Compositional dependence of intensity and electric field gradient tensors for Fe$^{2+}$ at the $M1$ site in Ca–rich pyroxene by single crystal Mössbauer spectroscopy

Daiki FUKUYAMA*, Keiji SHINODA*, Daigo TAKAGI* and Yasuhiro KOBAYASHI**

*Graduate School of Science, Osaka Metropolitan University, Osaka 558–8585, Japan
**Institute for Integrated Radiation and Nuclear Science, Kyoto University, Osaka 590–0494, Japan

The compositional dependence of the intensity and electric field gradient (EFG) tensors for Fe$^{2+}$ at the $M1$ sites, Fe$^{2+}$ at the $M2$ sites, and Fe$^{3+}$ at the $M1$ sites in Ca–rich pyroxene were obtained from Mössbauer spectra of crystallographically oriented single-crystal thin sections of four Ca–rich natural pyroxenes. Components of the intensity tensor ($I_{XX}$, $I_{YY}$, $I_{XY}$, and $I_{ZZ}$) for Fe$^{2+}$ at the $M1$ sites in Wo$_{50}$ Ca–rich pyroxene were almost the same; the averages of the $I_{XX}$, $I_{YY}$, $I_{XY}$, and $I_{ZZ}$ components were 0.342, 0.477, 0.039, and 0.681, respectively. Intensity tensor for Fe$^{2+}$ at the $M1$ sites of Wo$_{40}$ Ca–rich pyroxene was different from the Wo$_{50}$. Whereas principal axes of EFG tensors for Fe$^{2+}$ at the $M1$ sites of Wo$_{50}$ pyroxenes had the same direction, principal axes of $V_{XX}$ and $V_{YY}$ of EFG of Wo$_{40}$ had different directions from that from Wo$_{50}$. The difference of intensity and EFG tensors between Wo$_{50}$ and Wo$_{40}$ suggests that the intensity and EFG tensors for Fe$^{2+}$ at $M1$ sites are dependent on the Ca contents and are independent of Fe contents. Some intensity and EFG tensors for Fe$^{2+}$ at the $M2$ sites and Fe$^{3+}$ at the $M1$ sites in Ca–rich pyroxene were also obtained. However, the compositional dependence of the intensity and EFG tensors has yet to be clarified, because the number of examples is insufficient.

Keywords: Mössbauer spectroscopy, Intensity tensor, Electric field gradient (EFG) tensor, Ca–rich pyroxene

INTRODUCTION

Mössbauer spectra of single crystal of Ca–rich pyroxenes

Scanning Electron Microscope (SEM) with Energy Dispersive X-ray Spectrometer (EDS) and Electron Probe Micro Analyzer (EPMA) are usually used for chemical analyses of crystals in thin sections in mineralogy and petrology. Although almost elements except for the lighter elements than carbon can be analyzed by SEM/EDS and EPMA, valency of Fe cannot be distinguished by these methods. Kimura and Akasaka (1999) proposed an analytical method to measure Fe$^{2+}$/Fe$^{3+}$ ratio using $I_{eq}$ and $I_{eq}$ X-ray emission peaks by EPMA. However, this is a semiquantitative analytical method for Fe-silicates containing total FeO more than 5 wt%. $^{57}$Fe Mössbauer microspectroscopy is an important and unique method for the analysis of valency of Fe in minerals, as emphasized in the introduction by Shinoda and Kobayashi (2019). A γ-ray source in which $^{57}$Co radioisotope is diffused in a rhodium matrix is used for $^{57}$Fe Mössbauer measurements. The radius of the γ-ray source is approximately 5 mm. Due to the lack of a device to focus the γ-rays, $^{57}$Fe Mössbauer spectroscopy has not been used for microspectroscopy to measure a selected spot. Powdered samples are generally used for Mössbauer measurements, and this results in a low spatial resolution. To overcome the disadvantages of Mössbauer spectroscopy using powdered samples, a few Mössbauer microscopic methods have been proposed for spot analyses of thin sections (McCammon et al., 1991; Yoshida et al., 2009; Shinoda and Kobayashi, 2018). While such techniques offer advantages, a problem remains in the analysis of Mössbauer spectra of thin sections of multi–site solid solution minerals such as pyroxene.

Pyroxene is a typical multi–site solid solution mineral that includes $M1$ and $M2$ sites. The ideal chemical formula for natural calcium pyroxene is (Ca,Fe$^{2+}$,Mg)SiO$_3$. The $M1$ sites are almost regular octahedral sites. The $M2$
pyroxene is dependent on the sites that Fe$^{2+}$ ions occupy. 

Fe$^{2+}$ ions produce a quadrupole doublet in the $^{57}$Fe Mössbauer spectrum. Quadrupole splitting of Fe$^{2+}$ in pyroxene is dependent on the sites that Fe$^{2+}$ ions occupy. According to Dyar et al. (2013), Fe$^{2+}$ in M1 sites exhibits a wider quadrupole splitting doublet (2.0–2.6 mm/s) than that of Fe$^{2+}$ in M2 sites (1.7–2.1 mm/s), whereas isomer shifts of Fe$^{2+}$ of M1 and M2 sites are approximately 1.13–1.19 mm/s in common. Fe$^{3+}$ ions produce a quadrupole splitting as small as 0.3–0.7 mm/s, which is easily distinguished from Fe$^{3+}$. The wider quadrupole doublet due to Fe$^{2+}$ at M1 sites is termed the outer doublet and the narrower quadrupole doublet due to Fe$^{2+}$ at M2 sites is the inner doublet. At the beginning of the $^{57}$Fe Mössbauer spectroscopic study of Ca–rich pyroxene, assignments of quadrupole doublets to M1 and M2 sites were controversial. The outer doublet of hedenbergite was assigned to Fe$^{2+}$ at M2 sites and the inner doublet to Fe$^{2+}$ at M1 sites (Bancroft et al., 1967). Matsui et al. (1970) assigned the outer doublet to Fe$^{2+}$ at M2 sites and the inner doublet to Fe$^{2+}$ at M1 sites in the analysis of synthetic Ca–rich pyroxenes. Subsequently, the assignment was altered to the outer doublet being due to M1 sites and the inner doublet to M2 sites (Williams et al., 1971). Dyar et al. (2013) examined $658$ Mössbauer spectra of pyroxene that wholly covered the pyroxene quadrilateral and determined fundamental Mössbauer parameters (isomer shift, quadrupole splitting, and recoil-free fractions) for Fe$^{2+}$ at the M1 and M2 sites of pyroxenes as a function of composition. Reliable peak separation of the quadrupole doublet of a powdered pyroxene sample, where the inner and the outer doublets are strongly overlapped, can be achieved using the Dyar parameters because the intensities of the two peaks in each doublet can be assumed to be equal. On the other hand, the intensities of the two peaks of a doublet for a single crystal of pyroxene, such as a thin section, are not equal, and the intensity ratio changes by varying the angle between the incident γ-ray direction and the crystallographic orientation of single crystal pyroxene (Tennant et al., 2000, Shinoda and Kobayashi, 2019). Therefore, a quadrupole doublet for a single crystal is characterized by four parameters: isomer shift (IS), quadrupole splitting (QS), line width (LW) and peak intensity $I^b = \text{Area}^b (\text{Area}^b + \text{Area}^d)$. In this study, $I^b$ is represented as the ratio of the areal percentage of the higher Doppler velocity component ($\text{Area}^b$) to the sum of the area ($\text{Area}^b + \text{Area}^d$) of the higher and lower Doppler velocity components ($\text{Area}^d$). Peak separation of an overlapped doublet for a single crystal of pyroxene into the inner and outer doublets has a problem due to the fourth parameter above. For example, augite generally contains three types of Fe ions, such as Fe$^{2+}$ at M1 sites, Fe$^{2+}$ at M2 sites, and Fe$^{3+}$. Thus, augite yields a complex Mössbauer spectrum where three doublets are strongly overlapped. To separate the raw data for the Mössbauer spectrum into three doublets that include 12 parameters is very difficult because several combinations of peak intensities are possible. If the peak intensities of doublets are known for a given thin section, then the fourth parameter can be fixed, and reliable peak separation can be achieved for an overlapped doublet for a single crystal pyroxene thin section. Therefore, it is very important to determine the crystallographic dependence of the peak intensity against the incident γ-rays for pyroxene. The intensity of the quadrupole doublet of single crystals can be calculated from the intensity tensor. Zimmermann (1975, 1983) proposed equations to calculate the peak intensity and electric field gradient (EFG) tensors for quadrupole doublets for single crystals by setting a rectangular coordinate system (X, Y, Z) for monoclinic crystals. The intensity tensors of Fe of pyroxenes are important for $^{57}$Fe Mössbauer analyses of thin section of pyroxenes, because the fourth parameters for reliable peak separation can be fixed by the intensity tensors.

Tennant et al. (2000) determined the intensity and EFG tensors for Fe$^{2+}$ at M1 sites in natural Mg–hedenbergite [(CaFe$_{0.54}$Mg$_{0.46}$)$_{(2.00)}$Si$_2$O$_6$] (W096En23Fs27) from Sweden using the left-handed system $X/a*(//b \times c)$, $Y/c$ axis, and $Z/b$ axis. Shinoda and Kobayashi (2019) determined the intensity and EFG tensors for Fe$^{2+}$ at M1 sites in natural aegirine (NaFe$_3$Si$_2$O$_6$) from Malawi using the right-handed system $X/c*//(a \times b)$, $Y/a$ axis, and $Z/b$ axis. Figure 1 shows the polar coordinate that defines the relationship between the monoclinic axis and the rectangular coordinate, where $X//c*//(a \times b)$, $Y/a$ axis, and $Z/b$ axis, and the polar angles $\theta$ and $\phi$ for the incident γ-rays are shown. Although an intensity tensor for Ca–rich pyroxene for a single chemical component was revealed by Tennant et al. (2000), the intensity tensors for the other chemical compositions of Ca–rich pyroxene have not been measured, and the compositional dependence of the intensity tensor for Ca–rich pyroxene is unknown. The remaining problem in the Mössbauer spectra of pyroxenes is to determine the compositional and crystallographic dependence of the peak intensity tensor. In this study, the intensity and EFG tensors for Fe$^{2+}$ in the M1 and M2 sites in Ca–rich pyroxenes are revealed from Mössbauer spectra of crystallographically oriented thin sections.

Four Ca–rich pyroxenes are examined in this study: two diopsides, augite, and hedenbergite. In addition, the intensity and EFG tensors for Mg–hedenbergite by Tennant
et al. (2000) are recalculated using a right-handed system with \(X/e^r(//a \times b)\), \(Y/a\) axis, and \(Z/b\) axis. The modified intensity tensor is compared with those obtained in the present study. Finally, the chemical dependence of the tensor components \((I_{XX}, I_{YY}, I_{XY}, and I_{ZZ})\) for Fe\(^{2+}\) at \(M1\) and \(M2\) sites is discussed. The intensity tensors are practically useful for the analyses of Mössbauer spectra of multi-site solid solution minerals because peak intensity of quadrupole doublets can be calculated from \(\gamma\)-ray direction.

EFG tensor is a basic physical property and closely related to the intensity tensor as shown in the next section and Zimmermann (1975). The EFG tensor components are electric field gradient due to electrical charges around \(^{57}\)Fe Mössbauer nuclei, and proportional to \(r^3\), where \(r\) is distance between Mössbauer nuclei and the surrounding charges. Therefore, EFG tensor components are governed by the local structure around Mössbauer nuclei and can be principally calculated from atomic positions analyzed by crystal structure analyses. Shinoda and Kobayashi (2019) calculated the EFG tensor for Fe\(^{3+}\) at the \(M1\) site of aegirine from the atomic positions of the nearest neighbor oxygens and suggested that slight differences of atomic positions result in considerably different asymmetric parameter. Therefore, it is still necessary to determine experimentally EFG tensors.

### Calculating method of the intensity and EFG tensors of Ca-rich pyroxenes

The Ca-rich pyroxenes considered in the present study belong to space group \(C2/c\). The \(M1\) and \(M2\) sites in \(C2/c\) pyroxene occur in special positions on the diad axes of rotation parallel to the \(b\) axis (Cameron and Papke, 1980). As indicated by Zimmermann (1983) and derived by Shinoda and Kobayashi (2019), the EFG tensor for Fe\(^{2+}\) or Fe\(^{3+}\) on the diad axes can be expressed as

\[
V = \begin{pmatrix}
V_{XX} & V_{XY} & 0 \\
V_{XY} & V_{YY} & 0 \\
0 & 0 & V_{ZZ}
\end{pmatrix}
\]  
(1),

where \(V_{XX} + V_{YY} + V_{ZZ} = 0\). According to Zimmermann (1983), the EFG tensor components \(V_{ij}\) and intensity tensor components \(I_{ij}\) are related as

\[
I_{ij} = \frac{1}{2} \delta_{ij} \pm \frac{eQ}{8|\Delta E_Q|} V_{ij}
\]  
(2),

where \(\delta_{ij} = 0\) if \(i \neq j\), and \(\delta_{ii} = 1\) if \(i = j\). The positive and negative terms apply to higher and lower energy, respectively, \(e\) is the positive elementary charge, \(Q\) is the nuclear quadrupole moment, and \(\Delta E_Q\) is the quadrupole splitting. The traceless intensity tensor \(T\) is derived as \(T_{ij} = I_{ij} - (1/2) \delta_{ij}\) for the higher energy peak, so that the traceless intensity tensor \(T\) is proportional to the EFG tensor as:

\[
T_{ij} = \frac{eQ}{8|\Delta E_Q|} V_{ij}
\]  
(3).

\(T\) in italic font is the traceless intensity tensor before diagonalization of the matrix. From Eqs. (1) and (2), the intensity tensor \(I\) is given as:

\[
I = \begin{pmatrix}
I_{XX} & I_{XY} & 0 \\
I_{XY} & I_{YY} & 0 \\
0 & 0 & I_{ZZ}
\end{pmatrix}
\]  
(4),

where \(I_{XX} + I_{YY} + I_{ZZ} = 3/2\).

The peak intensity for a single crystal of pyroxene can be expressed as:

\[
I^h(\theta, \phi) = \begin{pmatrix}
e_X & e_Y & e_Z
\end{pmatrix}
\begin{pmatrix}
I_{XX} & I_{XY} & 0 \\
I_{XY} & I_{YY} & 0 \\
0 & 0 & I_{ZZ}
\end{pmatrix}
\begin{pmatrix}
e_X \\
e_Y \\
e_Z
\end{pmatrix}
\]  
(5),

where \(I^h(\theta, \phi)\) is the peak intensity, \(e_X = \sin \theta \cos \phi\), \(e_Y = \sin \theta \sin \phi\), and \(e_Z = \cos \theta\). In Eq. (5), the \(Z\) axis is selected as the diad axis, \(\theta\) and \(\phi\) are the polar angles of incident \(\gamma\)-rays in the rectangular coordinate system \((X, Y, Z)\), and \((e_X, e_Y, e_Z)\) is the direction cosine of incident \(\gamma\)-rays.

The Intensity tensor can be experimentally determined
by measuring Mössbauer spectra of crystallographically oriented thin sections with varying directions of γ-ray against crystallographic axes and applying least-squares fitting (LSQ) to peak intensities and γ-ray directions. From Eq. (5), the observation equation for LSQ is given as:

\[
\begin{align*}
& (\sin^2 \theta_i \cos^2 \phi_i - \cos^2 \theta_i) I_{XX} \\
& + (\sin^2 \theta_i \sin^2 \phi_i - \cos^2 \theta_i) I_{YY} \\
& + 2 (\sin^2 \theta_i \cos \phi_i \sin \phi_i) I_{XY} \\
& = I_0^\prime(\theta_i, \phi_i) - \frac{3}{2} \cos^2 \theta_i \\
& \text{where } i \text{ is the number of measurements, and } \theta_i \text{ and } \phi_i \text{ are the angles of } \gamma\text{-rays for the } i\text{-th measurements. An intensity tensor } I_0' \text{ can be obtained by solving simultaneous equations of Eq. (6). Traceless tensor } T'_{ij} = I_0' - (1/2) \delta_{ij} \text{ can be obtained from the experimentally determined } I_0. \text{ According to Zimmermann (1983), the components of the traceless intensity tensor } T \text{ must be scaled as:}
\end{align*}
\]

\[
I_\Delta = 16 \left\{ T^2_{ZZ} + \frac{1}{3} (T_{XX} - T_{YY})^2 \right. \\
\left. + \frac{4}{3} (T^2_{XY} + T^2_{XZ} + T^2_{YZ}) \right\} = 1
\]

As } T_{ij}' \text{ is not scaled traceless tensor, } T_{ij}' \text{ must be scaled by using } I_\Delta'

\[
I_{\Delta'} = 16 \left\{ T^2_{ZZ} + \frac{1}{3} (T_{XX} - T_{YY})^2 \right. \\
\left. + \frac{4}{3} (T^2_{XY} + T^2_{XZ} + T^2_{YZ}) \right\}
\]

as follows:

\[
T_{ij} = \sqrt{1/I_{\Delta}' T_{ij}'}
\]

\( T \) is proportional to \( V \) [Eq. (3)]. The traceless tensor \( T \) can be diagonalized with the Euler angle matrix \( U \), as

\[
U = \begin{pmatrix}
\cos \varphi & -\sin \varphi & 0 \\
\sin \varphi & \cos \varphi & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

(10)

gives the diagonalized traceless tensor \( T \) as follows:

\[
T = U^{-1} T U = \begin{pmatrix}
T_{XX} & 0 & 0 \\
0 & T_{YY} & 0 \\
0 & 0 & T_{ZZ}
\end{pmatrix}
\]

(11).

(12), so that the EFG components \([V_{XX}, V_{YY}, \text{ and } V_{ZZ} (\text{C/m}^3)]\) can be calculated using a \( QS \) of 1 mm/s = 4.80 × 10\(^{-4}\) (eV) = 7.69 × 10\(^{-27}\) (J), \( Q = 0.16 \text{ barn} \) (1 barn = 10\(^{-28}\) m\(^2\)) (Dufek et al., 1995), \( \Delta \theta = 8.854 \times 10^{-12} \) (F/m): the permittivity in vacuum, and the experimentally determined \( \eta \) (asymmetric parameter) and \( \Delta E_Q \) (mm/s).

**EXPERIMENTAL**

**Chemical analyses**

Four natural Ca-rich pyroxenes examined in this study are diopside (1) (Kamisano, Nambu-cho, Minamikoma-gun, Yamamashi Prefecture, Japan), diopside (2) (Horado, Seki, Gifu Prefecture, Japan), augite (Hinokuchisawa, Sarashina, Nagano Prefecture, Japan), and hedenbergite (Oshigahae, Nishiusuki-gun, Miyazaki Prefecture, Japan). Chemical compositions of Ca-rich pyroxenes were measured using SEM with EDS at the condition of 20 kV and 500 pA. All back scattered images of four samples were homogeneous, that suggests Ca-rich pyroxenes of this study are chemically homogeneous pyroxenes.

**X-ray diffraction**

Back Laue and precession X-ray cameras were used to adjust the crystallographic axes and to crystallographically orient the thin sections. Figure 2a shows a back Laue X-ray photograph of diopside (1) with a volume of 10 mm\(^3\) using a Mo X-ray tube operated with 35 kV and 15 mA. Distance between crystal and X-ray film is 35 mm. Width and height of X-ray film is 77 mm and 95 mm. X-ray exposure time is 6 h. A Laue analysis system (Laue Analysis program, 2022) was used for the analysis of diffraction spots on the back Laue photographs. The \( b^\ast \) axis in Figure 2a was adjusted to be parallel to the incident X-rays, and the \( a^\ast \) and \( c^\ast \) axes are indicated by arrows. Figure 2b shows a precession photograph of diopside (1) perpendicular to the \( b^\ast \) axis, and the \( a^\ast \) axis is adjusted to the horizontal dial axis of the X-ray precession camera; the \( c^\ast \) axis is indicated by an arrow. Distance between crystal and X-ray film is 60 mm. Width and height of
Intensity and EFG tensors for Fe" at M1 sites in Ca-rich pyroxene

X-ray film is 100 mm and 100 mm. X-ray exposure time is 4.5 h. This thin section can be rotated 360° around the horizontal axis (a* axis). Back Laue (Fig. 2a) and precession (Fig. 2b) photographs are informative for determining the c* axis. The (002) diffraction spot in Figure 2b is located at a similar position to the (202) spot. Although both spots have almost the same angle and distance from the a* axis and the origin of the reciprocal lattice, the intensity of the (002) spot is greater than that for the (202) spot. In the back Laue photograph (Fig. 2b), the c* and (101) reciprocal directions also have the same angle from the a* axis. Although the (051) and (151) spots occupy alternative positions, the intensity of the (051) spot is greater than that of the (151) spot.

Oriented thin sections were made in the following ways. A rod was fixed to parallel to the b* axis after determining b* axis parallel to X-ray on Laue camera (Fig. 2a). The oriented crystal with the rod was mounted on a glass slide with resin, where the b* axis was oriented perpendicular to the glass slide. The oriented crystal mounted on a glass slide was cut with a low-speed diamond wheel cutter. After polishing the cut plane, the crystal was fixed on a glass slide with an acetone-soluble adhesive and cut again with the low-speed cutter. The second cut plane was polished to an appropriate thickness, and the oriented thin section was recovered by dissolving the adhesive. The oriented thin section was then mounted on the goniometer again, and the crystallographic orientations were accurately adjusted by X-ray precession measurements within ±0.5°. The other oriented thin sections were prepared in the same way.

Mössbauer spectroscopy measurements

Mössbauer spectroscopy measurements were conducted in transmission mode on a constant acceleration spectrometer with a Si-PIN semiconductor detector (XR–100CR, AMPTEK, Inc.) and a multichannel analyzer with 1024 channels. The γ-ray source was 1.85 GBq 57Co in Rh with a diameter of 4 mm. An 57Fe–enriched iron foil was used as the velocity calibrant. Figure 3 shows the setup of the γ-ray source, Pb pinhole (PH), Si-PIN detector head, and an oriented thin section (C) on the goniometer head (G) fixed on a rotation stage (R) parallel to the dial axis of the X-ray precession camera. The two symmetric spectra were folded, and the Doppler velocity range was set to ±5 mm/s or ±3 mm/s. The MossWinn program was used for peak separation (MossWinn, 2018).

RESULTS AND DISCUSSION

Chemical analyses

The analytical results are shown in Table 1, where the weight percentages (wt%) for oxides are averages of ten measurement points, the wt% of Mg-hedenbergite was not shown in Tennant et al. (2000). Chemical analyses indicate the following formulae: diopside (1) from Kamisano: (Ca0.92Fe0.10Mg0.98Σ2.00)(Si1.96Al0.05)Σ2.00O6(Wo46En49Fs5), diopside (2) from Horado: (Ca0.97Fe0.06Mg0.79Σ2.07)Σ1.95(Si1.99Al0.03)Σ2.02O6(Wo49En04Fs16), hedenbergite from Sarashina: (Ca0.75Na0.03Fe0.31Mg0.84Ti0.02Σ1.95)Σ1.97(Si1.99Al0.03)Σ2.02O6(Wo40En45Fs16), hedenbergite from Nishiusuki: (Ca0.97Fe0.79Mg0.05Mn0.08Al0.04Σ1.93Si0.03Σ2.00O6(Wo35En23Fs44). Figure 4 shows the pyroxene quadrilateral with the four chemical compositions used in this study, and Mg-hedenbergite from Tennant et al. (2000).

Mössbauer analyses

Diopside (1): (Wo46En49Fs5). Chemical analysis of diopside (1) indicated the formula (Ca0.92Fe0.10Mg0.98Σ2.00)
Table 1. Chemical analyses of Ca-rich pyroxenes

|          | Di(1) | Di(2) | Augite | Hedenbergite | Tennant et al. |
|----------|-------|-------|--------|--------------|----------------|
| K wt%    | 0.98  | 0.97  | 0.97   | 0.97         | 0.97           |
| H wt%    | 0.98  | 0.92  | 0.92   | 0.92         | 0.92           |
| S wt%    | 3.2   | 3.1   | 3.1    | 3.1          | 3.1            |
| N wt%    | 4.3   | 4.3   | 4.3    | 4.3          | 4.3            |
| Sweden   | (O=6) | (O=6) | (O=6)  | (O=6)        | (O=6)          |
| SiO2     | 53.53 | 54.65 | 51.47  | 50.20        |                |
| TiO2     | 0.88  |       |        |              |                |
| Al2O3    | 2.31  | 2.04  | 9.37   | 23.51        |                |
| MgO      | 23.60 | 24.72 | 18.77  | 22.32        |                |
| MnO      | 0.41  |       |        |              |                |
| Na2O     |       |       |        |              |                |
| Total    | 99.65 | 99.40 | 99.68  | 99.89        |                |

End-member (%)

|        | Wo | En | Fs |
|--------|----|----|----|
| Di(1)  | 46.1 | 48.9 | 5.0 |
| Di(2)  | 49.2 | 47.6 | 3.2 |
| Augite | 39.7 | 44.8 | 15.5 |
| Hedenbergite | 53.4 | 2.8 | 43.9 |
| Tennant et al. | 50.1 | 22.3 | 27.6 |

Chemical compositions of Ca-rich pyroxenes in this study (1) and of Tennant et al. (2000) (2) in a pyroxene quadrilateral. 1, diopside (1) (Wo46En49Fs5); 2, diopside (2) (Wo53En3Fs44); 3, augite (Wo40En45Fs16); 4, hedenbergite (Wo45En3Fs4); 5, Mg-hedenbergite (Wo35En2Fs57) by Tennant et al. (2000).

Table 2 shows the Mössbauer dataset used to determine the intensity and EFG tensors for Fe2+ at the M2 site of diopside (1). Reliable intensity tensors for Fe2+ and Fe3+ at the M1 sites of diopside (1) were not obtained, because separated doublets of Fe2+ and Fe3+ at the M1 sites were too low to be calculated.

Equation (6) was employed for $I_{\theta_1}$ ($\theta$, $\phi$) with the $\theta$, $\phi$ listed in Table 2 in the LSQ calculation, from which the most probable values of $I_{XX}$, $I_{YY}$, and $I_{ZZ}$ were obtained as $I_{XX} = 0.494(5)$, $I_{YY} = 0.430(5)$, $I_{ZZ} = 0.041(8)$, and $I_{ZZ} = 0.576(10)$, where the estimated errors are given in parentheses. Therefore, the intensity tensor for Fe2+ at M2 sites in diopside (1) is given as

$$I_{Fe^{2+}(M2)Di(1)} = \begin{pmatrix}
0.494(5) & 0.041(8) & 0 \\
0.041(8) & 0.430(5) & 0 \\
0 & 0 & 0.576(10)
\end{pmatrix}
(13).$$

The EFG tensor and principal axes for EFG can be calculated from the intensity tensor (Eq. (13)) by applying Eqs. from (7) to (11) as follows. The traceless intensity tensor $T'$ and its components $T''_{ij}$ are set, so that $T'$ is given as:

$$T'_{Fe^{2+}(M2)Di(1)} = \begin{pmatrix}
-0.006 & 0.041 & 0 \\
0.041 & -0.070 & 0 \\
0 & 0 & 0.076
\end{pmatrix}
(14).$$
where $T'_{ij} = I_{ij} - (1/2)\delta_{ij}$. The $T'$ components are applied to Eq. (8), whereby $I'_{\Lambda}$ is calculated as $I'_{\Lambda} = 0.149$. Scaling $T'_{ij}$ using Eq. (9), the traceless intensity tensor $T$ is given as:

$$T_{Fe^{2+}(M2)\Delta l(1)} = \begin{pmatrix} -0.016 & 0.106 & 0 \\ 0.106 & -0.181 & 0 \\ 0 & 0 & 0.196 \end{pmatrix}. \quad (15)$$

The diagonalization of $T$ using the Euler angle matrix $U$,

$$U_{Fe^{2+}(M2)\Delta l(1)} = \begin{pmatrix} \cos(26.0^\circ) & -\sin(26.0^\circ) & 0 \\ \sin(26.0^\circ) & \cos(26.0^\circ) & 0 \\ 0 & 0 & \cos(26.0^\circ) \end{pmatrix}. \quad (16)$$

gives the diagonalized traceless intensity tensor $T$:

$$T_{Fe^{2+}(M2)\Delta l(1)} = U_{(16)}^{-1}T_{(15)}U_{(16)} = \begin{pmatrix} 0.036 & 0 & 0 \\ 0 & -0.232 & 0 \\ 0 & 0 & 0.196 \end{pmatrix}. \quad (17)$$

The $V_{XX}$, $V_{YY}$, and $V_{ZZ}$ components of the diagonalized EFG tensor $V$ are proportional to those in $T$ [Eq. (3)], whereas these should be rearranged as $|V_{XX}| \leq |V_{YY}| \leq |V_{ZZ}|$ (Travis, 1971) with non-italic fonts. The component 0.036 in Eq. (17) is the minimum absolute value, and the $V_{XX}$ axis of the EFG tensor is oriented along the X axis after diagonalization. The component of the maximum absolute value is $-0.232$ in Eq. (17); therefore, the $V_{ZZ}$ axis of the EFG tensor is oriented along the Y axis after diagonalization. The intermediate component is 0.196 in Eq. (17), and the $V_{YY}$ axis of EFG is oriented along the Z axis after diagonalization. Considering the Euler angles in the Euler angle matrix $U$ [Eq. (16)], the EFG principal axes for Fe$^{2+}$ are...
at M2 sites in diopside (1) are discussed in the later section. The asymmetry parameter \( \eta \) is determined as \( \eta = (T_{XX} - T_{ZZ})/T_{YY} = 0.690 \). Substituting \( QS = 2.002 \text{ mm/s} \) and \( \eta \) into Eq. (12) gives the EFG components \( (V_{XX}, V_{YY}, \text{ and } V_{ZZ}) \) of Fe\(^{2+} \) at M2 sites in diopside (1) to be \( 4.82 \times 10^{10}, 2.62 \times 10^{11}, \text{ and } -3.11 \times 10^{11} \text{ C/m}^3 \), respectively.

**Diopside (2): \((\text{Wo}_{49}\text{En}_{48}\text{Fs}_{3})\).** Chemical analysis of diopside (2) indicated the formula \((\text{Ca}_{0.97}\text{Fe}_{0.06}\text{Mg}_{0.94})\Sigma_{1.97} (\text{Si}_{1.99}\text{Al}_{0.03})\Sigma_{2.02}\text{O}_6\). The molar contents of Mg and Ca were 0.94 and 0.97, respectively. The results suggest that Ca ions almost fully occupy the M2 sites and that the Mg ions are not sufficient to occupy the M1 sites. Therefore, the major part of the Fe\(^{2+} \) ions occupy the M1 sites. Figure 6 shows the Mössbauer spectrum of a thin section of diopside (2) which was measured under the condition \( \gamma\text{-ray/}b^* \) axis. The single doublet in Figure 6 suggests that there is no Fe\(^{3+} \), but is due to Fe\(^{2+} \) at M1 sites, as determined from the chemical analyses. Table 3 shows the Mössbauer dataset used to determine the intensities and EFG tensors for Fe\(^{2+} \) at M1 sites in diopside (2). The averages of IS, QS, and LW for Fe\(^{2+} \) in the M1 sites of diopside (2) were 1.176, 1.919, and 0.310 mm/s, respectively.

Eq. (6) is applied to the dataset in Table 3, by which the intensity tensor for Fe\(^{2+} \) for M1 sites of diopside (2) is given as:

\[
I_{\text{Fe}^{2+}(\text{M1})} = \begin{pmatrix}
0.328(7) & 0.050(15) & 0 \\
0.050(15) & 0.480(5) & 0 \\
0 & 0 & 0.692(12)
\end{pmatrix}
\]

The same calculation processes in Eqs. (14) to (17) are applied to calculate the scaled traceless intensity tensor \( T \) as:

\[
T_{\text{Fe}^{2+}(\text{M1})} = \begin{pmatrix}
-0.197 & 0.057 & 0 \\
0.057 & -0.023 & 0 \\
0 & 0 & 0.219
\end{pmatrix}
\]

Diagonalization of \( T \) using the Euler angle matrix \( U \),

\[
U_{\text{Fe}^{2+}(\text{M1})} = \begin{pmatrix}
\cos(73.3^\circ) & -\sin(73.3^\circ) & 0 \\
\sin(73.3^\circ) & \cos(73.3^\circ) & 0 \\
0 & 0 & \cos(0^\circ)
\end{pmatrix}
\]


gives the diagonalized traceless intensity tensor \( T \):

\[
T_{\text{Fe}^{2+}(\text{M1})} = U_{(20)}^{-1} T_{(19)} U_{(20)}
\]=

\[
\begin{pmatrix}
-0.005 & 0 & 0 \\
0 & -0.214 & 0 \\
0 & 0 & 0.219
\end{pmatrix}
\]

From the absolute values of the components in Eq. (21),

| Table 3. Mössbauer dataset to determine the intensity and EFG tensors for Fe\(^{2+} \) at the M1 site of diopside (2) |
|---------------------------------------------------------------|
| **Diopside (2)** | **#1 (\text{\La})** | **#2 (\text{\Lb})** | **#3 (\text{\Lc})** |
| \( \gamma \text{-ray direction} \) | | | |
| \( \theta \) (°) | 60 | 90 | 60 | 0 | 30 | 30 | 90 | 60 |
| \( \phi \) (°) | 90 | 90 | 270 | 0 | 74 | 254 | 344 | 344 |
| \( \text{Fe}^{2+}(\text{M1}) \) intensity | | | |
| \( \text{Low peak (cts)} \) | 996 | 1761 | 1018 | 1088 | 1291 | 1436 | 1209 | 1777 |
| \( \text{High peak (cts)} \) | 1157 | 1635 | 1136 | 2555 | 2119 | 2646 | 549 | 1200 |
| \( \text{Peak intensity} \) | 0.537 | 0.481 | 0.527 | 0.701 | 0.621 | 0.648 | 0.312 | 0.403 |
| \( ^{57}\text{Fe Mössbauer parameter} \) | 1.168 | 1.175 | 1.172 | 1.174 | 1.170 | 1.175 | 1.188 | 1.187 | 1.176 | 0.002 |
| \( \delta \) [mm/s] | 1.888 | 1.938 | 1.921 | 1.905 | 1.942 | 1.909 | 1.929 | 1.918 | 1.919 | 0.004 |
| \( \Gamma \) [mm/s] | 0.329 | 0.318 | 0.300 | 0.283 | 0.299 | 0.304 | 0.336 | 0.314 | 0.310 | 0.004 |
the VXX, VYY, and VZZ axes of the EFG tensor are the X, Y, and Z axes after diagonalization, respectively. From the Euler angle in Eq. (20), the EFG principal axes for Fe²⁺ at M₁ sites in diopside (2) are discussed in the later section. The asymmetry parameter \( \eta \) is determined as \( \eta = \frac{TXX - TYY}{TZZ} = 0.954 \). Substituting QS = 1.919 mm/s and the \( \eta \) value into Eq. (12) gives the EFG components (VXX, VYY, and VZZ) for Fe²⁺ at M₁ sites in diopside (2) as \(-6.41 \times 10^9\), \(-2.74 \times 10^{11}\), and \(2.81 \times 10^{11}\) C/m³, respectively.

Augite; (Wo₄₀En₄₅Fs₁₆). Chemical analysis of augite indicated the formula \((Ca_{0.75}Na_{0.03}Fe_{0.31}Mg_{0.84}Ti_{0.02})\Sigma_{1.95}(Si_{1.91}Al_{0.16})\Sigma_{2.07}O_{6}\). The molar contents of Ca and Mg were 0.75 and 0.84, respectively, both of which were much less than 1.00. This chemical formula suggests that Fe ions occupy the M₁ and M₂ sites. From the molar contents of Ca (0.746) + Na (0.029) = 0.775 and Mg (0.843) + Ti (0.024) = 0.867, the ratio of Fe ions at M₁ and M₂ sites was estimated to be 0.133:0.225. Figures 7a and 7b show Mössbauer spectra of augite powder and an oriented thin section of augite perpendicular to the \( b^* \) axis, respectively. A small peak at 0.8 mm/s indicates the higher Doppler energy of the quadrupole doublet for Fe³⁺ ions in augite. The broad linewidth of the main doublet (~0.6 mm/s) in Figures 7a and 7b indicates that this represents an overlap of outer (M₁) and inner (M₂) doublets due to Fe²⁺. The results of peak separation for powdered augite (Fig. 7a) into three doublets due to Fe²⁺ at M₂ sites, Fe²⁺ at M₁ sites, and Fe³⁺ at M₁ sites, assuming equal intensity, indicated an Fe²⁺ (M₂) doublet of IS = 1.11, QS = 2.01, LW = 0.411 mm/s, an Fe²⁺ (M₁) doublet of IS = 1.11, QS = 2.53, LW = 0.411 mm/s, and an Fe³⁺ doublet of IS = 0.531, QS = 0.577, LW = 0.442 mm/s. Figure 7b shows the Mössbauer spectrum of an oriented thin section of an augite single crystal under the condition \( \gamma//b^* \). Peak separation for single-crystal thin sections was performed by fixing the IS, QS, and LW Mössbauer parameters obtained from powdered augite and by unfixing the intensity parameters. Table 4 shows the Mössbauer dataset used to determine the intensity and EFG tensor for Fe²⁺ at M₂ sites, Fe²⁺ at M₁ sites, and Fe³⁺ at M₁ sites. The averaged area ratio for Fe²⁺ (M₂), Fe²⁺ (M₁), and Fe³⁺ (M₁) is shown in Table 4 as 66.6:12.7:20.8. Mössbauer data suggest that the ratio of Fe ions in M₁ and M₂ sites is 33.5 (12.7 + 20.8): 66.6, and the ratio of Fe²⁺ and Fe³⁺ is 79.3 (66.6 + 12.7): 20.8. The ratio obtained from the Mössbauer spectra is almost consistent with the ratio obtained from the chemical analysis (0.133:0.225). The ratio of Fe²⁺:Fe³⁺ suggests the chemical formula of this augite is \((Ca_{0.75}Na_{0.03}Fe^{2+}_{0.25}Fe^{3+}_{0.06}Mg_{0.84}Ti_{0.02})\Sigma_{2.07}Si_{1.91}Al_{0.16}O_{6}\).

(a) Intensity and EFG tensors for Fe²⁺ at M₂ sites in augite. Eq. (6) is applied to the dataset for Fe²⁺ (M₂), Fe²⁺ (M₁), and Fe³⁺ (M₁) is shown in Table 4 as 66.6:12.7:20.8. Mössbauer data suggest that the ratio of Fe ions in M₁ and M₂ sites is 33.5 (12.7 + 20.8): 66.6, and the ratio of Fe²⁺ and Fe³⁺ is 79.3 (66.6 + 12.7): 20.8. The ratio obtained from the Mössbauer spectra is almost consistent with the ratio obtained from the chemical analysis (0.133:0.225). The ratio of Fe²⁺:Fe³⁺ suggests the chemical formula of this augite is \((Ca_{0.75}Na_{0.03}Fe^{2+}_{0.25}Fe^{3+}_{0.06}Mg_{0.84}Ti_{0.02})\Sigma_{2.07}Si_{1.91}Al_{0.16}O_{6}\).

\[
I_{Fe^{2+}(M_2)_{Aug}} = \begin{pmatrix}
0.617(12) & 0.054(12) & 0 \\
0.054(12) & 0.405(11) & 0 \\
0 & 0 & 0.478(23)
\end{pmatrix}
\]

The same calculation processes from Eqs. (14) to (17) are applied to calculate the scaled traceless intensity tensor T as:
Diagonalization of $T_{\text{Fe}^2+ (M2)}$ using the Euler angle matrix $U_{\text{Fe}^2+ (M2)}$ gives the diagonalized traceless intensity tensor $T_{\text{Fe}^2+ (M2)}$:

$$T_{\text{Fe}^2+ (M2)}_{\text{Aug}} = U_{\text{Fe}^2+ (M2)}^{\text{T}} T_{\text{Aug}} (U_{\text{Fe}^2+ (M2)})$$

with $T_{\text{Aug}}$ being the intensity tensor for Fe$^{2+}$ in the M2 site of augite. The diagonalized tensor $T_{\text{Fe}^2+ (M2)}$ is then used to determine the EFG principal axes and other parameters.

The same calculation processes from Eqs. (14) to (17) are applied to calculate the scaled traceless intensity tensor $T$ as:

$$I_{\text{Fe}^{2+} (M1)} = T_{\text{Aug}}^{\text{T}} T_{\text{Aug}}$$

where $I_{\text{Fe}^{2+} (M1)}$ is the intensity tensor for Fe$^{2+}$ in the M1 site of augite. The EFG principal axes for Fe$^{2+}$ in the M2 sites of augite are discussed in the later section.

### Table 4. Mössbauer dataset to determine the intensity and EFG tensors for Fe$^{2+}$ at the M1 site, Fe$^{2+}$ at the M2 site and Fe$^{3+}$ at the M1 site of augite

| Augite | #1 (Lα) | #2 (Lβ) | #3 (Lγ) |
|--------|---------|---------|---------|
| γ-ray direction | | | |
| $\theta$ (°) | 90 | 60 | 60 |
| $\phi$ (°) | 74 | 74 | 254 |

**Fe$^{2+}$ (M2) peak intensity**

- Low peak (cts): 6436, 7034, 10257
- High peak (cts): 5816, 6445, 8936
- Peak intensity: 0.475, 0.478, 0.466
- Area(%): 63.2, 65.2, 66.3

**Fe$^{2+}$ (M1) peak intensity**

- Low peak (cts): 1750, 1450, 2163
- High peak (cts): 1134, 1244, 2032
- Peak intensity: 0.393, 0.462, 0.484
- Area(%): 14.9, 13.0, 14.5

**Fe$^{3+}$ (M1) peak intensity**

- Low peak (cts): 2496, 2452, 2825
- High peak (cts): 1756, 2063, 2716
- Peak intensity: 0.413, 0.457, 0.490
- Area(%): 21.9, 21.8, 19.2

### Mössbauer parameters

- Fe$^{2+}$ (M1) [IS = 1.11, QS = 2.53, LW = 0.411]
- Fe$^{2+}$ (M2) [IS = 1.11, QS = 2.01, LW = 0.411]
- Fe$^{3+}$ (M1) [IS = 0.531, QS = 0.577, LW = 0.442]
\[
\mathbf{T}_{Fe^{3+}(M)_{Aug}} = \begin{pmatrix}
-0.183 & -0.042 & 0 \\
-0.042 & -0.049 & 0 \\
0 & 0 & 0.233
\end{pmatrix}
\] (27).

Diagonalization of \( \mathbf{T} \) using the Euler angle matrix \( \mathbf{U} \),
\[
\mathbf{U}_{Fe^{3+}(M)_{Aug}} = \begin{pmatrix}
\cos(16.1^\circ) & -\sin(16.1^\circ) & 0 \\
\sin(16.1^\circ) & \cos(16.1^\circ) & 0 \\
0 & 0 & \cos0^\circ
\end{pmatrix}
\] (28)
gives the diagonalized traceless intensity tensor \( \mathbf{T} \):
\[
\mathbf{T}_{Fe^{3+}(M)_{Aug}} = \mathbf{U}_{(29)}^{-1} \mathbf{T}_{(27)} \mathbf{U}_{(28)}
\] (29).

From the absolute values of the components in Eq. (29), the \( V_{XX}, V_{YY}, \) and \( V_{ZZ} \) axes of the EFG tensor are the \( Y, \) \( X, \) and \( Z \) axes after diagonalization, respectively. From the Euler angle in Eq. (28), the EFG principal axes for \( Fe^{3+} \) at \( M1 \) sites in augite are discussed in the later section. The asymmetry parameter \( \eta \) is determined as \( \eta = (T_{XX} - T_{YY})/T_{ZZ} = 0.682. \) Substituting \( QS = 2.53 \) mm/s and the \( \eta \) value into Eq. (12), the EFG components \( (V_{XX}, V_{YY}, \) and \( V_{ZZ} \)) for \( Fe^{3+} \) at \( M1 \) sites in augite are \(-6.24 \times 10^{10}, -3.31 \times 10^{11}, \) and \( 3.93 \times 10^{10} \) C/m\(^3\), respectively.

(c) Intensity and EFG tensors for \( Fe^{3+} \) at \( M1 \) sites in augite. Eq. (6) is applied to the dataset for \( Fe^{3+} \) (M1) in Table 4, whereby the intensity tensor for \( Fe^{3+} \) at \( M1 \) sites in augite is given as:
\[
I_{Fe^{3+}(M)_{Aug}} = \begin{pmatrix}
0.446(56) & 0.041(60) & 0 \\
0.041(60) & 0.532(55) & 0 \\
0 & 0 & 0.522(111)
\end{pmatrix}
\] (30).

The same calculation processes from Eqs. (14) to (17) are applied to calculate the scaled traceless intensity tensor \( \mathbf{T} \) as:
\[
\mathbf{T}_{Fe^{3+}(M)_{Aug}} = \begin{pmatrix}
-0.187 & 0.143 & 0 \\
0.143 & 0.110 & 0 \\
0 & 0 & 0.077
\end{pmatrix}
\] (31).

Diagonalization of \( \mathbf{T} \) using the Euler angle matrix \( \mathbf{U} \),
\[
\mathbf{U}_{Fe^{3+}(M)_{Aug}} = \begin{pmatrix}
\cos(68.0^\circ) & -\sin(68.0^\circ) & 0 \\
\sin(68.0^\circ) & \cos(68.0^\circ) & 0 \\
0 & 0 & \cos0^\circ
\end{pmatrix}
\] (32)
gives the diagonalized traceless intensity tensor \( \mathbf{T} \):
\[
\mathbf{T}_{Fe^{3+}(M)_{Aug}} = \mathbf{U}_{(32)}^{-1} \mathbf{T}_{(31)} \mathbf{U}_{(32)}
\] (33).

From the absolute values of the components in Eq. (33), the \( V_{XX}, V_{YY}, \) and \( V_{ZZ} \) axes of the EFG tensor are the \( Z, \) \( X, \) and \( Y \) axes after diagonalization, respectively. From the Euler angle in Eq. (32), the EFG principal axes for \( Fe^{3+} \) at \( M1 \) sites in augite are discussed in the later section. The asymmetry parameter \( \eta \) is determined as \( \eta = (T_{XX} - T_{YY})/T_{YY} = 0.369. \) Substituting \( QS = 0.577 \) mm/s and the \( \eta \) value into Eq. (12), the EFG components \( (V_{XX}, V_{YY}, \) and \( V_{ZZ} \)) for \( Fe^{3+} \) at \( M1 \) sites in augite are \(2.97 \times 10^{10}, 6.45 \times 10^{10}, \) and \(-9.42 \times 10^{10} \) C/m\(^3\), respectively.

Hedenbergite: \( \text{(Wos}_{0.53}\text{En}_{0.44}\text{Fs}_{0.04}) \). Chemical analysis of hedenbergite indicated the formula \( \text{(Ca}_{0.97}\text{Fe}_{0.79}\text{Mg}_{0.05}\text{Mn}_{0.06}\text{Al}_{0.001}\text{Si}_{1.93}\text{O}_{6}) \). The molar contents of Mg and Ca were 0.05 and 0.97, respectively, which suggests that Ca ions fully occupy the \( M2 \) sites and Mg ions are not sufficient to fully occupy the \( M1 \) sites. Therefore, the major part of \( Fe^{3+} \) ions occupy the \( M1 \) sites. Figure 8 shows a Mössbauer spectrum of a thin section of hedenbergite measured under the condition \( \gamma \)-ray/\( b^* \) axis. The single doublet in Figure 8 suggests that there is no \( Fe^{3+} \), and the single doublet is due to \( Fe^{2+} \) at \( M1 \) sites, which corresponds to the chemical analysis results. Table 5 shows the Mössbauer dataset used to determine the intensity and EFG tensors for \( Fe^{2+} \) at \( M1 \) sites in hedenbergite. The averages of IS, QS and LW for \( Fe^{2+} \) at \( M1 \) sites in hedenbergite were 1.185, 2.235, and 0.337 mm/s, respectively. Eq. (6) was applied to the dataset in Table 5, whereby the intensity tensor for \( Fe^{2+} \) at \( M1 \) sites in hedenbergite is given as:
\[
I_{Fe^{2+}(M)_{Hd}} = \begin{pmatrix}
0.370(11) & 0.019(10) & 0 \\
0.019(10) & 0.467(11) & 0 \\
0 & 0 & 0.663(22)
\end{pmatrix}
\] (34).

The same calculation processes from Eqs. (14) to (17) were applied to calculate the scaled traceless intensity tensor \( \mathbf{T} \) as:
\[
\mathbf{T}_{Fe^{2+}(M)_{Hd}} = \begin{pmatrix}
-0.187 & 0.27 & 0 \\
0.27 & -0.048 & 0 \\
0 & 0 & 0.235
\end{pmatrix}
\] (35).

Diagonalization of \( \mathbf{T} \) using the Euler angle matrix \( \mathbf{U} \),
\[ U_{\text{Fe}^{2+}(M1)\text{Hd}} = \begin{pmatrix} \cos(79.4^\circ) & -\sin(79.4^\circ) & 0 \\ \sin(79.4^\circ) & \cos(79.4^\circ) & 0 \\ 0 & 0 & \cos(0^\circ) \end{pmatrix} \]

(36)

gives the diagonalized traceless intensity tensor \( T \): 

\[ T_{\text{Fe}^{2+}(M1)\text{Hd}} = U_{\text{36}}^{-1}T_{\text{35}}U_{\text{36}} = \begin{pmatrix} -0.043 & 0 & 0 \\ 0 & -0.192 & 0 \\ 0 & 0 & 0.235 \end{pmatrix} \]

(37).

From the absolute values of the components in Eq. (37), the \( V_{XX}, V_{YY}, \) and \( V_{ZZ} \) axes of the EFG tensor are the \( X, Y, \) and \( Z \) axes after diagonalization, respectively. From the Euler angle in Eq. (36), the EFG principal axes for \( \text{Fe}^{2+} \) at \( M1 \) sites in hedenbergite are discussed in the later section. The asymmetry parameter \( \eta \) is determined as 

\[ \eta = \frac{T_{XX} - T_{YY}}{T_{ZZ}} = 0.634. \]

Substituting \( QS = 2.235 \text{ mm/s} \) and the \( \eta \) value into Eq. (12), the EFG components (\( V_{XX}, V_{YY}, \) and \( V_{ZZ} \)) for \( \text{Fe}^{2+} \) at \( M1 \) sites in hedenbergite are 

\[ -6.41 \times 10^{10}, -2.86 \times 10^{11}, \text{ and } 3.51 \times 10^{11} \text{ C/m}^3, \]

respectively.

### Compositional dependence of intensity tensor and orientations of principal axes of EFG tensor for \( \text{Fe}^{2+} \) at \( M1 \) sites

Figure 9a shows the relation between the Fs components and the \( I_{XX}, I_{YY}, I_{XY}, \) and \( I_{ZZ} \) components for \( \text{Fe}^{2+} \) at \( M1 \) sites extracted from Eqs. (18), (26), (34), and (A1). Three \( \text{Wo} \) components of diopside (2), hedenbergite and \( \text{Mg}-\text{hedenbergite} \) among the four pyroxenes are commonly almost 50, which indicates that the \( M2 \) sites in these three pyroxenes are fully occupied with \( \text{Ca} \) ions. The intensity tensor components (\( I_{XX}, I_{YY}, \) and \( I_{ZZ} \)) for the three pyroxenes show almost constant values independent of the Fs components. The averages of the \( I_{XX}, I_{YY}, I_{XY}, \) and \( I_{ZZ} \) components for \( \text{Fe}^{2+} \) at \( M1 \) sites in \( \text{Wo50} \) pyroxenes are 0.342, 0.477, 0.039, and 0.681, respectively. Solid lines in Figure 9a are linear fits of the intensity tensor components for \( \text{Wo50} \). In contrast to the \( \text{Wo50} \) pyroxenes, the intensity tensor components for \( \text{Wo40} \) augite are plotted outside of the fitting lines. Common lines of the intensity tensor component of \( \text{Wo50} \) and four plots of \( \text{Wo40} \) out of the fitting lines for \( \text{Wo50} \) suggest that the intensity tensor components for \( \text{Ca}-\text{rich} \) pyroxenes are independent of the \( \text{Fe} \) components and dependent on the \( \text{Ca} \) component. Dotted lines in Figure 9a show the estimated intensity tensor components for \( \text{Wo40} \) pyroxene.

Figure 9b shows the principal axes of the EFG tensors for \( \text{Fe}^{2+} \) at \( M1 \) sites obtained from Eqs. (20) and (21), (28) and (29), (36) and (37), and (A3) and (A4) in Appendix. The \( V_{ZZ} \) axis, which is represented by squares and a solid line is commonly oriented along the \( b_\ast \) axis. The \( V_{XX} \) (circles and dotted line) and \( V_{YY} \) (triangles and broken line) axes for \( \text{Wo50} \) pyroxenes are oriented along the \( a_\ast \) and \( c \) axes, respectively. Although the precise orienta-

### Table 5. Mössbauer dataset to determine the intensity and EFG tensors for \( \text{Fe}^{2+} \) at the \( M1 \) site of hedenbergite

| Hedenbergite | #1 (\( \perp a \)) | #2 (\( \perp c \)) | #3 (\( \perp b \)) |
|-------------|------------------|------------------|------------------|
| \( \gamma \)-ray direction | | |
| \( \theta \) (°) | 90 | 90 | 90 |
| \( \phi \) (°) | 74 | 104 | 90 |
| Peak intensity | |
| Low peak (cts) | 43811 | 21520 | 30770 |
| High peak (cts) | 40437 | 16375 | 24849 |
| Peak intensity | 0.480 | 0.432 | 0.447 |

\(^{57}\text{Fe} \) Mössbauer hyperfine parameter

| IS (mm/s) | 1.185 | 1.181 | 1.186 |
| QS (mm/s) | 2.233 | 2.235 | 2.236 |
| LW (mm/s) | 0.337 | 0.336 | 0.346 |

Average
tions of the VXX and VYY axes for Wo40 deviate from those for Wo50, the approximate orientations for Wo40 are consistent with Wo50.

In the pyroxene structure, M1 octahedra and M2 polyhedra share edges to form continuous sheets parallel to the c axis and in the (100) plane (Zussman, 1968). The general ionic radii of Fe$^{2+}$ and Mg$^{2+}$ in 6-coordinated sites are 0.86 and 0.80 Å, respectively, and that for Ca$^{2+}$ in 8-coordinated sites is 1.20 Å (Whittaker and Muntus, 1970). Considering the general ionic radii of Fe$^{2+}$, Mg$^{2+}$, and Ca$^{2+}$, ion exchange of Fe$^{2+}$ and Mg$^{2+}$ in the M1 sites to maintain full occupancy of Ca$^{2+}$ at M2 sites must not change dimensions of the M1 sites such as the M1-O distances and O-M1-O angles. On the other hand, the replacement of Ca$^{2+}$ by Fe$^{2+}$ at M2 sites must reduce the size of the M2 polyhedra and change the dimensions of the neighboring M1 sites. As a result, the intensity and EFG tensors must be modified dependently of Ca$^{2+}$ at M2 sites.

**Compositional dependence of intensity tensor and orientations of principal axes of EFG tensor for Fe$^{2+}$ at M2 sites**

Figure 10a shows the relation between the Fs components and the $I_{XX}$, $I_{YY}$, $I_{XY}$, and $I_{ZZ}$ components for Fe$^{2+}$ at M2 sites extracted from Eqs. (13) and (22). Figure 10a is not

---

**Figure 9.** (a) $I_{XX}$ (blue), $I_{YY}$ (red), $I_{XY}$ (green), and $I_{ZZ}$ (black) components of Fe$^{2+}$ at the M1 sites. Solid lines are linear fitting lines of three Wo50 pyroxenes [Di(2), diopside (2); Hd, hedenbergite; Mg-Hd, Mg-hedenbergite calculated from Tennant et al. 2000]. Error bars are as small as circles. Dotted lines show the estimated intensity tensor components for Wo40 pyroxene. (b) Principal axes of EFG tensors of Fe$^{2+}$ at the M1 sites. The principal axes of diopside (2), augite, hedenbergite, and Mg-hedenbergite are represented as red, blue, green, and black, respectively. V$^{XX}$ axis is represented by circle and dotted line. V$^{YY}$ is triangle and broken line. V$^{ZZ}$ is square and solid line.

**Figure 10.** (a) $I_{XX}$ (blue), $I_{YY}$ (red), $I_{XY}$ (green), and $I_{ZZ}$ (black) components of Fe$^{2+}$ at the M2 sites of Wo40 [Di(1), diopside (1)] and Wo40 (Aug, augite) pyroxenes. Error bars are as small as circles. (b) Principal axes of EFG tensors of Fe$^{2+}$ at the M2. The principal axes of diopside (1) and augite are represented as red and blue. V$^{XX}$ axis is represented by circle and dotted line. V$^{YY}$ is triangle and broken line. V$^{ZZ}$ is square and solid line.
as informative as Figure 9a, because the data between Fs20 and Fs50 are missing. Two limited components for diopside (1) and augite suggest that $I_{YY}$ and $I_{XY}$ are constant regardless of Fs and $I_{XX}$, so that $I_{ZZ}$ varies with Fs. Figure 10b shows the principal axes of the EFG tensors for Fe$^{2+}$ at the M2 sites. The principal axes for diopside (1) and augite are represented in red and blue, respectively.

**Intensity tensor and orientation of principal axes of EFG tensor for Fe$^{3+}$ at M1 sites**

To compare with the intensity tensor for Fe$^{3+}$ at M1 sites in augite (Wo40), the intensity tensor, traceless tensor, diagonalization matrix and diagonalized tensor for aegirine (Ae; NaFe$^{3+}$Si$_2$O$_6$) (Shinoda and Kobayashi, 2019) are given as:

$I_{Fe^{3+}(M1)Ae} = \begin{pmatrix} 0.666(5) & -0.144(5) & 0 \\ -0.144(5) & 0.331(5) & 0 \\ 0 & 0 & 0.503(10) \end{pmatrix} \text{(Ae1)}$,

$T_{Fe^{3+}(M1)Ae} = \begin{pmatrix} 0.163 & -0.141 & 0 \\ -0.141 & -0.166 & 0 \\ 0 & 0 & 0.003 \end{pmatrix} \text{(Ae2)}$,

$U_{Fe^{3+}(M1)Ae} = \begin{pmatrix} \cos(69.6^\circ) & -\sin(69.6^\circ) & 0 \\ \sin(69.6^\circ) & \cos(69.6^\circ) & 0 \\ 0 & 0 & \cos(0^\circ) \end{pmatrix} \text{(Ae3)}$,

and

$T_{Fe^{3+}(M1)Ae} = U^{-1}_{(Ae1)}T_{(Ae2)}U_{(Ae3)} = \begin{pmatrix} -0.218 & 0 & 0 \\ 0 & 0.215 & 0 \\ 0 & 0 & 0.003 \end{pmatrix} \text{(Ae4)}$.

Figure 11 shows the principal axes of the EFG tensors for Fe$^{3+}$ at M1 sites in augite (blue) and aegirine (Shinoda and Kobayashi, 2019) (orange). Although augite is a Ca-rich pyroxene and aegirine is a Na-rich pyroxene, the principal axes for Fe$^{3+}$ are consistent.

Shinoda mistook calculations of the EFG components ($V_{XX}$, $V_{YY}$, and $V_{ZZ}$) for Fe$^{3+}$ at M1 sites in aegirine in Shinoda and Kobayashi (2019), because $V_{ZZ}$ was not divided by 4$\pi$0 in Eq. (22) of the paper. The corrected $V_{XX}$, $V_{YY}$, and $V_{ZZ}$ values for Fe$^{3+}$ at M1 sites in aegirine are $5.99 \times 10^8$, $4.29 \times 10^9$, and $-4.35 \times 10^9$ C/m$^3$, respectively.

**CONCLUSION**

The compositional dependence of the intensity and EFG tensors for Fe$^{2+}$ at M1 sites, Fe$^{2+}$ at M2 sites, and Fe$^{3+}$ at M1 sites in Ca-rich pyroxene were obtained from Mössbauer spectra of crystallographically oriented single-crystal thin sections of four Ca-rich natural pyroxenes. The intensity tensors for Fe$^{3+}$ at M1 sites in Wo40 pyroxene were almost the same; the averages of the $I_{XX}$, $I_{YY}$, $I_{XY}$, and $I_{ZZ}$ components were 0.342, 0.477, 0.039, and 0.681, respectively. The intensity tensor for Fe$^{3+}$ at M1 sites in Wo40 was slightly different from that for Wo50. Although the principal axes of the EFG tensors for Fe$^{3+}$ at M1 sites in the Wo50 pyroxenes consistently had the same direction, the principal axes of $V_{XX}$ and $V_{YY}$ for the EFG tensors for Wo40 had different directions from that for Wo50. The difference in tensor properties between Wo50 and Wo40 suggests that the intensity and EFG tensors for Fe$^{3+}$ at M1 sites are dependent on the Ca content but independent of the Fe content. Some intensity and EFG tensors for Fe$^{3+}$ at M2 sites and for Fe$^{3+}$ at M1 sites in Ca-rich pyroxene were also obtained. However, the compositional dependence of the intensity and EFG tensors has yet to be clarified, because the number of examples is insufficient.

**ACKNOWLEDGMENTS**

We thank two anonymous reviewers for critical and valuable comments that improve the manuscript. This research was conducted at the Institute for Integrated Radiation and Nuclear Science, Kyoto University, within the Visiting Researcher Program.
REFERENCES

Bancroft, G.M., Maddock, A.G. and Burns, R.G. (1967) Applications of the Mössbauer effect to silicate mineralogy–I. Iron silicates of known crystal structure. Geochimica et Cosmochimica Acta, 31, 2219–2246.

Cameron, M. and Papike, J.J. (1980) Crystal chemistry of silicate pyroxenes. In Pyroxenes (Prewitt, C.T. Ed.), pp. 525, Reviews in Mineralogy and Geochemistry 7, Mineralogical Society of America, Washington D.C., 5–92.

Dufek, P., Blaha, P. and Schwarz, K. (1995) Determination of the Nuclear Quadrupole Moment of $^{57}$Fe. Physical Review Letters, 75, 3545–3548.

Dyar, M.D., Klima, R.L., Fleagle, A. and Peel, S.E. (2013) Fundamental Mössbauer parameters of synthetic Ca-Mg-Fe pyroxenes. American Mineralogist, 98, 1172–1186.

Kimura, Y. and Akasaka, M. (1999) Estimation of $^{57}$Fe/$^{56}$Fe and Mn$^{2+}$/Mn$^{3+}$ ratios by electron probe microanalyzer. Journal of the Mineralogical Society of Japan, 28, 159–166 (in Japanese).

Kozu, S., Seto, K. and Ueda, J. (1928) Volume changes of diopside from Sano, Kai due to optical, chemical and thermal changes. Chikyu, 9, 406–423 (in Japanese).

Laue Analysis program. Norm Engineering Co. http://www.din.or.jp/~norm/sub2_e.htm (accessed 2022/4/17).

Matsui, Y., Maeda, Y. and Syono, Y. (1970) Mössbauer study of synthetic calcium-rich pyroxenes. Geochemical Journal, 4, 15–26.

McCammon, C.A., Chaskar, V. and Richard, G.G. (1991) A technique for spatially resolved Mössbauer spectroscopy applied to quenched metallurgical slags. Measurement Science and Technology, 2, 657–662.

MossWinn – Mössbauer spectrum analysis and database software. http://www.mosswinn.com/ (accessed 2018/7/30).

Naito, Y. (1988) Gem-grade chromian diopside found at the upper stream of Sano River, Yamanashi Prefecture. Journal of the Gemmological Society of Japan, 13, 25–30 (in Japanese).

Shinoda, K. and Kobayashi, Y. (2018) Mössbauer microspectrometer with a multiperispective X-ray lens. Japanese Magazine of Mineralogical and Petrological Sciences, 47, 163–167 (in Japanese).

Shinoda, K. and Kobayashi, Y. (2019) Determination of the electric field gradient tensor of $^{57}$Fe in the M1 site of aegirine by single crystal Mössbauer spectroscopy. Journal of Mineralogical and Petrological Sciences, 114, 130–141.

Tennant, W.C., McCannon, C.A. and Miletich, R. (2000) Electric field gradient and mean-squared-displacement tensors in hedenbergite from single-crystal Mössbauer millprobe measurements. Physics and Chemistry of Minerals, 27, 156–163.

Travis, J.C. (1971) The electric gradient tensor. An introduction to Mössbauer spectroscopy (May, L. Ed.). Plenum Press. New York, 75–103.

Williams, P.G.L., Bancroft, G.M., Bown, M.G. and Turnock, A.C. (1971) Anomalous Mössbauer spectra of C2/c Clinopyroxenes. Nature, 230, 149–151.

Whittaker, E.J.W. and Muntus, R. (1970) Ionic radii for use in geochemistry. Geochimica et Cosmochimica Acta, 34, 945–956.

Yoshida, Y., Suzuki, K., Hayakawa, K., Yukihira, K. and Soejima, H. (2009) Mössbauer spectroscopic microscope. Hyperfine Interact, 188, 121–126.

Zimmermann, R. (1975) A method for evaluation of single crystal $^{57}$Fe Mössbauer spectra (FeCl$_2$·4H$_2$O). Nuclear Instruments and Methods, 128, 537–543.

Zimmermann, R. (1983) The intensity tensor formulation for dipole transitions (e.g., $^{57}$Fe) and its application to the determination of EFG tensor. In Advances in Mössbauer spectroscopy (Thosar, B.V. Ed.). Elsevier Scientific Publishing Co., Amsterdam, 273–315.

Zussman, J. (1968) The crystal chemistry of pyroxenes and amphiboles, 1 Pyroxenes. Earth Science Reviews, 4, 39–67.
APPENDIX

Tennant et al. (2000) reported an EFG tensor for Fe$^{2+}$ at the M1 sites in Mg–hedenbergite with a chemical composition of (Ca$_{1.00}$Fe$_{0.54}$Mg$_{0.46}$)$_{2}$Si$_{2}$O$_{6}$, by setting left-handed crystallographic axes. Table A1 shows the Mössbauer dataset used to analyze the intensity and EFG tensors for Fe$^{2+}$ at the M1 sites in Mg–hedenbergite. Appendix Table A1 is modified from the original dataset of Tennant et al. (2000) into that for the right-handed system shown in Figure 1. The intensity and EFG tensors for Mg–hedenbergite were obtained as:

\[
I_{Fe^{2+}(M1)Mg-Hd} = \begin{pmatrix}
0.328(3) & 0.049(4) & 0 \\
0.049(4) & 0.485(4) & 0 \\
0 & 0 & 0.687(7)
\end{pmatrix},
\]

(A1),

\[
T_{Fe^{2+}(M1)Mg-Hd} = \begin{pmatrix}
-0.199 & 0.057 & 0 \\
0.057 & -0.018 & 0 \\
0 & 0 & 0.217
\end{pmatrix},
\]

(A2),

\[
U_{Fe^{2+}(M1)Mg-Hd} = \begin{pmatrix}
\cos(73.9^\circ) & -\sin(73.9^\circ) & 0 \\
\sin(73.9^\circ) & \cos(73.9^\circ) & 0 \\
0 & 0 & \cos(\theta)
\end{pmatrix},
\]

(A3),

and

\[
T_{Fe^{2+}(M1)Mg-Hd} = U_{(A3)}^{-1} T_{(A2)} U_{(A3)} = \begin{pmatrix}
-0.001 & 0 & 0 \\
0 & -0.216 & 0 \\
0 & 0 & 0.217
\end{pmatrix}.
\]

(A4).

From the absolute values of the components in Eq. (A4), the $V_{XX}$, $V_{YY}$, and $V_{ZZ}$ axes of the EFG tensor are the X, Y, and Z axes after diagonalization, respectively. From the Euler angle in Eq. (A3), the EFG principal axes for Fe$^{2+}$ at the M1 sites in Mg–hedenbergite are summarized in Figure 9. The asymmetry parameter $\eta$ is determined as $\eta = (T_{XX} - T_{YY})/T_{ZZ} = 0.991$.

| Mg–hedenbergite | Crystal 1 | Crystal 2 |
|-----------------|------------|------------|
| $\gamma$-ray direction |           |            |
| $\theta$ (°)    | 165        | 180        |
| $\phi$ (°)      | 344        | 0          |
| Peak intensity  |            |            |
| Low peak        | 0.158      | 0.148      |
| High peak       | 0.323      | 0.319      |
| Peak intensity  | 0.672      | 0.683      |

* Modified from the original dataset of Tennant et al. (2000).