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MÖSSBAUER SPECTRA OF MINERALS ALONG THE DIOPSIDE-HEDENBERGITE TIE LINE

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ABSTRACT

The Mössbauer spectra of five $C2/c$ clinopyroxenes lying on, or close to, the diopside-hedenbergite tie-line are described. Four of the minerals give spectra containing a single doublet, which is assigned to Fe^{2+} in the $M1$ position. Parameters characteristic of this position are derived and discussed. Of particular importance is the large temperature dependence of the Q.S. of the $M1$ doublet, and the increase of the $M1$ Q.S. with increase of $Fe/(Fe+Mg)$.

The fifth sample is found to give more complex spectra. From Mössbauer spectra taken over a range of temperatures, it is concluded that there are three doublets present. The major doublet is assigned to Fe^{2+} in the $M1$ clinopyroxene position, with small doublets due to Fe^{2+} in the clinopyroxene $M2$ position and in the $M1$ position of actinolite (present as impurity). Although not conclusive, our present evidence suggests that the *Q.S.* of the $M1$ doublet decreases with increase in temperature until at ~450°K it becomes smaller than that of the $M2$ doublet, whose temperature dependence is very small.

INTRODUCTION

Although the Mössbauer spectra of orthopyroxenes are now well understood (Bancroft, Burns, and Maddock, 1967; Virgo and Hafner, 1969) very few spectra of $C2/c$ clinopyroxenes have been obtained, and there exists considerable confusion both as to the assignment of peaks and interpretation of areas. For example, three differing peak assignments have been made in the literature (Dundon and Lindsley, 1968; Bancroft, Burns, and Maddock, 1967; Matsui, Maeda, and Syono, 1970; Hafner and Virgo, 1970). In addition, "anomalous" areas in certain studies (Dundon *et al.*, 1967; Matsui *et al.*, 1970; Gay, Bancroft, and Bown, 1970) have made it difficult to be confident about any detailed interpretation. In this paper, we discuss the comparatively simple spectra of five minerals of the diopside-hedenbergite series. We indicate the great value of obtaining the spectra over a range of temperatures, both for these, and more complex spectra (Williams, Bancroft, Bown, and Turnock, 1971).

The composition of the minerals studied in this paper lie very close to the diopside-hedenbergite tie-line and can be represented by the formula $CaFe_XMg_{1-X}Si_2O_6 (0<X<1)$. Diopside has space group symmetry $C2/c$ (Clark, Appleman, and Papike, 1969) and although a detailed structure determination of hedenbergite has not been performed, the existence of complete solid solution along the diopside-hedenbergite tie-line indicates that hedenbergite and minerals along the diopside-hedenbergite tie-line also have space group symmetry $C2/c$.

The unit cell of a $C2/c$ pyroxene contains four formula units with four equivalent $M1$ positions and four equivalent $M2$ positions. Since Ca^{2+} ions enter the $M2$ position (Clark *et al.*, 1969 and references), the Mössbauer spectra of these minerals should consist of one doublet due to Fe^{2+} in the $M1$ position with perhaps a very small doublet due to Fe^{2+} entering any Ca^{2+} deficiency in the $M2$ position (Bancroft *et al.*, 1967). The simplicity of these spectra makes it possible to assign the $M1$ peaks with confidence, and enables a detailed study of the temperature dependence of the $M1$ quadrupole splitting to be performed.

EXPERIMENTAL

The chemical compositions of the four terrestrial and one synthetic clinopyroxene are listed in Table 1. The compositions range from one close to diopside (specimen 1) to two close to hedenbergite (specimens 4 and 5). Complete analyses were obtained for specimens 1, 4, and 5, while iron analyses were obtained for specimens 2 and 3. It should be noted that the calcium content of the diopside is 1.01 Ca^{2+} per formula unit; there should therefore be no calcium deficiency in the $M2$ position in this specimen. In specimens 2 and 3, the calcium content was assumed to be 1.00 ions per formula unit. The Mössbauer spectra of these two samples (vide infra) strongly support this assumption. These spectra gave no indication of more than one doublet, indicating little or no Fe^{2+} in the $M2$ position, and a very small, if any, Ca^{2+} deficiency in the $M2$ position.

Specimen 4 (2B) was examined by X-ray powder diffraction for impurities. No evidence for any impurities was found.

The Mössbauer spectrometer and methods are described in previous papers (Bancroft *et al.*, 1967). A 20 mC Co^{57} in Pd source was used for all spectra. All center shifts are quoted relative to sodium nitroprusside. Statistically acceptable χ^2 values were obtained for all spectra.

RESULTS AND DISCUSSION

a) *The M1 Peaks.* The Mössbauer parameters for the five specimens are summarized in Table 2. The center shift (*C.S.*) values are similar for all samples, but the quadrupole splittings (*Q.S.*) vary widely from mineral to mineral (1.89 mm/sec to 2.32 mm/sec at 295°K). All spectra gave relatively narrow symmetric lines (full widths at half height between 0.33 and 0.37 mm/sec), and with the exception of specimen 4, all spectra consisted of one narrow doublet (*e.g.*, Figure 1). As stated previously, the narrow symmetric lines strongly indicate that Fe^{2+} only enters one site in the clinopyroxene structure. The major doublet in specimen 4 (Table 2) gave parameters which are consistent with those of other samples. Details of this spectrum will be discussed later in this paper.

The major doublet in all these spectra can immediately be assigned to Fe^{2+} in the $M1$ position since there is little or no Ca^{2+} deficiency in the

TABLE 1

The composition of the minerals lying close to the diopside-hedenbergite tie-line expressed as atoms per formula unit

$X^{+2}Y^{+2}Si_2O_6$.

Mineral	Composition		
	Ca^{2+}	$(Mg^{2+} + Mn^{2+})$	Fe^{2+}
1) 80819[1]	1.01	0.94	0.05
2) R6955[2]	1.00	0.46	0.54
3) 103182[2]	1.00	0.23	0.77
4) 2B[3]	0.95	0.20	0.85
5) D9-35[4]	1.00	0.10	0.90

1. Analyst: J.H. Scoon
2. Partial Analysis: J.H. Scoon. Analysis for Fe^{2+} only. Ca^{2+} is assumed to occupy all the M_2 position. The Mössbauer spectra (see text) are consistent with this assumption.
3. Mueller (1960).
4. Analyst: A.C. Turnock - synthetic hedenbergite.

*M*2 position. Other Mössbauer evidence is consistent with this assignment. Firstly, the temperature dependence of the *Q.S.* for all specimens is very large and decreases with increase in Fe^{2+} content. This large temperature dependence is also characteristic of the orthopyroxene *M*1 doublet (Bancroft *et al.*, 1967; Hafner and Virgo, 1970). In contrast, the Fe^{2+} *Q.S.* in *M*2 pyroxene positions has been found to be very insensitive to temperature between 77°K and 295°K (Hafner and Virgo, 1970; Williams *et al.*, 1971). These temperature dependencies are expected considering the much larger distortion from octahedral symmetry of the *M*2 site (Ingalls, 1964). Secondly, the quadrupole splittings for this doublet show the same compositional trend as those observed for the *M*1 orthopyroxene doublet (Figure 2): as the iron content increases, the *Q.S.* increases for the terrestrial samples. In contrast, the orthopyroxene *M*2 doublet shows the reverse trend (Bancroft *et al.*, 1967). The synthetic sample (quenched rapidly from above 1000°C) shows a significantly

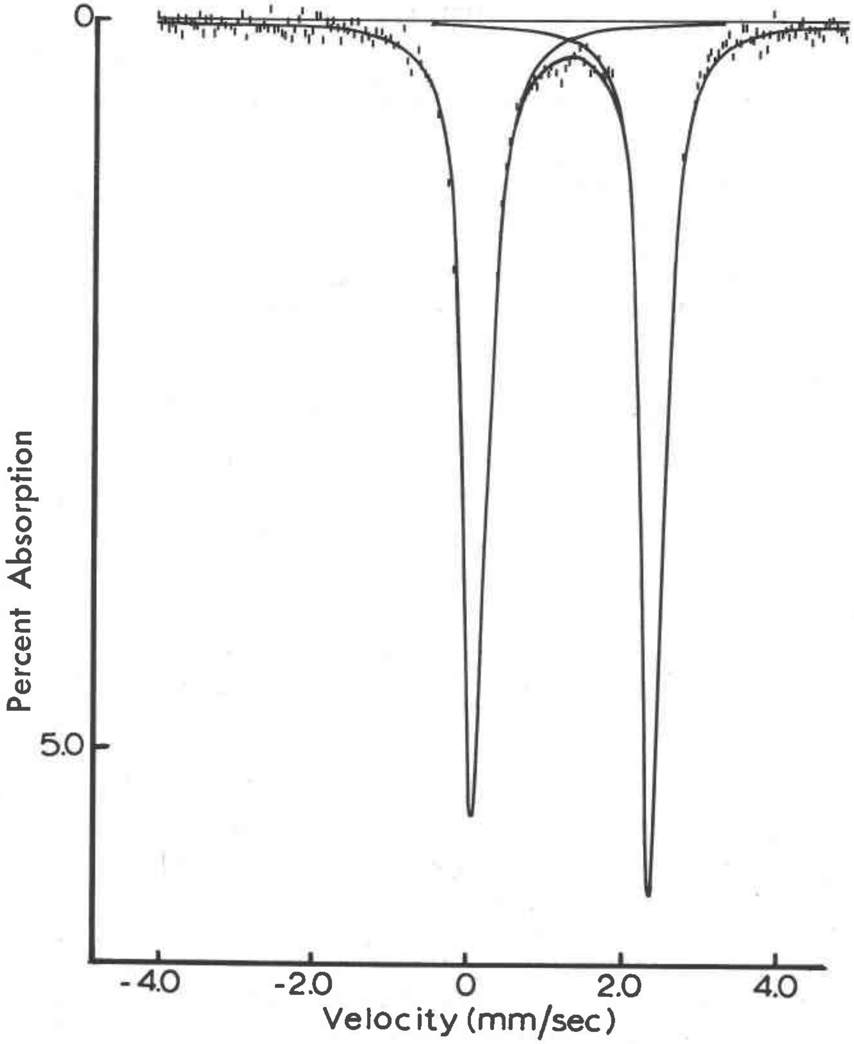


FIG. 1. Mössbauer spectrum of specimen 3 at 295°K.

lower *Q.S.* than the other hedenbergites. This result indicates that the *Q.S.* may be quite sensitive to the conditions of formation.

Surprisingly, however, the values of the *Q.S.* vary markedly from sample to sample at all temperatures and the *Q.S.* values are much smaller than any previously observed for the orthopyroxene or clinopyroxene *M*1 position (Bancroft *et al.*, 1967; Hafner *et al.*, 1970; Williams

TABLE 2

Mössbauer Parameters for ^{57}Fe in the M1 Position
in the Diopside-Hedenbergite Series*

Specimen	Temperature °K	Centre Shift mm/sec+	Q.S. mm/sec	Temperature-variation of the Q.S. mm/sec - °K
1	77	1.54	2.45	
	210	1.49	2.12	2.5×10^{-3}
	295	1.43	1.89	
2	77	1.54	2.57	
	295	1.56	2.13	2.0×10^{-3}
3	295	1.47	2.32	
4	77	1.50	2.71	1.9×10^{-3}
	210	1.51	2.41	
	295	1.50	2.32	
	680	1.22	1.46	
	815	1.05	1.08	
5	77	1.52	2.58	2.3×10^{-3}
	210	1.46	2.33	
	295	1.45	2.07	

* The full widths at half height are between 0.33 and 0.37 mm/sec for all spectra.

\+ All centre shifts are quoted relative to sodium nitroprusside.

et al., 1971). In fact, the room temperature *Q.S.* for the diopside is significantly smaller than almost all *M*2 *Q.S.* values in pyroxenes. This result shows that the *M*2 *Q.S.* may not always be smaller than the *M*1 *Q.S.* in pyroxenes, and indicates the necessity of obtaining spectra over a range of temperature to assign the lines in complex pyroxene spectra (Williams *et al.*, 1971).

b) *Specimen 4* (*2B*). As mentioned previously, the spectra of specimen 4 strongly indicate that there is more than one doublet present. In a previous room temperature spectrum of this sample (Bancroft *et al.*, 1967), a small doublet having a *Q.S.* of 2.7 mm/sec was fitted and assigned to the *M*2 position to fill the small Ca^{2+} deficiency (Table 1) of 0.05 per formula unit. Our present more detailed study indicates that there is *another* doublet on the *inside* of the main peaks at low temperatures having a *Q.S.* of about 2.1 mm/sec at 77°K. In no spectra of this

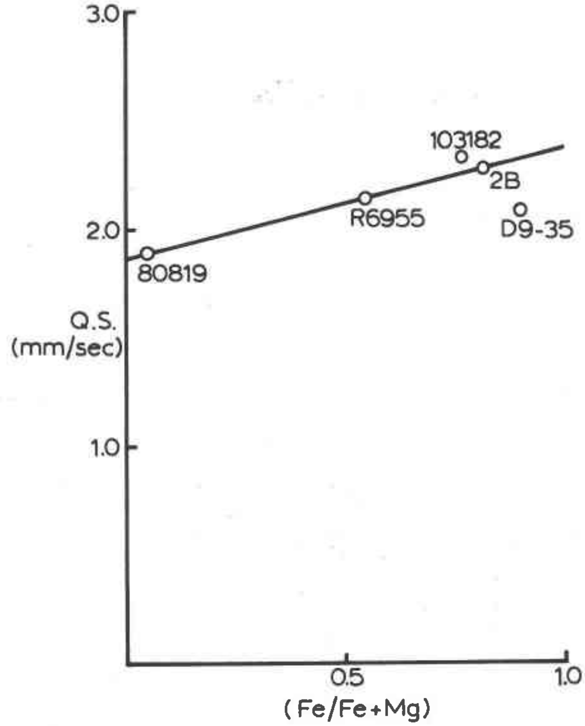
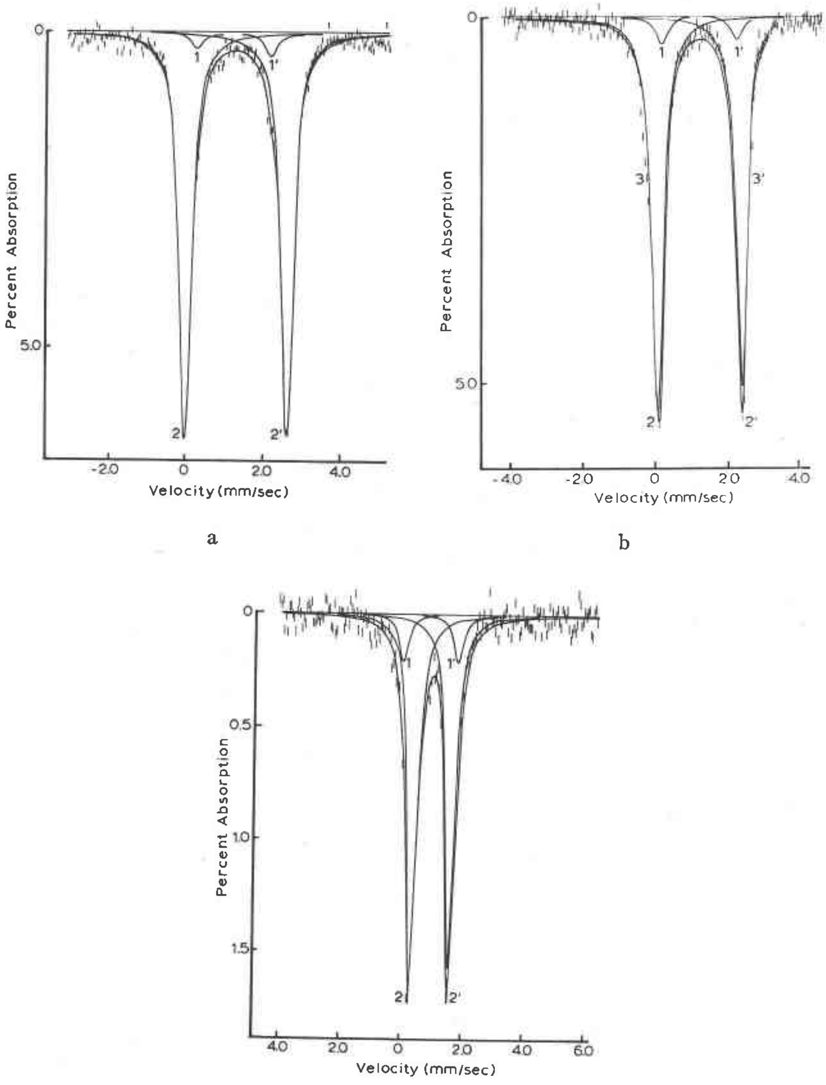


FIG. 2. Quadrupole splitting plotted against Fe/(Fe+Mg) at 295°K.

sample is there any evidence for the Fe^{3+} reported in the chemical analysis (Mueller, 1960).

The spectra of specimen 4 at 77°K, 295°K, and 815°K are shown in Figure 3. At 77°K, there is a distinct shoulder on the *inside* of the major $M1$ peaks (Figure 3a). The two additional peaks fitted (1 and 1′) have a *Q.S.* of about 2.1 mm/sec, and comprise 7 percent of the total area. At 815°K, there is a distinct shoulder on the *outside* of the main peaks (Figure 3c). The two peaks fitted (1 and 1′) have a *Q.S.* of 1.6 mm/sec. These peaks are quite likely due to the same Fe^{2+} in the same site in both spectra, and the peaks have "crossed over" the main $M1$ peaks.

At room temperature, although there is no visual evidence for peaks having a *Q.S.* between 1.6 and 2.1 mm/sec (Figure 3b), two peaks were fitted on the inside of the main peaks, constraining the relative areas to be equal to those in the 77°K spectrum. These peaks (1 and 1′) gave a *Q.S.* of 2.1 mm/sec. Figure 3b now emphasizes the shoulder on the *outside* of the main peaks. These small peaks (3 and 3′) are not seen at other temperatures—presumably because the temperature dependence of the



a

b

c

FIG. 3. Mössbauer spectra of specimen 4 at a) 77°K b) 295°K c) 815°K.

Q.S. is such that the peaks approach the *M*1 peaks both at high and low temperatures.

The complete results for this specimen are summarized in Figure 4. Peaks 1 and 1′ have a very similar *Q.S.* and $\partial(Q.S.)/\partial T$ to those of *M*2

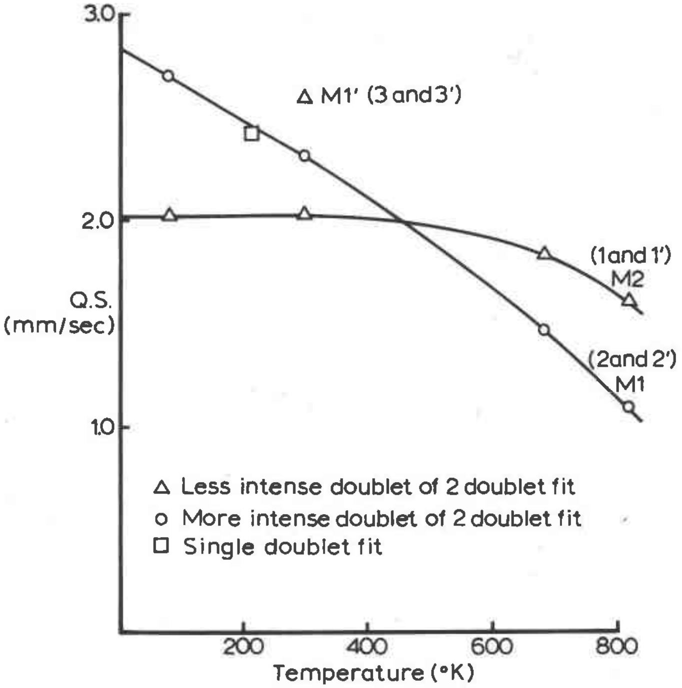


FIG. 4. Quadrupole splitting plotted against temperature for specimen 4. The peaks 1 and 1′, 2 and 2′, and 3 and 3′ refer to those in Figure 3.

positions in other clinopyroxenes (Hafner *et al.*, 1970; Williams *et al.*, 1971). Consistent with the suggestion of Ghose and Hafner (1968), it seems likely then that peaks 1 and 1′ are due to Fe^{2+} in the $M2$ position in specimen 4, and that peaks 3 and 3′ are *not* due to Fe^{2+} in $M2$ as assigned in the previous study (Bancroft *et al.*, 1967). The assignment of peaks 3 and 3′ presents considerable difficulties. As mentioned previously, X-ray examination gave no indication of impurities. However, this clinopyroxene coexisted with actinolite (Mueller, 1960), and since actinolite gives one set of peaks having a *Q.S.* of about 2.8 mm/sec at 295°K (Bancroft *et al.*, 1967), we feel that it is likely that these peaks are due to actinolite $M1$ peaks (Greaves, Burns, and Bancroft, 1971). This actinolite must be finely intergrown with hedenbergite. This conclusion has since been confirmed by optical examination by S. Ghose (personal communication). It is also possible that peaks 1 and 1′ are due to Fe^{2+} in the actinolite $M2$ position, although these peaks are usually much smaller than the actinolite $M1$ peaks (Greaves *et al.*, 1971).

On balance, we feel that peaks 1 and 1′ are mostly due to Fe^{2+} in the clinopyroxene *M*2 position. This result indicates the difficulties that small, impurities may make in the detailed analyses of Mössbauer spectra.

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REFERENCES

BANCROFT, G. M., R. G. BURNS, AND A. G. MADDOCK (1967) Applications of the Mössbauer effect to silicate mineralogy—I. Silicates of known crystal structure. *Geochim. Cosmochim. Acta* **31,** 2219–2246.

CLARK, J. R., D. E. APPLEMAN, AND J. J. PAPIKE (1969) Crystal chemical characterization of clinopyroxenes based on eight new structure refinements. *Mineral Soc. Amer. Spec. Pap.* **2,** 31–50.

DUNDON, R., AND D. H. LINDSLEY (1968) Mössbauer study of synthetic Ca-Fe clinopyroxenes. *Carnegie Inst. Wash. Year Book* **66,** 366–369.

GAY, P., G. M. BANCROFT, AND M. G. BOWN (1970) Diffraction and Mössbauer studies from lunar soils and rocks. *Science* **167,** 626–628.

GHOSE, S., AND S. S. HAFNER (1968) Application of ^{57}Fe Mössbauer resonance in silicates. *In Applications of Nuclear and Electronic Resonance Spectroscopy in Mineralogy, AGI Short Course Lecture Notes*, Amer. Geol. Inst., Wash., D. C., p. G.H. 1–31.

GREAVES, C., R. G. BURNS, AND G. M. BANCROFT (1971) Resolution of actinolite spectra into three ferrous doublets. *Nature*, **229,** 60–61.

HAFNER, S. S., AND D. VIRGO (1970) Temperature-dependent cation distributions in lunar and terrestrial pyroxenes. *Geochim. Cosmochim. Acta, Suppl. 1, Vol.* **3,** 2183–2198.

INGALLS, R. (1964) Electric field gradient tensor in ferrous compounds. *Phys. Rev.* **133,** A787–795.

MATSUI, Y., Y. MAEDA, AND Y. SYONO (1970) Mössbauer study of synthetic calcium rich pyroxenes. *Geochim. J.* **4,** 15–26.

MUELLER, R. F. (1960) Compositional characteristics and equilibrium relationships in mineral assemblages of a metamorphosed iron formation. *Amer. J. Sci.* **258,** 449–497.

VIRGO, D. AND S. S. HAFNER (1969) Fe^{2+}-Mg order disorder in heated orthopyroxenes. *Mineral. Soc. Amer. Spec. Pap.* **2,** 83–93.

WILLIAMS, P. G. L., G. M. BANCROFT, M. G., BOWN, AND A. C. TURNOCK (1971) The "anomalous" Mössbauer spectra of *C*2/*c* pyroxenes *Nature*, **230,** 149–151.

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