MÖSSBAUER AND INFRARED STUDY OF A
VOLCANIC AMPHIBOLE

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Abstract

Mössbauer spectra have been obtained from an analysed volcanic cummingtonite at 4.2, 55, 78 and 298°K. The spectra are essentially the same except at the lowest temperature where new lines appear. Analysis of the 298°K Mössbauer spectrum and an infrared spectrum shows that the cation distribution is not greatly different from that previously recorded for metamorphic cummingtonites of similar composition.

Introduction

Although cummingtonite is usually found in metamorphic rocks it is occasionally present in plutonic or even volcanic rocks. Kuno (1938), for example, has recorded cummingtonite from a hypersthene dacite. Cummingtonite also occurs in a Pleistocene rhyolitic pumice breccia belonging to the Rotoiti Pumice Breccia Formation at Rotoiti, New Zealand. The material consists of phenocrysts of plagioclase (andesine), quartz, cummingtonite and minor hypersthene, magnetite and ilmenite embedded in fresh pumiceous glass.

A. Ewart, in a paper in preparation on the acid volcanic rocks of the Rotorua region, has estimated that the conditions in the magma chamber prior to extrusion were 700–800°C and about 2 kbar H_2O pressure. After initial rapid fall in temperature the flow probably cooled to about 200°C in the two weeks following the extrusive episode.

Ghose and Hafner (1967) have shown that the cations in some volcanic orthopyroxenes are considerably more disordered than their metamorphic equivalents. It would perhaps be expected that the more disordered cation distributions characteristic of higher temperature would be frozen into the volcanic amphiboles. Testing this prediction was the reason for the present investigation.

Recent studies on cummingtonites have indicated that it is a simple matter to obtain information about the distribution of Fe and Mg over the nonequivalent cation sites using Mössbauer and infrared spectroscopy. Although with Mössbauer (Ghose and Hafner, 1968; Gibb and Greenwood 1965) or infrared (Burns and Strens, 1966) alone, it has only been possible to determine a partial ordering scheme, Bancroft, *et al.* (1967) have shown that by combining data from both techniques it is possible to determine the distributions completely.

In the present paper the results of infrared and liquid nitrogen (78°K) and liquid helium (4.2°K) Mössbauer examinations are recorded and compared with room temperature data. It will be shown that the 4.2°K spectrum provides much additional information though an unequivocal interpretation is not possible at present.

Chemical Analysis

The chemical analysis of the amphibole as presented in Table 1 is rather high in Al and Ca but still within the cummingtonite range of composition. The material will be described in more detail by A. Ewart.

Infrared

A high resolution infrared spectrum taken with a grating instrument with spectral slit width set at 1.5 cm^{-1} again shows the features of an iron-poor cummingtonite. In Figure 1 its hydroxyl spectrum is compared with that of a metamorphic cummingtonite DH7-484 (Mueller, 1960). It will be observed that although the frequencies of the bands are almost identical in comparison as expected, bandwidths of the volcanic speci-

Table 1. Chemical Analysis and Structural Formula of Cummingtonite
(Ewart 1971)

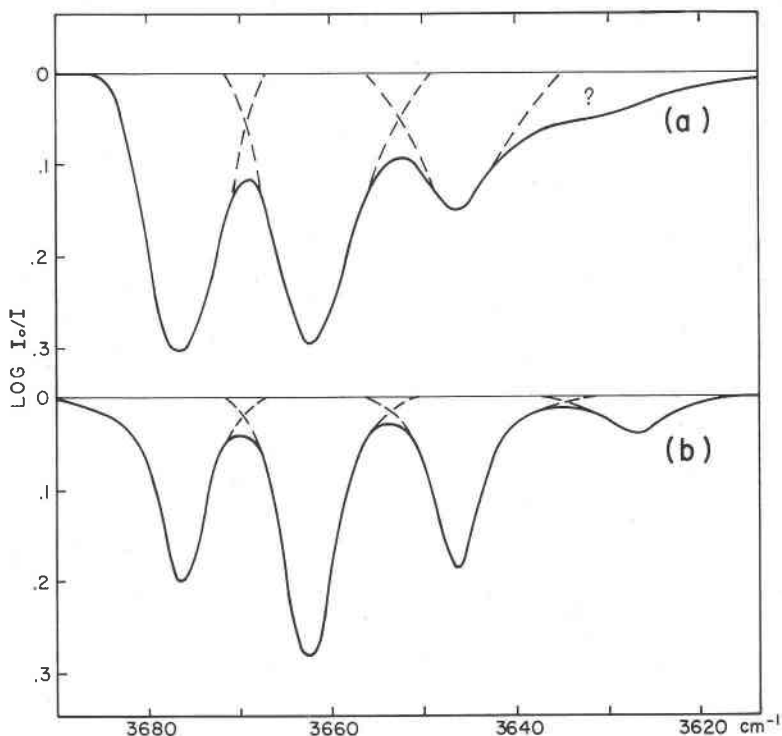|	Weight %		Number of ions on the basis of 24 (O, OH, F)	
SiO_2	53.6	Si^{4+}	7.742	8.00
		Al^{3+}	.258	
Al_2O_3	1.84	Al^{3+}	.054	
TiO_2	0.46	Ti^{4+}	.050	
FeO	17.4	Fe^{2+}	2.102	
Fe_2O_3	1.26	Fe^{3+}	.137	
MgO	18.8	Mg^{2+}	4.048	7.06
MnO	1.29	Mn^{2+}	.158	
CaO	2.25	Ca^{2+}	.348	
Na_2O	0.51	Na^+	.142	
K_2O	0.10	K^+	.019	
H_2O	2.00	OH^-	1.927	2.00
F	0.18	F^-	.082	
Total	99.69			
O≡F	.08			
	99.61			

FIG. 1. Infrared spectra of cummingtonites in the hydroxyl stretching region. (a) Volcanic cummingtonite P30407 (b) Metamorphic cummingtonite DH7-484 (Mueller, 1960).

men ($\backsim$10 cm^{-1}) are appreciably larger than those of the metamorphic specimen ($\backsim$6 cm^{-1}). The same feature has been observed in a comparison of talc and mica (Wilkins, 1967) and is almost certainly related to the degree of Al substitution for Si. The broader bandwidths in the volcanic cummingtonite may have the same origin since there are 0.3 Al atoms in 8 tetrahedral sites compared to negligible substitution for the metamorphic example. The volcanic cummingtonite also contains appreciable Fe^{3+}. This is not obviously in the $M(1)$, $M(3)$ sites but should it be present absorption will occur mainly below 3640 cm^{-1}, as inferred from results on other amphiboles (Burns and Prentice, 1968; Wilkins and Vedder, 1969). For this reason, $Fe^{2+}/Fe^{2+}+Mg$ for $M(1)$, $M(3)$ sites (0.27) has been calculated from the relative intensities of the two high frequency bands only.

MÖSSBAUER

A powder of the volcanic cummingtonite was pelleted in polypropylene

to form an absorber of thickness 10 mg natural iron per cm². Mössbauer spectra were determined at 298, 78, 55 and 4.2°K, with a 10 mCi source of ^{57}Co in Pd kept at the same temperature as the absorber by means of helium exchange gas (so that second order Doppler shifts should be negligible). In the same source-absorber geometry as used for the cummingtonite, the source gave a thickness-corrected observed linewidth (full width at half height) of 0.23 mm/sec with sodium nitroprusside dihydrate. Ghose and Hafner (1968), reporting the results of a liquid nitrogen temperature (78°K) examination of metamorphic cummingtonite, noted only minor differences between the 298°K and 78°K spectra. The same can be said of the spectra of our specimen down to 55°K, but at 4.2°K, the spectrum is considerably more complicated. The 298°K and 78°K Mössbauer spectra are shown in Figure 2, and a comparison of the spectral parameters is provided in Table 2. The computed fit shown is the best fit obtained using Lorentzian lineshapes in the iterative curve fitting procedure. Much better fits were obtained using non-Lorentzian lineshapes as discussed later.

Several features of the spectra require comment. The central peak of low intensity which appears has been assigned to Fe^{3+}. The Fe^{3+}/Fe^{2+} ratio estimated from the spectral intensities at room temperature (where this small peak is best resolved) is 0.053 compared to 0.065 from chemical analysis.

In our room temperature spectra, the width of the outer doublet components is much the same as the width of the inner doublet components. This is to be compared with the results quoted by Bancroft *et al.* (1967) in which the outer lines were broader than the inner. They used this as further evidence for the outer doublet being a superposition. The quadrupole splitting for the inner doublet ranges between 1.50 and 1.64 mm/sec in the specimens examined by Bancroft *et al.* This compares with our value of 1.71 mm/sec at 298°K. These effects can be attributed mainly to differences in composition, since our material is unusually magnesian and outside the range of composition studied by Bancroft *et al.*

At room temperature, integral asymmetry is also conspicuous. For both doublets the component at the more negative relative velocity is more intense by about 14 percent. This asymmetry is probably due to the Karyagin effect (anisotropy in the recoil-free fraction) as the absorber was prepared in such a way as to avoid preferred orientation of the crystallites. At 78°K the outer doublet exhibits no integral asymmetry, as expected if the Karyagin effect were in fact the reason for the asymmetry at 298°K. The inner doublet, however, still appears to be asymmetric, most probably because of the uncertainty in the position of the
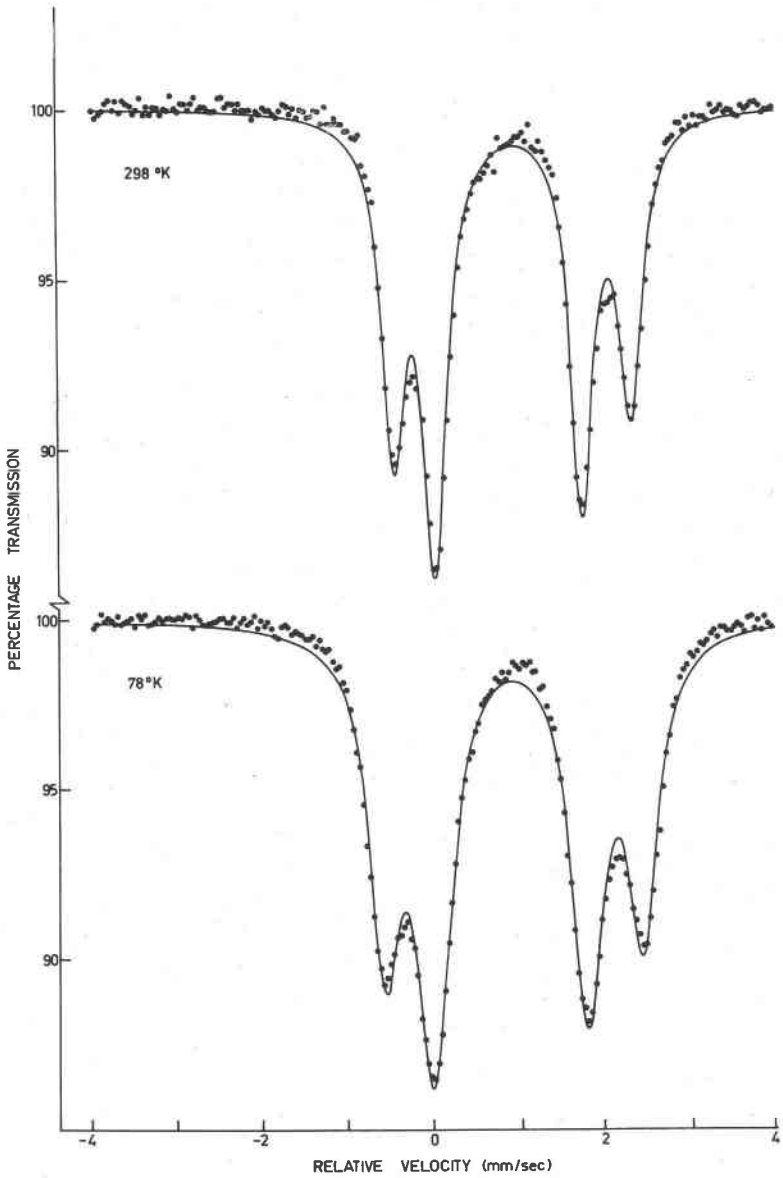
FIG. 2. 298°K and 78°K Mössbauer spectra of volcanic cummingtonite P30407.
Lines shown are computed best fits using Lorentzian line shapes.

TABLE 2. MÖSSBAUER PARAMETERS FOR LORENTZIAN FITS TO VOLCANIC
CUMMINGTONITE SPECTRA AT 298°K, 78°K AND 4.2°K

T°K	Peak	Peak position (mm/sec)	Width (mm/sec)	Fractional Area	Doublet	Isomer shift[a] (mm/sec) ±0.02	Quadrupole splitting (mm/sec) ±0.02
298	3	−0.42	0.33	0.21			
	4	0.07	0.35	0.30	3+7	0.97	2.77
	5	0.60	0.32	0.05			
	6	1.78	0.34	0.26	4+6	0.93	1.71
	7	2.35	0.32	0.18			
78	3	−0.55	0.43	0.20			
	4	0.02	0.48	0.30	3+7	0.97	3.03
	5	(0.23)	(0.44)	(0.03)[b]			
	6	1.83	0.46	0.27	4+6	0.93	1.81
	7	2.48	0.45	0.20			
4.2	1	−1.53	1.22	0.05			
	2	−0.75	1.21	0.10	1+9	1.40	5.86
	3	−0.51	0.67	0.10			
	4	0.03	0.44	0.23	2+8	0.87	3.25
	5	0.93	0.82	0.06			
	6	1.77	0.53	0.22	3+7	0.92	2.85
	7	2.34	1.24	0.08			
	8	2.48	0.82	0.11	4+6	0.90	1.80
	9	4.33	1.42	0.06			

[a] With respect to ^{57}Co in Pd.
[b] Parameters doubtful for this peak.

contribution from the Fe^{3+}, *i.e.*, the asymmetry might be caused by a superposition of the Fe^{3+} peak. As mentioned below, it is thought that relaxation effects are evident at 4.2°K, giving rise to the possibility that even at 78°K one quadrupole doublet component might be relaxation broadened. This would only give rise to peak height asymmetry, however, not integral asymmetry. Nevertheless, since the outer doublet, consisting of contributions from the $M(1)$, $M(2)$ and $M(3)$ sites is being fitted with one quadrupole doublet only, and since the outer doublet is not completely resolved from the inner doublet, an apparent area asymmetry may result unless all of the three sites are subject to relaxation of the same rate.

In going from room to liquid nitrogen temperature, the isomer shifts for the two groups of sites remain unchanged whereas the inner doublet splitting has increased slightly. The quadrupole splitting of the outer

doublet, on the other hand, has increased considerably, but the doublet contributions from the $M(1)$, $M(2)$ and $M(3)$ sites are still not resolved. As pointed out by Ghose and Hafner (1968), this is understandable since these three sites have quite similar environments and might be expected to exhibit similar temperature dependences for the quadrupole splitting.

In view of this difference in the temperature dependences of the quadrupole splittings, a spectrum at 4.2°K was determined to see whether the two doublets could be further resolved and whether differential changes in symmetry might cause the outer doublet to be resolved into its three doublet components, although a spectrum taken at 55°K was not appreciably different to the 78°K spectrum.

As shown in Figure 3, the liquid helium temperature spectrum no longer consists of two doublets; this is demonstrated by Figure 3(A) where the best fit to four Lorentzians is shown. A fit to nine Lorentzians was attempted, the best fit being shown in Figure 3(B) and the corresponding parameters listed in Table 2. However it can be seen from the fitted parameters that it is most unlikely that the spectrum now consists of four quadrupole doublets with quite different splittings (together with the small peak in the middle); the isomer shift and quadrupole splitting for the outermost fitted doublet are too extreme to be reasonable. Also the width of the resolved peak at ca 4.3 mm/sec suggests that relaxation effects might be present, consequently the parameters for the 4.2°K spectrum listed in Table 2 are to be considered as having limited significance.

It is proposed that the 4.2°K spectrum exhibits the effects of paramagnetic relaxation, although the observation of magnetic hyperfine structure in paramagnetic ferrous compounds by Mössbauer spectroscopy (in zero applied field) is most unusual, even at 4.2°K, since the spin-lattice relaxation times involved are usually much too short. Recently, however, Shenoy $et\ al.$ (1969) have reported the observation of such spectra in orthopyroxenes, $Fe_xMg_{1-x}SiO_3$, $x < 0.4$. The spectrum that these workers observe for the orthopyroxene with $x = 0.269$ at 4.2°K exhibits many of the features present in our 4.2°K cummingtonite spectrum. In this orthopyroxene, essentially only one of the two possible Fe^{2+} sites is occupied, so that the magnetic hyperfine pattern produced is virtually a unique one. The cummingtonite spectrum here is complicated by the fact that all four sites are occupied. The inner doublet, assumed to be associated with the $M(4)$ sites, is still well defined at 4.2°K, so that the Fe^{2+} in these sites is relaxing considerably faster than the nuclear Larmor precession frequency. This is not unreasonable since the more distorted $M(4)$ site might be expected to have a smaller hyperfine field than the other three sites ($c.f.$ orthopyroxenes). It is difficult
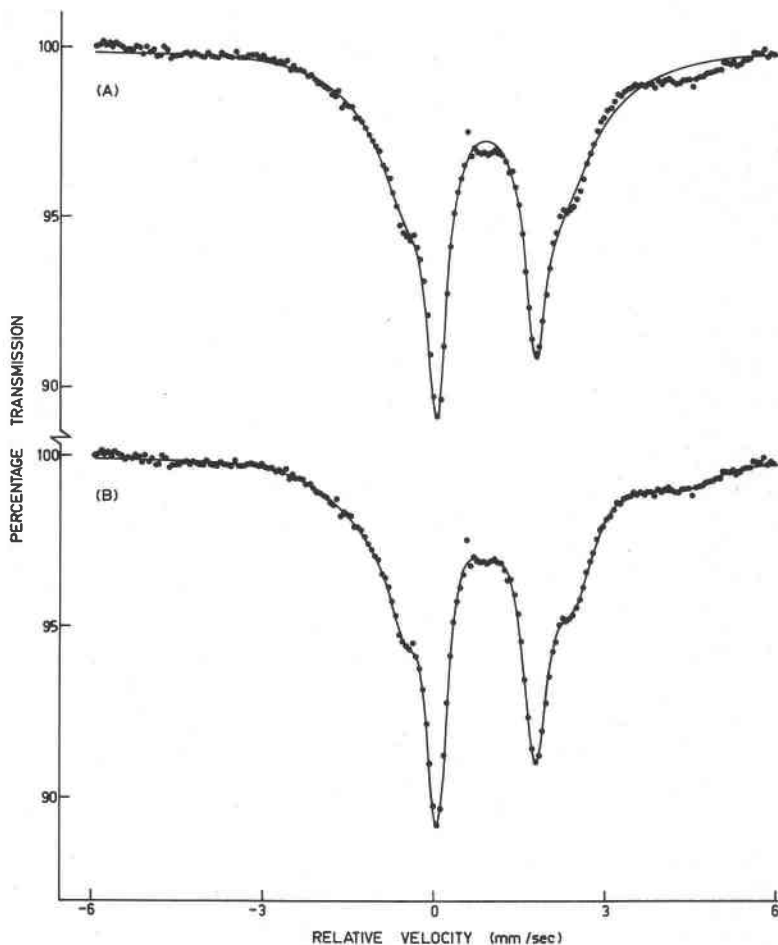
Fig. 3. Liquid helium (4.2°K) Mössbauer spectrum of volcanic cummingtonite P30407. (A) Best fit to four Lorentzians (B) Best fit to nine Lorentzians.

to say whether all of the other three sites are giving rise to magnetic hyperfine structure, or just one or two of the sites. The latter possibility seems likely as there still seems to be a quadrupole doublet contribution in roughly the same position as the outer doublet of the higher temperature spectra.

Even if the low temperature spectrum could be unequivocally interpreted, fitting to a sufficient accuracy to determine site occupancy information would be extremely difficult. In principle, this information could be obtained from a spectrum determined at a considerably lower tem-

perature (*e.g.* 0.5°K), particularly if the hyperfine fields at each site were different.

The ratio of Fe^{2+} in the $M(4)$ sites to the other three sites has been calculated from the room temperature spectral intensity data (the 78°K data give rise to the same ratio). Bancroft *et al.* (1967) obtained the relationship

$$A_4/A_{1,2,3} = 0.9n_4/n_{1,2,3}$$

where subscripts refer to the $M(1)$, $M(2)$, $M(3)$, and $M(4)$ positions, A is the peak (doublet) area and n is the number of Fe^{2+} ions. The factor 0.9, implying essentially that the recoil-free fraction for the $M(4)$ site is *ca* 10% lower than a weighted mean recoil-free fraction for the other three sites, seems somewhat low. Virgo and Hafner (1968) found that the recoil-free fractions for the two Fe^{2+} sites in $FeSiO_3$ were very nearly the same, and as the $M(1)$ and $M(2)$ sites in $FeSiO_3$ are quite similar to the $(M(1),M(2),M(3))$ and $M(4)$ sites in cummingtonite respectively, a factor close to 1.0 is expected here also. It is possible that an apparent recoil-free fraction difference arises out of using the areas of computed best-fit Lorentzians. These areas might be different from the actual areas under the two doublets, as the lineshapes are probably not exactly Lorentzian. We obtained much better fits to the spectra using "pseudo-Lorentzians" involving exponents slightly greater than 2.0,[1] but Lorentzian line shapes, as well as Bancroft's 0.9 factor are used here to facilitate comparison with the published work on metamorphic cummingtonite.

DISCUSSION

The cation distribution as calculated from the infrared and 298°K Mössbauer data are given in Table 3 where it is compared with the cation distribution in a metamorphic cummingtonite of similar composition. There is some arbitrariness in placing the Fe^{3+}, Al^{3+}, Ca^{2+}, Na^+ and Mn^{2+}. The infrared spectrum indicates that these ions are not present in any significant concentration in $M(1)$, $M(3)$ sites and they have been allocated to $M(2)$ and $M(4)$ sites on the basis of amphibole crystal chemical considerations.

It is interesting to observe that when allowance is made for the different proportions of impurity ions the cation distrubutions in the metamorphic and volcanic specimens are not dissimilar. This could mean that

[1] Lorentzian = background $- \dfrac{\text{peak height}}{1 + \left(\dfrac{2}{\text{width}}\right)^2 (x - \text{peak posn.})^{2.0}}$

TABLE 3. CATION DISTRIBUTION IN CUMMINGTONITE PER FORMULA UNIT

Site	35.4% Fe metamorphic cummingtonite[a]	Volcanic cummingtonite 30407 298°K data
$M(4)$	Fe^{2+} 1.65 Mg 0.14 Ca 0.13 Mn 0.08	Fe^{2+} 1.29 Mg 0.10 Ca 0.35 Mn 0.16 Na 0.10
$M(2)$	Fe 0.11 Mg 1.89	Fe^{2+} 0.00 Mg 1.76 Fe^{3+} 0.14 Al^{3+} 0.05 Ti^{4+} 0.05
$M(1)$	Fe^{2+} 0.48 Mg 1.52	Fe^{2+} 0.54 Mg 1.46
$M(3)$	Fe^{2+} 0.24 Mg 0.76	Fe^{2+} 0.27 Mg 0.73

[a] Data from Bancroft et al. (1967).

a conspicuous degree of disordering was not present in the amphibole at equilibrium at magmatic temperatures. Alternatively, cooling of the flow would have been slow enough for the present degree of ordering to have developed.

REFERENCES

BANCROFT, G. M., R. G. BURNS, AND A. G. MADDOCK (1967) Determination of cation distribution in the cummingtonite-grunerite series by Mössbauer spectra. *Amer. Mineral.* **52,** 1009–1026.

BURNS, R. G., AND F. J. PRENTICE (1968) Distribution of iron cations in the crocidolite structure. *Amer. Mineral.* **53,** 770–776.

———, AND R. G. J. STRENS (1966) Infrared study of the hydroxyl bands in clinoamphiboles. *Science,* **153,** 890–892.

GHOSE, S., AND S. S. HAFNER (1967) Mg^{2+}–Fe^{2+} distribution in metamorphic and volcanic orthopyroxenes. *Z. Kristallogr.* **125,** 157–162.

———, AND ——— (1968) Mg–Fe distribution over (M_1, M_2, M_3) and M_4 sites in cummingtonite. *Geol. Soc. Amer. Annu. Meet. Prog. Abstr.* **1968** 110–111.

GIBB, T. C., AND N. N. GREENWOOD (1965) Chemical applications of the Mössbauer effect. Part 2. Oxidation states of iron in crocidolite and amosite. *Trans. Faraday Soc.* **61,** 1317–1323.

KUNO, H. (1938) On the occurrence of primary cummingtonitic hornblende in some dacites from Japan. *Proc. Imp. Acad. Tokyo,* **14,** 221.

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

SHENOY, G. K., G. M. KALVIUS, AND S. S. HAFNER (1969) Magnetic behaviour of the FeSiO$_3$-MgSiO$_3$ orthopyroxene system from N.G.R. in ^{57}Fe. *J. Appl. Phys.* **40,** 1314–1316.

VIRGO, D., AND S. S. HAFNER (1968) Re-evaluation of the cation distribution in orthopyroxenes by the Mössbauer effect. *Earth Planet. Sci. Lett.* **4,** 265–269.

WILKINS, R. W. T. (1967) The hydroxyl stretching region of the biotite mica spectrum. *Mineral. Mag.* **36,** 325–333.

——, AND W. VEDDER (1969) Mechanisms of thermal decomposition in micas and amphiboles. *Proc. 6th Int. Symp. Reactiv. Solids,* 227–235.