor effects on ferrous iron in the *M1* site. Surprisingly, the Ca,Na ordering about *M1* does not change appreciably on going from the *P2/n* to the *C2/c* space group.

Experimental

The omphacite compositions (atomic proportions relative to six oxygens) are reported in Table 1, and listed in order of decreasing Ca/(Na+Ca) ratio. Mössbauer spectra of five of these minerals—JD1054, 113RGC, 102RGC, Ca1059, and Cam958—were recorded in previous studies (Bancroft *et al.*, 1969; Williams, 1970), but because of our different fitting procedure and interpretation, we include the new fits and appropriate fits from Williams (1970) for these minerals. Most of the minerals have been well characterized by X-ray diffraction. Refinements in the *P2/n* space group have been published for the Japanese omphacite SB26C (Matsumoto *et al.*, 1975)

Table 1. Omphacite compositions: atomic proportions relative to six oxygen atoms

	JD1054[a]	Cam958[b]	JD1013[a]	113-RGC-58[c]	102-RGC-58[c]	SB26C[d]	Ca1059[e]	Ti-Omp.[f]	JD951[a]
Si	1.97	1.96	1.99	1.95	1.97	1.92	1.98	1.95	1.99
Al	0.03	0.04	0.01	0.05	0.03	0.08	0.02	0.05	1.01
Al	0.14	0.26	0.23	0.40	0.38	0.40	0.51	0.44	0.39
Ti	----	----	----	0.01	0.00	0.01	0.01	0.05	----
Fe^{3+}	0.06	0.01	0.09	0.05	0.12	0.14	0.03	0.14	0.15
Fe^{2+}	0.08	0.04	0.11	0.11	0.09	0.08	0.05	0.33	0.02
Mn	----	----	----	0.00	0.00	----	----	----	----
Mg	0.72	0.70	0.55	0.41	0.43	0.39	0.42	0.05	0.42
Ca	0.82	0.75	0.69	0.58	0.50	0.52	0.47	0.45	0.47
Na	0.19	0.23	0.34	0.41	0.47	0.48	0.48	0.54	0.56
Ca/(Ca+Na)	0.81	0.77	0.67	0.59	0.52	0.52	0.49	0.46	0.46

[a] Dixon (1968).

[b] Essene, personal communication and Bancroft, Williams and Essene (1969).

[c] Coleman et al. (1965).

[d] Matsumoto, Tokonami and Morimoto (1975).

[e] Morgan (1970).

[f] Curtis et al. (1975), average of two analyses.

and the titanium ferro-omphacite (Ti–Omp., Curtis *et al.*, 1975). The two Californian specimens 102-RGC-58 and 113-RGC-58, and the Venezuelan omphacite Cal059, have been refined in the *P2* space group (Clark and Papike, 1968; Clark *et al.*, 1969), but all of these omphacites probably have the *P2/n* space group (Matsumoto *et al.*, 1975). For Cal059, single-crystal X-ray diffraction study has confirmed the suggestion of Matsumoto *et al.* that the true space group is *P2/n* (Fleet *et al.*, 1978). In the two *P2* structures refined by Clark *et al.* (1969, Table 10), the occupancies of positions which are equivalent in *P2/n* are more-or-less the same, and the distinction between the *P2* and *P2/n* structures of a given omphacite must be rather subtle. Hence, cation occupancies for the *P2/n* structure of Cal059 (Table 2) have been calculated by simply averaging the data for the near-equivalent position pairs in the Clark *et al.* refinement, and a separate least-squares refinement of the *P2/n* structure of Cal059 using the structure factor data of Clark *et al.* (1969, Table 12) gave identical results. On the basis of compositional criteria (Clark and Papike, 1968), both JD1054 and Cam958 should have the *C2/c* space group, and we have confirmed the *C2/c* symmetry for Cam958 using single-crystal precession techniques.

Samples of Cal059 and JD951 were heated under pressures of 15 to 18 kbar for one day at temperatures of 300, 500, 700, 900, and 1000°C (Fleet *et al.*, 1978). The products of the runs at 300, 500 and 700°C are unchanged from the unheated material. The 900 and 1000°C run products are, respectively, largely and wholly converted to the *C2/c* structure. Mössbauer spectra were obtained for most of the heated products, but only representative data are included in Table 3.

Mirror-image Mössbauer spectra were recorded in 512 channels using an Austin Science Associates spectrometer and a 50 mCi ^{57}Co in Cu source. The spectrometer was calibrated using a 99.99 percent natural Fe foil. All center shifts are given relative to sodium nitroprusside; subtract 0.26 mm/sec to convert to natural Fe (Bancroft, 1973). Between 75–150 mg of omphacite was used as the absorber, corresponding to between 1 and 5 mg/cm^2 natural Fe in the absorbers. Because of the very small amount of iron in most of these samples, long accumulation times were required to obtain reasonable statistics, and between 2×10^6 and 8×10^6 baseline counts were recorded for each spectrum. For Cal059, the small amounts required for the heating experiments (Fleet *et al.*, 1978) resulted in only about 1 mg/cm^2 of natural iron in the absorber, leading to absorptions of only about 1 percent.

Table 2. Cation occupancy factors in *P2/n* omphacites

Mineral	Cation Site	Fe	Al	Mg	Ca	Na
Cal059	M1	0.10	0.04	0.86		
Clark et al. (1969)	M1(1)	0.04	0.96			
	M2				0.28	0.72
	M2(1)				0.72	0.28
SB26C	M1	0.18		0.82		
Matsumoto	M1(1)	0.13	0.87			
et al. (1975)	M2				0.31	0.69
	M2(1)				0.72	0.28
Ti-Omp.	M1	0.78		0.22		
Curtis et al.	M1(1)	0.17	0.83			
(1975)	M2				0.28	0.72
	M2(1)				0.70	0.30

The spectra were fitted to Lorentzian line shapes using methods described earlier (Bancroft, 1973) and a program written by one of us (L.P.A.).

Results

Room-temperature Mössbauer spectra of four omphacite samples are shown in Figures 1–3, and the Mössbauer parameters are given in Table 3 for the spectra in this paper and the unpublished fits by Williams (1970), in order of increasing Ca/(Ca+Na) ratios. The titanium ferro-omphacite spectrum (Fig. 2) and the Cal059(700) spectrum (Fig. 1a) are entirely consistent with the other *P2/n* omphacite spectra recorded earlier. Two ferrous doublets are readily resolved visually. However, as detailed in the previous studies, the inner ferrous doublet is much broader than the outer doublet, and at least three doublets are required to obtain reasonable widths and statistically reasonable χ^2 values. In the previous study (Bancroft *et al.*, 1969), four ferrous doublets were fitted for crystal-chemical reasons, as outlined in the introduction. Statistically, however, it is not possible to choose between the three and four ferrous doublet fits (Williams, 1970), and with Fe^{2+} mainly in one *M1* position in the *P2/n* structure, there is no crystal-chemical reason for fitting more than three ferrous doublets. We therefore take three ferrous doublets to be the correct general fit to omphacite clinopyroxenes. The next-nearest-neighbor treatment below confirms this approach.

Similar constraints in the fitting procedure have been employed here as in the previous study (Bancroft *et al.*, 1969). The widths of all Fe^{2+} peaks are set

Table 3. Mössbauer parameters[a]

		Fe^{2+} peaks										Fe^{3+} peaks			$\frac{Fe^{3+}}{\text{total iron}}$ (%)		χ^{2}[e]	Ref.[f]
		1,1'			2,2'			3,3'										
Sample[b]	T,K[c]	C.S.	Q.S.	Rel.[d] Area	C.S.	Q.S.	Rel.[d] Area	C.S.	Q.S.	Rel.[d] Area	FWHM	C.S.	Q.S.	FWHM	Mössbauer	Chemical Analysis		
JD1054	295	not observed			1.45	2.55	0.32	1.46	1.95	0.68	0.47,0.35	0.78	0.41	0.49	27	43	412(418)	W
	110	not observed			1.51	2.82	0.40	1.52	2.36	0.60	0.45,0.40	0.74	0.53	0.50	26	43	403(428)	W
Cam958	295	not observed			1.48	2.41	0.47	1.46	1.99	0.53	0.49	0.63	0.33	0.43	10	11	529	TW
Cam958(1000)	295	not observed			1.45	2.55	0.39	1.43	1.90	0.61	0.46		not fit		--	--	564	TW
	110				1.59	3.09	0.38	1.61	2.37	0.62	0.41		not fit		--	--	446	TW
JD1013	295	1.49	2.81	0.27	1.45	2.27	0.27	1.46	1.89	0.46	0.41	0.74	0.41	0.43	56	45	435	TW
113-RGC-58	295	1.44	2.86	0.32	1.46	2.22	0.34	1.43	1.86	0.33	0.36	0.70	0.40	0.40	21	32	482(435)	W
102-RGC-58	295	1.43	2.86	0.31	1.46	2.27	0.30	1.37	1.99	0.39	0.42	0.71	0.36	0.43	48	56	404(431)	W
SB26C	295	1.43	2.84	0.44	1.41	2.13	0.44	1.45	1.77	0.12	0.42	0.67	0.43	0.43	58	64	923	TW
	110	1.53	3.13	0.40	1.54	2.55	0.33	1.58	2.07	0.27	0.37	0.74	0.46	0.46	60	64	578	TW
Cal059	295	1.45	2.88	0.40	1.44	2.23	0.30	1.42	1.85	0.30	0.34	0.69	0.42	0.44	19	33	518	TW
Cal059(700)	295	1.47	2.85	0.40	1.43	2.21	0.27	1.42	1.92	0.33	0.34	0.67	0.35	0.52	20	33	489	TW
Cal059(900)	295	1.46	2.84	0.40	1.44	2.24	0.31	1.46	1.77	0.29	0.39	0.65	0.41	0.38	19	33	552	TW
Cal059(1000)	295	1.43	2.82	0.41	1.42	2.25	0.31	1.42	1.69	0.28	0.36	0.67	0.41	0.34	12	33	564	TW
Cal059	110	1.53	3.15	0.41	1.53	2.47	0.34	1.51	2.26	0.25	0.38	0.74	0.37	0.45	18	33	556	TW
Cal059(700)	110	1.52	3.18	0.32	1.55	2.69	0.27	1.51	2.24	0.41	0.35	0.76	0.28	0.45	24	33	421	TW
Cal059(900)	110	1.52	3.12	0.44	1.53	2.59	0.29	1.51	2.12	0.27	0.34	0.75	0.43	0.51	21	33	460	TW
Cal059(1000)	110	1.52	3.06	0.43	1.54	2.49	0.32	1.49	1.93	0.25	0.34	0.78	0.34	0.43	12	33	566	TW
Ti-Omp.	295	1.45	2.96	0.47	1.42	2.31	0.27	1.41	1.94	0.26	0.31	0.69	0.56	0.32	22	29	761	TW
	110	1.52	3.22	0.48	1.52	2.67	0.30	1.53	2.29	0.23	0.31	0.80	0.38	0.31	22	29	608	TW
JD951[g]	295	1.38	2.84	0.34	1.32	2.38	0.34	1.24	2.11	0.32	0.38	0.68	0.48	0.38	78	88	812	TW
JD951(900)	295	1.39	2.79	0.41	1.37	2.27	0.31	1.36	1.63	0.28	0.45	0.67	0.44	0.49	71	--	484	TW
JD951(1000)	295	1.43	2.84	0.38	1.43	2.30	0.35	1.40	1.70	0.27	0.38	0.66	0.45	0.49	47[h]	--	597	TW

[a] All C.S. (center shift), Q.S. (quadrupole splitting) and FWHM (full width half maximum) are given in mm/sec. The C.S. values are quoted relative to sodium nitroprusside. Subtract 0.26 mm/sec to convert to Fe metal. The errors in the C.S. and Q.S. are ±0.05 mm/sec, except for JD951 for which the errors are ±0.10 mm/sec. The errors in the FWHM value are ±0.03 mm/sec.

[b] Whenever the sample has been heated for one day, the temperature (°C) is given in brackets.

[c] Temperature of measurement.

[d] The relative areas are given as fractions of the total absorption by ferrous iron. Errors are ±10%.

[e] The sum of the squares of the deviations (Bancroft, 1973, p.59). The number of degrees of freedom are 500 unless given in brackets.

[f] W refers to Williams (1970), and TW refers to this work.

[g] Poor quality Fe^{2+} data because of the very small Fe^{2+} intensity.

[h] Fe^{3+} has been reduced during the heating process.

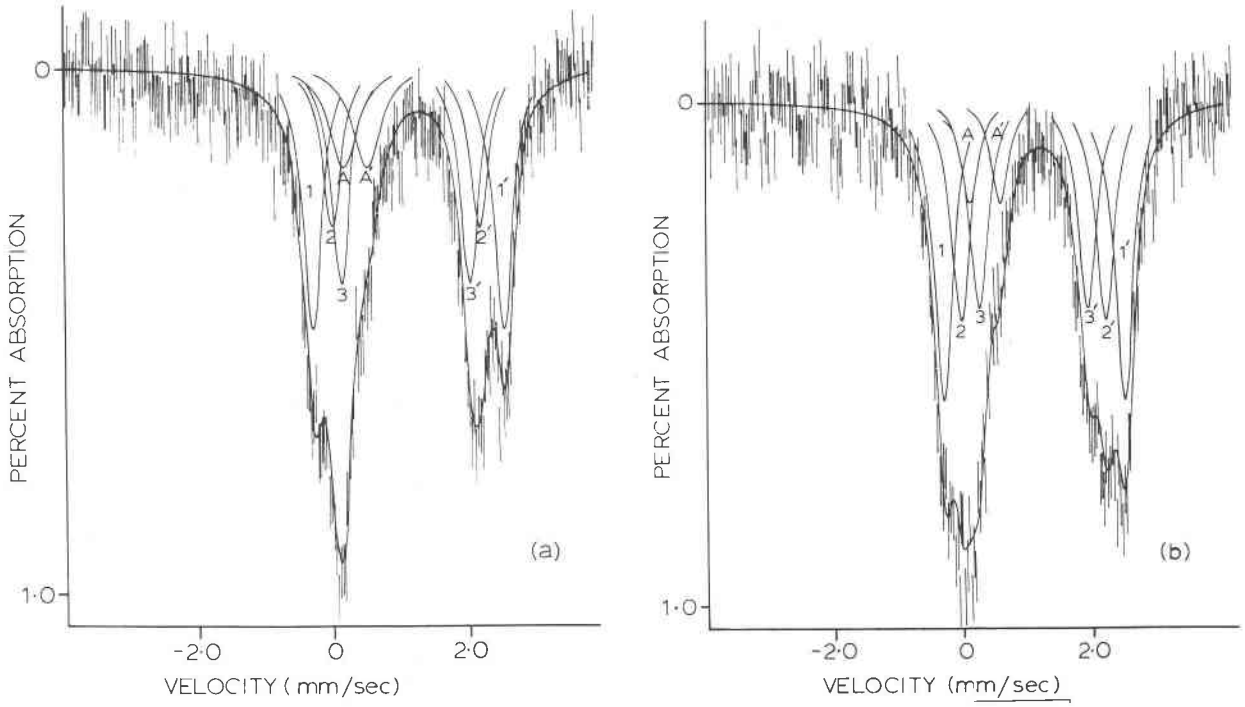

Fig. 1. Room-temperature Mössbauer spectra of Ca1059 after (a) heating to 700°C (*P2/n* space group) and (b) heating to 1000°C (*C2/c* space group)—both for one day. The 700°C spectrum is identical to the spectrum of the unheated sample published earlier (Bancroft *et al.*, 1969; Williams, 1970). Peaks A and A′ are the Fe^{3+} doublet, and doublets 1,1′, 2,2′, and 3,3′ correspond to the Fe^{2+} doublets as numbered in Tables 5 and 6.

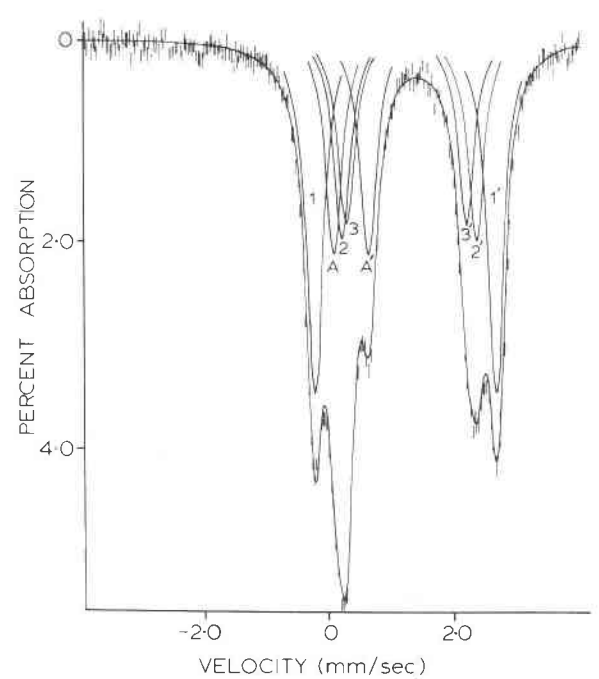

Fig. 2. Room-temperature Mössbauer spectrum of the titanium ferro-omphacite.

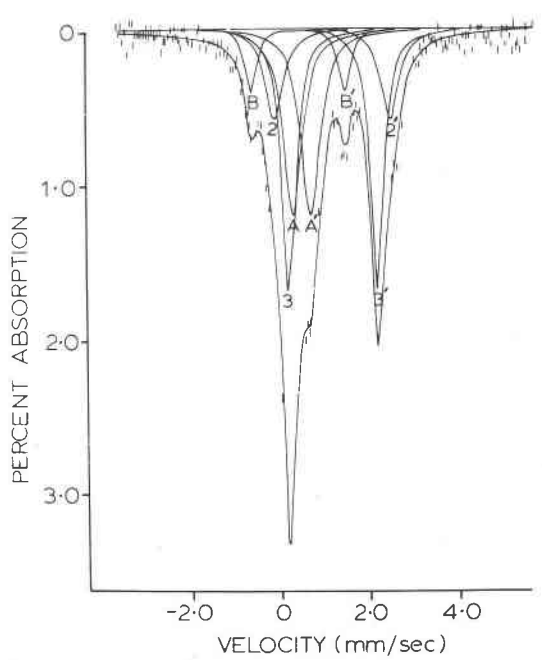

Fig. 3. Mössbauer spectrum of JD1054 at room temperature. Peaks B and B′ have a C.S. and Q.S. of 0.76 mm/sec and 1.98 mm/sec respectively, and are due to impurity epidote (Bancroft *et al.*, 1967).

equal to each other (but not at a fixed value), the Fe^{3+} peak widths are set equal, and the areas of the component peaks of a doublet are constrained to be equal. For JD951 and SB26C spectra, additional position constraints had to be employed. Because of the very small amount of Fe^{2+} in JD951 (Table 1), the errors in the parameters are substantially larger than the errors for other samples (footnotes a and g to Table 3).

The use of three ferrous doublets in this study, as opposed to four ferrous doublets in our previous study, illustrates the difficulties in computing such complex spectra, and reinforces the computing philosophy outlined previously (Bancroft, 1973). First, one *must* use the well justified width and area constraints if one wishes to even begin interpreting such complex spectra. Second, because the χ^2 values for both three and four doublet fits are *very* similar, one *must* resort to other physical evidence to fit the spectra. The crystal-chemical and Mössbauer evidence in 1969 suggested that a four ferrous doublet fit was more reasonable than a three doublet fit, and a four ferrous doublet fit gave *consistent* Mössbauer parameters. On the basis of the 1977–78 crystal-chemical and Mössbauer evidence, it is apparent that a three doublet fit (which also gives consistent results) is more reasonable than a four doublet fit, and the results below strongly suggest that we now have the correct interpretation of the spectra. However, it is always possible that we do not yet fully understand the crystal chemistry of omphacites (as tends to happen in science!), and there is still a possibility (albeit small) that the Mössbauer fits will have to be slightly modified at a later date.

The spectra of the *P2/n* and *C2/c* Ca1059 samples (Figs. 1a and 1b respectively, and Table 3) are qualitatively similar, and show conclusively that a *C2/c* sample, with only one possible *M1* site, also gives rise to a three ferrous doublet pattern. The outer two doublets in the two samples have the same C.S. and Q.S. within errors, while the inner ferrous doublet in the *C2/c* sample has a smaller Q.S. than in the *P2/n* sample. Even the relative ferrous peak areas are equal within the error in the two different space groups. The spectra of the high Ca *C2/c* samples JD1054 and Cam958 only show the two inner ferrous doublets (doublets 2 and 3), but the broad outer peaks (doublet 2 of width >0.45 mm/sec compared to ≤ 0.42 mm/sec for all other doublets in these two and all other samples) suggest a small contribution to the spectra from doublet 1 (≤ 10 percent of the total ferrous area).

The three ferrous doublet fits give consistent ferric and ferrous C.S. and Q.S. values for all samples. The ferric C.S. and Q.S. values are all 0.7 mm/sec and ~ 0.4 mm/sec respectively at room temperature. The three ferrous doublets have very similar C.S. values of ~ 1.4 mm/sec, as expected for Fe^{2+} in six-coordination (Bancroft, 1973), and the Q.S. values fall into three distinct groups: 2.8–2.9 mm/sec, 2.1–2.3 mm/sec, and 1.7–1.9 mm/sec for doublets 1, 2, and 3 respectively. JD1054 and Cam958 have larger doublet 2 Q.S. values of ~ 2.5 mm, at least partially due to the neglect of the small doublet 1 peaks which are almost certainly present. All the ferrous Q.S. values have a large temperature dependence. Thus, all Q.S. values increase by 0.3–0.4 mm/sec from 295 K to 110 K.

There are also several noticeable trends in the relative areas of the ferrous peaks with decrease in the Ca/(Na+Ca) ratio. The area of doublet 1 increases as the Ca/(Na+Ca) ratio decreases, while the area of doublet 3 decreases with a decrease in the Ca/(Na+Ca) ratio (Fig. 4). Thus the relative areas of doublets 1 and 3 in JD1054 [Ca/(Na+Ca) = 0.81] are ~ 0 and ≥ 0.6 respectively, while the corresponding relative areas for Ti-Omp [Ca/(Na+Ca) = 0.46] are ~ 0.5 and ~ 0.3 respectively.

Discussion

The available X-ray site occupancies (Table 2) strongly suggest that nearly all of the Fe^{2+} in *P2/n* omphacites is present in the *M1* position, and the Fe^{2+} content of the *M2*, *M2(1)* positions is negligible. The Mössbauer results are totally consistent with this suggestion, and indeed lend considerable support to it. In particular, the three ferrous Q.S. values are all temperature-dependent, and have a similar temperature-dependence to other ferrous Q.S. in pyroxene *M1* positions (Bancroft *et al.*, 1971; Dowty and Lindsley, 1973). In contrast, the more distorted *M2* site gives rise to a very small temperature-dependence of the Fe^{2+} Q.S. (Bancroft, 1973). None of the three ferrous doublets can be attributed then to Fe^{2+} in the *M2* or *M2(1)* positions. The similarity of the titanium ferro-omphacite spectrum with the spectra of other omphacites with similar Ca/(Na+Ca) ratio also argues strongly against any significant contribution of *M2*[or *M2(1)*] Fe^{2+} to these spectra. In the omphacites with very small Fe^{2+} contents (0.02–0.11 pfu Fe^{2+}), it always seemed possible that a substantial percentage of Fe^{2+} (although only ~ 0.01–0.03 Fe^{2+} pfu) could be present in *M2* or *M2(1)* if the Na+Ca chemical content was slightly overestimated. How-

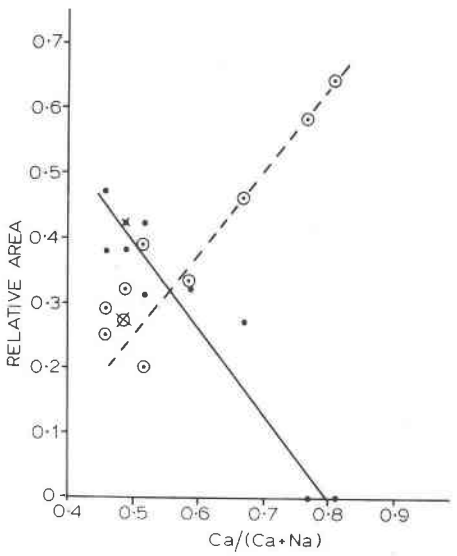

Fig. 4. Plot of relative area of the ferrous doublets 1 and 3 *vs.* Ca/(Ca+Na) ratio. Doublet 3 relative areas are denoted by circled dots, and doublet 1 relative areas are given by dots. The inverted *C2/c* Ca1059 samples are denoted by circled ×'s (doublet 3) and ×'s with dots (doublet 1). The data points are taken from the average of the 295 and 110 K results in Table 3. The lines (----, doublet 3; ——— doublet 1) are drawn only for clarity in defining the trends.

ever, the large Fe^{2+} content of the ferro-omphacite (0.33 Fe^{2+} pfu) makes it highly unlikely that greater than about 0.03 pfu (10 percent of the Fe^{2+}) could enter *M2* or *M2(1)*. On chemical grounds alone, the titanium ferro-omphacite spectrum must be due to Fe^{2+} in just the *M1* positions.

We conclude then that the three ferrous doublets are due to Fe^{2+} in just the *M1* position in both *C2/c* and *P2/n* omphacites. Following from Dowty and Lindsley's work on Ca,Fe next-nearest-neighbor effects in pyroxenes, we attribute the three ferrous doublets to the differing field gradients (and resulting Q.S.) presented by the three neighboring *M2* [and *M2(1)*] ions Na^+ and Ca^{2+} on Fe^{2+} in *M1*. Using the chemical analysis Na and Ca values for *C2/c* samples, and the site occupancy data from chemical analysis and X-ray work for the *P2/n* samples, we compute the probability (considering a random distribution) of having 3Ca, 2Ca 1Na, 1Ca 2Na, or 3Na in the three *M2* type sites surrounding the *M1* iron. The occupancy factors are different for the *C2/c* and *P2/n* specimens [see the results (Table 4) for Ca/(Na+Ca) = 0.50 for both space groups] because of the partial *M2(1)*, *M2* site ordering of Ca^{2+} and Na^+ in *P2/n* omphacite. The ordering of Ca^{2+} in *M2(1)* biases the statistical calculation to give a greater proportion of high Ca configurations (2Ca 1Na, 3Ca) in *P2/n* omphacite.

The three doublets 1, 2, and 3 can be associated readily with the *M2* configurations 1Ca 2Na, 2Ca 1Na, and 3Ca respectively. This assignment is based on two strong pieces of evidence. First, the calcium-rich JD1054 omphacite has a similar chemical content and a similar Q.S. (1.95 mm/sec) for its major doublet to the Q.S. (1.89 mm/sec) of a diopside of composition $Ca(Mg_{0.94}Fe^{2+}_{0.05})Si_2O_6$ (Bancroft *et al.*, 1971). Second, there is semiquantitative agreement between experimental and theoretical relative ferrous intensities. Thus, the Ca-rich omphacites such as JD1054 and Cam958 have the largest doublets, which are associated with the 3Ca configuration in *M2*; while the highest-Na members (such as titanium ferro-omphacite) have a much smaller doublet 3 and a larger doublet 1 (associated with 1Ca 2Na in *M2*). The lack of a ferrous doublet associated with the 3Na configuration in *M2* is not surprising, because on charge-balance considerations one would certainly not expect three monovalent Na ions in *M2* associated with ferrous ion in *M1*. Note here that the *M1* doublet associated with $3Na^+$ ions would likely have a Q.S. of greater than 3 mm/sec, giving a range of *M1* pyroxene Fe^{2+} Q.S. of much greater than 1 mm/sec.

The agreement between predicted and observed intensities for *C2/c* samples is semiquantitative. Thus for the 1000°C heated Ca1059 sample *(C2/c)*, the observed (and calculated) relative intensities are: 0(0.13), 0.42(0.37), 0.31(0.37), and 0.27(0.13) for the 3Na configuration and doublets 1, 2, and 3 respectively. The doublet associated with the 3Ca configuration (doublet 3) would be expected to have a larger intensity than expected on the random hypothesis because of charge balance considerations, *i.e.* Ca^{2+} in

Table 4. Probabilities of the four next-nearest-neighbor *M2* configurations of the *M1* sites in *P2/n* and *C2/c* omphacites

Space Group	Ca Na+Ca	Ca occupancy M2	Ca occupancy M2(1)	Na occupancy M2	Na occupancy M2(1)	3Na	2Na+Ca (1)	Na+2Ca (2)	3Ca[a] (3)
C2/c	0.81	0.81		0.19		0.01	0.09	0.37	0.53
	0.75	0.75		0.25		0.02	0.14	0.42	0.42
	0.67	0.67		0.33		0.04	0.22	0.44	0.30
	0.50	0.50		0.50		0.13	0.37	0.37	0.13
P2/n	0.50	0.27	0.73	0.73	0.27	0.05	0.31	0.50	0.14
	0.46	0.28	0.70	0.72	0.30	0.06	0.33	0.47	0.14

[a] Note that the M1 ferrous doublets correspond to: (1), 2Na+Ca in neighboring M2, M2(1); (2), Ca+2Na in M2, M2(1); (3), 3Ca in M2, M2(1).

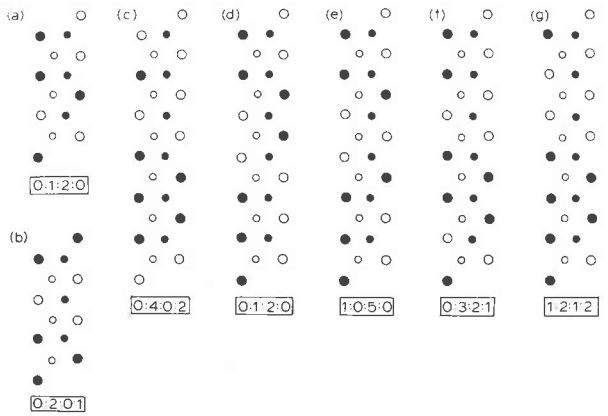

Fig. 5. Schematic arrangements of Ca^{2+} and Na^{+} adjacent to the $x = 1/4$ octahedral strip of *P2/n* omphacite, with Ca/(Na+Ca) = 0.5 and site occupancies of 1/3 Ca, 2/3 Na for M2 and 2/3 Ca, 1/3 Na for M2(1). The relative areas of the Fe^{2+} Mössbauer peaks are given below each strip for the M2(1), M2 cation combinations 3Na:1Ca 2Na:2Ca 1Na:3Ca respectively. Solid large circles, Ca; open large circles, Na; solid small circles, Al; open small circles, (Mg,Fe^{2+}).

M2 will tend to surround Fe^{2+} in *M1*, while Na^{+} in *M2* will tend to surround Al^{3+} in *M1*. Similarly, for JD1054, the observed (and calculated) intensities are: 0(0.01), ~0(0.09), 0.36(0.37), and 0.64(0.53). However, the agreement is not as good for the *P2/n* samples. The observed (and calculated) relative intensities for the *P2/n* Ca1059 samples are: 0(0.05), 0.38(0.31), 0.30(0.50), and 0.32(0.14). Clearly, charge-balance requirements modify the random population of the *M2(1)* and *M2* sites. Several arrangements of Ca^{2+} and Na^{+} cations in *P2/n* omphacite are illustrated in Figure 5. None of the ratios of the relative peak intensities for these arrangements compares with the corresponding observed ratio for *P2/n* Ca1059 samples. However, certain combinations of them (for example, f plus g) do give ratios approaching the observed data, and thus afford an impression of the type of short-range $Ca^{2+}$and Na^{+} clustering in *P2/n* omphacite.

Table 5. Average deviations from the mean of *M1*-O bond lengths and room temperature quadrupole splittings

Pyroxene	Average deviation of M1-O bond length from mean	Q.S. or (Average Q.S.)	Range of Q.S.
$CaMg(Fe^{2+})Si_2O_6$ diopside	0.026[a]	1.89[b]	---
$CaFeSi_2O_6$ hedenbergite	0.028[c]	2.22[d]	---
$FeMgSi_2O_6$ orthopyroxene	0.040-0.048[e]	2.35-2.49[f]	---
$Ca_{0.5}Fe_{1.5}Si_2O_6$ Hd-Fs	0.040[g]	(2.43)[d]	2.05-2.69[d]
$Ca_{0.3}Fe_{1.7}Si_2O_6$ Hd-Fs	0.040[g]	(2.40)[d]	2.10-2.69[d]
$Ca_{0.5}Na_{0.5}(MgFeAl)Si_2O_6$ omphacite	0.042[h]	(2.43)[i]	1.8-2.9[i]

[a] Clark, Appleman and Papike (1969).
[b] Bancroft, Williams and Burns (1971).
[c] Cameron, Sueno, Prewitt and Papike (1973).
[d] Dowty and Lindsley (1973), (weighted averages).
[e] Burnham, 1966, and Morimoto and Koto (1969).
[f] Bancroft, Maddock and Burns (1967).
[g] Ohashi, Burnham and Finger (1975).
[h] Average of the M1-O average deviation in SB26C (Matsumoto, Tokonami and Morimoto, (1975) and Ti-Omp. (Curtis, Gittins, Kocman, Ruckledge, Hawthorne and Ferguson (1975).
[i] This work, weighted averages from structures in three P2/n omphacites, Ca1059, SB26C and Ti-Omp.

The observed (and calculated) relative intensities for the *P2/n* Ca1059 samples are: 0(0.05), 0.38(0.31), 0.30(0.50), and 0.32(0.14). Clearly, charge-balance requirements modify the random population of the *M2(1)* and *M2* sites. Several arrangements of Ca^{2+} and Na^{+} cations in *P2/n* omphacite are illustrated in Figure 5. None of the ratios of the relative peak intensities for these arrangements compares with the corresponding observed ratio for *P2/n* Ca1059 samples. However, certain combinations of them (for example, f plus g) do give ratios approaching the observed data, and thus afford an impression of the type of short-range $Ca^{2+}$and Na^{+} clustering in *P2/n* omphacite.

As noted earlier, the Mössbauer spectra for the *P2/n* and inverted *(C2/c)* Ca1059 samples are very similar. Thus, the (Mg,Fe^{2+})–Al disorder, most probably associated with the $P2/n \rightleftarrows C2/c$ inversion, has not changed the overall proportion of the various possible nearest-neighbor Fe^{2+} environments in the inverted samples. The most obvious explanation for this phenomenon is that Ca^{2+} and Na^{+}, being intrinsically more mobile than the *M1* and *M1(1)* cations, have simply readjusted to new equilibrium distributions in response to charge-balance and space-fitting requirements.

The *M1* Q.S. values are of considerable interest. The range of *M1* Q.S. values in this study is greater than 1 mm/sec—considerably larger than that (~0.6 mm/sec) observed for the Ca–Fe pyroxenes (Dowty and Lindsley, 1973). Our larger range of Q.S. values results in better resolved spectra for omphacites than for the Ca–Fe pyroxenes. Following the Dowty and Lindsley interpretation of Ca–Fe pyroxenes, the data in Table 5 show that the *M1* Q.S. increases as the *M2* cation changes from Ca^{2+} to Fe^{2+} to Na^{+}; and that the Q.S. (or the weighted average of the *M1* Q.S.) increases as the distortion from octahedral symmetry of the *M1* site increases. Because the range of Q.S. values in omphacites is much larger than that for the Ca–Fe pyroxenes, it follows that the range of *M1* site distortions in the omphacites is larger than in the Ca–Fe pyroxenes. As argued by Dowty and Lindsley, this Q.S.-distortion correlation strongly suggests that these Q.S. values are associated with the positive slope of the F-distortion curve (Ingalls, 1964). For such small distortions from octahedral symmetry, the Q.S. increases greatly with small increases in distortion from octahedral symmetry.

The evidence in favor of the association of the three *M2* cation combinations 1Ca 2Na, 2Ca 1Na,

and 3Ca with the three Fe^{2+} doublets in omphacites appears most compelling. However, we recognize that we have left at least one problem unanswered. The positional disorder of the oxygen atoms in omphacites, as indicated by the magnitude of the thermal parameters, whilst somewhat greater than the corresponding data for the end-member composition (Clark *et al.*, 1969; Matsumoto *et al.*, 1975), is much less than that observed in Ca–Fe clinopyroxenes (Ohashi *et al.*, 1975). In contrast, the *M1* Q.S. values (above paragraph) suggest that the positional disorder of the oxygen atoms in omphacites should be larger than in the Ca–Fe clinopyroxenes—if the distortion of the oxygen polyhedra is the controlling factor on the *M2* Q.S. values. In addition, the site symmetry of the *M1* site in omphacite requires two different stereochemical configurations for each of the *M2* nearest-neighbor combinations, 1Ca 2Na and 2Ca 1Na. Presumably, these two configurations lead to very similar Q.S. values.

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