THE AMERICAN MINERALOGIST, VOL. 52, JULY–AUGUST, 1967

DETERMINATION OF CATION DISTRIBUTION IN THE CUMMINGTONITE-GRUNERITE SERIES BY MÖSSBAUER SPECTRA

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Abstract

Mössbauer spectra for the cummingtonite-grunerite and manganoan cummingtonite series give the proportion of Fe^{2+} ions in the $M(4)$ and $(M(1)+M(2)+M(3))$ positions of the amphibole structure. These results, together with data for the Fe^{2+} ion distribution between the $(M(1)+M(3))$ and $(M(2)+M(4))$ positions determined by infrared spectroscopy, enable total site populations to be estimated for each specimen.

Fe^{2+} ions occupy the $M(4)$ position preferentially, and discriminate against the $M(2)$ position. In manganoan cummingtonite, Mn^{2+} ions favor the $M(4)$ position more strongly than iron.

Detection of cation ordering and estimations of site populations in ferromagnesian silicates by the Mössbauer technique are more rapid, direct and accurate than conventional X-ray methods. The Mössbauer technique also provides a method for detecting $Fe^{2+}-Mn^{2+}$ ordering in silicate minerals.

Introduction

The Mössbauer effect can provide a rapid, direct and accurate method for estimating site populations in the crystal structures of iron-containing minerals. A study of various silicate series—olivine, pyroxene, amphibole, garnet and epidote—has been made (Bancroft and Burns, 1966*a*, *b*). In the present paper results for the cummingtonite-grunerite series[2] $(Mg, Fe)_7Si_8O_{22}(OH)_2$ are described.

Ordering of Fe^{2+} ions in ferromagnesian silicates has been detected in the structures of hypersthene (Ghose, 1965a), pigeonite (Morimoto Applemann and Evans, 1960) and cummingtonite (Ghose, 1961; Fischer, 1966; Ghose and Hellner, 1959) by X-ray diffraction. In the cummingtonite structure, ordering has also been inferred from infrared spectroscopy (Burns and Strens, 1966) and chemical analysis (Klein, 1964).

Ghose (1965b) has stated that detection of cation ordering by X-ray diffraction can lead to ambiguous results, especially if some of the ele-

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[2] The nomenclature of W. A. Deer, R. A. Howie and J. Zussman, *Rock-Forming Minerals*, v. 2, p. 235 (Longmans, London, 1963) is adopted in this paper. Cummingtonite refers to minerals containing less than 70 mole percent $Fe_7Si_8O_{22}(OH)_2$; grunerite is applied to compositions exceeding 70 mole percent of the Fe (II) component.

ments involved, such as Fe and Mn, have similar scattering factors. Even in actinolite, where Fe and Mg have appreciably different scattering factors, ordering was not detected by X-ray methods (Zussman, 1955), although infrared (Burns and Strens, 1966) and Mössbauer (Bancroft and Burns, 1966*b*) measurements have indicated that significant ordering does occur. In addition, the inherent experimental errors in the X-ray techniques can amount to at least 10 percent of the estimated values (Ghose, 1965*a*). Infrared spectra of the cummingtonite-grunerite series may indicate ordering (Burns and Strens, 1966), but the method generally provides partial site populations only. Chemical analysis, together with optical and density measurements, may suggest ordering (Klein, 1964), but site populations cannot be estimated.

The variation of Mössbauer spectra with the distortion of the coordination polyhedra provides a potential method for estimating cation distribution in the cummingtonite-grunerite series from the peak areas. These data, together with results obtained from infrared measurements (Burns and Strens, 1966) enable total site populations to be determined in the cummingtonite structure.

Previous Mössbauer measurements on silicates (de Coster, Pollak and Amelinckx, 1963; Sprenkel-Segel and Hanna, 1964; Gibb and Greenwood, 1965) have indicated that the unusually large line widths in some minerals are due to a superposition of lines. Lines due to Fe^{2+} usually have widths at a half height of less than 0.45 mm/sec for a stainless steel source. Since Mössbauer data are obtained in digital form, rather than analog form as in many spectroscopic techniques, they are readily amenable to detailed computer processing. This will resolve lines not resolvable visually, and compute areas under peaks (Stone, 1966). Site populations obtained in the present study have been estimated from computer-fitted spectra.

THE MÖSSBAUER EFFECT

The Mössbauer effect is the term used to describe the recoilless emission and resonant absorption of nuclear gamma rays, discovered in 1957 by R. L. Mössbauer. As in most resonant experiments, a measurement is made of the absorption of electromagnetic radiation by an absorber after emission by a source. In this instance, the nuclear absorption of γ rays is measured. Resonant absorption is difficult to observe because the emitting and absorbing atoms recoil, causing the emitted γ ray to have insufficient energy to be absorbed. Mössbauer found that using solid sources and absorbers, a certain fraction of the γ rays is emitted and absorbed without recoil of the atom, so that the γ ray has just the right energy to be absorbed. The absorption band extends over a very narrow range of energies. Thus, the ratio of the linewidth of the absorption band to the energy of the γ ray is about 3 parts in 10^{13} for Fe^{57}. Such a narrow linewidth permits nearby energy levels of the nucleus to be observed by changing the energy of the emitted γ rays using the Doppler effect.

Experiments are carried out using a radioactive source, an absorber and standard counting techniques. The energy of the γ ray emitted by the source is shifted by moving the source relative to the absorber. The source is usually mounted on a vibrator, a range of velocities is scanned repetitiously for a period of hours, and the γ rays transmitted through the absorber are recorded in a multichannel analyser. The γ rays received during a given portion of the velocity cycle of the source are always recorded in the same channel. Thus, each channel records γ rays detected when the source is moving at some given average velocity. If a stainless-steel source and absorber are used, one peak is obtained at zero velocity. If a different paramagnetic absorber is used, one or two peaks may be observed at different velocities, corresponding to different energies.

The two characteristic parameters obtained from the Mössbauer spectrum of a paramagnetic compound are the chemical isomer (C.I.) shift and the quadrupole quadruple splitting (Q.S.). The C.I. shift is defined for a one-line spectrum, as the displacement of the resonance line from zero velocity, obtained with a reference source. In the cese of a two-line spectrum the C.I. shift refers to the displacement of the midpoint of the doublet from zero velocity. The C.I. shift is a measure of electron density at the nucleus and can be related to chemical bonding. The quadruple splitting is the separation between the doublet peaks in a Mössbauer spectrum. It is determined by the asymmetry of the electric field at the nucleus, and can be related to the symmetry of the electronic configuration of the absorbing atom and to the symmetry and effective charge of the surrounding atoms in the lattice.

The Mössbauer effect has been observed in about 30 isotopes but only two, Fe^{57} and Sn^{119}, have been widely studied by chemists. Recent descriptions of the theory and application of Mössbauer spectroscopy are given by Wertheim (1964) and DeVoe and Spijkerman (1966).

DESCRIPTION OF METHOD

The area, A, under a peak in the Mössbauer spectrum of a thin absorber is given by (Preston, Hanna and Heberle, 1962)[1]

$$A = \tfrac{1}{2}\pi n f_a f_s \sigma_o \Gamma G(n, f_a, \sigma_o) \qquad (1)$$

where

n is defined in this paper as the number of Fe atoms per formula unit

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[1] Equation (1) is not strictly true for a two-line spectrum. For a full discussion of the difficulties and assumptions involved in the method, see Bancroft, to be published.

f_a is the Mössbauer fraction of the absorber—the fraction of atoms which absorb resonantly without recoil
f_s is the Mössbauer fraction of the source
σ_0 is the maximum resonant absorption cross section
Γ is the width of the peak at half height
$G(n, f_a, \sigma_0)$ depends on the thickness and homogeneity of the absorber, as well as f_a and σ_0.

In theory, n should be directly determinable from A, but in practise such determinations have been rather unsuccessful. Sprenkel-Segal and Hanna (1964), who attempted to estimate mineral concentrations in stone meteorites using external standards, have discussed some of the difficulties involved.

The method used in the present study employs one specimen as standard, and this minimizes or eliminates many of the difficulties usually encountered.[1] If a mineral contains iron atoms in two distinct sites each of which gives rise to different Mössbauer spectra, the ratio of iron in the two sites, n_1/n_2, in the *same* mineral absorber is proportional to the ratio of the areas under the peaks. Thus

$$\frac{A_1}{A_2} = C\frac{n_1}{n_2} \tag{2}$$

where

$$C = \frac{f_1}{f_2}\cdot\frac{\Gamma_1}{\Gamma_1}\cdot\frac{G(n_1, f_{a_1}, \sigma_0)}{G(n_2, f_{a_2}, \sigma_0)} \tag{3}$$

In equation (2), the areas A_1 and A_2 are expressed as (channels×counts), but A_1/A_2 and n_1/n_2 are dimensionless. The ratio A_1/A_2 may be calculated directly from the spectra, and if n_1/n_2 is assumed for one mineral of a series, C may be determined. Then n_1/n_2 may be calculated for each of the remaining specimens from the areas under the Mössbauer peaks, if it is assumed that (1) C is a constant over the entire composition range, and (2) The Fe^{57} fraction is the same in each mineral, and no isotope fractionation takes place between sites.

THE CUMMINGTONITE CRYSTAL STRUCTURE

The crystal structure of a cummingtonite with 35.8 mole percent $Fe_7Si_8O_{22}(OH)_2$ was determined by Ghose (1961). It has the basic components of the amphibole structure and consists of infinite double chains of Si_4O_{11} groups linked by bands of cations, which extend along the *c* axis. There are four distinct positions of six-fold coordination which are designated M(1), M(2), M(3) and M(4). These are in the proportions M(1):M(2):M(3):M(4)=2/7:2/7:1/7:2/7. Cations in the M(1) and M(3) positions are coordinated to four oxygen and two hydroxyl (or, occasionally, F^-) ions, whereas six oxygen ions surround the cation in the M(2) position. The oxygen ions surrounding these positions are each linked to only one silicon ion. Cations in the M(4) position (which is the calcium position in the actinolite structure) are surrounded by four oxygen ions each linked to one silicon ion, and two oxygen atoms which are each shared by two silicon ions.

The coordination polyhedra about the M(1) and M(3) positions are flattened slightly along the *O*(1)-*O*(1) and *O*(3)-*O*(3) axes, respectively, whereas the M(2) coordination polyhedron is slightly compressed along the *b* axis (Fig. 1). The oxygen coordination polyhedron about the M(4) position is distorted considerably from octahedral symmetry, and is compressed along the *O*(4)-*O*(4) axis and elongated along the *b* axis (Fig. 1). Average metal-oxygen distances in the four coordination sites are: *M*(1) site, 2.099 Å; M(2) site, 2.084 Å; M(3) site, 2.092 Å; M(4) site, 2.306 Å. Therefore, the M(4) site is appreciably different, both structurally and energetically (Mueller, 1962; Burns, 1965), from the M(1), M(2) and M(3) sites.

The structure of a cummingtonite with 67.3 mole percent $Fe_7Si_8O_{22}(OH)_2$ is similar (Ghose and Hellner, 1959), and average metal-oxygen distances are: M(1) site, 2.114 Å; M(2) site, 2.108 Å; M(3) site, 2.110 Å; M(4) site, 2.295 Å;

EXPERIMENTAL

Measurements were made on six minerals of the cummingtonite-grunerite series, and one manganoan cummingtonite. All specimens, except the 35.4 percent Fe^{2+} cummingtonite, had been analysed previously. The compositions and sources of the specimens are summarized in Table 1. Concentrations are expressed as mole percentages of Fe (II), Mg (II), Mn (II) and Ca (II) components, and the number of each cation per formula unit is given in parenthesis. All analyses were checked by the electron-probe microanalyser, and are considered to have an accuracy better than ±2 percent.

The Mössbauer instrumentation and technique are described elsewhere (Bancroft, Maddock and Ward, 1966). A two millicurie source of Co^{57} in stainless steel was used. This gives a minimum line width of 0.35 mm/sec. with sodium nitroprusside as the absorber. All the spectra in the present study were measured with both the source and absorber at room temperature. Total counts in excess of 2×10^5 per channel were obtained for each spectrum.

Absorbers were prepared by mixing the finely ground mineral (150 mesh) with two grams of ground perspex and pressing the mixture into a disc about 1 mm thick. Each disc, except that of manganoan cummingtonite, contained an iron concentration of about 10 mg/cm^2. In the manganoan cummingtonite, enough sample was available to have a concentration of only 3 mg/cm^2.

The mirror image spectra obtained from the spectrometer were fit by computer to Lorentzian line shapes, the theoretical line shape. A good fit, defined by the value of χ^2 (Stone, 1966), was obtained for each spectrum, which confirmed the number and shape of lines fitted to the spectra.

RESULTS

The Mössbauer spectra obtained for the cummingtonite-grunerite series are shown in Figure 2. Each spectrum, taken directly from the computer plot, has been fitted to four Lorentzian curves with line widths between 0.36 and 0.42 mm/sec. The width of the outer two lines is slightly larger than the inner two lines in each spectrum. The relative in-

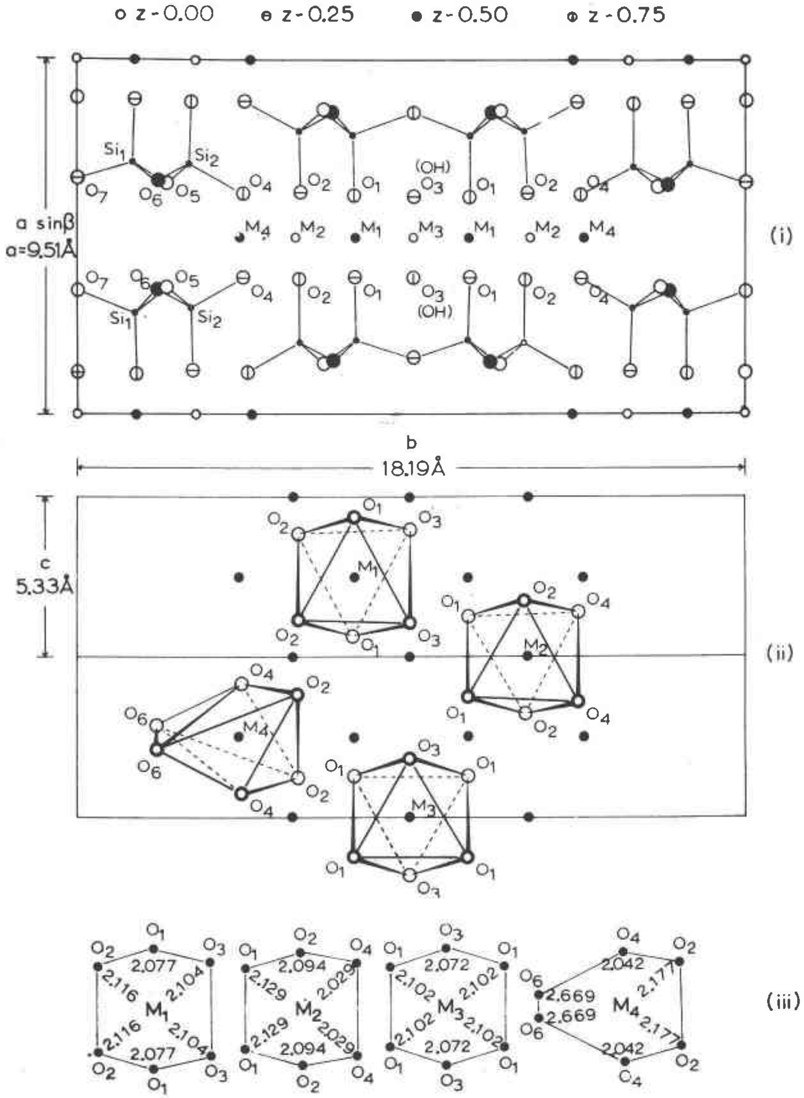


FIG. 1. The cummingtonite crystal structure. (i) Projection of the structure onto (001). (ii) Projection of the M(1), M(2), M(3) and M(4) coordination polyhedra onto (100). Bands of cations at $x=0.50$ are shown. (iii) Metal—oxygen distances in each coordination polyhedron. Atomic coordinates and cell parameters from Ghose (1961).

TABLE 1. CHEMICAL ANALYSES OF SPECIMENS

Specimen Cation	(1)	(2)	(3)	(4)	(3)	(4)	(3)
Iron mole % Fe (II) component	35.4	51.8	63.0	85.0	87.5	95.3	19.7
(Fe^{2+} per formula unit)	(2.48)	(3.63)	(4.41)	(5.95)	(6.13)	(6.67)	(1.38)
Magnesium mole % Mg (II) component	61.7	45.2	34.9	11.0	11.0	1.9	53.8
(Mg^{2+} per formula unit)	(4.32)	(3.17)	(2.44)	(0.77)	(0.77)	(0.13)	(3.76)
Manganese mole % Mn (II) component	1.1	1.8	1.9	1.4	0.7	1.2	23.7
(Mn^{2+} per formula unit)	(0.08)	(0.13)	(0.13)	(0.10)	(0.05)	(0.09)	(1.66)
Calcium mole % Ca (II) component	1.8	1.2	0.3	2.6	0.8	1.6	2.8
(Ca^{2+} per formula unit)	(0.13)	(0.08)	(0.02)	(0.18)	(0.06)	(0.11)	(0.20)

(1) Cummingtonite, from Bare Hills copper mine, Baltimore Co., Maryland. U. S. U. S. Nat. Mus. spec. no. 118125. (analyst: Burns, electron-probe).

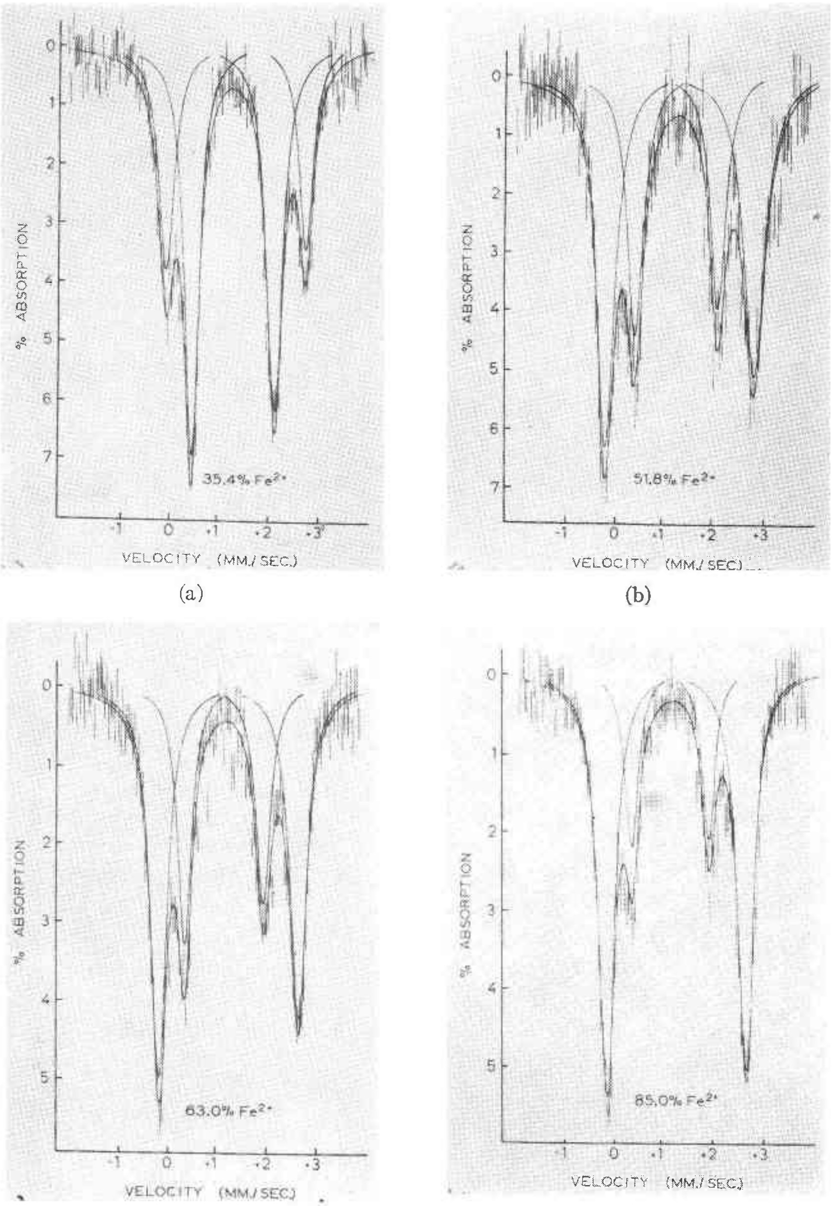
(2) Cummingtonite, in quartz-rich cummingtonite—garnet schist, from Mikonui River, Westland, New Zealand. (analyst: Mason, 1953).

(3) Cummingtonite, grunerite, and manganoan cummingtonite, from the Wabash Iron Formation, Labrador. (analyst: Klein, 1964).

(4) Grunerites, from the Quebec Iron Formation. (analyst: Mueller, 1960).

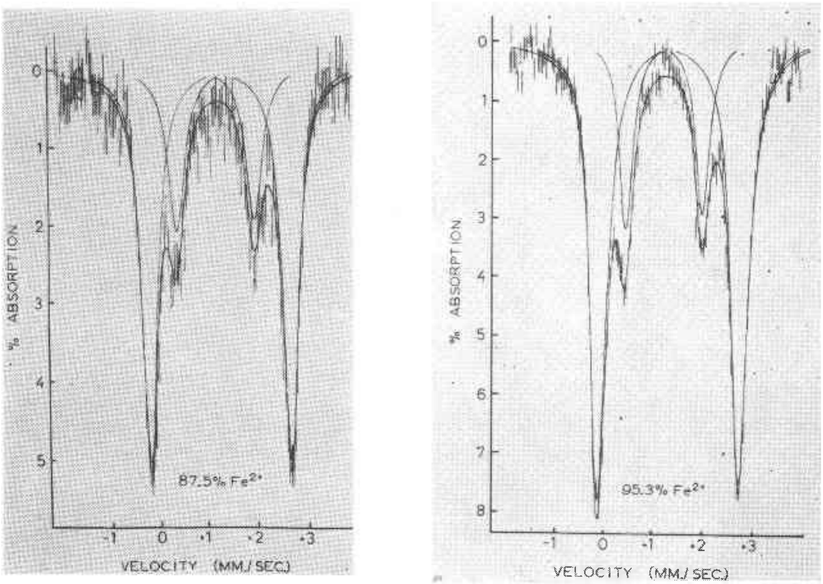
tensity of the peaks changes with composition: the inner two peaks decrease in intensity with increasing Fe^{2+} ion concentration. The quadruple splitting and isomer shift of the outer peaks are about 2.80 and 1.25 mm/sec., respectively, and for the inner two peaks 1.60 and 1.16 mm /sec., respectively. These parameters will be discussed in a later paper.

The first problem to be resolved is the assignment of the observed peaks to iron atoms in the appropriate sites in the cummingtonite structure. Because all "high-spin" Fe^{2+} compounds give rise to peaks with large quadruple splitting and intensities of quadruple pairs are generally equal, the four peaks observed in each spectrum must arise from at least two different types of iron. The inner two peaks are assigned to the M(4)


% ABSORPTION
VELOCITY (MM./SEC.)
35.4% Fe²⁺
51.8% Fe²⁺
63.0% Fe²⁺
85.0% Fe²⁺
-1
0
+1
+2
+3

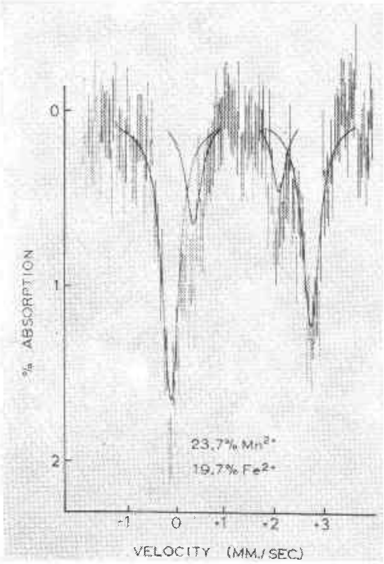
(a) (b)

(c) (d)



(e)

(f)



(g)

FIG. 2. Computer plots of the Mössbauer spectra of amphiboles of the cummingtonite-grunerite series. In each spectrum, the four Lorentzian line fits are shown.

(*a*) 35.4 percent Fe^{2+} cummingtonite;
(*b*) 51.8 percent Fe^{2+} cummingtonite;
(*c*) 63.0 percent Fe^{2+} cummingtonite;
(*d*) 85.0 percent Fe^{2+} grunerite;
(*e*) 87.5 percent Fe^{2+} grunerite;
(*f*) 95.3 percent Fe^{2+} grunerite;
(*g*) 19.7 percent Fe^{2+}, 23.7 percent Mn^{2+} cummingtonite.

TABLE 2. PEAKS AREAS IN THE MÖSSBAUER SPECTRA

Mole % $Fe_7Si_8O_{22}(OH)_2$	A_{123} (counts×channels×10^{-5})	A_4 (counts×channels×10^{-5})
35.4	1.99±0.06	3.58±0.06
51.8	1.20±0.03	0.74±0.03
63.0	2.40±0.05	1.39±0.04
85.0	3.07±0.05	1.07±0.04
87.5	2.05±0.04	0.87±0.05
95.3	5.74±0.05	1.91±0.05
19.7	1.43±0.09	0.47±0.09

position and the outer two to the M(1), M(2) and M(3) positions for the following reasons:

First, the M(4) site is highly distorted compared to the other three (Fig. 1). It is also different energetically from the remaining sites (Mueller, 1962; Burns, 1965). Calculations of the magnitude of the quadruple splitting for the Fe^{2+} ion (Ingalls, 1964) indicate that the value decreases with increasing distortion of a site from octahedral symmetry. This prediction has been confirmed by measurements on many silicate minerals (Bancroft and Burns, 1966*a, b*). For example, gillespite, which contains iron in square planar coordination (Pabst, 1943; Burns, Clark and Stone, 1966), gives the smallest quadruple splitting known for a "high-spin" Fe (II) compound (Bancroft, Clark and Stone, *to be published*).

Second, the width of the outer two lines is always slightly larger than the inner two which suggests that the outer two lines consist of a superposition of unresolvable lines due to Fe^{2+} ions in the M(1), M(2) and M(3) positions. Indeed, in actinolite, in which the M(2) site is slightly more distorted (Zussman, 1955) than the cummingtonite M(2) site (Ghose, 1961), the peak due to Fe^{2+} ions in the M(2) position is resolved in the computer plot of the Mössbauer spectrum (Bancroft and Burns 1966*b*).

Third, it has been shown from X-ray diffraction measurements (Fischer, 1966; (Ghose, 1961) that most of the iron in a cummingtonite with 35.8 mole percent $Fe_7Si_8O_{22}(OH)_2$ is in the M(4) position. This may be correlated with the Mössbauer spectrum of the 35.4 percent Fe^{2+} cummingtonite, in which the inner two peaks are the more intense.

Fourth, the relative intensities of the peaks in the 95.3 percent Fe^{2+} grunerite are about 0.~~250~~ 33 (Table 2), which is in reasonable agreement with the value expected from the proportion of M(4) positions (2/~~7~~5 ~~=0.286~~). = 0.4

Thus, there is no doubt that the peak assignment is correct. It is then immediately obvious from the spectrum of the 35.4 percent Fe^{2+} cummingtonite that Fe^{2+} ions enter the M(4) position preferentially. Note, however, that the spectra also show that Mn^{2+} ions enter the M(4) position preferentially in the manganoan cummingtonite at the expense of iron.

In order to determine the proportion of iron in each position use is made of equation (2) and the computer-calculated areas under the peaks (Table 2). Thus

$$\frac{A_4}{A_{123}} = C\frac{n_4}{n_{123}} \tag{4}$$

where the subscript 4 refers to the M(4) position, and the subscript 123 refers to the M(1), M(2) and M(3) positions.

To obtain C, the following assumptions are made for the cation distribution in the 95.3 percent Fe^{2+} grunerite: first, all the 0.2 Mn^{2+} plus Ca^{2+} per formula unit enter the M(4) position; second, the remaining 1.80 M(4) positions are occupied by Fe^{2+} ions. The basis for these assumptions is that, although Fe^{2+} ions favor the M(4) position, they will be displaced by the larger Ca^{2+} ions (which fill the M(4) position in the actinolite structure) and Mn^{2+} ions (which enter the M(4) position preferentially in the manganoan cummingtonite).

Applying these assumptions, and using the calculated areas (Table 2), $A_4/A_{123} = 1.91\times10^5/5.74\times10^5 = 0.333$; $n_4/n_{123} = 1.80/4.87 = 0.370$; and $C = 0.900$. Having obtained C, the ratios n_4/n_{123} (or $n_4/(n_4+n_{123})$) may be calculated for the remaining specimens from the ratios A_4/A_{123} (or $A_4/A_4+A_{123})$) using the assumptions made earlier.

The results of these calculations are given in Table 3. Column 3 of this table summarizes the ratios $A_4/(A_4+A_{123})$, together with the standard deviations. The amounts of iron in the M(4) and (M(1)+M(2)+M(3)) positions are given in the last two columns of Table 3, and columns 4 and 5 of Table 4. The results for the 87.5 percent Fe^{2+} grunerite and the manganoan cummingtonite show that the amount of Ca^{2+}, Mn^{2+} and Fe^{2+} ions in the M(4) positions exceeds 2.00. The result for the 87.5 percent Fe^{2+} grunerite lies within the statistical error of the calculations, but the data for the manganoan cummingtonite suggest that a proportion of the Mn^{2+} ions occupy the M(1), M(2) and M(3) positions. These aspects are discussed later.

Infrared measurements of the fundamental and first overtone bands of the hydroxyl stretching frequency of amphiboles (Burns and Strens, 1966) enable the proportions of Fe^{2+} ions in the (M(1)+M(3)) and (M(2)+M(4)) positions to be calculated in each of the cummingtonites and grunerites. These data are summarized in columns 6 and 7 of Table 4.

TABLE 3. DISTRIBUTION OF Fe^{2+} IONS IN THE CUMMINGTONITE-GRUNERITE SERIES FROM THE MÖSSBAUER SPECTRA

Mole % $Fe_7Si_8O_{22}(OH)_2$	Total Fe^{2+} (per formula unit)	$\frac{A_4}{A_4+A_{123}}$	$\frac{n_4}{n_4+n_{123}}$	Fe^{2+} in M(4) position (per formula unit)	Fe^{2+} in (M(1)+M(2)+M(3) positions (per formula unit)
35.4	2.48	0.643±0.017	0.667±0.019	1.65 ±0.05	0.83 ±0.04
51.8	3.63	0.382±0.030	0.406±0.032	1.47 ±0.13	2.16 ±0.11
63.0	4.41	0.367±0.025	0.392±0.027	1.73 ±0.13	2.68 ±0.11
85.0	5.95	0.259±0.023	0.280±0.025	1.67 ±0.16	4.28 ±0.12
87.5	6.13	0.298±0.028	0.320±0.030	1.96 ±0.19	4.17 ±0.16
95.3	6.67	0.250±0.015	0.270±0.017	1.80 ±0.12	4.87 ±0.10
19.7	1.38	0.247±0.091	0.267±0.098	0.37 ±0.14	1.01 ±0.13
1	2	3	4	5	6

Using these values, the amount of iron in the M_2 position may be calculated as follows:

$$Fe_{M(1),M(2),M(3)_{(Möss)}} - Fe_{M(1),M(3)_{(ir)}} = Fe_{M(2)}$$

The results are given in column 8 of Table 4.

All errors quoted in Tables 2 and 3 are standard deviations. It is difficult to estimate errors in the infrared method so that standard deviations are not quoted for the M(2) position. It should be noted, however, that in the estimate of the standard deviation for the M(4) position in the 35.4 percent Fe^{2+} cummingtonite there is only about 3 percent error, which is a considerable improvement over the accuracy of the X-ray technique (Ghose, 1961). In principle, the standard deviation in the Mössbauer measurements could be lowered further by counting over a longer time interval, or using a stronger Co^{57} source. In no case, however,

TABLE 4. DISTRIBUTIONS OF Fe^{2+} IONS IN THE CUMMINGTONITE-GRUNERITE SERIES FROM MÖSSBAUER AND INFRARED SPECTRA

Mole % $Fe_7Si_8O_{22}(OH)_2$	Mole % Ca(II)+Mn(II) components	Total $Mn^{2+}+Ca^{2+}$	Fe^{2+} in M(4) position	Fe^{2+} in M(1)+M(2)+M(3) positions	Fe^{2+} in M(1)+M(3) positions	Fe^{2+} in M(2)+M(4) positions (i)	Fe^{2+} in M(2) position
35.4	2.9	0.21	1.65	0.83	0.72	1.76	0.11
51.8	3.0	0.21	1.47	2.16	1.50	2.13	0.66
63.0	2.2	0.15	1.73	2.68	1.96	2.45	0.72
85.0	4.0	0.28	1.67	4.28	2.62	3.33	1.66
87.5	1.5	0.11	1.96	4.17	2.56	3.57	1.61
95.3	2.8	0.20	1.80	4.87	2.95	3.72	1.92
19.7	26.5	1.86	0.37	1.01	0.44	0.94	0.07
1	2	3	4	5	6	7	8

(i) The values for the ((M(2)+M(4)) positions differ slightly from those reported in the earlier study (Burns and Strens, 1966), in which concentrations were expressed in terms of iron (II) and magnesium components only.

is a standard deviation quoted in Table 3 larger than ±10 percent of the amount stated, except for the manganoan cummingtonite which gave a poor spectrum on account of the small amount of sample available.

Table 5 summarizes the results and gives the percentages of each position in the amphibole structure occupied by iron in the cummingtonite-grunerite series. The results are shown graphically in Figure 3.

DISCUSSION

The measurements show that in the cummingtonite-grunerite series Fe^{2+} ions strongly favor the M(4) position, and discriminate against the M(2) position in cummingtonites. In some grunerites, however, Fe^{2+} ions become enriched in the M(2) position. These trends influence the proportion of Fe^{2+} ions in the M(1) and M(3) positions, but Figure 3 suggests that Fe^{2+} ions are randomly distributed over the M(1) and M(3) positions. This conforms with results from infrared measurements (Burns and Strens, 1966) in which no cation clustering could be detected in the cummingtonite-grunerite series. This behavior is in contrast with other amphibole series where cation clustering (tendency for the distributions MgMgMg or FeFeFe to occur more often in the two M(1) and one M(3) position than expected for random mixing) has been observed (Strens, 1966). The points for the M(2) and M(4) positions are very scattered about smooth curves. This may be a reflection of different temperatures and pressures of crystallization, for the specimens used in this study were not all derived from the same locality. Closer fits to smooth curves might be obtained from a study of suites of specimens from the same formation, such as metamorphosed iron formations in Quebec (Mueller, 1960; Kranck, 1961) and Labrador (Klein, 1964). The points for the M(4)

TABLE 5. PERCENTAGE OF EACH POSITION IN THE AMPHIBOLE STRUCTURE OCCUPIED BY IRON IN THE CUMMINGTONITE—GRUNERITE SERIES

Mole % $Fe_7SI_8O_{22}(OH)_2$	% Fe^{2+} in M(1)+M(3) positions	% Fe^{2+} in M(2) position	% Fe^{2+} in M(4) position
35.4	24.0	5.5	82.5
51.8	50.0	33.0	73.5
63.0	65.3	36.0	86.5
85.0	87.3	83.0	83.5
87.5	85.3	80.5	98.0
95.3	98.3	96.0	90.0
19.7	14.7	3.5	18.5

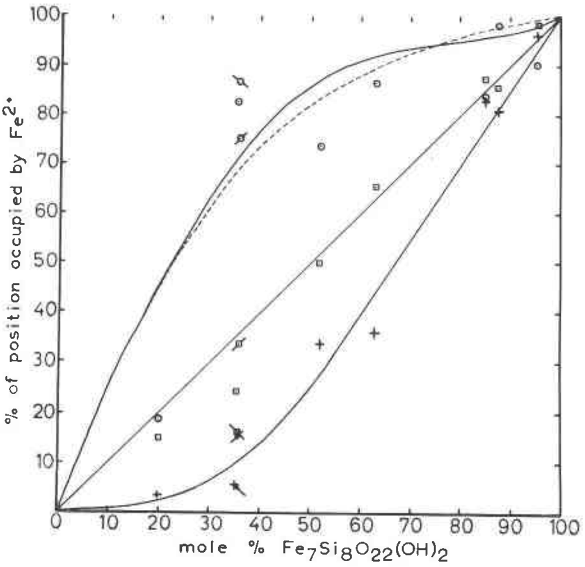


FIG. 3. Percentages of each position in the amphibole structure occupied by iron in the cummingtonite-grunerite series. A line at 45° is drawn for reference. The lines through the points for the M(4) position are adapted from curves by Mueller (1962) for a regular (full-line) and ideal (dashed line) solid solution. ⊙ M(4) position; + M(2) position; ⊡ M(1), M(3) positions. ⊘ ⊬ ⊡ Ghose, 1961; ⦸ ⊹ ⧄ Fischer, 1966.

position, which are strongly affected by the presence of Ca^{2+} and Mn^{2+} ions in the specimens (compare the results for the 85.0 and 87.5 percent Fe^{2+} grunerites in Table 4), are related to theoretical curves constructed by Mueller (1962) from thermodynamic arguments. The significance of this feature will be discussed in a later paper. Note that there is excellent agreement between results obtained in this study for the 35.4 percent Fe^{2+} cummingtonite and those obtained by Fischer (1966) for a 35.8 percent Fe^{2+} cummingtonite by X-ray diffraction measurements.

The results for the manganoan cummingtonite indicate that Mn^{2+} ions favor the M(4) position more strongly than Fe^{2+} ions, although Fe^{2+} ions still prefer the M(4) position and discriminate against the M(2) position. The preference of Mn^{2+} ions for the M(4) position was also suggested indirectly by infrared spectroscopy (Burns and Strens, 1966) and chemical analysis (Klein, 1964). Klein (1964) noted that naturally occurring cummingtonites rarely exceed 30 mole percent $Mn_7Si_8O_{22}(OH)_2$, and suggested that the maximum amount of manganese that could enter the cummingtonite structure corresponds to complete filling of the M(4) positions (*i.e.* 28.6% Mn). The present study, however, shows that, although Mn^{2+} favor the M(4) position, all of the manganese does not enter the M(4) position. The Mössbauer measurements give 0.37 ± 0.14 Fe^{2+} per formula unit occupying the M(4) position (Table 3). Assuming that the 0.20 Ca^{2+} (Table 1) enter only the M(4) position and that no Mg^{2+} ions are present, the remaining 1.43 ± 0.14 M(4) positions ($71.5 \pm 7\%$) are occupied by Mn^{2+} ions, leaving $(1.66 - 1.43)$ or 0.23 Mn^{2+} per formula unit to be distributed over the M(1), M(2) and M(3) positions. It may be noted that manganactinolites have been reported with up to 15 atom percent Mn and two Ca^{2+} ions per formula unit (Deer, Howie, and Zussman, 1963, v. 2, p. 253). Unfortunately, the errors in the calculation of site populations in the manganoan cummingtonite are rather large because of the poor quality of the Mössbauer spectrum for this specimen. Nevertheless, the results for the manganoan cummingtonite indicate a technique for estimating Fe/Mn ratios in crystallographic positions, which at the present time is impossible by X-ray techniques. Analogous Mössbauer measurements of the orthopyroxene series show that Mn^{2+} ions favor the M(2) position of the orthopyroxene structure (Bancroft and Burns, 1966b).

The results in Tables 3, 4, and 5 and Figure 3 are based on the assumption that, in order to evaluate C, iron occupies 90 percent of the M(4) positions in the 95.3 percent Fe^{2+} grunerite. This figure was obtained by assuming that all the Ca^{2+} and Mn^{2+} ions in the grunerite occupy M(4) positions only, and that the small amount of magnesium is present entirely in the M(1), M(2) and M(3) positions. If, however, some of the magnesium also occupies the M(4) positions, thereby reducing the proportion of this position occupied by iron to about 87 percent, C becomes 0.943. Using the 35.4 percent Fe^{2+} cummingtonite as an example, n_4 becomes 1.63 and n_{123} becomes 0.85 (compare Table 3 in which $n_4 = 1.65$ and $n_{123} = 0.83$). On the other hand, if some of the manganese (or, perhaps, calcium) in the 95.3 percent Fe^{2+} grunerite is present in the M(1), M(2) or M(3) positions and the M(4) position contains instead 93 percent Fe^{2+}, then C becomes 0.862, and $n_4 = 1.67$ and $n_{123} = 0.81$ in the 35.4 percent Fe^{2+} cummingtonite. These calculations show how insensitive the results are to small errors in C arising from the choice of cation distribution in the 95.3 percent Fe^{2+} grunerite. All factors considered, the choice adopted in the present study of 1.80 Fe^{2+} in the M(4) positions appears to be reasonable, especially when account is taken of the possibility that Mg^{2+} and Mn^{2+} ions may interchange on the M(1), M(2), M(3) and M(4) positions, respectively, and leave the Fe^{2+} content of the M(4) position unchanged.

Obviously, a more rigorous prodecure would be to use computer-calculated areas under Mössbauer peaks for the pure, natural or synthetic, grunerite end-member $Fe_7Si_8O_{22}(OH)_2$.

CONCLUSIONS

Quantitative Mössbauer measurements of the M(4) site populations have been obtained for seven minerals of the cummingtonite-grunerite series. Combined with infrared measurements, the M(2) site populations have been estimated together with the M(1)+M(3) site populations. This paper indicates the advantages of using Mössbauer techniques for estimating site populations. The spectrum is recorded in a matter of hours, and can be analysed on the computer in a matter of minutes. The accuracy of the method enables more precise calculations to be made than have previously been possible.

ACKNOWLEDGMENTS

The authors wish to thank the following people for analysed specimens: Dr. R. F. Mueller, Dr. C. Klein, Jr., Dr. B. Mason, and Professor C. S. Hurlbut. We also wish to thank Dr. A. J. Stone for assistance with the computer program, Dr. R. G. J. Strens for infrared measurements and helpful discussions, Dr. M. G. Bown for reading the manuscript, and Mrs. V. M. Burns for editing and typing the manuscript. This study was supported by grants from the British Council and Science Research Council (R.G.B.). G.M.B. wishes to acknowledge the award of a Shell Canada Postgraduate Scholarship.

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Manuscript received, July 29, 1966; accepted for publication, October 24, 1966.