Shirozulite, KMn\textsuperscript{2+}(Si\textsubscript{3}Al)O\textsubscript{10}(OH)\textsubscript{2}, a new manganese-dominant trioctahedral mica: Description and crystal structure

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ABSTRACT

Shirozulite is a new Mn-dominant trioctahedral mica from the Taguchi mine, Aichi Prefecture, Japan. The mineral occurs in tephroite-rhodochrosite ores in contact with a Ba-bearing, K-feldspar vein. Shirozulite formed during regional low-P/T metamorphism and, thereafter, suffered thermal metamorphism from a local granodiorite. Grains of shirozulite are up to 0.5 mm across and have a typical micaceous habit. Color: dark reddish brown. Cleavage: (001), perfect. Optical properties: biaxial negative, 2V = very small. Strongly pleochroic: X = pale yellow, Y = pale brown, absorption X < Y = Z. Refractive indices: n\textsubscript{a} = 1.592(2), n\textsubscript{b} = n\textsubscript{c} = 1.635(2). The structural formula is (K\textsubscript{0.9}Ba\textsubscript{0.09})(Mn\textsuperscript{2+}1.53Mg\textsubscript{0.04}Fe\textsuperscript{2+}0.20T\textsubscript{0.06}Al\textsubscript{0.29})(Si\textsubscript{3.34}Al\textsubscript{1.66})O\textsubscript{10}[(OH)\textsubscript{0.9}F\textsubscript{0.01}], and the end-member composition is KMn\textsuperscript{2+}3AlSiO\textsubscript{4}(OH). Density: obs. = 3.20(3) g/cm\textsuperscript{3}. Shirozulite is monoclinic, C2/m, 1M polytype, a = 5.3791(7), b = 9.3197(9), c = 10.2918(9) Å, β = 100.186(9)°, V = 507.8(1) Å\textsuperscript{3}. The six strongest lines in the powder X-ray diffraction pattern are as follows: d (Å), l (%), hkl: 1.635, 100, (001); 2.654, 96, (131); 3.386, 51, (003); 1.556, 48, (313); 2.467, 46, (32); 2.202, 36, (133). The crystal structure has been refined to an R value of 4.1% based on 663 observed reflections collected with MoK\textalpha X-radiation from a single crystal. The mean bond lengths, tetrahedral rotation, and octahedral flattening angles are as follows: <T-O> = 1.668, <M1-O> = 2.118, <M2-O> = 2.202, <K-O> (inner) = 2.995, and <K-O> (outer) = 3.376 Å, α = 8.36°, β\textsubscript{M1} = 58.5°, β\textsubscript{M2} = 58.2°. The apparent element distribution coefficient analyses among coexisting manganese or manganoan silicate minerals indicate that the trioctahedral mica structure cannot contain larger amounts of Mn\textsuperscript{2+} relative to Mg and Fe\textsuperscript{2+} than in olivine, pyroxenoid, and garnet.

INTRODUCTION

Trioctahedral micas along the phlogopite-annite join occur as rock-forming minerals in a wide range of geological environments. They usually contain only minor Mn\textsuperscript{2+}, and micas containing dominant octahedral Mn\textsuperscript{2+} have not been reported until now. Synthesis work on trioctahedral micas with Mn-bearing starting materials suggests that micas with a tetrahedral composition of (Si\textsubscript{3}Al) cannot contain more than about one Mn\textsuperscript{2+} pfu (per formula unit) (Hazen and Wones 1972). However, a new Mn\textsuperscript{2+}-dominant trioctahedral mica has been found at the Taguchi mine, a regionally and thermally metamorphosed strata-bound Mn ore deposit in Aichi Prefecture, Japan. This mineral is named shirozulite in honor of Dr. Haruo Shirozu, Professor Emeritus of Kyushu University, for his outstanding contributions to the crystal-chemistry of sheet-silicate minerals, particularly the chlorite group. Shirozulite has been approved as a new mineral by the International Mineralogical Association’s Committee on New Minerals and Mineral Names. Type material is deposited at the Graduate School of Social and Cultural Studies, Kyushu University, Japan.

SAMPLE DESCRIPTION

Occurrence

The Taguchi mine is located at Yatuhashi, Kita-shitara County, Aichi Prefecture, Japan. The mine is in a strata-bound Mn ore deposit in the Ryoke metamorphic belt and is renowned for an abundance of mineral species: e.g., yoshimuritaite (Hirowatari and Isono 1963), richterite (Shoda and Bunno 1973), alleghanyite, sonolite, manganoite, jacobsite, and galaxite. Manganese-rich layers are up to 2 m wide and show a zonal arrangement: hausmannite + rhodochrosite, tephroite, and pyroxenoid (rhodonite, pyroxmangite) ores (Hirowatari and Isono 1963). Shirozulite formed during low P/T-type regional metamorphism of Cretaceous age, and thereafter, was thermally metamorphosed by an adjacent granodiorite. Shirozulite occurs in tephroite-rhodochrosite ores in contact with a Ba-bearing K-feldspar vein, as subhedral grains closely associated with tephroite, rhodochrosite, and apatite. Grains of barite (a few μm in diameter) are dispersed throughout the rhodochrosite, giving it a turbid appearance in thin section. A back-scattered electron image is shown in Figure 1; the mottled appearance of the mica is due to minor chemical heterogeneity involving the substitution Ba\textsuperscript{2+}Al\textsuperscript{3+}K\textsuperscript{4+}Si\textsuperscript{4+}.  

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**Physical properties**

Grains of shirozulite are up to 0.5 mm across and have a typical micaceous appearance. Color: dark reddish brown. Cleavage: (001) perfect. Optical properties: biaxial negative, 2V = very small. Strongly pleochroic: X = pale yellow, Y = Z = pale brown, absorption X < Y = Z. Refractive indices: nα = 1.592(2), nβ = nγ = 1.635(2). Density: obsd. = 3.20 g/cm³ by pycnometer, calc. = 3.14 g/cm³. Vickers hardness was measured on the (001) surface with an Akashi model MVK: VHN = 100–130; Mohs hardness = 3.

**Chemical composition**

Preliminary chemical analyses of the mica and coexisting minerals were done using a scanning electron microscope JEOL SEM35CF-II equipped with a Link System 800-2-500 energy-dispersive spectrometer and a ZAF-4/FLS quantitative-analysis software system. Operating conditions were as follows: accelerating voltage 15 kV, beam current 1.5 nA on Fe metal, and 100 s collecting time.

The crystal used to collect single-crystal XRD data was mounted on a Siemens P4 automated four-circle diffractometer with a graphite monochromator and a Mo X-ray tube. Twenty-five reflections were centered; a constrained monoclinic cell was determined from the setting angles and refined using a least-squares technique (Table 2). Single-crystal intensity data were measured from 4 to 60 °2θ with a scan range of 1.2° and scan-speeds from 2.5 to 29.3 °/min. Psi-scan data were measured on 20 reflections out to 60 °2θ at increments of 5°; an absorption correction was done with the crystal modeled as a thin plate.

**Single-crystal diffraction and structure refinement**

A crystal was mounted on a Siemens P4 automated four-circle diffractometer with a graphite monochromator and a Mo X-ray tube. Twenty-five reflections were centered; a constrained monoclinic cell was determined from the setting angles and refined using a least-squares technique (Table 2). Single-crystal intensity data were measured from 4 to 60 °2θ with a scan range of 1.2° and scan-speeds from 2.5 to 29.3°/min. Psi-scan data were measured on 20 reflections out to 60 °2θ at increments of 5°; an absorption correction was done with the crystal modeled as a thin plate.

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**X-ray powder pattern**

Powder diffraction data were collected with a Rigaku Rint-2100V diffractometer using curve-graphite monochromatized CuKα X-rays and operating at 40 kV and 40 mA with a step-width of 0.01 °2θ and a step-interval of 16 s. A Rietveld analysis was done using the program Rietan-2000 (Izumi and Ikeda 2000): the single-crystal structural data described above were used as the initial parameters, and the isotropic-displacement factors were used. Table 8 shows the observed and calculated d-values, and the observed intensities; Figure 2 shows the fitted powder-diffraction pattern. Within the estimated standard deviations, the resultant unit-cell parameters are consistent with the values from the single-crystal data.

*For a copy of Table 7, document item AM-04-052, contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. Deposit items may also be available on the American Mineralogist web site at http://www.minsocam.org.*
The \textit{T} site

The unit formula calculated from the chemical analysis (Table 1) has 1.464 $^{23}$Al \textit{apfu}, and the $<$T-O$>$ distance is 1.668 Å. Figure 3 shows the variation in $<$T-O$>$ as a function of $^{23}$Al content in some recent structure-refinements of mica. Although some scattering occurs around 1.2 $^{23}$Al, there is a well-developed linear relation between $^{23}$Al content and the $<$T-O$>$ bond-length. Hazen and Burnham (1973) gave the line: $<$T-O$>$ = 0.0408 $^{23}$Al + 1.608 [therein $x_{_{\text{W}}}/(x_{_{\text{H}}})$ is converted to $^{23}$Al]. Both regression lines coincide well, although the line in this study gives slightly shorter values than that given by Hazen and Burnham (1973): 0.001~0.003 Å shorter when $^{23}$Al = 1.0~1.5, respectively, and they coincide at $^{23}$Al = 0.744. The data for shirozulite lie on this trend, indicating that the structure refinement and electron-microprobe results are compatible.

The \textit{M} sites

The relations between mean bond length at the octahedral sites, $<$M1-O$>$ and $<$M2-O$>$, are shown in Figure 4. In almost all samples, the M1 octahedra are larger than the M2 octahedra, and the $<$M1-O$>$ for almost all trioctahedral micas are less than 2.125 Å (Fig. 4), suggesting that this value is the maximum possible value in these micas.

Dimensional misfit between tetrahedral and octahedral sheets

The structure of shirozulite would seem, at first sight, to be rather unusual relative to other trioctahedral 1M micas, as it has a very large principal octahedrally coordinated cation (Mn$^{2+}$, $r = 0.83$ Å; Shannon 1976) and a large tetrahedral rotation angle $\alpha$ (8.36°). Donnay et al. (1964) showed that the principal mechanisms whereby the octahedral and tetrahedral layers in mica accommodate their dimensional differences are octahedral flattening ($\psi$) and tetrahedral rotation ($\alpha$). Hazen and Wones (1972) showed that there is an inverse relation between the tetrahedral rotation angle and the mean ionic radius ($<$<\text{r}$>$) of the octrahedrally coordinated cation(s). In particular, the ideal relation between $\alpha$ and $<$<\text{r}$>$ (Hazen and Wones 1972) indicates that $<$<\text{r}$>$ cannot exceed 0.76 Å (i.e. at 0.76 Å, $\alpha = 0^\circ$), and at larger values of ionic radius, the octahedral sheet should be too large to link to the tetrahedral layer. The mean constituent radius of the octrahedrally coordinated cations in shirozulite is 0.76 Å, exactly equal to the maximum size of octahedral cation possible according to the $\alpha$-$<$<\text{r}$>$ relation of Hazen and Wones (1972). However, instead of $\alpha$ being equal to 0°, as predicted for this specific ionic radius, $\alpha$ = 8.36°, one of the largest values of $\alpha$ observed in trioctahedral micas (Table 6, Fig. 5). How can the octahedral layer in shirozulite link to the tetrahedral layer with such a large value of tetrahedral rotation? First, the octahedral flattening in shirozulite is small compared with most other trioctahedral micas (Fig. 6), effectively reducing the size of the octahedral layer. Second, the tetrahedral layer in shirozulite contains significantly more Al (1.46) than the 1.00 Al \textit{apfu} present in the synthetic trioctahedral micas considered by Hazen and Wones (1972). This additional $^{23}$Al increases the size of the tetrahedral

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|}
\hline
Atom  & x & y & z & $U_{_{\text{iso}}}$ & $U_{_{11}}$ & $U_{_{22}}$ & $U_{_{33}}$ & $U_{_{12}}$ & $U_{_{13}}$ & $U_{_{23}}$ \\
\hline
Si & 0.7574(2) & 0.16685(4) & 0.22491(14) & 126(4) & 108(6) & 63(6) & 207(7) & -3(5) & 28(5) & 0(5) \\
Mn1 & 0 & 0.5 & 0.5 & 113(6) & 82(9) & 38(8) & 222(11) & 0 & 34(7) & 0 \\
Mn2 & 0.1681(2) & 0.8313(15) & 0.5 & 171(4) & 79(6) & 49(6) & 222(8) & 0 & 27(5) & 0 \\
K & 0 & 0 & 0 & 319(8) & 335(13) & 273(12) & 344(14) & 0 & 48(10) & 0 \\
Na & 0.8265(7) & 0.2288(4) & 0.1681(4) & 218(12) & 178(18) & 186(19) & 30(2) & -31(17) & 62(15) & -65(15) \\
O2 & 0.5141(11) & 0 & 0.1676(6) & 231(17) & 25(3) & 92(2) & 28(3) & 0 & -823 & 0 \\
O3 & 0.6303(7) & 0.1675(4) & 0.3885(4) & 163(10) & 161(16) & 105(13) & 219(18) & 6(14) & 19(14) & 4(14) \\
O4 & 0.1283(11) & 0 & 0.3949(6) & 191(16) & 18(3) & 19(3) & 20(3) & 0 & 20(20) & 0 \\
H & 0.105(18) & 0 & 0.2982(8) & 100(--) & \\
\hline
\end{tabular}
\caption{Final parameters for the crystal structure of shirozulite}
\end{table}
layer, promotion leading to the tetrahedral layer and a large octahedral layer. Increasing amounts of octahedrally coordinated AI will have a similar effect. These arguments account for the large tetrahedral rotation in shirozulite, and also suggest that end-member shirozulite, K Mn\(^{2+}\) Al Si, O\(_{10}\) (OH)\(_{2}\), will not be stable as the octahedral layer is very large without any compensating increase in the size of the tetrahedral layer.

### Table 4. Interatomic distances (Å) and angles (°) in shirozulite

<table>
<thead>
<tr>
<th>T-O1</th>
<th>1.667(4)</th>
<th>M1-O3a</th>
<th>×4</th>
<th>2.128(4)</th>
<th>M2-O3a</th>
<th>×2</th>
<th>2.102(4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-O1a</td>
<td>1.674(4)</td>
<td>M1-O4a</td>
<td>×2</td>
<td>2.099(5)</td>
<td>M2-O5b</td>
<td>×2</td>
<td>2.113(3)</td>
</tr>
<tr>
<td>T-O2</td>
<td>1.674(3)</td>
<td>&lt;M1-O&gt;</td>
<td>2.118</td>
<td>M2-O4c</td>
<td>×2</td>
<td>2.095(4)</td>
<td></td>
</tr>
<tr>
<td>T-O3</td>
<td>1.657(4)</td>
<td>&lt;M2-O&gt;</td>
<td>2.103</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<\(\text{T-O}<\)

### Table 5. Refined site-scattering (epfu) and assigned site-populations (apfu)

<table>
<thead>
<tr>
<th>Site</th>
<th>Refined site-scattering value</th>
<th>Assigned site-populations</th>
<th>Calculated site-scattering value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>56</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M1</td>
<td>19.8(2)</td>
<td>0.04 Ti + 0.29 Al + 0.20 Fe(^{3+})</td>
<td>59.3</td>
</tr>
<tr>
<td>M2</td>
<td>37.9(3)</td>
<td>+ 0.94 Mg + 1.53 Mn</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>23.1(3)</td>
<td>0.90 K + 0.09 Ba</td>
<td>22.1</td>
</tr>
</tbody>
</table>

### Table 6. Calculated structure parameters for shirozulite

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha^(*))</td>
<td>8.36</td>
</tr>
<tr>
<td>(\psi^(*))</td>
<td>58.5</td>
</tr>
<tr>
<td>(\beta^(*))</td>
<td>58.2</td>
</tr>
<tr>
<td>(T_{\text{m}}^(*))</td>
<td>110.2</td>
</tr>
<tr>
<td>Sheet thickness (t)</td>
<td>2.216</td>
</tr>
<tr>
<td>tetrahedral (\Delta);</td>
<td>2.224</td>
</tr>
<tr>
<td>Interlayer separation (\Delta);</td>
<td>3.468</td>
</tr>
<tr>
<td>(\Delta(A)^{**})</td>
<td>0.479</td>
</tr>
<tr>
<td>(&lt;\text{K-O}&gt;) (outer) – (&lt;\text{K-O}&gt;) (inner)</td>
<td>0.381</td>
</tr>
<tr>
<td>(\beta_{\max}(\text{K})^*)</td>
<td>100.02</td>
</tr>
</tbody>
</table>

\(^*\) \text{tan} \alpha = 4b(0.25 - y_{30})/a \ (\text{Hazen and Burnham 1973})\.

\(^\dagger\) \text{cos} \psi = t_{2}/(2d_{3})\.

\(^\ddagger\) mean \(O_{\text{mean}}\) - T-O\(_{\text{mean}}\).

\(^\S\) \(t_{2} = 2d_{3}\cos \psi, t_{3} = 4d_{3}/t_{2} = c \sin \beta, 2d_{3}\cos \psi \times (8/3d_{3})\) (Donnay et al. 1964).

\(^\|\) Dimensional misfit between tetrahedral and octahedral sheets defined as \(\Delta = (2\sqrt{3}(\text{Obs} - \text{Shr}) - 3\sqrt{3})\) (Toraya 1981).

\(^\#\) 180° - \text{co} \theta/\langle 003\rangle (Tyrra and Guggenheim 1991).

### Figure 4. \(<\text{M1-O}\>\) and \(<\text{M2-O}\>\) relations. Nor = norrishite (Tyrra and Guggenheim 1991); Hnd = hendricksite (Robert and Gasperin 1985); Fkn = ferrokinoshitalite (Guggenheim and Frimmel 1999); Ann = annite (Hazen and Burnham 1973); Shr(star) = shirozulite (the present study). Other data from Brigatti and Davoli (1990), Brigatti et al. (1991), Brigatti and Popp (1993), Bigni and Brigatti (1994), Alletti et al. (1995), Brigatti et al. (1998), Hawthorne et al. (1999), Russell and Guggenheim (1999), Schingaro et al. (2001), and Brigatti et al. (2001).
There is an inverse relation between tetrahedral rotation and charge of the constituent interlayer cations will strongly affect the interlayer separation and the interlayer separation and tetrahedral rotation in shirozulite, are similar to those in Mg-rich micas.

The interlayer site

The interlayer site in shirozulite contains significant K and Ba, and the refined site-scattering value of 23.1 epfu is in excellent accord with the effective scattering value of 22.1 epfu calculated from the unit formula (Table 5). The interlayer-cation site occurs between the T-O-T (tetrahedral-octahedral-tetrahedral) layers that stack in the z direction. Thus, both variation in size and charge of the constituent interlayer cations will strongly affect the interlayer separation and the c-dimension of the unit cell. In C2/m 1M annite, the interlayer separations (3.35–3.37 Å; α = 1.5–2.0°) are somewhat smaller than in analogous Mg-rich micas (3.45–3.48 Å; α = 8.9–10.2°) (Bailey 1984; Brigatti and Guggenheim 2002); the interlayer separation and tetrahedral rotation in shirozulite, are similar to those in Mg-rich micas.

There is an inverse relation between tetrahedral rotation and interlayer separation (Fig. 5), but there are significant perturbations from a monotonic relation; these are presumably due to factors that affect the relative dimensions of the tetrahedral and octahedral layers, e.g., F content, variation in T-site populations (Al, Fe$^{3+}$ substituting for Si), variation in tri- and tetra-valent cation content of the octahedral sites, and type of interlayer cation. Further studies are needed to untangle the effects of these variations on linkage of the tetrahedral and octahedral layers.

**Element partition among coexisting minerals**

Chemical compositions of trioctahedral micas of the manganobarian phlogopite-kinoshitalite series are strongly dependent on the different types of coexisting minerals (Fig. 7), particularly with regard to the $^{10}$Si, $^{8}$O, $^{6}$Al substitutions in the kinoshitalite-annite series. Kinoshitalite occurs in hausmannite-rhodochrosite ores in which Mn is the predominant transition-metal cation, but its octahedral sites are rich in Mg rather than Mn, and contain negligible Fe$^{3+}$ and Fe$^{2+}$ (Fig. 7a). Shirozulite occurs in rhodochrosite-tephroite ore (Fig. 7b). However, micas in rhodochrosite-tephroite ore are generally of manganobarian phlogopite compositions, and its octahedral Mn are usually under one-third. Micas that coexist with pyroxmangite, manganocummingtonite-grunerite amphiboles, and/or garnet are commonly rich in Fe$^{3+}$, and they belong to the manganobarian phlogopite-annite series (Figs. 7c and 7d). Judging from the chemical compositions of the coexisting minerals, it is supposed that the minerals are in chemical equilibrium (at least the manganese or manganoo-silicate minerals). As the chemical compositions of garnets are in the spessartine-almandine-grossular system (Mg-Fe$^{2+}$-Ca) and have a low pyrope component (Mg), mineral formation is assumed to have occurred at low pressure.

To compare the element distributions of the trioctahedral mica with coexisting silicate minerals (i.e., monoclinic amphibole, pyroxmangite, olivine, and garnet), we examined the apparent partition coefficients of these minerals. We may define the apparent partition coefficients between, for example, garnet, and trioctahedral mica for Mg-Mn and Fe$^{2+}$-Mn as follows:

$$K'_{\text{DMg-Mn}} = \frac{(X_{\text{Mg}}/X_{\text{Mn}})_{\text{Phl}}}{(X_{\text{Mg}}/X_{\text{Mn}})_{\text{Grt}}}$$

$$K'_{\text{DFe-Mn}} = \frac{(X_{\text{Fe}}/X_{\text{Mn}})_{\text{Phl}}}{(X_{\text{Fe}}/X_{\text{Mn}})_{\text{Grt}}}$$

and

$$K'_{\text{DMg-Fe}} = \frac{(X_{\text{Mg}}/X_{\text{Fe}})_{\text{Phl}}}{(X_{\text{Mg}}/X_{\text{Fe}})_{\text{Grt}}} = K'_{\text{DMg-Mn}} / K'_{\text{DFe-Mn}}$$
where \( X_{\text{Mg}}, X_{\text{Mn}}, \) and \( X_{\text{Fe}} \) denote the mole fraction of Mg, Mn, and Fe\(^{2+}\) end-members of the relevant solid solutions, and superscripts \( \text{Phl} = \text{mica} \) and \( \text{Grt} = \text{garnet} \). These \( K' \) values correspond to the exchange reactions of the following type:

\[
R_3\text{Al}_2\text{Si}_3\text{O}_{12} + KMn_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2 = Mn_3\text{Al}_2\text{Si}_3\text{O}_{12} + KR_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2
\]

where \( R \) denotes Mg or Fe\(^{2+}\). Supposing that mineral-formation conditions (i.e., temperature, pressure, and \( H_2O \) fugacity) were the same, but the chemical potentials were different in each zone, and supposing also that each coexisting mineral can be treated as an ideal solid solution, the same \( K' \) values would apply for each set of element- and mineral-pairs.

Element distribution among coexisting minerals is shown in Figures 8a, 8b, and 8c. Samples are from Japanese thermally metamorphosed strata-bounded Mn ore deposits with formation conditions (\( T-P \)) similar to those of the Taguchi mine: Noda-Tamagawa mine, Iwate Pref.; Tatehira mine, Hokkaido; Kuranosawa mine, Tochigi Pref.; Hamayokogawa mine, Gunma Pref.; Hokkejino mine, Kyoto; Fukumigawa mine, Ehime Pref.; and Shimozuru mine, Miyazaki Pref. Relative to Mn\(^{2+}\), Mg preferentially partitions into coexisting minerals in the following order: micas (octahedral sites, \( M1 \) and \( M2 \)) > manganoan cummingtonite-grunerite (\( M1, M2, M3, \) and \( M4 \) sites) > tephroite (\( M1 \) and \( M2 \) sites) > pyroxmangite (\( M \) sites) > garnet (dodecahedral site) (Fig. 8a). Iron (Fe\(^{2+}\)) more easily replaces Mn\(^{2+}\) than Mg, and shows the following preference: micas > amphiboles > tephroite > pyroxmangite > garnet (Fig. 8b). Substitution of Mg and Fe\(^{2+}\) in coexisting minerals is more extensive, and Mg shows the preference: micas > amphiboles > tephroite > pyroxmangite > garnet (Fig. 8c). Mn\(^{2+}\) normally partitions preferentially into other minerals relative to mica, and hence shirozulite will seldom occur in ordinary parageneses.

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REFERENCES CITED


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