Roweite from the Fuka mine, Okayama Prefecture, Japan

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Roweite occurs as reddish to dark brown granular crystals up to 0.8 mm across in crystalline limestone near gehlenite-spurrite skarns at the Fuka mine, Okayama Prefecture, Japan. It is closely associated with uralborite. Associated minerals include shimazakiite, frolovite, bultfonteinite, fluorite and calcite. An electron microprobe analysis of roweite gave an empirical formula $\text{Ca}_{2.006}(\text{Mn}_{1.410}\text{Fe}_{0.333}\text{Mg}_{0.181}\text{Zn}_{0.036}\text{Co}_{0.004})\Sigma_{1.964}\text{B}_{4.017}\text{O}_{6.989}(\text{OH})_{6.011}$ based on O = 13. The unit cell parameters are $a = 9.057(2)$, $b = 13.335(3)$, $c = 8.284(3)$ Å. The calculated density is 2.92 g cm^{-3} . The roweite from the Fuka mine was probably formed as a secondary mineral from calcium borates such as uralborite in a reaction with manganese-bearing late hydrothermal solution.

Keywords: Roweite, Calcium manganese borate, Skarn, Fuka

INTRODUCTION

Roweite, $\text{Ca}_2\text{Mn}_2\text{B}_4\text{O}_7(\text{OH})_6$, is a rare calcium manganese hydroxide borate. The mineral was first identified as a new mineral reported by Berman and Gonyer (1937). It was found in a single small specimen from hydrothermal vein of a metamorphosed stratiform zinc ore in the zinc mines of Franklin, New Jersey, USA. The specimen was occurred in a narrow veinlet of almost pure roweite intimately associated with a silky white fibrous thomsonite. The wall-forming minerals of the roweite veinlet were franklinite, zincite and willemite, which were also recognized as inclusions of the roweite crystal. Subsequently, Moore and Araki (1974) determined the crystal structure of the mineral from the type locality. X-ray diffraction, and physical and optical properties data were obtained by Aristarain et al. (1974). On the other hand, Malinko et al. (1972) found that magnesian roweite in borate ores of the Solongo contact metasomatic deposit in Buryat, USSR, and the Mg-dominant analogue of roweite was described as a fedorovskite $\text{Ca}_2(\text{Mg}, \text{Mn})_2\text{B}_4\text{O}_7$

$(\text{OH})_6$ by Malinko et al. (1977).

During a mineralogical survey of gehlenite-spurrite skarns at the Fuka mine, roweite was found as fine several granular crystals in crystalline limestone. This is the first occurrence of roweite in Japan. The Mn-bearing minerals have not been found in the Fuka mine to date. The present paper deals with the mineralogical properties and mode of occurrence of roweite from the Fuka mine.

OCCURRENCE

Roweite was discovered as aggregates of several fine crystals in borate mineral assemblage block mainly consisting of shimazakiite (Kusachi et al., 2013) in crystalline limestone close to gehlenite-spurrite skarns which were formed as pyrometasomatic products of limestone at the Fuka mine, Okayama Prefecture, Japan ($34^\circ 46' \text{N}$, $133^\circ 26' \text{E}$). Several roweites occur as an aggregate of radial column crystals and a granular crystal from 0.1 to 0.8 mm in diameter in an uralborite crystal (Figs. 1 and 2A), which is one of the minerals in the block consisting of uralborite (Kusachi et al., 2000) and frolovite (Kusachi et al., 1995) without shimazakiite in the crystalline limestone. As indicated by the arrows in the photomicrograph

Figure 1. Photograph of roweite from the Fuka mine. Abbreviations: Rw, roweite; Ur, uralborite.

Figure 2. Photomicrograph (plane-polarized light) of roweite. (A) An overview showing the grains of roweite (Rw), uralborite (Ur) and calcite (Cal). L shows lack of a mineral from section. A white rectangular frame indicates the area of enlarged view. (B) An enlarged view showing fine crystals of roweite within the crystal of uralborite. Two black arrows indicate the fine crystals of roweite growing into uralborite.

(Fig. 2B), roweite seems to replace to and grow up in uralborite. The other associated minerals are bultfonteinite, calcite and fluorite.

Figure 3. Infrared absorption spectra of roweite.

PHYSICAL AND OPTICAL PROPERTIES

Roweite is reddish brown or dark brown with a vitreous luster and non-fluorescent in hand specimens. In thin section, the mineral is pale yellowish brown to dark brown, and transparent. The mineral shows pleochroism, and grains are darker brown when the trace of cleavage is vertical to the polarizer. The Fe free roweite from Franklin is colorless in thin section (Aristarain et al., 1974). Therefore, it is seemed that color density increases with increase in the Fe content. Cleavage is perfect on {100}. The calculated density of roweite from the Fuka mine is 2.92 g cm^{-3} based on the empirical formula and refined unit cell parameters. The data was slightly small than 2.933 g cm^{-3} [measured as $2.935(5) \text{ g cm}^{-3}$] reported from Franklin by Aristarain et al. (1974), whereas the data was larger than 2.74 g cm^{-3} [measured as $2.73(1) \text{ g cm}^{-3}$] reported from Solongo by Malinko et al. (1972).

The infrared absorption spectrum of roweite from the Fuka mine was measured by transmission method using an infrared spectrometer (JASCO FT/IR-6200typeA) for the wave number range from 4000 to 650 cm^{-1} , as shown in Figure 3. The resolution of wave number is 4 cm^{-1} . The sharp absorption bands at 3525 and 3503 cm^{-1} and the broad bands at 3188 cm^{-1} are attributed to the OH stretching vibration. The numerous absorption bands in the range from 1400 to 865 cm^{-1} are characteristic to the borates. The spectrum of roweite shows no absorption bands for CO_3 .

X-RAY CRYSTALLOGRAPHY

The powder X-ray diffraction data of roweite from the Fuka mine were obtained by using a Gandolfi camera with diameter = 114.6 mm employing Ni-filtered $\text{CuK}\alpha$

Table 1. Powder X-ray diffraction data of roweite

Fuka, Okayama, Japan (present study)						Calculated data based on the crystal structure (Moore and Araki, 1974)		Fuka, Okayama, Japan (present study)						Calculated data based on the crystal structure (Moore and Araki, 1974)	
			I/I_0	$d_{\text{obs.}}$	$d_{\text{calc.}}$	$I_{\text{calc.}}$	$d_{\text{calc.}}$				I/I_0	$d_{\text{obs.}}$	$d_{\text{calc.}}$	$I_{\text{calc.}}$	$d_{\text{calc.}}$
0 0 1	16	8.30	8.28	43	8.29	4 3 2	5	1.814	1.814	4	1.815				
1 1 0	4	7.51	7.49	7	7.50	3 5 2			1.800	1	1.802				
1 2 0	25	5.39	5.37	15	5.38	3 6 0	9	1.789	1.790	5	1.792				
1 2 1	20	4.52	4.51	13	4.51	4 0 3			1.751	2	1.751				
2 1 0			4.29	3	4.29	3 6 1	5	1.748	{	1.750	2	1.751			
0 0 2	4	4.14	4.14	9	4.14	5 2 0				1.748	2	1.748			
2 0 1	99	3.98	3.97	100	3.97	4 4 2	27	1.706	1.707	30	1.708				
2 1 1			3.81	3	3.81	4 5 1	5	1.696	1.690	1	1.691				
1 1 2	10	3.63	3.62	8	3.63	0 8 0	9	1.667	1.667	8	1.670				
1 2 2	22	3.28	3.28	17	3.28	0 0 5			1.657	2	1.658				
0 4 1	14	3.10	3.09	15	3.10	3 2 4	5	1.653	1.654	4	1.655				
2 0 2	24	3.06	3.06	26	3.06	3 6 2	6	1.644	1.643	3	1.645				
2 1 2	8	2.98	2.98	3	2.98	2 4 4			1.640	20	1.641				
2 3 1	10	2.95	2.96	2	2.96	0 8 1	24	1.637	1.634	7	1.637				
3 1 0	6	2.92	2.94	4	2.94	5 2 2	6	1.610	1.611	3	1.611				
1 3 2	4	2.87	2.87			4 5 2	5	1.591	1.593	2	1.594				
0 0 3	22	2.75	2.76	4	2.76	2 8 0			1.564	1	1.567				
3 2 0			2.75	13	2.75	2 0 5			1.556	2	1.557				
2 4 0	5	2.69	2.68	6	2.69	4 4 3	9	1.549	1.550	11	1.551				
3 2 1	2	2.64	2.61			2 8 1			1.537	4	1.539				
0 4 2	100	2.60	2.60	81	2.60	4 0 4	4	1.526	1.528	4	1.529				
1 1 3			2.59	4	2.59	4 1 4			1.518	2	1.519				
1 5 0			2.56	1	2.56	0 4 5			1.484	2	1.485				
2 4 1	11	2.56	2.55	12	2.56	2 8 2	8	1.463	1.463	7	1.465				
3 3 0	6	2.50	2.50			4 7 0			1.458	1	1.459				
1 4 2			2.50			6 0 2			1.418	2	1.418				
1 2 3	7	2.45	2.46	2	2.46	2 4 5			1.410	1	1.411				
1 5 1			2.44	3	2.45	6 1 2			1.410	1	1.410				
3 1 2	8	2.40	2.40	6	2.40	4 4 4			1.389	2	1.390				
2 1 3	5	2.33	2.32	5	2.32	0 0 6			1.381	2	1.382				
2 5 0			2.30	1	2.30	6 4 0			1.375	2	1.376				
3 2 2	17	2.29	2.29	13	2.29	3 6 4			1.354	2	1.355				
4 0 0	19	2.27	2.26	17	2.26	4 8 0	5	1.342	1.342	5	1.344				
2 4 2			2.25	2	2.26	1 2 6			1.337	2	1.338				
4 1 0			2.23	1	2.23	4 0 5	5	1.336	{	1.337	4	1.338			
4 0 1	31	2.19	2.18	28	2.18	5 2 4				1.336	1	1.336			
1 5 2			2.18	1	2.18	4 8 1	4	1.326	1.325	4	1.327				
1 6 0	15	2.16	2.16	5	2.16	2 0 6	4	1.317	1.321	3	1.321				
4 1 1			2.16	7	2.16	0 8 4	4	1.299	1.299	3	1.300				
0 4 3	40	2.13	2.13	35	2.13	0 4 6			1.276	3	1.277				
1 6 1			2.09	1	2.09	6 4 3	5	1.231	1.231	3	1.231				
0 0 4	10	2.07	2.07	13	2.07	0 8 5			1.175	1	1.176				
3 1 3	5	2.01	2.01	5	2.01	5 6 4			1.162	1	1.163				
3 5 0			2.00	1	2.00	6 4 4			1.146	2	1.146				
3 5 1			1.943	1	1.945	2 0 7			1.145	2	1.146				
1 2 4			1.932	10	1.934	2 8 5			1.137	1	1.139				
2 4 3			1.925	12	1.927	8 1 0			1.128	1	1.128				
1 6 2	18	1.916	1.914	11	1.917	4 8 4	4	1.126	1.126	3	1.128				
2 1 4			1.865	2	1.866	4 4 6			1.111	3	1.112				
4 4 1	5	1.826	1.827	5	1.828										

$a = 9.057(2)$, $b = 13.335(3)$, $c = 8.284(3)$ Å, $V = 1000.6(5)$ Å³.

radiation. The data were recorded on an imaging plate, and processed with a Fuji BAS-2500 bio-image analyzer using computer program written by Nakamuta (1999). The powder X-ray diffraction data of roweite are given in Table 1, with calculated data based on the crystal structure of Moore and Araki (1974). The unit cell parameters were refined from the powder X-ray diffraction data with an internal SiO₂ standard reference material using a computer program by Toraya (1993). The unit cell parameters are $a = 9.057(2)$, $b = 13.335(3)$, $c = 8.284(3)$ Å, and in close agreement with the $a = 9.057(2)$, $b = 13.357(2)$, $c = 8.289(1)$ Å obtained by Aristarain et al. (1974). On the other hand, the unit cell parameters from Solongo were $a = 9.01(2)$, $b = 13.25(3)$, $c = 8.27(2)$ Å. The unit cell dimensions of roweite from the Fuka mine were slightly larger than those reported from Solongo by Malinko et al. (1972).

CHEMISTRY

Roweite is easily soluble in dilute hydrochloric acid. The chemical composition was determined by means of an electron microprobe (JEOL JXA-8900R; WDS mode, 15 kV, 12 nA, and 5 µm beam diameter). The standard materials were; takedaite (Ca and B), manganosite (Mn), periclase (Mg), hematite (Fe), willemite (Zn) and CoO (Co). Detection limit for CoO was about 0.06 wt% (3σ level). F and Cl were not detected in EDS analyses. The H₂O was not determined directly due to a lack of pure material and was estimated by difference. The average of 10 analytical points is given in Table 2, together with the data by Berman and Gonyer (1937) and Malinko et al. (1972) for comparison.

Berman and Gonyer (1937) first reported the chemical formula of roweite to be CaMnB₂O₄(OH)₂ after their analytical result. Subsequently, Moore and Araki (1974) solved the structure and showed that the structural formula was Ca₂Mn₂²⁺(OH)₄[B₄O₇(OH)₂]. The empirical formula of roweite from the Fuka mine (based on O = 13 apfu), Ca_{2.006}(Mn_{1.410}Fe_{0.333}Mg_{0.181}Zn_{0.036}Co_{0.004})Σ1.964 B_{4.017}O_{6.989}(OH)_{6.011}, is very close to the ideal formula. The roweite from the Fuka mine shows higher content of Fe²⁺ than those from other localities, and is characterized with a small amount of Co in it.

DISCUSSION

Roweite, Ca₂Mn₂B₄O₇(OH)₆, and fedorovskite, Ca₂Mg₂B₄O₇(OH)₆, Mg-analogue of roweite, form isomorphous solid solution series (Malinko et al., 1977). Unit cell dimensions of roweite-fedorovskite series relate to the Mn content, and they show a positive correlation to the ratio

Table 2. Chemical compositions of roweite

(wt%)	1			2	3
	n* = 10	Range	SD		
B ₂ O ₃	31.71	30.70 - 32.71	0.55	32.40	34.15
CaO	25.51	25.01 - 26.89	0.54	25.40	23.96
MnO	22.69	20.56 - 23.21	0.84	28.30	17.87
MgO	1.65	1.39 - 1.86	0.16	1.66	7.59
FeO	5.42	4.83 - 5.62	0.27	-	1.20
Fe ₂ O ₃	-			-	0.13
ZnO	0.67	0.28 - 0.89	0.22	3.13	-
CoO	0.07	0.00 - 0.09	0.03	-	-
SiO ₂	-			-	1.37
H ₂ O	12.28**			8.51	13.4
Insol.	-			0.84	-
Total	100			100.24	99.67
Number of ions on the basis of O = 13					
B	4.017			4.321	4.052
Ca	2.006			2.103	1.765
Mn	1.410			1.852	1.040
Mg	0.181			0.191	0.788
Fe	0.333			-	0.069
Fe ³⁺	-			-	0.007
Zn	0.036			0.179	-
Co	0.004			-	-
Si	-			-	0.094
H	6.011			4.386	6.114

* Number of analyzed spots.

** Calculated by the difference from 100% total.

1. Fuka, Okayama Prefecture, Japan. The present work.
2. Franklin, USA. Berman and Gonyer (1937).
3. Solongo, USSR. Malinko et al. (1972).

Figure 4. The relation between the unit cell parameters and Mn/(Mn + Mg + Fe + Zn + Co + Si) (apfu) ratios.

Figure 5. Correlation diagram of the calculated densities and Mn/(Mn + Mg + Fe + Zn + Co + Si) (apfu) ratios.

Figure 6. Chemical composition of roweite. (A) Mn-Mg-Fe (apfu) series. (B) Mn-Mg-Zn (apfu) series.

of Mn/(Mn + Mg + Fe + Zn + Co + Si) in apfu as shown in Figure 4. The calculated densities of roweite show a positive correlation to the ratio of Mn/(Mn + Mg + Fe + Zn + Co + Si) (Fig. 5). Moreover, refractive index shows a positive correlation, whereas dispersion has negative correlation to the Mn content (Malinko et al., 1977).

Roweite from the Fuka mine shows higher concentrations of Fe compared to those from the other localities (Fig. 6A). Roweite from Solongo is characterized with higher content of Mg and small amounts of Fe (Fig. 6A). Roweite from Franklin is higher content of Zn (Fig. 6B).

Roweite is closely associated with uralborite, which is formed by a hydrothermal alteration (Kusachi et al., 2000). The ideal B/Ca ratios are 2 in both roweite and uralborite. The mode of occurrence, namely the replacing growth (Fig. 2B), and the same B/Ca ratio suggest that roweite from the Fuka mine was formed as a secondary mineral from uralborite in a late hydrothermal reaction with Mn bearing solution.

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