Vimsite from the Fuka mine, Okayama Prefecture, Japan

Shoichi KOBAYASHI^{*}, Manami YUASA^{*}, Mitsuo TANABE^{**}, Shigetomo KISHI^{***} and Isao KUSACHI^{****}

^{*}Department of Earth Sciences, Faculty of Science, Okayama University of Science, Okayama 700-0005, Japan

^{**}2058-3 Niimi, Okayama 718-0011, Japan

^{***}534 Takayama, Kagamino-cho, Tomada-gun, Okayama 708-0345, Japan

^{****}509-6 Shiraishi, Kita-ku, Okayama 701-0143, Japan

Vimsite was found as a mass or a veinlet in crystalline limestone associated with gehlenite-spurrite skarns at the Fuka mine, Okayama Prefecture, Japan. Vimsite occurs as colorless to white aggregates of anhedral or prismatic transparent crystals up to 1 mm in length in association with shimazakiite, sibirskite, priceite, uralborite, calciborite, kurchatovite, and calcite. It is also formed as a 0.5 mm wide veinlet. An electron microprobe analysis of vimsite gave an empirical formula $(\text{Ca}_{0.993}\text{Mg}_{0.009}\text{Fe}_{0.003}\text{Mn}_{0.001})_{\Sigma 1.006}\text{B}_{1.996}\text{O}_2(\text{OH})_4$ based on O = 6. The unit cell parameters are $a = 10.021(3)$, $b = 9.566(4)$, $c = 4.447(2)$ Å, $\beta = 91.231(9)^\circ$. The calculated density is 2.523 g cm^{-3} . The Vickers microhardness is 186–206 kg mm⁻² (25 g load). It is likely that vimsite from the Fuka mine was formed by subsequent hydrothermal alteration, as with uralborite and priceite, of sibirskite produced by the hydrothermal alteration of shimazakiite.

Keywords: Vimsite, Calcium metaborate, Skarn, Fuka

INTRODUCTION

Vimsite, $\text{CaB}_2\text{O}_2(\text{OH})_4$, is a rare calcium hydroxide borate. The mineral was first identified as a new mineral reported by Shashkin et al. (1968). It was found in a specimen of marble skarn from a zone of extensive borate mineralization on a contact metasomatic copper deposit in the Urals, Russia. Vimsite occurs in colorless, transparent crystals up to 2 mm in size. The mineral was closely intergrown with uralborite and formed an aggregate of transparent crystals overgrowing garnet and magnesite grains with calciborite, sibirskite and frolovite as a borate mineral in marble skarn. After that, Malinko and Kuznetsova (1970) found vimsite in a contact metasomatic iron deposit in Siberia, Russia. The mineralogical data of vimsite from the type locality has been reported only for impure specimen. The Siberian specimen is much purer than vimsite from the Ural deposit, but a small amount of SiO_2 (0.55%) has also been detected as an impurity in the chemical analysis of the sample from Siberia. The crystal structure of vimsite has been determined by Shashkin et al. (1969). Subsequently, it has been refined by Simonov et al. (1976). Vimsite is one of the calcium metaborate,

which are characterized by a constant molar ratio $\text{CaO}:\text{B}_2\text{O}_3 = 1:1$. Shashkin et al. (1971) summarized the powder X-ray diffraction data for seven metaborate minerals including vimsite from the Urals. The vimsite ($C2/c$) from the Urals is associated with uralborite ($P2_1/n$) in a polymorphic relationship (Shashkin et al., 1968).

During a mineralogical survey of gehlenite-spurrite skarns at the Fuka mine, vimsite was found as a mass or a veinlet in near the boundary between crystalline limestone and aggregate of calcium borate minerals close to near gehlenite-spurrite skarn. This is the first occurrence of vimsite in Japan. The present paper deals with the mineralogical properties and mode of occurrence of vimsite from the Fuka mine.

OCCURRENCE

Vimsite was discovered closely associated with shimazakiite (Kusachi et al., 2013) in crystalline limestone close to gehlenite-spurrite skarn at the Fuka mine, Okayama Prefecture, Japan ($34^\circ 46' \text{N}$, $133^\circ 26' \text{E}$), which was formed as pyrometasomatic products of limestone. Vimsite occurs as colorless to white aggregates of anhedral or prismatic transparent crystals up to 1 mm in length with sibirskite, priceite, and calcite (Fig. 1). On the other hand, a veinlet consisting of only vimsite was observed up to

Figure 1. Composition image of vimsite from Fuka. Vim, vimsite; Sib, sibirskite; Pri, priceite; Cal, calcite.

Figure 2. Photograph of vimsite veinlet from Fuka. Vim, vimsite; Sib, sibirskite.

0.5 mm in width (Fig. 2). In the either case, vimsite occurs closed association with uralborite (Kusachi et al., 2000), priceite (Kobayashi et al., 2017), and sibirskite (Kusachi et al., 1997) in the zone between the block consisting mainly shimazakiite and surrounding limestone. Vimsite occurs with uralborite and priceite in the aggregate of sibirskite, but it is not in direct contact with uralborite in a polymorphic relationship. The other associated minerals are borate minerals such as calciborite (Kobayashi et al., 2014) and kurchatovite (Hayashi et al., 2017) which are spotted in shimazakiite rich parts in the zone, and fluorite, apophyllite, and calcite.

PHYSICAL AND OPTICAL PROPERTIES

Vimsite is colorless or white with a vitreous luster and non-fluorescent in hand specimens. In thin section, the mineral is colorless and transparent. Cleavage is perfect along elongation of the prismatic crystal. The Vickers microhardness that was measured using a microhardness

Figure 3. Infrared absorption spectra of vimsite from Fuka.

tester (Akashi M-400 MVK-E) is 186–206 kg mm⁻² (25 g load). The calculated density of vimsite from the Fuka mine is 2.523 g cm⁻³ based on the empirical formula and refined unit cell parameters. The calculated data is slightly smaller than 2.54 g cm⁻³ reported for the specimen from the Urals (Shashkin et al., 1968).

The infrared absorption spectrum of vimsite from the Fuka mine was measured by transmission method using an infrared spectrometer (Nicolet iS50 FT-IR) 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 3556, 3337, and 3250 cm⁻¹ are attributed to the O–H stretching vibration. The numerous absorption bands in the range from 1440 to 720 cm⁻¹ are characteristic to the borates. The spectrum of vimsite shows no absorption bands for CO₃.

X-RAY CRYSTALLOGRAPHY

The X-ray powder diffraction data of vimsite from Fuka are shown with those from the Urals, Russia by Shashkin et al. (1968) and pdf card data (#01-073-2458) calculated on the basis of single-crystal data by Simonov et al. (1976) in Table 1. The data of vimsite from the Fuka mine were obtained by using an X-ray diffractometer (Rigaku RINT-2500V) with graphite-monochromatized CuK α 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 nonreflective plate and measured. Data of Shashkin et al. (1968) were obtained by X-ray photographic film in an RKU-114 camera utilizing unfiltered Fe radiation (35 kV, 12 mA), and the line intensities were visually read on a ten-point scale. 20 positions of all diffraction peaks of the sample from Fuka could be attributed to vimsite except for one weak peak, which might correspond to the strongest peak of sibirskite. On the other hand, when relative peak intensities are compared, posi-

Table 1. X-ray powder diffraction data of vimsite

			1			2		3	
<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{calc.}	<i>d</i> _{obs.}	<i>I</i> _{obs.}	<i>d</i> _{obs.}	<i>I</i> _{obs.} *	<i>d</i> _{calc.}	<i>I</i> _{calc.}
1	1	0	6.92	6.92	32	6.87	6	6.92	57
2	0	0	5.01	5.01	1	5.01	2	5.01	4
0	2	0	4.78	4.78	<1	4.78	1	4.78	2
1	1	1	3.72	3.71	1	3.72	7	3.71	56
2	2	0	3.46	3.46	100	3.48	10	3.46	100
0	2	1	3.26	3.26	3	3.26	5	3.25	19
3	1	0	3.15	3.15	1	3.15	2	3.15	4
1	3	0	3.04	3.04	22	3.04	6	3.04	31
2	2	1	2.71	2.71	1	2.71	4	2.71	19
3	1	1	2.60	2.60	4			2.60	43
3	1	1	2.55	2.55	1	2.55	6	2.55	32
4	0	0	2.50	2.50	2	2.50	6	2.50	22
0	4	0	2.39	2.39	1	2.46	4	2.39	3
3	3	0	2.31	2.31	7	2.305	2	2.31	8
0	0	2	2.22	2.22	4			2.22	57
4	2	0				2.223	8		
0	4	1	2.11	2.10	1			2.10	7
1	1	2				2.105	1		
3	3	1	2.06	2.06	1			2.06	43
2	0	2				2.060	6		
3	3	1	2.03	2.03	2	2.037	5	2.03	38
0	2	2	2.02	2.02	1	2.017	4	2.01	26
4	2	1	2.00	2.00	1	2.001	4	2.00	19
4	2	1	1.970	1.968	1			1.969	9
5	1	0						1.962	10
2	4	1				1.961	3	1.948	17
2	4	1				1.949	4	1.933	1
1	5	0				1.906	1		
2	2	2	1.883	1.880	5	1.881	7	1.881	14
2	2	2				1.854	1	1.855	3
5	1	1						1.810	6
1	3	2				1.813	2	1.798	9
3	1	2				1.800	1		
5	1	1	1.781	1.779	1			1.780	5
1	5	1	1.728	1.729	1			1.727	8
6	0	0	1.670	1.670	2	1.672	5	1.671	15
4	0	2				1.646	1	1.643	1
4	4	1	1.604	1.603	1			1.603	13
5	3	1				1.606	4	1.595	1
5	3	1	1.575	1.574	1			1.575	11
6	2	0				1.577	5		
<i>a</i> (Å)			10.021(3)			10.02(2)		10.026(2)	
<i>b</i> (Å)			9.566(4)			9.71(2)		9.558(3)	
<i>c</i> (Å)			4.447(2)			4.440(5)		4.440(1)	
β (°)			91.231(9)			92		91.31(2)	
<i>V</i> (Å ³)			426.1(3)			431.7		425.4	

1. Fuka, Okayama, Japan. The present work.

2. The Urals, Russia. (Shashkin et al., 1968).

3. pdf # 01-073-2458. Calculated on the basis of single-crystal data by Simonov et al. (1976).

* The line intensities were estimated visually from a ten-point scale.

tion of the maximum intensity peak coincides in the both data, while other peaks are in different order of intensity in each data set. This difference in intensity is most probably

due to preferred orientation of particles and/or poor particle statistics arising from a small amount of sample, where in the oriented sample, the intensity ratio of the oriented

plane may be stronger than the actual one. As shown in Table 1, the intensity ratios of vimsite from Fuka and Ural differ somewhat compared to the calculated intensity ratio of the pdf card data presented by Simonov et al. (1976), and only the ratio of vimsite from the Fuka mine do not seem to differ significantly.

The 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 $a = 10.021(3)$, $b = 9.566(4)$, $c = 4.447(2)$ Å, $\beta = 91.231(9)^\circ$. The lattice constants of vimsite from the Urals (Shashkin et al., 1968) determined by powder method are $a = 10.02(2)$, $b = 9.71(2)$, $c = 4.440(5)$ Å, $\beta = 92^\circ$ (Table 1). The b -axis and β of vimsite from the Fuka mine were slightly smaller, whereas c -axis was slightly longer than those reported by Shashkin et al. (1968), respectively. The notable difference in lengths of the b -axis is possibly related to the fact that the observed d -value of the 040 diffraction is somewhat larger than the value expected from the 020 diffraction in Shashkin et al. (1968). The unit cell parameters reported here is comparable to the values obtained from single-crystal data by Simonov et al. (1976), $a = 10.026(2)$, $b = 9.558(3)$, $c = 4.440(1)$ Å, $\beta = 91.31(2)^\circ$ (converted from originally reported $B2/b$ setting to $C2/c$ setting for comparison).

CHEMICAL COMPOSITION

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). The standard materials were; takedaite (B and Ca), periclase (Mg), hematite (Fe), and manganosite (Mn). The H₂O was not determined directly due to a lack of pure material and was calculated by stoichiometry on the basis of 6 O (atom per formula unit). F and Cl were not detected in EDS analyses. The average of 6 analytical points is given in Table 2, together with the data by Shashkin et al. (1968) for comparison. The data from the type locality is re-calculated by deducting the chemical composition of coexisting magnesite and andradite-grossular garnet. The empirical formula of vimsite from the Fuka mine is $(\text{Ca}_{0.993}\text{Mg}_{0.009}\text{Fe}_{0.003}\text{Mn}_{0.001})_{\Sigma 1.006}\text{B}_{1.996}\text{O}_2(\text{OH})_4$. The formula supports the ideal formula of $\text{CaB}_2\text{O}_2(\text{OH})_4$ indicated by Shashkin et al. (1968).

DISCUSSION

Vimsite, ideally $\text{CaB}_2\text{O}_2(\text{OH})_4$, shows the highest B_2O_3 content among the hydrous metaborate minerals from the Fuka mine as well as uralborite (Fig. 4). The metaborate minerals are characterized by a constant molar ratio

Table 2. Chemical compositions of vimsite

No.	1	2
B ₂ O ₃ (wt%)	42.92 (41.64-43.89)	42.2
CaO	34.38 (32.50-36.60)	34.0
MgO	0.22 (0.00-1.09)	
FeO	0.13 (0.00-0.57)	
MnO	0.03 (0.00-0.12)	
H ₂ O	22.25*	23.8
Total	99.94	100
Number of ions on the basis of O = 6		
B	1.996	1.94
Ca	0.993	0.97
Mg	0.009	
Fe	0.003	
Mn	0.001	
H	4.000	4.23

1. Fuka, Okayama, Japan. The present work.

2. The Urals, Russia. Shashkin et al. (1968).

* Calculated based on the stoichiometry.

$\text{CaO}:\text{B}_2\text{O}_3 = 1:1$. Metaborate minerals confirmed from the Fuka mine are vimsite, calciborite (Kobayashi et al., 2014), uralborite (Kusachi et al., 2000), nifontovite (Kusachi and Henmi, 1994), frolovite (Kusachi et al., 1995), pentahydroborite (Fujiwara et al., 1982), and hexahydroborite (Kusachi et al., 1999) (Fig. 4). On the other hand, Shashkin et al. (1971) also represented endogenic calcium metaborate group such as calciborite, korszhin-

Figure 4. Minerals from the Fuka mine in the system $\text{CaO}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$. 1, takedaite ($\text{Ca}_3\text{B}_2\text{O}_3$); 2, shimazakiite ($\text{Ca}_2\text{B}_2\text{O}_5$); 3, calciborite (CaB_2O_4); 4, sibirskite ($\text{Ca}_2\text{B}_2\text{O}_5 \cdot \text{H}_2\text{O}$) and parasibirskite ($\text{Ca}_2\text{B}_2\text{O}_5 \cdot \text{H}_2\text{O}$); 5, priceite [$\text{Ca}_2\text{B}_5\text{O}_7(\text{OH})_5 \cdot \text{H}_2\text{O}$]; 6, vimsite [$\text{CaB}_2\text{O}_2(\text{OH})_4$] and uralborite [$\text{CaB}_2\text{O}_2(\text{OH})_4$]; 7, nifontovite [$\text{Ca}_3\text{B}_6\text{O}_6(\text{OH})_{12} \cdot 2\text{H}_2\text{O}$]; 8, olshanskyite [$\text{Ca}_3\text{B}_4(\text{OH})_{18}$]; 9, frolovite [$\text{CaB}_2(\text{OH})_8$]; 10, pentahydroborite ($\text{CaB}_2\text{O}_4 \cdot 5\text{H}_2\text{O}$); 11, hexahydroborite [$\text{CaB}_2(\text{OH})_8 \cdot 2\text{H}_2\text{O}$].

skite, uralborite, nifontovite, frolovite, and pentahydroborite, which have been discovered in skarn-formed limestones from the Novofrolovsk copper deposit of the skarn type in the Turinsk district, the Central Urals. Though there was no korzhinskite in the Fuka mine, the mineral assemblages are similar between the Fuka mine and the Urals mine. The molecular numbers of water within the minerals varies from 0 for calciborite to 6 H₂O in the molecule of hexahydroborite. According to Kobayashi et al. (2014), the density shows a tendency to decrease with increase in the water content in metaborate minerals, and the density calculated for vimsite from the Fuka mine is also in agreement with this tendency. The B₂O₃ content is almost constant in shimazakiite, sibirskite, priceite, uralborite, and vimsite, and the H₂O content increases from shimazakiite to vimsite and uralborite, or priceite (Fig. 4). On the other hand, as mentioned above, vimsite is formed in the aggregate of sibirskite as well as uralborite and priceite. Therefore, vimsite is presumed to be formed by the subsequent hydrothermal alteration, as with uralbolite (Kusachi et al., 2000) and priceite (Kobayashi et al., 2017), from sibirskite produced by the hydrothermal alteration of shimazakiite.

Kobayashi et al. (2017) concluded that priceite from the Fuka mine formed by a late-hydrothermal alteration of shimazakiite. The occurrence of the priceite in this study (Fig. 1) indicates that the mineral is a hydrothermal alteration product of sibirskite that can be inferred to have been generated by hydrothermal alteration of shimazakiite.

In the Fuka mine, vimsite occurs as a mass or a veinlet with uralborite and priceite in the aggregate of sibirskite though vimsite is not in direct contact with uralborite in a polymorphic relationship. Therefore, vimsite from the Fuka mine was probably formed by the reaction of sibirskite with a late hydrothermal solution as well as uralborite, though the difference between the formation condition of both minerals is not known.

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