Fedorovskite from the Fuka mine, Okayama Prefecture, Japan

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Fedorovskite was found as aggregates in crystalline limestone associated with gehlenite–spurrite skarns at the Fuka mine, Okayama Prefecture, Japan. Fedorovskite occurs as gray to dark gray aggregates of anhedral translucent crystals up to 0.8 mm across in association with shimazakiite, uralborite, vimsite, cuspidine, fluorite, and calcite. An electron microprobe analysis of fedorovskite gave an empirical formula Ca$_{2.013}$(Mg$_{1.901}$Fe$_{0.072}$Mn$_{0.023}$Zn$_{0.002}$Co$_{0.001}$Ni$_{0.001}$)$_{Σ2.000}$(B$_{3.852}$Si$_{0.104}$)$_{Σ3.956}$O$_{7.000}$(OH$_{5.421}$F$_{0.579}$)$_{Σ6.000}$ based on O = 7 and OH + F = 6. The mineral is orthorhombic, and the unit cell parameters refined from X-ray diffraction are $a = 8.915(7)$ Å, $b = 13.086(16)$ Å, $c = 8.295(9)$ Å, and $V = 967.7(18)$ Å$^3$. The calculated density is 2.692 g cm$^{-3}$. The fedorovskite from the Fuka mine was probably formed as a secondary mineral from calcium borates such as shimazakiite in a reaction with magnesium-bearing late hydrothermal solution.

Keywords: Fedorovskite, Calcium magnesium borate, Skarn, Fuka

INTRODUCTION

Fedorovskite, Ca$_2$Mg$_2$B$_4$O$_7$(OH)$_6$, is a rare calcium magnesium hydroxide borate that forms a solid solution with Roweite [Ca$_2$Mn$_2$B$_4$O$_7$(OH)$_6$]. Malinko et al. (1972) found magnesian Roweite in a borate ore at the Solongo contact metasomatic deposit in Buryatia, Transbaikal region, USSR. Subsequently, Malinko et al. (1977) described it as a new mineral fedorovskite, the end member of Mg-dominant analogue of Roweite, and reported the chemical composition, physical properties, and X-ray diffraction data. Fedorovskite from the Solongo occurs with sakhaite, frolovite, datolite, botryolite and uralborite, and as monomineralic veinlets and nests in svabite-containing garnet-vesuvianite-svabite skarn. On the other hand, Ando et al. (2015) reported Roweite from the Fuka mine which contains a small amount of Fe, poor in Mg, and close to its endmember. The crystal structure of Roweite from the type locality is determined by Moore and Araki (1974). Yamnaya et al. (1975) has shown that fedorovskite and Roweite are isostructural based on X-ray structural studies.

During a mineralogical survey of gehlenite–spurrite skarns at the Fuka mine, fedorovskite was found as fine several granular crystals in crystalline limestone. This is the first occurrence of fedorovskite in Japan and is the closest to the fedorovskite end member reported so far. Minerals containing Mg as a major component are rare in the Fuka mine, and the mineral is the second case after borcarite (Kusachi et al., 1997). The present paper deals with the mineralogical properties and mode of occurrence of fedorovskite from the Fuka mine.

OCCURRENCE

Fedorovskite was discovered closely associated with shimazakiite (Kusachi et al., 2013) in crystalline limestone close to gehlenite–spurrite skarns at the Fuka mine, Okayama Prefecture, Japan. An irregular shaped vein with a width of 10–20 cm is found between the block and surrounding limestone. The block is 1–1.5 m in diameter, mainly composed of shimazakiite. Various hydrous borate minerals such as uralborite (Kusachi et al., 2000) and vimsite (Kobayashi et al., 2019) have formed within...
the zone, and these minerals and occurrences have been shown in previous reports (e.g., Kobayashi et al., 2019). Fedorovskite also occurs with these borate minerals in this zone and is characteristically found in samples with cuspidine and fluorite. In thin section, fedorovskite occurs as an aggregate of fine crystals with a diameter of 1 mm or less (Fig. 1A). The crystals are richer in Fe, Mg, and S. EPMA analysis shows this is possibly Fe and Mg sulfate mineral.

Fedorovskite and roweite, which are in solid solution with each other, are extremely rare minerals in the Fuka mine, and both have never been identified in the same section. The former is observed as an aggregate of fine minerals as described above, and its close relationship with other borate minerals is not clear, whereas the latter occurred as a fine grain of 0.8 mm or less and does not coexist with the undetermined sulfate mineral. Roweite is closely related to uralborite and is formed as a secondary mineral of uralborite (Ando et al., 2015).

PHYSICAL AND OPTICAL PROPERTIES

Fedorovskite is gray or dark gray with a vitreous luster and non-fluorescent in hand specimens. In thin section, the mineral is dark gray to black and translucent. Pleochroism and cleavage are unclear. The calculated density of fedorovskite from the Fuka mine is 2.692 g cm$^{-3}$ based on the empirical formula and refined unit cell parameters. The data was slightly smaller than 2.74 g cm$^{-3}$ [measured as 2.73(1) g cm$^{-3}$] for magnesian roweite, whereas the data was larger than 2.60 g cm$^{-3}$ [measure as 2.65(1) g cm$^{-3}$] for fedorovskite reported from Solongo by Malinko et al. (1977). The densities of fedorovskite–roweite series tend to decrease with the increase of the Mg/(Mg + Mn + Fe + Zn + Co + Ni) in apfu in Figure 3. However, 2.73 and 2.65 g cm$^{-3}$ of density from Solongo which are measured values are plotted below the line connecting fedorovskite and roweite. The former from Solongo is measured on a sample mixed with frolovite having 2.22 g cm$^{-3}$ (Kusachi et al., 1995). On the other hand, the density of the latter is also calculated from the lattice constant (2 in Table 1) and the chemical data (Malinko et al., 1977). The value is 2.82 g cm$^{-3}$ and is plotted on the line. Therefore, fedorovskite–roweite series show a negative correlation with the ratio of Mg/(Mg + Mn + Fe + Zn + Co + Ni) in apfu.

X-RAY CRYSTALLOGRAPHY

The X-ray powder diffraction data of fedorovskite from Fuka are shown with those from Solongo, Russia by Malinko et al. (1977) in Table 1. The data of fedorovskite from the Fuka mine were obtained by using an X-ray diffractometer (Rigaku RINT-2500V) with graphite-monochromatized CuKa radiation generated at 40 kV and 260 mA. Because the amount of the sample was small, the powder sample was pasted with water on a silicon non-reflective plate and measured. The powder X-ray diffraction data of fedorovskite are given in Table 1, with calculated data based on the crystal structure of Malinko et al. (1977). Since the intensity of the diffraction line indicated by Malinko et al. (1977) was read on a ten-point scale, each data was multiplied by ten. When relative peak intensities are compared, position of the maximum intensity peak coincides in the both data, while other peaks show different intensity in each data set. This difference...
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in intensity is probably due to preferred orientation of particles and/or poor particle statistics arising from the small amount of sample, where in the oriented sample, the intensity ratio of the oriented plane may be stronger than the actual one. Fedorovskite is orthorhombic system ($Pbam$), and cell parameters calculated by least-squares refinement for a list of $hkl$ indices and $d$-values of peak positions read automatically by PDXL (Rigaku) are $a = 8.915(7)$, $b = 13.086(16)$, $c = 8.295(9)$ Å and $V = 967.7(18)$ Å$^3$. The unit cell parameters from Solongo were $a = 8.96(2)$, $b = 13.15(2)$, $c = 8.15(1)$ Å and $V = 960.27$ Å$^3$. The $a$ and $b$-axis of unit cell dimensions of fedorovskite from the Fuka mine were slightly smaller than those reported from Solongo by Malinko et al. (1977), but the $c$-axis was larger.

CHEMISTRY

The chemical composition was determined by means of an electron microprobe (JEOL JXA-8230; WDS mode, 15 kV, 12 nA, and 5 μm beam diameter) in Okayama University of Science. The standard materials were takedaite (B and Ca), periclase (Mg), wollastonite (Si), rhodochrosite (Mn), hematite (Fe), willemite (Zn), CoO (Co), NiO (Ni), fluorite (F), and marcasite (S). The H$_2$O was estimated stoichiometrically because there was not enough pure mineral for direct determination. The average of 10 analytical points is given in Table 2 and is compared with the

![Figure 2. Composition image and X-ray images of element distribution map of fedorovskite from Fuka. (A) Composition image. (B) S$_{K\alpha}$ image. (C) Fe$_{K\alpha}$ image. (D) Mg$_{K\alpha}$ image. Fed, fedorovskite; Und, undetermined mineral. Color version is available online from https://doi.org/10.2465/jmps.200512.](image-url)
theoretical composition for the ideal formula of Ca$_2$Mg$_2$B$_4$O$_7$(OH)$_6$. The fedorovskite from the Fuka mine is characterized by a high Mg content, no intermediate composition with roweite, and small amounts of Si and F. Figure 4 shows the relationship between B and Si. Moore and Araki (1974) show that the roweite anion group $[\text{B}_4\text{O}_7(\text{OH})_2]^{4-}$ is a polyborate tetramer consisting of two triangles and two tetrahedra. It is considered that Si in fedorovskite with the same structure as roweite replaces B in the tetrahedron. Therefore, the empirical formula of fedorovskite from the Fuka mine (based on O = 7 and OH + F = 6 apfu) is shown as Ca$_{2.013}$(Mg$_{1.901}$Fe$_{0.072}$Mn$_{0.023}$Zn$_{0.002}$Co$_{0.001}$Ni$_{0.001}$)$\Sigma$2.000(B$_{3.852}$Si$_{0.104}$)$\Sigma$3.956O$_{7.000}$$(\text{OH})_{5.421}\text{F}_{0.579}\Sigma6.000$, which is very close to the ideal formula with high Mg content in the octahedral site.

**DISCUSSION**

Fedorovskite [Ca$_2$Mg$_2$B$_4$O$_7$(OH)$_6$] forms isomorphous solid solution series with roweite [Ca$_2$Mn$_2$B$_4$O$_7$(OH)$_6$] (Malinko et al., 1977). Unit cell dimensions of fedorovskite-roweite series are related to the Mg content, and

| Table 1. X-ray powder diffraction data of fedorovskite |
|------------------------------------------|
| $h$ | $k$ | $l$ | $d_{calc.}$ | $d_{obs.}$ | $I_{obs.}$ |
| --- | --- | --- | --- | --- | --- |
| 1 | 1 | 0 | 7.36 | 7.32 | 44 |
| 1 | 2 | 0 | 5.28 | 5.29 | 28 |
| 2 | 0 | 0 | 4.46 | 4.45 | 48 |
| 1 | 3 | 0 | 3.92 | 3.98 | 40 |
| 2 | 0 | 1 | 3.92 | 3.92 | 100 |
| 1 | 1 | 2 | 3.61 | 3.61 | 30 |
| 1 | 3 | 1 | 3.54 | 3.56 | 30 |
| 1 | 2 | 2 | 3.26 | 3.25 | 46 |
| 2 | 0 | 2 | 3.03 | 3.02 | 14 |
| 2 | 1 | 2 | 2.96 | 2.96 | 12 |
| 3 | 1 | 0 | 2.90 | 2.90 | 20 |
| 1 | 3 | 2 | 2.85 | 2.85 | 31 |
| 3 | 2 | 0 | 2.70 | 2.72 | 24 |
| 2 | 4 | 0 | 2.64 | 2.68 | 30 |
| 3 | 2 | 1 | 2.57 | 2.59 | 63 |
| 1 | 2 | 3 | 2.45 | 2.43 | 20 |
| 3 | 1 | 2 | 2.38 | 2.39 | 14 |
| 2 | 1 | 3 | 2.31 | 2.28 | 60 |
| 4 | 0 | 0 | 2.23 | 2.24 | 21 |
| 4 | 1 | 0 | 2.20 | 2.20 | 2 |
| 4 | 0 | 1 | 2.15 | 2.16 | 30 |
| 4 | 2 | 0 | 2.11 | 2.11 | 37 |
| 1 | 6 | 1 | 2.05 | 2.067 | 40 |
| 4 | 3 | 0 | 1.98 | 2.004 | 40 |
| 3 | 2 | 3 | 1.934 | 1.926 | 58 |
| 2 | 6 | 1 | 1.907 | 1.909 | 60 |
| 4 | 4 | 1 | 1.798 | 1.803 | 30 |
| 3 | 5 | 2 | 1.775 | 1.779 | 30 |
| 0 | 4 | 4 | 1.751 | 1.732 | 20 |
| 2 | 7 | 1 | 1.688 | 1.693 | 45 |
| 3 | 2 | 4 | 1.646 | 1.632 | 10 |
| 4 | 6 | 1 | 1.532 | 1.539 | 40 |
| 1 | 7 | 3 | 1.525 | 1.523 | 20 |
| 3 | 6 | 4 | 1.341 | 1.333 | 40 |
| 4 | 0 | 5 | 1.330 | 1.318 | 20 |
| 0 | 8 | 5 | 1.165 | 1.158 | 20 |
| 1 | 6 | 6 | 1.157 | 1.145 | 20 |

| Parameter | Value |
|-----------|-------|
| $a$ (Å) | 8.915(7) |
| $b$ (Å) | 13.086(16) |
| $c$ (Å) | 8.295(9) |
| $V$ (Å$^3$) | 967.7(18) |

1. Fuka, Okayama, Japan. The present work.
2. Solongo, Buryatia, USSR. Malinko et al. (1977).

| Table 2. Chemical composition of fedorovskite |
|------------------------------------------|
| (wt%) | $n^*$ = 10 | Range | SD |
|-------|-----------|-------|---|
| B$_2$O$_3$ | 34.24 | 32.44 - 35.61 | 0.93 | 36.07 |
| SiO$_2$ | 1.60 | 0.10 - 4.31 | 1.37 |
| CaO | 28.82 | 26.87 - 30.28 | 1.06 | 29.05 |
| MgO | 19.56 | 18.21 - 20.69 | 0.86 | 20.88 |
| FeO | 1.32 | 0.44 - 1.94 | 0.38 |
| MnO | 0.41 | 0.33 - 0.52 | 0.06 |
| ZnO | 0.04 | 0.00 - 0.23 | 0.07 |
| CoO | 0.02 | 0.00 - 0.05 | 0.01 |
| NiO | 0.01 | 0.00 - 0.03 | 0.01 |
| F | 2.81 | 2.28 - 3.31 | 0.32 |
| H$_2$O | 12.47 | 14.00 |
| O=F | -1.18 | |
| Total | 100.12 | 100.00 |

Number of ions on the basis of O = 7 and OH + F = 6

- B: 3.852
- Si: 0.104
- Ca: 2.013
- Mg: 1.901
- Fe: 0.072
- Mn: 0.023
- Zn: 0.002
- Co: 0.001
- Ni: 0.001
- F: 0.579
- H: 5.421

- Analyzed spots. ** Calculated based on the stoichiometry.

1. Fuka, Okayama, Japan. The present work.
2. Theoretical composition for Ca$_2$Mg$_2$B$_4$O$_7$(OH)$_6$. 

[B$_2$O$_3$(OH)$_3$]$^{4-}$ is a polyborate tetramer consisting of two triangles and two tetrahedra. It is considered that Si in fedorovskite with the same structure as roweite replaces B in the tetrahedron. Therefore, the empirical formula of fedorovskite from the Fuka mine (based on O = 7 and OH + F = 6 apfu) is shown as Ca$_{2.013}$(Mg$_{1.901}$Fe$_{0.072}$Mn$_{0.023}$Zn$_{0.002}$Co$_{0.001}$Ni$_{0.001}$)$\Sigma$2.000(B$_{3.852}$Si$_{0.104}$)$\Sigma$3.956O$_{7.000}$(OH$_{5.421}$F$_{0.579}$)$_{2.6000}$, which is very close to the ideal formula with high Mg content in the octahedral site.
they show a negative correlation to the ratio of Mg/(Mg + Mn + Fe + Zn + Co + Ni) in apfu as shown in Figure 5. The lattice constant of fedorovskite in the figure is obtained using the d-value of the common index that is also recognized in roweite. The a and b axes tend to decrease as this ratio increases, but the change of c axis is not so remarkable and seems to be almost constant except for the ratio of 0.61. It is shown by Moore and Araki (1974) that Mn in roweite, which has isomorphous relationship with fedorovskite, is distributed on the sheet-like structure the a-b axis plane. Therefore, it is considered that the substitution of Mg at the Mn position has a greater effect on the a and b axes than on the c axis.

Fedorovskite from the Fuka mine contains a small amount of Fe and Mn but is rich in Mg and very close to the end member of fedorovskite (Fig. 6). The distribution of chemical compositions from the Fuka, Solongo and Franklin mines indicates that fedorovskite and roweite are almost continuous solid solution. The fedorovskite from Fuka has a lower Fe content, which replaces Mg and Mn, than roweite from the same locality (Ando et al., 2015).

Roweite from the Fuka mine was formed as a secondary mineral from uralborite in a late hydrothermal reaction with Mn bearing solution (Fig. 6). The distribution of chemical compositions from the Fuka, Solongo and Franklin mines indicates that fedorovskite and roweite are almost continuous solid solution. The fedorovskite from Fuka has a lower Fe content, which replaces Mg and Mn, than roweite from the same locality (Ando et al., 2015).

In the Fuka mine, the chemical compositions of fedorovskite and roweite are close to their end members, and no mineral with an intermediate chemical composition between them has been found. On the other hand, although the number of analyses between fedorovskite and roweite is small, compositions distribute widely between the end members, indicating continuous solid solution (Fig. 6). Therefore, in the Fuka mine, fedorovskite produced by the reaction with Mg bearing hydrothermal

**Figure 4.** The relation between B and Si contents of fedorovskite from Fuka.

**Figure 5.** The relation between the unit cell parameters and Mg/(Mg + Mn + Fe + Zn + Co + Ni) (apfu) ratios.
solution and Roweite produced by the reaction with Mn bearing solution should have formed at different reaction stages (and/or areas).

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SUPPLEMENTARY MATERIAL

Color version of Figure 2 is available online from https://doi.org/10.2465/jmps.200512.

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