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The Mössbauer Spectra of Various Natural Minerals

Yoshimasa TAKASHIMA and Shigeru OHASHI

Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Fukuoka

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The Mössbauer spectra have been measured for sixteen samples of natural minerals, including siderite, vivianite, garnets, olivines, pyroxenes, and other silicate minerals, The spectra were analyzed for the isomer shifts and quadrupole splittings, and the information thus obtained was correlated with the oxidation states of irons and the crystal structure of minerals. The relative abundances of the various sites present in a given mineral were also estimated by measuring the relative intensities of the absorption peaks in the resolved spectrum of the mineral. All the basic Mössbauer spectral patterns observed for the natural minerals are presented in graphic form.

In recent years considerable attention has been paid to the chemical application of the Mössbauer effect. There are a number of papers that allow one to evaluate the usefulness of Mössbauer spectroscopy as a tool for studying chemical bonding. Although a number of works have dealt with synthetic chemical compounds, however, comparatively little work has been done in measuring the Mössbauer spectra of naturally-occurring substances. The suggestion that Mössbauer spectroscopy can be well applied to a study of natural minerals was first made by Pollak¹⁾ (1962). More recently, a similar studies of different types of minerals have been done successfully by Herzenberg *et al.*²⁾ and Sprenkel-Segel *et al.*³⁾ The chief application of Mössbauer spectroscopy to minerals has thus far been associated with the mineral structure as well as the oxidation states of iron atoms. In practice, the characteristic features of the spectra are well related to the chemical environment around the Mössbauer nucleus.

The present work on natureal minerals was performed with emphasis on the mineral structure. However, the possibilities of identifying the oxidation states and of determining their ratios were also discussed. It seems that we may expect the Mössbauer spectroscopic technique to be applied to many other areas of mineralogy in the futrue.

Experimental

Apparatus and Procedure. The apparatus and procedure employed were essentially the same as those described in a previous paper.⁴⁾ A part of the instrument, however, was altered so that the measurements could be made more easily and accurately. Namely, γ rays were detected with a thin NaI(Tl) crystal coupled to a 400-channel pulse-height analyzer.

All measurements were made at room temperature. In general, runs were made with total counts in excess of 10^4 per Doppler velocity. Statistical error was taken into account in drawing the spectral lines. The isomer shifts are all expressed in mm/sec relative to stainless steel.

Mineral Samples. Most of the mineral samples used were bought from the Japan Earth Science Company, Kyoto. The vivianites, axinite, and biotite were obtained from our own collection. Some olivines and pyroxenes were provided by Mr. Kiyoshi Ishibashi of Kyushu University, Department of Geology. The sixteen minerals studied are summarized in Table 1.

The bulk of the mineral was first crushed into small pieces. Then the sample was carefully selected through a microscope so as to exclude any impurity. Finally, the sample was pulverized in an agate mortar. The powder (*ca.* 100 meshes) was mounted as uniformly

TABLE 1. MINERAL SAMPLES AND THEIR LOCALITIES

Sample	Locality
Siderite	Ogoya, Ishikawa Pref.
Vivianite	Himeshima, Ohita Pref.
Vivianite	Kobe, Hyogo Pref.
Lievrite	Unknown
Andradite	Kamaishi, Iwate Pref.
Almandite	Ishikawa, Ishikawa Pref.
Forsterite	Karasu, Saga Pref.
Fayalite	Kosei, Shiga Pref.
Augite	Nishigadake, Saga Pref.
Augite	Karatsu, Saga Pref.
Diopside	Karatsu, Saga Pref.
Hedenbergite	Kitahira, Yamaguchi Pref.
Axinite	Obira, Ohita Pref.
Biotite	Sugiyama, Saga Pref.
Tourmaline	Ishikawa, Ishikawa Pref.
Hornblende	Matsuyama, Ehime Pref.

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1) H. Pollak, M. de Coster and S. Amelinckx, *Phys. Stat. Sol.*, **2**, 1653 (1962).

2) C. L. Herzenberg and D. Toms, *J. Geophys. Res.*, **71**, 2661 (1966).

3) E. L. Sprenkel-Segel and S. S. Hanna, *Geochim. Cosmochim. Acta*, **28**, 1913 (1964).

4) Y. Takashima and S. Ohashi, This Bulletin, **38**, 1684 (1965).

as possible on an absorber disk. The samples ranged in thickness from 10 to 24 mg Fe/cm², depending on the iron content in the minerals.

Chemical Analysis of Iron. The determination of the iron(II) and iron(III) in minerals was carried out by means of the permanganate titration technique. The pulverized mineral was brought into the solution by treating it with sulfuric acid and hydrofluoric acid, with special care taken to prevent the oxidation of iron(II) in the process. The solution in a platinum crucible was transferred without removing the cover to 80 ml of a cold, saturated boric acid solution. The sample solution thus obtained was titrated at once with a 0.1 N potassium permanganate standard solution. Then the total iron content was determined in the same way by using the same solution after the iron in the solution had been reduced to the bivalent state with a zinc-amalgam reductant. The iron(III) content can be found by deducting the iron(II) content from the total iron content. This method is sufficiently accurate to be useful.

Results and Discussion

It is well known that there are three basic Mössbauer spectral patterns, *i. e.*, a single absorption line, double absorption lines, and six-splitted absorption lines. The last one is produced by a Zeeman splitting resulting from the interaction of the nuclear magnetic dipole with the magnetic field produced at the nuclear site by the electrons. Such spectra were observed in the cases of iron oxides[5] and sulfides.[6,7] In our measurements, however, such samples were intentionally avoided because they have already been extensively studied and our instrument is not suited for the measurement of such a wide range of velocity. Most of the samples studied were of a silicate form, but some were of phosphate and carbonate forms.

The spectra were analyzed for the isomer shifts and quadrupole splittings, and the information thus obtained was correlated with the oxidation states of iron and the crystal structures of the minerals. In principle, however, numerous difficulties are inherent in any detailed analysis of the Mössbauer spectrum. The trial-and-error method is necessary to make possible a reasonable analysis of the spectrum. The absorption peak intensity was roughly evaluated in order to obtain an estimate of the iron content in any particular crystal site. To eliminate the saturation effect in the absorption, the absorbers were made thin ranging, from 10 mgFe/cm² to 15 mgFe/cm². In some cases, however, thicker absorbers were used because of the difficulty inherent in the preparation technique. The saturation was observed in samples with thicknesses of >15 mgFe/cm².

Siderite ($FeCO_3$). The siderite exhibits only a sharp doublet Mössbauer pattern similar to a typical ionic ferrous compound. The isomer shift (δ) and the quadrupole splitting (ε) observed were $\delta = 1.38$ mm/sec and $\varepsilon = 0.94$ mm/sec respectively. The former value is typical of the ferrous ion, while the latter is somewhat small for the ferrous ion in ferrous compounds. This means that the binding of iron atoms in the siderite is similar to that of a typical ionic ferrous salt, but that the iron is in a nonspherical environment.

Vivianite [$Fe_3(PO_4)_2 \cdot 8H_2O$]. The spectrum of vivianite shows three absorption lines. The authors have resolved the spectrum into two doublets. The spectra of two vivianites are reproduced in Fig. 1. The first two bands are due to trivalent-state iron, and the second two bands, to bivalent-state iron. The spectrum of Himeshima vivianite was compared with that of Kobe vivianite by measuring each absorber with the same areal iron density. A difference in the intensity of the trivalent iron peak between the two vivianites was observed. On the contrary, the general trends of the X-ray powder patterns of the two minerals are very similar. The above facts suggest that, *in some cases*, the Mössbauer absorption pattern can be used in the locality identification of minerals.

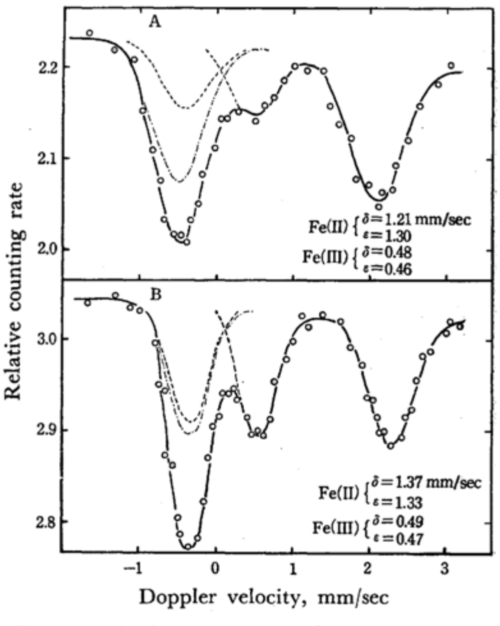

Fig. 1. Mössbauer spectra of vivianites.
Thickness = 15 mg Fe/cm²
A: Himeshima vivianite, B: Kobe vivianite

The presence of the trivalent iron in these minerals may be attributed to the erosive oxidation in the light of the δ and ε values, *i. e.*, the isomer shift and the quadrupole splitting of Fe_2O_3 are similar to those of the vivianites.

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[5] G. Shirane, D. E. Cox and L. Ruby, *Phys. Rev.*, **125**, 1158 (1962).

[6] K. Ôno, A. Ito and E. Hirahara, *J. Phys. Soc. Japan*, **17** 1615 (1962).

[7] I. Solomon, *C, R. Acad. Sci., Paris*, **250**, 3818 (1960).

Garnets. The garnet group is repersented by the general formula, $A_3B_2Si_3O_{12}$, where A=Fe, Ca, Mg, Mn, *etc.*, and where B=Al, Fe, Cr, *etc.* As is shown in Fig. 2, the silicon-oxygen tetrahedra exist as independent groups linked to the octahedra of the trivalent ions, while the bivalent metal ions are situated in the center of the oxygen dodecahedra. Of the many kinds of garnets, andradite and almandite were chosen as samples. The Mössbauer spectra of these two minerals are compared with each other in Fig. 3. In this case, the absorbers were so prepared that the areal iron density was approximately 10 mgFe/cm². The andradite spectrum can be resolved into a single line with a high intensity and a doublet with a weak intensity. The intense single line may be an unresolved doublet, for its half-width is a little larger than that of stainless steel. The values of both the isomer shifts lie in the range characteristic of the trivalent state iron. The intense line indicates a more covalent nature in bonding than the weak one. This supports the assumptions that there are two different iron sites in the crystal, and that most of the iron atoms are at the B site and only a few, at the A site.

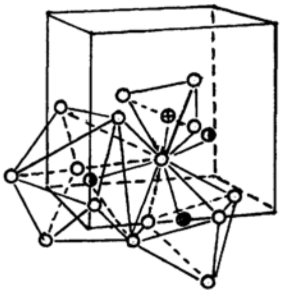

Fig. 2. Crystal structure of garnet ($A_3B_2Si_3O_{12}$).
○: O
●: Al, Fe, Cr,··· (B)
◑: Fe, Ca, Mg, Mn,··· (A)
⊕: Si

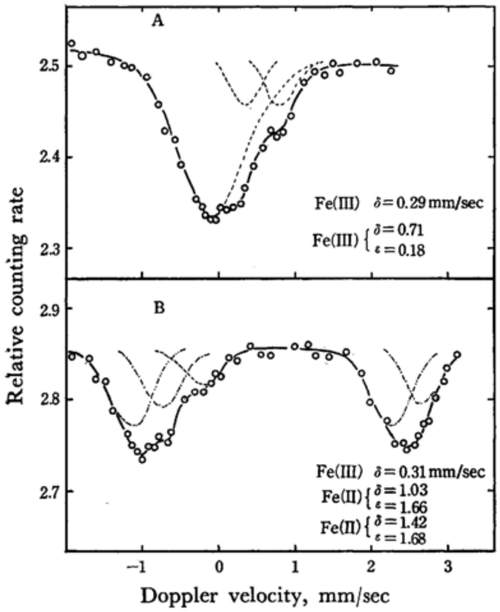

Fig. 3. Mössbauer spectra of garnets.
Thickness=10 mg Fe/cm².
A: Andradite, B: Almandite

The spectrum of almandite showed a relatively complex structure. It is resolved into two doublets characteristic of bivalent iron and a single line characteristic of trivalent iron. Since the isomer shift of the trivalent iron in the almandite is close to that of the covalently-bonded iron atoms, the trivalent iron must be located at the B site, together with a large amount of bivalent iron. Accordingly, the other bivalent iron, of about an equal amount, must be located at the A site.

Olivines. The Mössbauer spectra of two kinds of olivine, forsterite and fayalite, are shown in Fig. 4. The isomer shift and quadrupole splitting were of the same order as for almandite, showing the ionic nature of the iron bonding present.

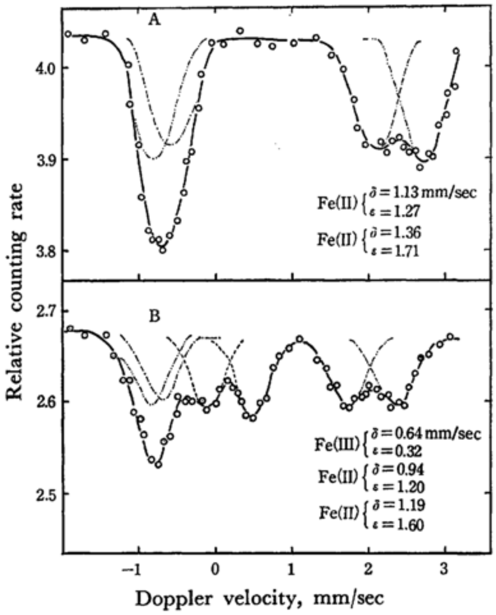

Fig. 4. Mössbauer spectra of olivines.
Thickness=24 mg Fe/cm².
A: Forsterite, B: Fayalite

The compositions of olivines vary from that of forsterite, Mg_2SiO_4, to that of fayalite, Fe_2SiO_4, there being a complete diadocky between manganese and iron atoms. The crystal structure parallel to the (100) plane is shown in Fig. 5. In Fig. 5, the silicon atoms at the center of the tetrahedra are not shown. Small open circles (Mg or Fe atoms) are at $x=0$, while small solid circles (Mg or Fe atoms) are at $x=1/2$. The fact that the Mössbauer spectrum has resolved into two

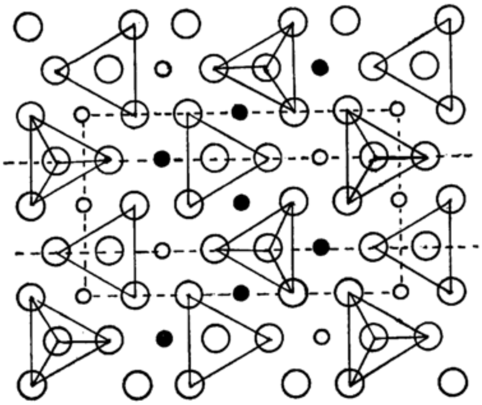

Fig. 5. Crystal structure of olivine.
○: O; ○ ●: Mg, Fe

doublets of equal intensities is consistent with the crystal structure. Namely, half of the metal (Mg or Fe) is located at the site having as nearest neighbors two oxygen atoms from two adjacent tetrahedra, but the other half is located at the other site, having two oxygens from one adjacent trahedron. In these two Mössbauer spectra the predominant absorption patterns correspond to that of bivalent state iron. Only fayalite gave a weak absorption pattern corresponding to that of trivalent state iron.

Pyroxenes. The pyroxenes include varieties which have orthorhombic and monoclinic symmetries. The authors used four monoclinic samples, *i. e.*, two augites, a diopside, and a hedenbergite, for the measurement. The Mössbauer spectra obtained are shown in Figs. 6 and 7. The locality difference in the Mössbauer patterns was observed between the two augites as for the vivianites. The resolution of the spectra is shown by the dotted curves. The results indicate that the single site is available to the bivalent iron in the crystal structure of augite, while two sorts of sites are available in the cases of diopside and hedenbergite. No peak attributable to trivalent state iron was observed in the hedenbergite spectrum.

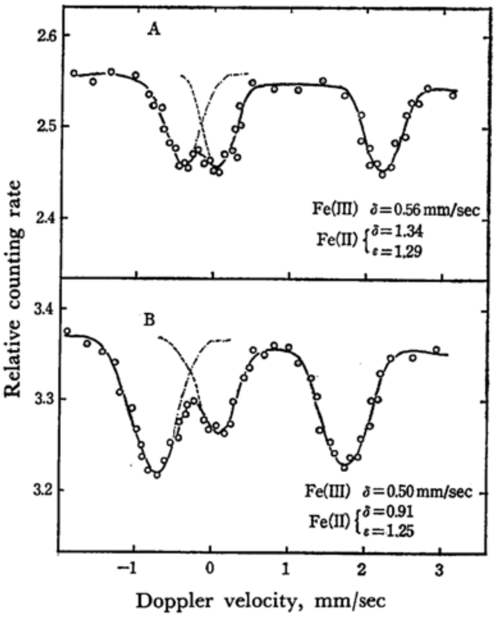

Fig. 6. Mössbauer spectra of pyroxenes.
Thickness = 14 mg Fe/cm^2.
A: Nishigadake augite, B: Karatsu augite

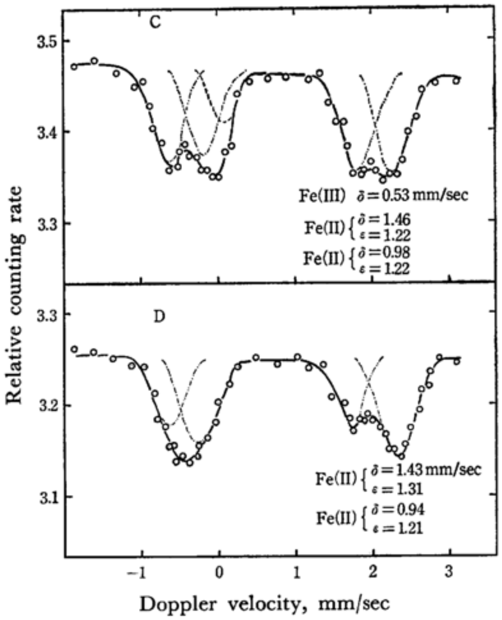

Fig. 7. Mössbauer spectra of pyroxenes.
Thickness = 15 mg Fe/cm^2.
C: Diopside, D: Hedenbergite

TABLE 2. ISOMER SHIFTS AND QUADRUPOLE SPLITTINGS OF SEVERAL SILICATE MINERALS

	Fe(II)		Fe(II)		Fe(III)	
	δ(mm/sec)	ε(mm/sec)	δ(mm/sec)	ε(mm/sec)	δ(mm/sec)	ε(mm/sec)
Axinite	1.39	1.2			0.60	0.14
Biotite	1.18	1.32	1.46	1.60	0.48	0
Tourmaline	1.06	0.98	1.42	1.34	0.89	0
Hornblende	0.98	1.13	1.38	1.62	0.66	0.20
Lievrite	1.30	1.37	1.25	0.89	0.54	0.32

Other Silicate Minerals. As has been discussed above, the Mössbauer spectrum measured for each mineral can be interpreted in terms of valency state, lattice sites, the covalency of bonding, and crystal distortion. Among the number of silicate minerals, axinite, biotite, tourmaline, hornblende, and lievrite were investigated by the present authors. Some of the same sort of minerals had already been measured by other people.[1,2] The silicate minerals generally give complicated Mössbauer spectra, the most complicated patterns being obtained in the cases of the hornblende and lievrite. They both consist of three doublets, our analysis shows. The values of the isomer shift and of the quadrupole splitting for these minerals are summarized in Table 2.

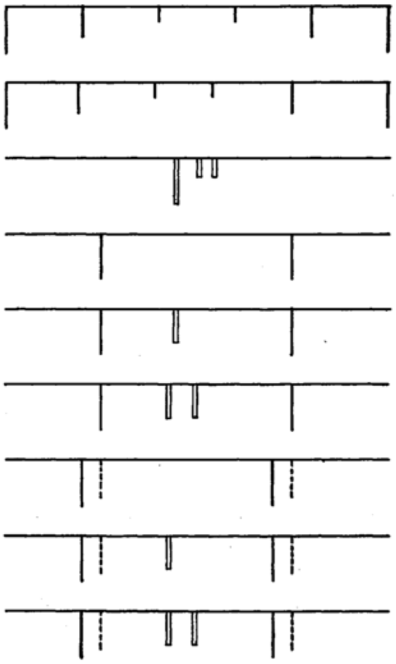

Fig. 8. Basic Mössbauer patterns observed in the natural minerals.
Solid and dotted lines represent bivalent iron.
Open lines represent tivalent iron.

Summary of the Mössbauer Spectra of Minerals. The absorption of resonant gamma rays produces various patterns characteristic of the various minerals. Nine basic patterns and their modifications have so far been observed for the natural minerals. Of these patterns, seven were observed in the wide variety of minerals examined here. The other two resulted from such ferromagnetic iron minerals as iron sulfides. The basic patterns are illustrated in Fig. 8, where the absorption peaks are abbreviated by the single lines, and where the intensity, peak position, and splitting scales are arbitrarily chosen.

Relationship between Peak Intensity and Iron Content. The amount of iron in a sample can be determined from the intensity of the Mössbauer spectrum if the nuclei are located in fairly identical environments. The correlation between the peak intensity (peak area) and the iron content was examined by using a stainless steel and a vivianite mineral of varying thicknesses. As the thickness was increased, the intensity increased, as is shown in Table 3.

TABLE 3. COMPARISON OF ABSORBER THICKNESS AND PEAK INTENSITY

Sample	Stainless steel	Vivianite
Ratio of iron content taken	1* : 4 : 12	1** : 2 : 3
Ratio of absorption peak area observed	1 : 2.1 : 4.5	1 : 1.6 : 1.9

* Thickness=6 mg Fe/cm²
** Thickness=15 mg Fe/cm²

The next point examined was the relation between the Fe(II)/Fe(III) ratios and their peak

TABLE 4. RELATION BETWEEN Fe(II)/Fe(III) RATIO AND RATIO OF ABSORPTION PEAK

Sample	Absorber thickness (mgFe/cm²)	From chemical analysis data			From the Mössbauer spectrum
		Fe(II) %	Fe(III) %	Fe(II)/Fe(III)	Ratio of absorption peak area due to Fe(II) and Fe(III)
Vivianite (Himeshima)	15	22.7	9.1	2.49	2.49
Vivianite (Kobe)	15	13.2	12.6	1.05	1.12
Almandite	10	18.3	2.0	9.15	8.81
Fayalite	24	31.1	15.1	2.06	2.10
Augite (Nishigadake)	14	4.5	2.1	2.14	2.21
Augite (Karatsu)	14	5.4	2.0	2.70	2.96
Diopside	15	6.5	1.4	4.64	8.60
Axinite	10	4.4	1.5	2.93	2.96
Biotite	15	19.0	1.9	10.00	9.80
Tourmaline	10	5.2	1.4	3.64	5.11
Hornblende	12	7.1	4.2	1.69	1.73
Lievrite	20	27.4	12.2	2.28	2.15

intensity ratios. The results obtained are summarized in Table 4. It may be seen from Table 4 that there is in most cases a fairly good agreement between the ratios of the iron content determined by chemical analysis and the ratios of peak intensity obtained from the Mössbauer spectrum. The apparent discrepancies observed in several cases could result from several causes: 1) drift of the pulse-height analyzer, 2) nonidentical environment around the iron nuclei, 3) counting error, 4) effect of higher energy γ rays on 14.4 keV γ rays, and 5) saturation effect in the absorption. In view of the spectrometer employed, further discussion of the subject is premature. Experiments to elucidate this subject would need to be conducted with a better spectrometer.

The Mössbauer absorption peak does not appear when the iron content in the mineral is less than 1%. This would seem to be the limit of detection in this experiment.

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