

⁵⁷Fe Mössbauer spectral analysis of the sodic clinopyroxenes

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Abstract

Iron-bearing clinopyroxenes were synthesized under hydrothermal, controlled oxygen fugacity conditions at 20 mole% intervals along six binary joins; diopside ($\text{CaMgSi}_2\text{O}_6$)–hedenbergite ($\text{CaFeSi}_2\text{O}_6$), diopside–acmite ($\text{NaFeSi}_2\text{O}_6$), hedenbergite–acmite, acmite– $\text{NaCrSi}_2\text{O}_6$, hedenbergite– $\text{NaCrSi}_2\text{O}_6$, and acmite– $\text{LiFeSi}_2\text{O}_6$.

⁵⁷Fe Mössbauer spectra of these, and of naturally occurring specimens of related compositions, reveal several different types of spectral change as a function of composition. In isovalent solid solutions only small to moderate changes in quadrupole splitting of normal, narrow-line ferrous or ferric doublets are observed. In solid solutions where atoms with different valences are mixed on the same sites, substitution results in marked changes involving line broadening, strong changes in quadrupole splitting and even break-up of single peaks into temperature-dependent, irregularly shaped absorption bands. Lack of a simple one doublet–one site correspondence requires use of more complicated fitting models. The spectra can be fit with multiple doublets having large quadrupole splitting differences. These doublets can be interpreted as either due to different near-neighbor configurations or to a combination of temperature and less specifically localized compositional effects. However, considering the lack of a theoretical basis, the larger number of variables and the generally broadened character of the spectra, neither present interpretation can be considered as firmly established.

Introduction

The pyroxenes show a broad variety of isovalent and charge compensated solid solutions in which the participating sites can usually be inferred with some confidence. End member and intermediate compositions can be prepared in the laboratory and in many cases compared to naturally occurring analogues. This study seeks to relate Mössbauer spectral changes to chemical changes and ultimately to inferred structural and electronic changes in sodic clinopyroxene solutions.

Experimental methods

Synthesis

Clinopyroxenes were synthesized from moist oxide mixes sealed in Ag–Pd or Au capsules treated in

conventional cold-seal hydrothermal pressure vessels. Where needed, oxygen fugacities were buffered by an outer capsule containing an appropriate oxygen buffering assemblage. Synthesis temperatures, pressures, buffer types and run durations are compiled in Table 1. In most cases several synthesis attempts were required to achieve an acceptably pure clinopyroxene product. Many trials failed for such reasons as inappropriate buffer, too low a temperature usually resulting in formation of some amphibole, too high a temperature resulting in some melting or finally, incomplete reaction of the starting materials, especially Cr_2O_3 . For a few bulk compositions these problems of synthesis were never completely overcome and for those pyroxenes only rough qualitative conclusions may be drawn. From the results of the synthesis experiments and previous literature reports it is believed

Table 1. Experimental synthesis conditions

Comp. ¹	Buffer ²	T(C°)	P(bars)	t(hrs)
Ac ₁₀₀	—	660	1000	139
La ₁₀₀	—	655	1000	113
Ac ₈₀ La ₂₀	HM	585	1000	139
Ac ₆₀ La ₄₀	HM	580	1000	139
Ac ₄₀ La ₆₀	HM	593	1000	139
Ac ₂₀ La ₈₀	HM	598	1000	139
Ac ₂₀ Ks ₈₀	—	588	500	240
Ac ₄₀ Ks ₆₀	—	583	500	240
Ac ₆₀ Ks ₄₀	—	586	500	240
Ac ₈₀ Ks ₂₀	—	581	500	240
Ac ₂₀ Hd ₈₀	FMQ	632	500	166
Ac ₄₀ Hd ₆₀	FMQ	627	500	166
Ac ₆₀ Hd ₄₀	FMQ	627	500	166
Ac ₈₀ Hd ₂₀	FMQ	622	500	166
Hd ₁₀₀	FMQ	690	2000	380
Ac ₂₀ Di ₈₀	HM	890	500	68
Ac ₄₀ Di ₆₀	HM	880	500	68
Ac ₆₀ Di ₄₀	HM	890	300	99
Ac ₈₀ Di ₂₀	HM	885	300	99
Hd ₂₀ Ks ₈₀	FMQ	655	350	236
Hd ₄₀ Ks ₆₀	FMQ	645	350	236
Hd ₆₀ Ks ₄₀	FMQ	655	350	236
Hd ₈₀ Ks ₂₀	FMQ	645	350	236

¹Ac=NaFeSi₂O₆, La=LiFeSi₂O₆, Ks=NaCrSi₂O₆
Hd=CaFeSi₂O₆, Di=CaMgSi₂O₆
²HM=hematite-magnetite, FMQ=fayalite-magnetite-quartz

that continuous solid solutions exist at the temperatures of synthesis along all the joins studied here.

Run products were examined under the microscope for homogeneity and presence of other phases, and powder X-ray diffraction patterns were run on all samples. The diffraction patterns were used to check for other phases, to determine gross chemical homogeneity as assessed by diffraction line-width and in most cases, to determine the cell dimensions of the pyroxene. No noticeable line broadening or splitting of the diffraction lines was observed in any case. Agreement between measured cell dimensions and previously published values or those calculated from the equations of

Ribbe and Prunier (1977) are within estimated errors.

Spectra

Mössbauer spectra were measured on a conventional constant acceleration, Kankelite-type spectrometer. Mirror image spectra were accumulated in 512 channels of a multichannel analyzer. A velocity increment of about 0.3 mm/sec-channel was employed. Background counts of about one to three million counts per channel were obtained. Samples were prepared by mixing the powdered synthetic run product with an inert adhesive in a polyethylene sample holder. No evidence of preferred orientation was observed with any synthetic sample although special mixing with an inert filler was necessary with a few of the natural acmites due to their fibrous nature. All sample densities were kept below 0.2 mg ⁵⁷Fe/cm² in order to minimize thickness or saturation effects.

Velocity versus channel number calibration, instrumental line aberration and the magnitude of the small sinusoidal variation in the background counting rate due to variation in source to detector distance were all evaluated from long counting time measurements on standards (iron metal, ferrous oxalate dihydrate, sodium nitroprusside and hematite). Careful fitting of the low-noise spectra of these standards demonstrates that the spectral line shape, due to various sample and instrumental causes, is slightly nonlorentzian. The observed shape was found to be about 90% lorentzian and 10% gaussian and consequently this hybrid line shape was used to fit all the spectra. Although such small deviations in line shape have little effect on fitted parameters such as isomer shift (IS), quadrupole splitting (QS), or even linewidth, use of the actually observed lineshape aids in the resolution of overlapped spectra and in evaluating the statistical quality of the fits.

In all spectral fits doublets were constrained to be symmetric in both area and linewidth. Observed linewidths of standards are 0.30 mm/sec or less and repeated measurements on standards suggests that IS and QS values are accurate to about 0.01 to 0.02 mm/sec. All isomer shifts are quoted relative to the source line with which they were measured, *i.e.*, Fe in Pd. To convert to IS relative to iron metal add 0.18 mm/sec to the quoted value. The quality of the spectrum and adequacy of the fit in reproducing the observations, is given by the Ruby "misfit" parameter and its estimated error (Ruby, 1973). Except

for a few spectra of very low iron content samples, misfits are generally one quarter of one percent or less.

Mössbauer spectra of the synthetic pyroxene series

Diopside ($\text{CaMgSi}_2\text{O}_6$)–*hedenbergite* ($\text{CaFeSi}_2\text{O}_6$)

The diopside–hedenbergite series provide the simple M(1) ferrous doublet against which more complex pyroxene spectra may be compared. Along this isovalent substitution join, Mg and Fe^{2+} substitute for each other in the M(1) octahedral site. The Mössbauer spectra of a series of natural and synthetic clinopyroxenes on or near this join have been the subject of several papers (Matsui *et al.*, 1970; Bancroft *et al.*, 1971; Matsui *et al.*, 1972). In addition spectra of natural pyroxenes of related composition have been reported (Bancroft *et al.*, 1967; Marzolf *et al.*, 1967; Valter *et al.*, 1970; Ionescu *et al.*, 1971; and Ekimov *et al.*, 1973).

Samples along the diopside–hedenbergite join were prepared by Dr. W. P. Freeborn at 800°C, 2 kbar as part of a study of Mg–Fe partitioning between clinopyroxene and olivine (Freeborn, 1976). The sample of composition $\text{Di}_{98}\text{Hd}_{02}$ was prepared with 89% enriched ^{57}Fe . Mössbauer spectra gathered at 85 K and 298 K are summarized in Table 2. Each spectrum consists of a single symmetric quadrupole-split doublet of relatively narrow line width. The data of Matsui *et al.* (1972) match the values obtained here except that their QS values are consistently higher by about 0.03 to 0.04 mm/sec. The Mössbauer spectral parameters reported for natural clinopyroxenes in the studies mentioned are similar to those for the synthetic minerals although the compositions of most of the samples are not sufficiently close to the Di–Hd join to allow exact comparisons. Mössbauer parameters for a number of manganoan hedenbergites have been reported (Matsui *et al.*, 1972; Ionescu *et al.*, 1971; and Bancroft *et al.*, 1971). The QS values of the Mn-bearing pyroxenes are significantly larger than those on the Di–Hd join having equivalent iron content.

Acmite ($\text{NaFe}^{3+}\text{Si}_2\text{O}_6$)–*LiFe}^{3+}\text{Si}_2\text{O}_6*

In acmite the Na atom is in eightfold coordination in the M(2) site whereas in the Li-pyroxenes, the Li atom in M(2) is only sixfold coordinated (Clark *et al.*, 1969). The Mössbauer spectra of these pyroxenes are extremely simple, consisting of one, narrowly split, symmetric doublet. The fitted param-

Table 2. Mössbauer parameters of synthetic clinopyroxenes fit with one Fe^{2+} or Fe^{3+} doublet

Composition ¹	Misfit	IS ^{2,3}	QS ³	Γ ³
room temperature spectra:				
$\text{Di}_{98}\text{Hd}_{02}$	0.24%	1.00(1)	1.85(2)	0.30(1)
$\text{Di}_{70}\text{Hd}_{30}$	0.11	1.02(1)	2.04(2)	0.31(1)
$\text{Di}_{60}\text{Hd}_{40}$	0.28	0.99(1)	2.07(2)	0.31(1)
$\text{Di}_{50}\text{Hd}_{50}$	0.15	1.00(1)	2.10(2)	0.31(1)
$\text{Di}_{40}\text{Hd}_{60}$	0.10	1.00(1)	2.13(1)	0.33(1)
$\text{Di}_{20}\text{Hd}_{80}$	0.18	1.01(1)	2.19(1)	0.32(1)
Hd_{100}	0.14	1.00(1)	2.24(1)	0.31(1)
La_{100}	0.03	0.20(1)	0.29(1)	0.29(1)
$\text{Ac}_{20}\text{La}_{80}$	0.04	0.19(1)	0.29(1)	0.31(1)
$\text{Ac}_{40}\text{La}_{60}$	0.05	0.20(1)	0.29(1)	0.32(1)
$\text{Ac}_{60}\text{La}_{40}$	0.03	0.20(1)	0.29(1)	0.32(1)
$\text{Ac}_{80}\text{La}_{20}$	0.08	0.23(1)	0.28(1)	0.30(1)
Ac_{100}	0.03	0.22(1)	0.29(1)	0.29(1)
$\text{Ac}_{80}\text{Ks}_{20}$	0.05	0.21(1)	0.29(1)	0.30(1)
$\text{Ac}_{60}\text{Ks}_{40}$	0.05	0.19(1)	0.30(1)	0.31(1)
$\text{Ac}_{40}\text{Ks}_{60}$	0.05	0.19(1)	0.30(1)	0.31(1)
$\text{Ac}_{20}\text{Ks}_{80}$	0.09	0.19(1)	0.31(1)	0.31(1)
$\text{Ac}_{80}\text{Di}_{20}$	0.09	0.22(1)	0.36(1)	0.30(1)
$\text{Ac}_{60}\text{Di}_{40}$	0.30	0.22(1)	0.45(2)	0.35(1)
$\text{Ac}_{40}\text{Di}_{60}$	0.22	0.23(1)	0.49(2)	0.38(2)
$\text{Ac}_{20}\text{Di}_{80}$	0.48	0.21(2)	0.59(3)	0.49(2)
liquid nitrogen temperature spectra:				
$\text{Di}_{98}\text{Hd}_{02}$	0.37	1.12(2)	2.52(2)	0.35(2)
Hd_{100}	0.17	1.15(2)	2.81(2)	0.35(2)

¹Di=diopside, Hd=hedenbergite, Ac=acmite, La= $\text{LiFeSi}_2\text{O}_6$, Ks= $\text{NaCrSi}_2\text{O}_6$

²IS=isomer shift relative to Fe in Pd, for IS relative to iron metal add 0.18

³IS, QS (quadrupole splitting) and Γ (peakwidth) in mm/sec

ters are reported in Table 2. Despite the considerable change of structure, all Mössbauer parameters remain constant across the join.

Acmite–kosmochlor ($\text{NaCrSi}_2\text{O}_6$)

In this series ferric iron and chromium substitute in the M(1) sites. X-ray diffraction analysis of the synthesized pyroxene run-products showed a small proportion of a second phase, Cr_2O_3 . It appears that Cr_2O_3 persists metastably even for long synthesis times and thus the compositions of the intermediate pyroxenes will be slightly off their nominal composition.

The results of fitting room temperature Mössbauer spectra of these pyroxenes with one symmetric doublet are included in Table 2. The spectra are

very similar to those observed for acmite- $\text{LiFe}^{3+}\text{Si}_2\text{O}_6$ series. IS is approximately constant, peak width is narrow and constant and QS is nearly constant or perhaps increases very slightly towards the Cr-end member.

Acmite-diopside

In this solid solution the replacement of magnesium by ferric iron on M(1) is coupled with a sodium for calcium replacement on the M(2) site. Although X-ray diffraction analysis of the pyroxenes synthesized on this join failed to reveal a second phase, the Mössbauer spectra showed in each case a very weak ferrous peak, possibly due to minor loss of Na to the fluid phase. This ferrous iron content amounts to only 0.016 to 0.03 mole Hd component.

The Mössbauer spectra of this aliovalent series present a major difference from the previous isovalent series. The ferric QS splitting does not remain constant but approximately doubles from about 0.3 to 0.6 mm/sec across this join. Even more significantly, the Mössbauer line-width undergoes a drastic increase from a normal narrow line at acmite to a highly broadened line towards the diopside end-member. This marked line broadening involves introduction of asymmetry in shape in the sense that the two lines of the ferric doublet are broadened much more to the outside than between the two peaks. An extreme example of such a spectrum is shown in Figure 1. Because of the obvious shape asymmetry, the spectrum cannot be well fitted by one doublet. In order to quantitatively describe the

observed spectral envelope a series of increasingly wider spaced symmetric doublets of decreasing intensity were employed. No significance can be attached to the number, location and widths of the component peaks used to achieve this fit as equally good fits could be achieved with other combinations.

The location of a composite peak can be defined as the centroid or weighted average of the several component peak locations. The width reported for normal symmetric peaks is the full peak-width measured at half peak height. A corresponding full width at half maximum height can be assigned to any composite peak which is everywhere concave to the baseline, and this working definition is used here, as the best available, single parameter. The parameters of the composite peaks as so defined are reported in Table 2. The IS is constant and the same as observed in the other ferric pyroxenes reported here. Ohashi and Hariya (1970) reported the Mössbauer spectrum of a synthetic sodic clinopyroxene of composition $\text{Di}_{20}\text{Ac}_{80}$ but fit a broad singlet rather than a narrowly split doublet.

Acmite-hedenbergite

On this join both Fe^{2+} and Fe^{3+} are present in the M(1) octahedral sites and charge balance is maintained by an appropriate mix of Na and Ca on the M(2) sites. The proportion of ferric iron that should be present for each ideal composition (20 mole% intervals) compared to the values measured from the Mössbauer spectra taken at room and liquid

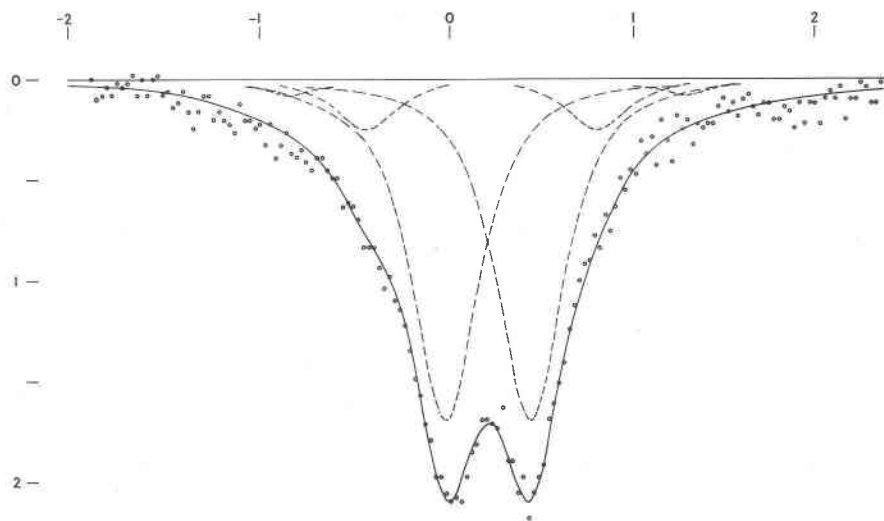


Fig. 1. Mössbauer spectrum of diopside₈₀-acmite₂₀ at room temperature.

nitrogen temperature respectively are 80% vs. 79 and 77; 60% vs. 60 and 59; 40% vs. 41 and 42; and 20% vs. 23 and 23, for the four acmite-hedenbergite intermediates. Systematic differences between the ideal and measured values could be attributed to possible differences between the recoil-free-fraction of ferric and ferrous iron, changes in the ratio of recoil-free-fraction with temperature, or synthesis errors. The generally good agreement between these sets of numbers indicates that such effects are within estimated errors in the determination of ferrous-ferric ratio (*ca.* 2%) and in the synthesis (*ca.* 2%).

The spectra of the intermediate acmite-hedenbergites are the most complex and most interesting of all those investigated. Both room temperature and liquid nitrogen temperature spectra are illustrated in Figure 2. The behavior of the ferric absorption features in this series is reminiscent of the acmite-diopside series. The narrowly split and narrow line Fe^{3+} doublet seen in acmite widens in both quadrupole splitting and peak width as hedenbergite component is increased. The peak broadening is again asymmetric. For the most extreme case, $\text{Hd}_{80}\text{Ac}_{20}$, the ferric peaks were simulated as in the Di-Ac cases, by adding a second weak component to the outside of the main ferric doublet.

At hedenbergite the spectrum consists of only one well split, symmetric doublet due to Fe^{2+} in the M(1) site. The ferrous doublet in $\text{Hd}_{80}\text{Ac}_{20}$ is slightly and asymmetrically broadened relative to Hd_{100} . Specifically, the Fe^{2+} doublet seems to be broadened more on the outside than between the peaks, especially at room temperature. With increasing acmite substitution the ferrous absorption features can be seen to broaden asymmetrically, forming a wide, irregularly shaped absorption band. In order to fit the observed distribution, the ferrous absorption band was considered the sum of several peaks. Two different fitting models were employed here: one in which the ferrous portion of the spectrum was fitted with two doublets and one in which this part of the spectrum was fitted with three doublets. To anticipate the results, it may be noted that either model equally well reproduces the observed spectra and choosing between them rests more on the interpretation than on the quality of fit.

In the first model the ferrous band was fitted with two symmetric doublets, each having the same isomer shift and all four peaks having the same width. This constrained two doublet fit has the fewest number of peaks and smallest number of

variables found to adequately reproduce the observed spectra. The good fit, reasonable widths and smooth variation of all peak parameters with composition attest to the *sufficiency* of the two-ferrous-doublet fit. The results of this model fitted to the acmite-hedenbergite series are listed in Table 3. Of the two ferrous components, the outer doublet intensity increases as acmite component increases. The proportions differ however at the two temperatures of measurement and neither set bears any simple relationship to the stoichiometry.

A fit employing three ferrous doublets was investigated in order to compare results with Mössbauer spectra of omphacitic pyroxenes recently published by Aldridge *et al.* (1978). As omphacites are composed mainly of jadeite, diopside, acmite and hedenbergite components, their spectra are likely to be similar to those reported here. Aldridge *et al.* adopt an earlier proposal by Dowty and Lindsley (1973) that Fe^{2+} in clinopyroxene M(1) sites yield discernably different Mössbauer doublets depending upon occupancy of the adjacent M(2) sites. These authors propose that the ferrous absorption band in omphacite is therefore the sum of three discrete doublets representing Fe^{2+} in M(1) surrounded by (a) 3 Ca (b) 2 Ca + 1 Na, (c) 1 Ca + 2 Na. (A fourth possible doublet representing a 3 Na configuration is thought in the case of omphacitic compositions to be too weak in intensity to fit.)

Using three doublets it is possible to choose area ratios that are the same at room and liquid nitrogen temperatures. In order to retain constant area ratios it was necessary, however, to fix the doublet areas during the fitting procedure. Final values for peak areas were determined, through trial and error, as those giving acceptable fits at both temperatures. Because of the greater overlap with the large number of peaks, it was in some cases necessary to fix peak locations to avoid singular normal-equation matrices in the least-squares fitting procedure. Results are given in Table 4. The quality of the fits are good but not statistically better than the two doublet fits and linewidths are about the same in either case.

Hedenbergite-kosmochlor ($\text{NaCrSi}_2\text{O}_6$)

This is another aliovalent solid solution series in which substitution of Fe^{2+} and Cr^{3+} is compensated by substitution of Ca for Na in M(2). As a result iron should be present in only the ferrous state. However, all syntheses of this series produced both Fe^{2+} and Fe^{3+} as shown by the Mössbauer spectra. X-

Table 3. Mössbauer parameters of synthetic and natural clinopyroxenes fit with one Fe³⁺ and two Fe²⁺ doublets

Composition ¹	Misf. ²	- ferric doublet -				-inner ferrous-			-outer ferrous-		
		Area ³	IS ^{4 5}	QS ⁵	Γ ⁵	Area ³	IS ^{4 5}	QS ⁵	Area ³	QS ⁵	Γ ⁵
room temperature spectra:											
Hd ₈₀ Ac ₂₀	0.16	23	0.25(2)	0.46(2)	0.36(3)	70	1.01(2)	2.13(2)	7	2.69(3)	0.35(1)
Hd ₆₀ Ac ₄₀	0.16	41	0.23(2)	0.42(2)	0.35(2)	40	0.99(2)	2.06(2)	19	2.72(2)	0.43(1)
Hd ₄₀ Ac ₆₀	0.14	60	0.22(1)	0.38(1)	0.33(1)	22	0.96(2)	2.00(2)	18	2.73(2)	0.41(2)
Hd ₂₀ Ac ₈₀	0.07	79	0.23(1)	0.35(1)	0.31(1)	9	0.99(2)	1.91(3)	12	2.74(2)	0.39(2)
Hd ₇₄ Ac ₂₆ Ks ₀₀	0.21	26	0.23(2)	0.45(3)	0.41(2)	60	0.99(2)	2.12(2)	14	2.64(3)	0.38(2)
Hd ₅₀ Ac ₂₇ Ks ₂₄	0.27	34	0.22(2)	0.43(3)	0.37(2)	47	0.99(2)	2.07(2)	19	2.70(3)	0.39(2)
Hd ₂₃ Ac ₂₉ Ks ₄₈	0.41	56	0.25(3)	0.39(3)	0.34(1)	20	0.98(3)	1.97(3)	24	2.70(3)	0.38(2)
Hd ₀₈ Ac ₁₅ Ks ₇₇	0.32	64	0.22(2)	0.35(2)	0.32(1)	12	0.97(3)	1.77(4)	24	2.80(3)	0.36(2)
ML-81-21	0.42	31	0.26(2)	0.44(2)	0.36(1)	57	0.97(2)	1.98(2)	12	2.59(3)	0.36(2)
L-169-1	0.27	49	0.24(1)	0.46(2)	0.39(1)	35	0.98(2)	2.00(2)	16	2.68(2)	0.40(2)
LA-1	0.07	71	0.23(1)	0.38(1)	0.35(1)	15	0.96(2)	2.00(2)	14	2.75(2)	0.46(2)
liquid nitrogen temperature spectra:											
Hd ₈₀ Ac ₂₀	0.13	23	0.34(2)	0.47(2)	0.36(2)	43	1.11(2)	2.66(2)	34	2.96(2)	0.36(1)
Hd ₆₀ Ac ₄₀	0.19	42	0.33(1)	0.43(2)	0.33(1)	23	1.10(2)	2.58(2)	35	3.01(2)	0.40(1)
Hd ₄₀ Ac ₆₀	0.11	59	0.33(1)	0.40(1)	0.33(1)	9	1.09(2)	2.36(3)	32	3.01(2)	0.39(1)
Hd ₂₀ Ac ₈₀	0.07	77	0.33(1)	0.36(1)	0.32(1)	5	1.10(2)	2.32(2)	16	3.08(2)	0.36(1)
L-169-1	0.30	48	0.35(2)	0.47(2)	0.37(1)	23	1.11(2)	2.44(2)	29	2.93(2)	0.40(2)

¹Hd=hedenbergite, Ac=acmite, Ks=NaCrSi₂O₆, for natural sample compositions see Table 5²Misf.= Misfit in %³Area (±2) in %⁴IS= isomer shift relative to Fe in Pd, for IS relative to iron metal add 0.18; IS(inner)=IS(outer)⁵IS, QS (quadrupole splitting) and Γ (peakwidth) in mm/sec; Γ(inner)=Γ(outer)Table 4. Mössbauer parameters of hedenbergite-acmite series fit with three Fe²⁺ doublets

Comp. ¹	Misf. ²	- inner -			- middle -			- outer -			Γ ⁵
		Area ³	IS ^{4 5}	QS ⁵	Area ³	IS ^{4 5}	QS ⁵	Area ³	IS ^{4 5}	QS ⁵	
room temperature spectra:											
Hd ₂₀ Ac ₈₀	0.08	16	0.96	1.83	28	0.95	2.18	56	0.97	2.77	0.36
Hd ₄₀ Ac ₆₀	0.15	25	0.96	1.87	38	0.95	2.19	37	0.97	2.79	0.36
Hd ₆₀ Ac ₄₀	0.17	33	1.00	1.99	40	0.98	2.17	27	0.99	2.77	0.43
Hd ₈₀ Ac ₂₀	0.34	56	1.01	2.08	44	1.00	2.28	0	-	-	0.42
liquid nitrogen temperature spectra:											
Hd ₂₀ Ac ₈₀	0.10	16	1.12	2.24	28	1.10	2.95	56	1.10	3.10	0.36
Hd ₄₀ Ac ₆₀	0.13	25	1.12	2.40	38	1.09	2.96	37	1.09	3.08	0.37
Hd ₆₀ Ac ₄₀	0.18	33	1.11	2.49	40	1.10	2.91	27	1.08	3.14	0.35
Hd ₈₀ Ac ₂₀	0.13	56	1.11	2.66	44	1.11	2.96	0	-	-	0.36

¹Hd=hedenbergite, Ac=acmite²Misf.= Misfit in %³Areas in % total ferrous component, ferric parameters see Table 3⁴IS=isomer shift relative to Fe in Pd, for IS relative to iron metal add 0.18⁵IS, QS (quadrupole splitting) and Γ(peakwidth) in mm/sec, all Fe²⁺ peaks have equal Γ

ray diffraction patterns showed pyroxene and Cr_2O_3 . In addition a white amorphous film, which appears to be a sodium silicate gel, was found coating the sample. It seems likely that because of

the low reactivity of Cr_2O_3 , the Na and Si components attack the iron oxide producing an acmite component even at low oxygen fugacities. The resulting pyroxenes then fall in the hedenbergite-

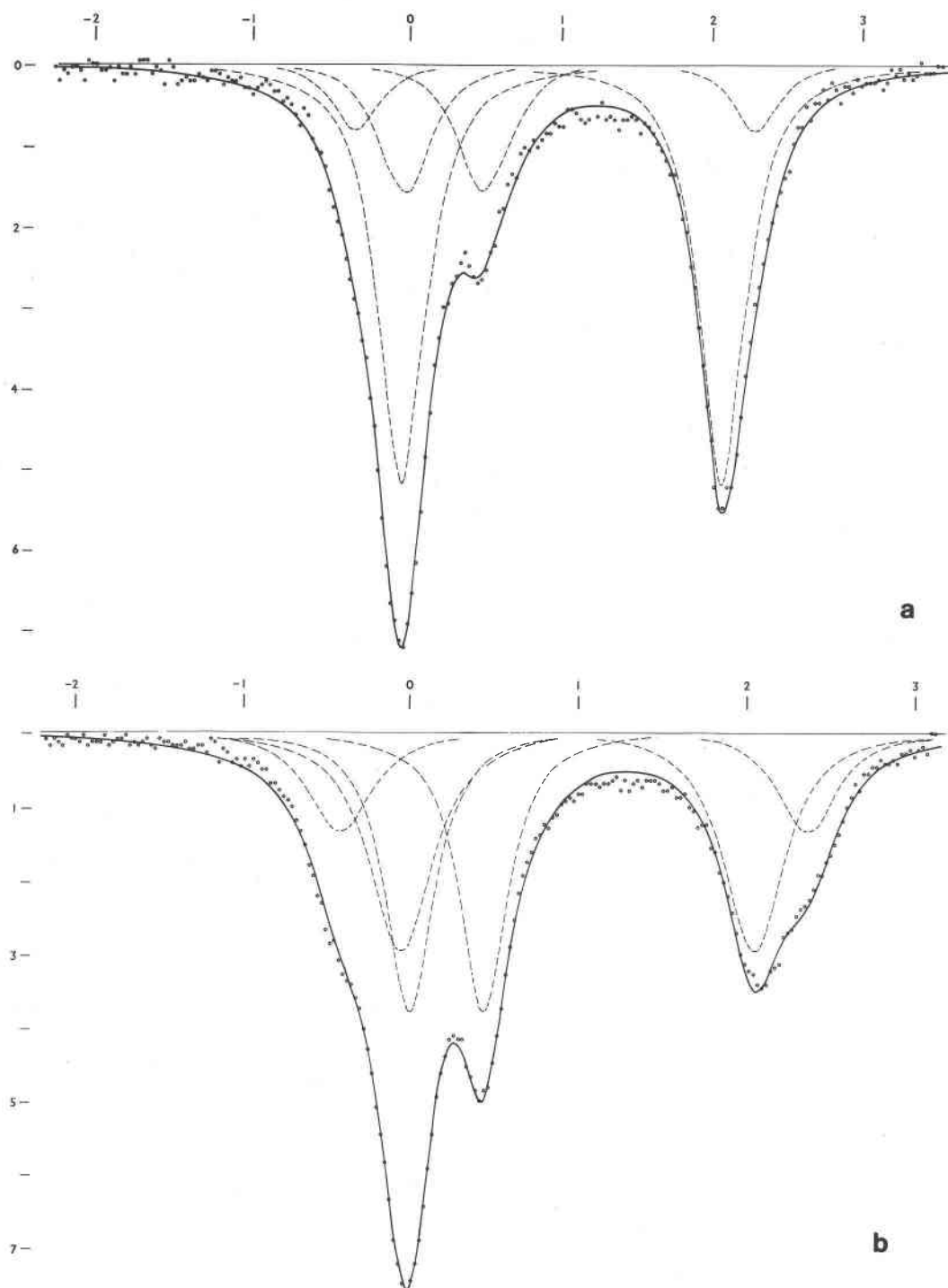


Fig. 2. Mössbauer spectra of the hedenbergite-acmite series at 20 mol % intervals. (a) $\text{Hd}_{80}\text{Ac}_{20}$ at RT, (b) $\text{Hd}_{60}\text{Ac}_{40}$ at RT.

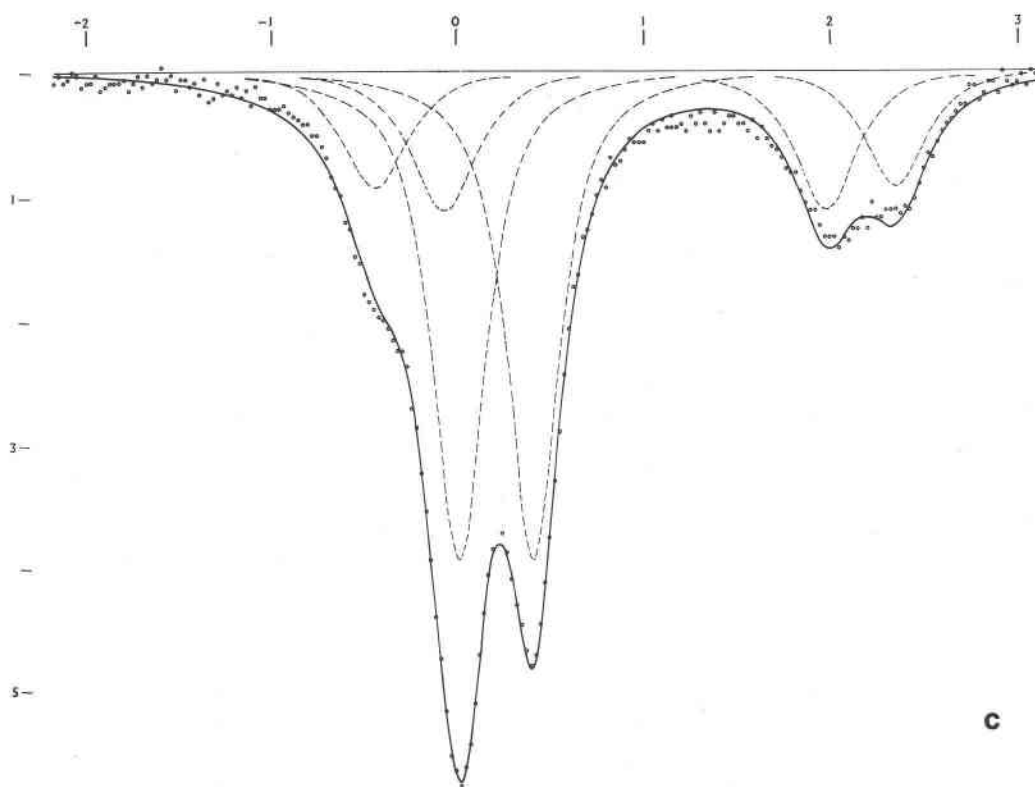


Fig. 2c. Mössbauer spectra of the hedenbergite-acmite series at 20 mol % intervals, Hd₄₀Ac₆₀ at RT.

kosmochlor-acmite ternary system. A rough estimate of composition can be made from the ferrous-ferric ratio and assignment of all sodium in the original charge to the pyroxene. Although these samples are well off the originally desired composition, their spectra show trends which are analogous to those of other mixed valence pyroxenes. These data thus contribute to the overall structure-chemistry-spectra systematics.

The compositions inferred for the ternary clinopyroxenes are given in Table 3 along with their Mössbauer spectral parameters. The ferrous absorption band was fit with two constrained doublets exactly as in the acmite-hedenbergite case.

Natural sodic clinopyroxenes

In addition to the synthetic series, a few natural sodic clinopyroxenes were chemically analyzed by conventional electron microprobe analysis. Ferrous-ferric ratios were obtained from Mössbauer spectra. Only three of 17 analyzed samples showed full or nearly full occupancy of the M(2) sites by Ca + Na, their cation proportions being given in Table 5. The remaining pyroxenes could have significant

amounts of ferrous iron in the M(2) sites. At room temperature the M(2) ferrous doublet has an isomer shift similar to that of the M(1) ferrous doublet(s) and a quadrupole splitting of about 2.0 mm/sec or less and the doublet is therefore largely superimposed on the M(1) ferrous features. At liquid nitrogen temperature the M(2) ferrous doublet shows little increase in its quadrupole splitting whereas the M(1) ferrous doublet increases in QS markedly. Thus resolution of M(2) spectral features is generally improved at lower temperatures.

The Mössbauer spectra of the natural samples show no indication of Fe²⁺ in M(2). Their spectra closely match those of the acmite-hedenbergite series. The same type of constrained two ferrous doublets and one ferric doublet fitting was employed (Table 3), but no doubt a three ferrous doublet fit could be used.

Mössbauer spectra of natural sodic clinopyroxenes have also been reported (Marzolf *et al.*, 1967, an aegirine; Bancroft *et al.*, 1969, an acmite-jadeite and four omphacites; Ekimov *et al.*, 1973, several sodic augites; and Aldridge *et al.*, 1978, nine omphacites). Where the spectra are illustrated it can be

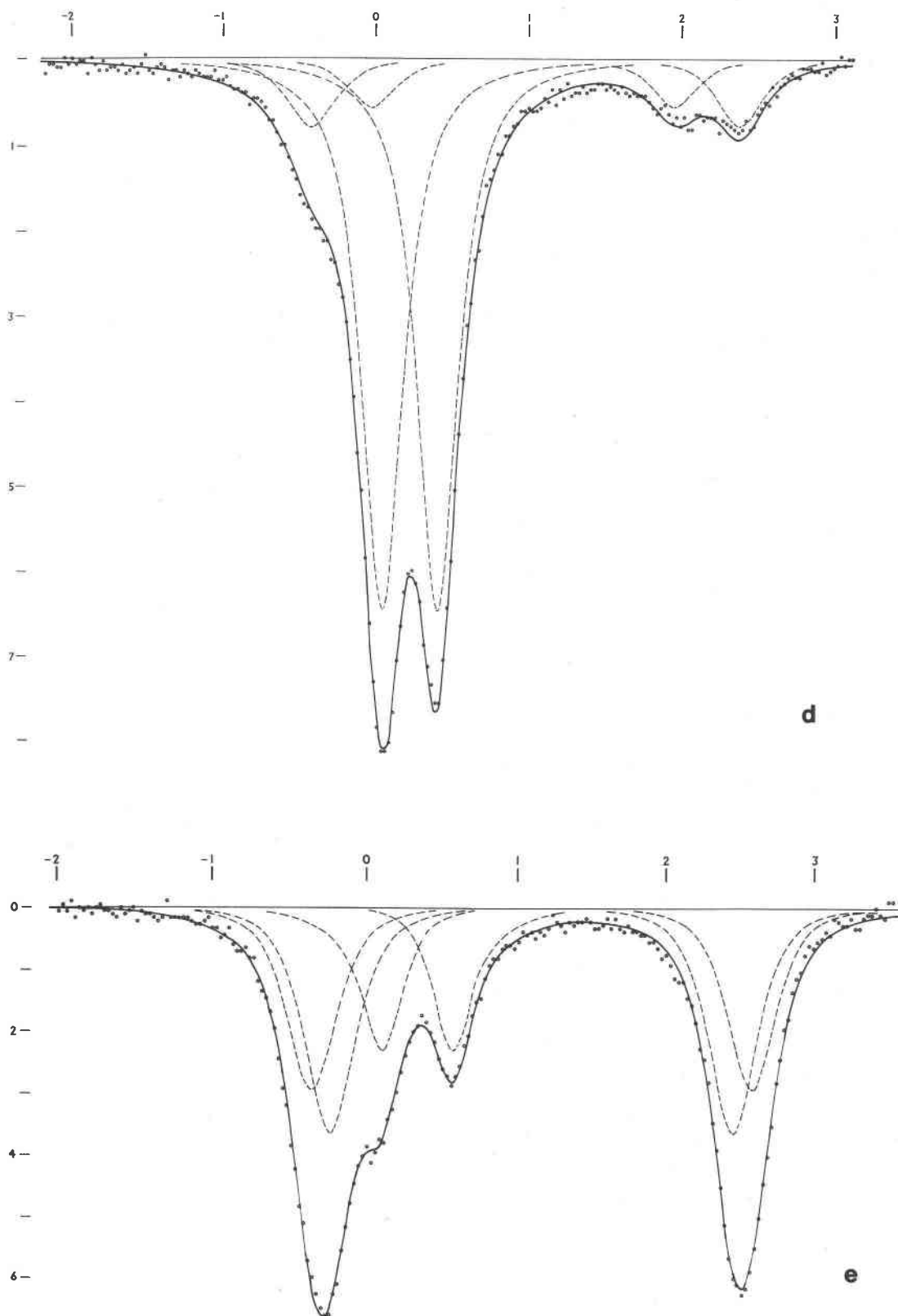


Fig. 2. Mössbauer spectra of the hedenbergite-acmite series at 20 mol % intervals, (d) $\text{Hd}_{20}\text{Ac}_{80}$ at RT, (e) $\text{Hd}_{80}\text{Ac}_{20}$ at 85 K.

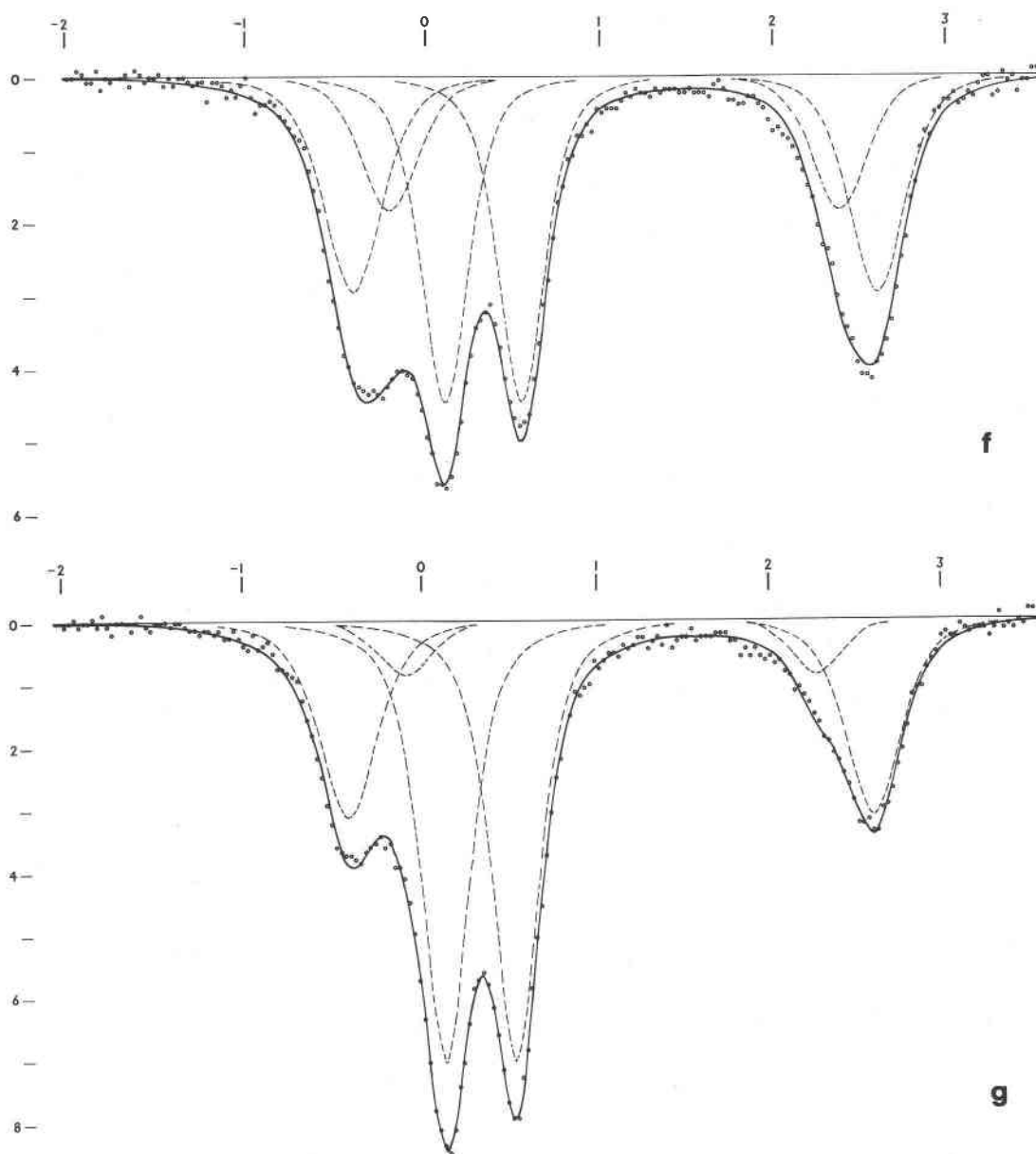


Fig. 2. Mössbauer spectra of the hedenbergite-acmite series at 20 mol % intervals, (f) $\text{Hd}_{60}\text{Ac}_{40}$ at 85 K, (g) $\text{Hd}_{40}\text{Ac}_{60}$ at 85 K.

seen that the ferrous absorption features are asymmetrically broadened, sometimes with the appearance of two separated peaks in the high velocity part of the spectrum. Such visual resolution of two ferrous peaks is not achieved in the spectra of the synthetic pyroxenes reported here although the more sodic samples approach this appearance (Fig. 2). The spectra of these natural sodic clinopyroxenes have been fitted by the various authors using one, two, three or four ferrous doublets in addition to a ferric doublet. Comparison of the illustrations

and fitted parameters of the literature reported spectra with those measured in this study suggests, however, that there are few differences in the observations but major differences in the interpretations.

Interpretation of the spectral results

Analysis of the entire group of 32 pyroxenes reported here discloses that the spectral variations follow a few simple, orderly trends. These are summarized and their relationships to chemical,

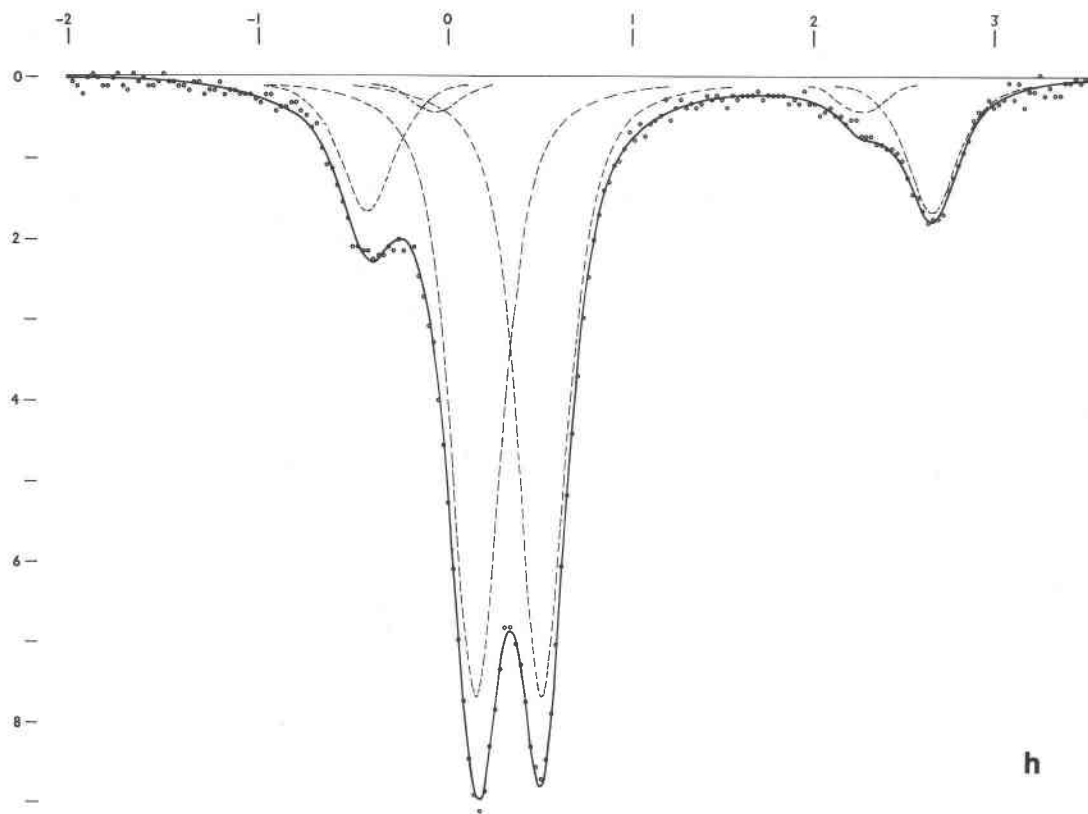


Fig. 2h. Mössbauer spectra of the hedenbergite-acmite series at 20 mol % intervals, $\text{Hd}_{20}\text{Ac}_{80}$ at 85 K.

electronic and crystal structural changes in sodic clinopyroxenes are explored.

Ferric iron in M(1) octahedral sites

Crystal structure analysis, optical and Mössbauer spectroscopy all suggest that Fe^{3+} resides only in M(1) or tetrahedral sites in sodic pyroxenes. Tetrahedral ferric iron in clinopyroxene has been recognized by Hafner and Huckenholz (1971) and by Ohashi and Hariya (1970, 1973). The tetrahedral ferric doublet has a much larger quadrupole splitting (about 1.5 mm/sec) than does the octahedral ferric doublet and in addition a characteristically smaller IS (about 0.0 mm/sec) reflecting the smaller coordination number. There is no evidence that ferric iron is present in any sites other than octahedral M(1) in any of the compounds reported in this paper.

The isomer shift of the doublet associated with Fe^{3+} in M(1) sites in all the sodic clinopyroxenes shows a value of about $0.22 \pm .02$ mm/sec at room temperature. There are no obvious systematic variations observed in any of the series within the accuracy of this study. At 85 K observed IS values

are about 0.1 mm/sec higher than at room temperature due to decreased mean square atomic velocity (the so-called second order Doppler effect). Its expected magnitude using the Debye approximation in the high temperature limit is 0.13 mm/sec for this temperature difference (Greenwood and Gibb, 1971).

For Fe^{3+} , highly symmetrical environments normally associated with undistorted or only slightly distorted coordination polyhedra give rise to small QS values while lower symmetry environments and highly distorted polyhedra yield QS values as high as 2.0 mm/sec in extreme cases. The pure ferric end member pyroxenes, $\text{NaFeSi}_2\text{O}_6$ and $\text{LiFeSi}_2\text{O}_6$ have the smallest QS of 0.29 mm/sec. Substitution of Cr^{3+} for Fe^{3+} results in a barely perceptible increase to about 0.31 mm/sec. In a natural acmite-jadeite near $\text{Ac}_{50}\text{Jd}_{50}$ the Fe^{3+} QS is reported to be 0.33 mm/sec (Bancroft *et al.*, 1969). Thus it appears that QS (and hence the local Fe^{3+} environment) is essentially unaffected by isovalent substitution into neighboring M(1) sites. The $\text{NaFeSi}_2\text{O}_6$ – $\text{LiFeSi}_2\text{O}_6$ series similarly indicates no effect on QS due to isovalent M(2) substitutions. Considering the size

Table 5. Chemical compositions of natural clinopyroxene samples

	(1)	(2)	(3)
Si	1.97	1.96	1.95
Ti	0.04	0.01	0.01
Al	0.03	0.07	0.04
Fe (3)	0.10	0.26	0.69
Fe (2)	0.24	0.28	0.30
Mn	0.01	0.02	0.04
Mg	0.65	0.40	0.05
Ca	0.84	0.73	0.33
Na	0.13	0.27	0.57
Σ	3.99	3.99	3.96
O	6.00	6.00	6.00

(1)	ML-81-21 sodic augite, Kola Peninsula
(2)	L-169-1 aegirine augite, Alnö, Sweden
(3)	LA-1 aegirine, Akerholmen, Norway

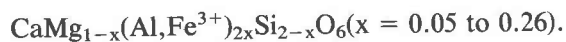
disparity between replacing atoms (the Li for Na substitution in addition results in a coordination number change from 8 to 6) and the high degree of edge sharing with neighboring M(1) and M(2) polyhedra, this lack of change of QS is remarkable.

Solid solutions of ferric end member pyroxenes with those having divalent M(1) and M(2) atoms result in a marked increase in QS (Fig. 3). The scattered observations fall largely between the Ac-Di and Ac-Hd trends shown as dashed lines. Evidently the electric field is more strongly perturbed by changing the valence of neighboring M(1) or M(2) atoms than by mere isovalent replacement at these same sites.

The value of the QS near the pure divalent pyroxene end members is imprecise due to the extreme asymmetric broadening of the ferric doublet. Figure 3 suggests a roughly linear relationship between composition and QS, but a strong change in slope near the divalent end members is not precluded by the data at hand.

It appears that an even greater increase in QS of octahedral M(1) ferric iron is produced by a change in valence of the tetrahedral site atoms. The M(1) octahedra share all six corners with TO_4 groups. Hafner and Huckenholz (1971) and Ohashi and Hariya (1973) report quadrupole splitting of 1.01 to

1.09 mm/sec for octahedral Fe^{3+} when the tetrahedral Si atoms have been partially replaced with Al and/or Fe^{3+} in the series,



Many of the Mössbauer absorption peaks of clinopyroxenes reported here show appreciable broadening over the minimum line-widths of about 0.27 to 0.29 mm/sec observable with the experimental configuration used. A number of causes of line broadening have been shown to exist but the simplest and most prevalent concept is that the broadened-line doublet consists of several closely spaced subcomponents each reflecting a different local environment with its own electric field gradient and resulting quadrupole splitting. In a solid solution, different environments could be related to sample inhomogeneity and/or different configurations of substituent atoms surrounding the iron atom sites. The presence of a large range of local environments and particularly a large change in QS from one local environment to another would produce the greatest broadening.

In the pyroxenes reported here the broadest lines are indeed observed where QS values are larger and rapidly changing with composition, as in the $\text{Di}_{80}\text{Ac}_{20}$ case (Fig. 1). In detail, however, this model is likely to be too simple. The widest variety of configurations and thus presumably the broadest peaks ought to occur midway in a solid solution series whereas, for example, the Di-Ac line widths appear to keep increasing towards diopside. Furthermore, fitting such broadened peaks requires use of components whose quadrupole splitting values appear to fall well beyond those of the (extrapolated) pure end members.

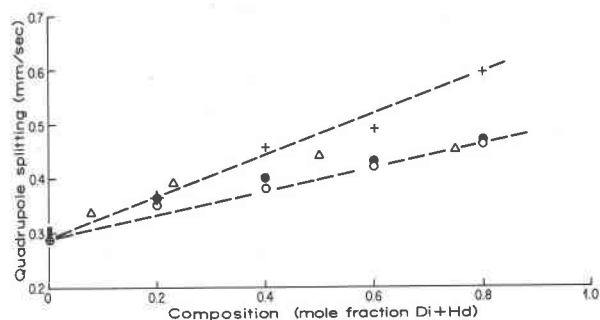


Fig. 3. Fe^{3+} quadrupole splitting versus composition. Crosses refer to Ac-Di, open circles to Ac-Hd at room temperature, closed circles to Ac-Hd at 85 K, triangles to Ac-Hd-Ks compositions. The acmite- $\text{NaCrSi}_2\text{O}_6$ - $\text{LiFeSi}_2\text{O}_5$ range is shown by the short vertical bar at zero mole fraction Di.

Ferrous iron in *M*(1) octahedral site—Summary of spectral observations

Due either to constraints or insignificant differences among fitted values the multiple doublets employed here can be characterized by one IS value, one linewidth and either two or three QS values. Ferrous isomer shift values show only a weak dependence on composition. The average IS of the predominantly calcic clinopyroxenes reported here is about 1.00 mm/sec at room temperature while an average of about 0.98 mm/sec is found for the sodic clinopyroxenes. The IS values are about 0.10 to 0.11 mm/sec larger at 85 K due to the second order Doppler effect. The quadrupole splitting trends of the sodic pyroxenes, which depend somewhat upon the number of doublets fitted, are considered first for the 2-doublet case. With two ferrous doublets the trends from hedenbergite towards acmite or acmite- $\text{NaCrSi}_2\text{O}_6$ are illustrated in Figure 4. The inner doublet, which is of greatest intensity near the calcium end member, shows a moderate decrease in QS with increase in acmite or kosmochlor component. This trend is almost exactly the same in both slope and magnitude as in the hedenbergite-diopside series where QS decreases from about 2.2 mm/sec at hedenbergite to about 1.9 mm/sec near diopside.

On cooling to 85 K the average increase in QS of the inner doublet is 0.48 mm/sec. The average increase in QS for this temperature change for four clinopyroxenes near the diopside-hedenbergite tie-line (Bancroft *et al.*, 1971) is also 0.48/mm sec. Thus in magnitude of quadrupole splitting, dependence on composition, and thermal behavior, the inner ferrous doublet of the Na-Ca clinopyroxenes is similar to the single *M*(1) quadrupole split doublet observed in the calcic clinopyroxene spectra.

The outer ferrous doublet is distinct from the inner doublet in its compositional and thermal dependence. Figure 4 shows the outer doublet slightly increasing in QS from hedenbergite towards the sodic clinopyroxenes, which is opposed to the inner doublet trend, and furthermore the total change is much smaller. The average increase in QS of the outer doublet on cooling to liquid nitrogen temperature is only 0.30 mm/sec. The intensity of the outer doublet increases from zero at hedenbergite to a maximum in the samples with the largest sodic clinopyroxene component. The area ratios of the two doublets are temperature dependent with the outer doublet increasing in area at lower tempera-

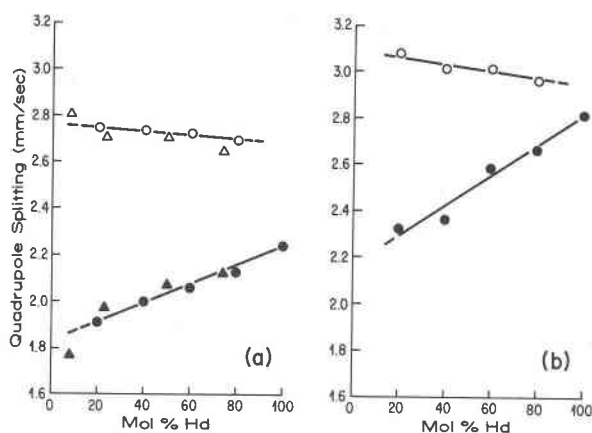


Fig. 4. Quadrupole splitting of inner and outer Fe^{2+} doublets in the Ac-Hd series (circles) and the Ac-Hd-Ks series (triangles) at (a) room temperature and (b) at 85 K.

tures, at the expense of the inner doublet. This effect is greatest near hedenbergite and least near the sodic clinopyroxenes. Although the diopside-hedenbergite series shows only one quadrupole split doublet, the subcalcic clinopyroxenes, with Ca less than 1.0 per formula unit and the *M*(2) deficit made up by Fe and/or Mg, show a definite outwards broadening of the *M*(1) doublet (Williams *et al.*, 1971, $\text{Ca}_{0.82}\text{Fe}_{1.02}\text{Mg}_{0.16}\text{Si}_2\text{O}_6$ and $\text{Ca}_{0.80}\text{Fe}_{0.6}\text{Mg}_{0.6}\text{Si}_2\text{O}_6$; Matsui *et al.*, 1972, five compositions $\text{Ca}_{0.8}(\text{Mg}, \text{Fe})_{1.2}\text{Si}_2\text{O}_6$; Dowty and Lindsley, 1973, compositions on the hedenbergite- $\text{Fe}_2\text{Si}_2\text{O}_6$ join; and Dollase and Freeborn, unpublished, $\text{Ca}_{0.9}(\text{Fe}, \text{Mg})_{1.1}\text{Si}_2\text{O}_6$). Except for the work of Dowty and Lindsley the spectra have been fitted with three doublets—an inner *M*(2) doublet, the principal *M*(1) doublet and an additional weaker outer doublet. Individual peaks are not visually resolvable in the broadened *M*(1) envelope and two doublets are adequate to reproduce the *M*(1) spectral features.

The additional outer ferrous doublet that appears in the subcalcic clinopyroxenes is similar to the outer doublet observed in sodic clinopyroxenes. Its QS at room temperature is similar at about 2.6 to 2.8 mm/sec depending upon sample composition with the more magnesian samples having the smaller values. Like the sodic clinopyroxene outer doublet, the increase in QS on cooling is significantly less than that of the inner doublet with the result of greater spectral overlap at lower temperatures. Furthermore, as in the case of the sodic clinopyroxenes, it appears that the relative area ratios of the inner and outer *M*(1) doublet change with temperature, the outer doublet again increasing somewhat

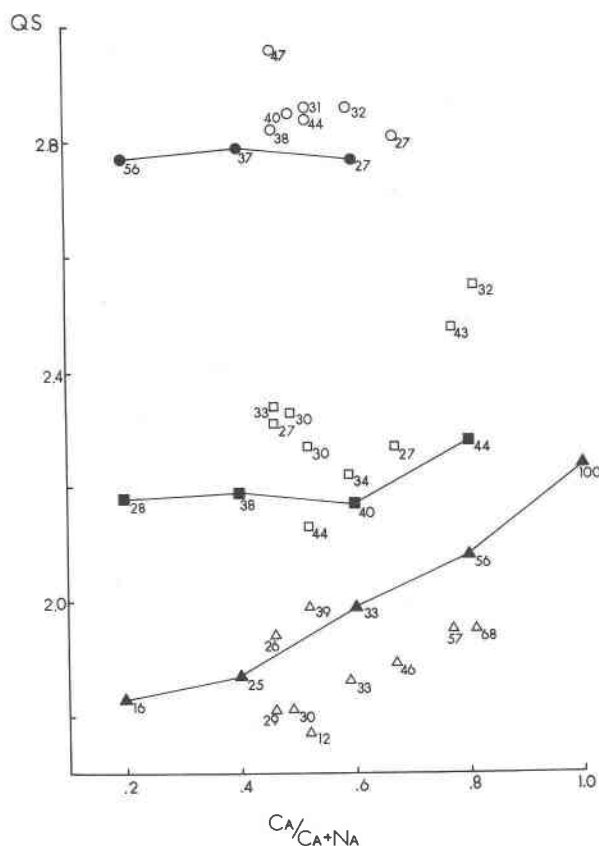


Fig. 5. Room temperature quadrupole splitting from three-doublet fits to the Ac-Hd series (solid symbols) and the omphacites reported by Aldridge *et al.* (1978) (open symbols).

on cooling to lower temperature. This effect is reported by Williams *et al.* (1971) and was seen on the subcalcic samples studied in this laboratory.

The trends resulting from fitting three ferrous doublets to the hedenbergite-acmite solid solution series are shown in Figure 5 which plots QS versus composition expressed as the $\text{Ca}/(\text{Ca}+\text{Na})$ ratio. The points connected by lines are from this study whereas the other data points are those reported by Aldridge *et al.* (1978) for omphacites lying near the jadeite-diopside or jadeite-hedenbergite compositional joins. Although there is scatter, the omphacite data cluster around the hedenbergite-acmite data. The number associated with each point is the percentage of the total Fe^{2+} content represented by the particular doublet. Note that the proportions of the omphacite doublets are similar to those shown for the hedenbergite-acmite series. In addition, the IS and line-width values reported for these omphacites do not differ significantly from those listed in Table 4. From the strong similarity of the fitted

results it may be concluded that the Mössbauer spectra of these two groups are closely similar.

Ferrous iron in M(1) sites and interpretation of multiple doublets

In the case of sodic and subcalcic clinopyroxenes it is evident that multiple doublets are required to reproduce the absorption features. Because different numbers of doublets yield fits of equal quality, it is necessary to examine the interpretations of the doublets in order to determine how many peaks ought to be fitted.

The individual doublets of a multidoublet fit have substantially different QS values (0.4 to 1.0 mm/sec in the present cases) thereby implying the existence of iron atom sites with different nuclear electric field gradients. The electric field gradient is the sum of two effects: the deviation from cubic symmetry of the atomic arrangement surrounding an iron atom (the so-called "lattice" term) and the deviation from cubic symmetry of the six 3d-electrons of the Fe^{2+} atom itself (The "valence" term) (Dowty and Lindsley, 1973). In order to produce such different doublets from different local environments either the lattice term or the valence term, or both, must change markedly as a function of composition. The compositional sensitivity of the lattice term can be estimated from consideration of the ferric doublets, where, because of the spherical symmetry of the $3d^5$ configuration, the lattice term is the only contributing effect. The Fe^{3+} doublets in the pyroxenes studied show a variation of only 0.0 to 0.3 mm/sec across an entire binary join, and considering the similarity of structure it seems likely that the compositional variation in the Fe^{2+} lattice term is of similar magnitude. If the QS differences between multiple Fe^{2+} doublets are too large to be accounted for by variations in the lattice term alone, then the different doublets must represent Fe^{2+} atoms also differing in valence terms, *i.e.* having different d-electron distributions (different orbital configurations or occupancies). Dowty and Lindsley (1973) clearly pointed out the importance to their model of the valence term variations. Their model postulated that significantly different valence terms were possible due to an unusually small distortion from octahedral symmetry of Fe^{2+} in the pyroxene M(1) site (that is, near degeneracy of orbital energy levels) and that a change in occupancy of the surrounding M(2) sites results in a change of orbital configuration. The model predicts that there should

be as many discrete orbital configuration states as there are different M(2) occupancy arrangements.

Use of three or four doublets as predicted by this model makes it possible to reproduce the observed spectra of the sodic and subcalcic clinopyroxenes at both room and liquid nitrogen temperatures. Furthermore, the component peak areas obtained are in "semiquantitative" agreement with those calculated for random M(2) occupancy (Aldridge *et al.* 1978). These successes in fitting support the model but do not prove its correctness. Consideration of some of the underlying assumptions and resulting fit parameters, in fact, suggests that the model is not entirely satisfactory in either the subcalcic or sodic clinopyroxene cases. For example it seems rather *ad hoc* that different orbital configurations result from different numbers of Na and Ca (or Fe and Ca) neighbors in M(2) sites but do not depend upon their spatial arrangement, nor on the degree of order in the M(2) sites, nor on the size, valence or ordering of the atoms occupying the two equally close, edge shared M(1) sites. Thus, for example, the lack of detectable spectral differences between cation ordered *P2/n* omphacite and the heat-treated, cation disordered *C2/c* equivalent pyroxene (Aldridge *et al.*, 1978) is not well explained by an occupancy sensitive model. Furthermore, if QS is a sensitive function only of M(2) site occupancy which implies that all other effects are too weak to produce further discernable doublets, then a given doublet ought to be fairly constant with composition. Aldridge *et al.* (1978) recognized this implication and proposed that their three fitted doublets have QS values of about 1.8 mm/sec for the CaCaCa environment, about 2.2 mm/sec. for the CaCaNa case and about 2.8 mm/sec in the CaNaNa case. However, pure hedenbergite, with a 100% CaCaCa configuration has a QS value of 2.24 mm/sec (Table 2) agreeing better with their CaCaNa value. Consideration of a wider range of compositions than those investigated by Aldridge *et al.* demonstrates (see Fig. 5) that in a three-ferrous doublet fit the CaCaCa doublet must change its QS value with composition, in fact by about 0.4 mm/sec from typical omphacite compositions to hedenbergite. Such a change is numerically equal to the QS difference between the CaCaCa and CaCaNa doublets which implies that the M(2) site occupancy is no more critical in determining QS than those changes in M(1) and more remote M(2) sites that represent the omphacite-to-hedenbergite composition shift. In the case of the subcalcic pyroxenes the variation of QS of a given doublet

with composition has been reported (Dowty and Lindsley, 1973) as up to nearly twice as large as the QS difference from one doublet to the next. For this solid solution series with no M(1) site occupancy variation, such large QS changes imply that more distant M(2) occupancy variations produce greater effects than do nearer M(2) occupancy variations!

Recently a near-neighbor variation model has been applied more convincingly to explain the Mössbauer spectra of a series of ferrous thiospinel solid solutions (Reidel and Karl, 1980). As a result of the energy level degeneracy of Fe^{2+} atoms on the $43m$ tetrahedral sites, separate doublets are indeed ascribable to different near-neighbor configurations. However, in contrast to the pyroxene results, the arrangements of substituents were found to be equally as important as their number and QS values of a given doublet did not change materially with composition.

An alternative interpretation of the broadened pyroxene absorption band may be obtained by further consideration of the implications of the two-ferrous-doublet fits. Insofar as such a model is applicable, the two doublets would represent two different populations of iron atoms with two different orbital configurations. The observed change of doublet area with temperature then implies that some atoms change from one configuration to the other as a result of the temperature change. Relatively minor changes in quadrupole splitting with temperature are well known and commonly result in a small QS increase as the temperature is lowered. On the other hand, large discontinuous QS changes, though less common, may also be produced by temperature changes. For example, a very large 2 mm/sec QS increase occurs at ca. 240 K in $\text{Fe}^{2+}(\text{H}_2\text{O})_6(\text{ClO}_4)_2$ (Reiff *et al.*, 1973) when the orbital ground state configuration flips from a doublet state to a singlet state. The change in distortion of the Fe^{2+} coordination octahedron that occurs at this transition has been attributed to a minor rearrangement in the hydrogen bonding scheme (Brunot, 1974).

The QS increases, whether large or small, reflect an increasingly asymmetric (less degenerate) orbital configuration. With nearly degenerate d-orbital energy levels the effect will be greater. In the sodic pyroxenes the difference between the QS changes with temperature suggest that the inner-doublet Fe^{2+} is in a less distorted site than the outer-doublet Fe^{2+} . As the inner doublet proportion increases with both hedenbergite component as well as with

temperature, it can be inferred that the Fe^{2+} site is generally less distorted in hedenbergitic pyroxenes and at high temperatures but becomes more distorted with either an increase in jadeite-acmite component or temperature decrease.

Considering both temperature and compositional effects on Fe^{2+} d-orbital configurations, the two-doublet model can be interpreted as follows. At some temperature and as a result of all neighboring atomic interactions, each M(1) ferrous atom in the sample adopts one of two possible orbital configurations. Sufficient change of either temperature or chemical environment will cause a flip from one configuration to the other. In a solid solution atoms will occur in each of the two postulated orbital states, although the proportions will gradually change across the compositional series and the exact fraction will depend on the temperature. Because of the range of environments there would be no sharp transition temperature akin to a phase transformation. At sufficiently high or sufficiently low temperature this model would predict there to be only one orbital state and consequently only one M(1) doublet. The peakwidth, however, would be influenced by compositional variation in the same way as seen with other pyroxene series reported earlier in this paper.

The two doublet model suffers, however, from some of the same problems as the three or four doublet model by assuming a small number of discrete orbital configurations for which no independent evidence exists. Nothing precludes there being in reality a larger number of discrete states or simply a continuum of states. It would seem prudent at this point to accept neither of these simple models with any certainty until these more fundamental questions of configuration variation are better resolved.

Optical spectroscopic investigations of orbital configurations and splittings, single-crystal Mössbauer investigations of nuclear electric field gradient tensor orientations and variable temperature Mössbauer studies of mixed Na-Ca clinopyroxenes could provide further evidence. Explanations are also needed as to why multiple doublets from one crystallographic site seem to be restricted to pyroxenes or possibly a few other minerals such as the thiospinels mentioned above.

Electron hopping in sodic clinopyroxenes

Rapid electron hopping between cations of different valence states occupying neighboring edge-

shared polyhedra has been recognized in silicates and other minerals (for a recent review see Burns, 1981). The ease of such hopping is in part related to the temperature, extent of edge sharing, atomic separations and the degree of similarity of the two sites involved. When this hopping is rapid relative to the Mössbauer-effect timescale, an averaging of the two valence states occurs with the appearance of new absorption areas intermediate between normal ferrous and ferric peaks. M(1)-M(1) hopping in aegirine has been reported by Amthauer and Rossman (1979, 1980). Comparison of the hedenbergite-acmite series spectra, at the two temperatures of measurement shown in Figure 2, also demonstrates that a very small, but finite, continuous absorption band can be seen in the room temperature spectrum in the region between the ferrous and ferric peaks. As this absorption is very weak it suggests that neighboring M(1) sites containing Fe^{2+} and Fe^{3+} are sufficiently distinct, perhaps due to attendant local ordering of Ca and Na atoms, to nearly suppress hopping, at least at or below room temperature.

Conclusions

The ^{57}Fe Mössbauer spectra of synthetic and natural sodic clinopyroxenes reported here and in earlier studies have established the general spectral effects resulting from compositional variations within this major mineral group. In brief, isovalent replacements produce negligible to modest, regular changes in Fe^{2+} and Fe^{3+} quadrupole splittings and linewidths. Allovalent substitutions, on the other hand, produce larger spectral changes expressed primarily as widening of ferrous or ferric absorption peaks into broad absorption bands. The increased energy range over which Mössbauer absorption occurs undoubtedly reflects the increased range of crystal structure environments experienced by the probe iron atoms. It is not known, however, whether this increased range consists of a few discrete environments or a more or less continuous range of environments. Lacking this information the appropriate number of peaks to be fitted to these clinopyroxenes remains unresolved, thereby presently inhibiting the full potential application of Mössbauer spectroscopy to site occupancy determination or other quantitative aspects of structure probing.

Acknowledgments

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hedenbergite join were prepared by W. P. Freeborn. The hydrothermal laboratory facilities were provided by W. G. Ernst and partially supported by NSF grant EAR 79-23615. We thank W. M. Thomas, G. R. Rossman and G. A. Waychunas for many helpful discussions as well as for their reviews of the manuscript. This study was supported in part by the National Science Foundation.

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