

Calciborite from the Fuka mine, Okayama Prefecture, Japan

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Calciborite was found as a veinlet or a mass in crystalline limestone associated with gehlenite-spurrite skarns at the Fuka mine, Okayama Prefecture, Japan. Calciborite occurs as milky white aggregates up to 1 mm in diameter with shimazakiite, fluorite, bornite and calcite. An electron microprobe analysis of calciborite gave an empirical formula $(\text{Ca}_{0.999}\text{Mn}_{0.001}\text{Co}_{0.001})_{\Sigma 1.001}\text{B}_{1.999}\text{O}_4$ based on $\text{O} = 4$. The unit cell parameters are $a = 8.373(2)$, $b = 13.811(8)$, $c = 5.012(4)$ Å. The mineral is optically biaxial (-), $\alpha = 1.594(2)$, $\beta = 1.654(2)$, $\gamma = 1.672(2)$ and $2V_{\text{calc.}} = 56^\circ$. The Vickers microhardness is 177 kg mm^{-2} (50 g load), and the Mohs hardness number is 3.5. The measured and calculated densities are 2.88(2) and 2.881 g cm^{-3} , respectively. The calciborite from the Fuka mine was probably formed by a reaction of boron-bearing fluids with limestone at a temperature between 250 and 300°C .

Keywords: Calciborite, Calcium borate, Skarn, Fuka

INTRODUCTION

Calciborite, CaB_2O_4 , is a very rare mineral of calcium borates. The mineral was first identified as a new mineral reported by Petrova (1955). It was found in deep drill cores at the contact of Middle Devonian limestone with quartz diorite intrusive in the Novofrolovo skarn type copper deposit in the Turinsk district, Central Urals, Russia. It was associated with calcite and dolomite, with minor amounts of garnet, magnetite, and pyroxene. The mineral also filled fissures in limestone and was observed to replace calcite. Malinko et al. (1963) re-examined the type material, and gave the chemical formula of CaB_2O_4 . Subsequently, Shashkin et al. (1970) determined the crystal structure of the mineral from the type locality. Moreover, powder X-ray diffraction data were obtained by Shashkin et al. (1971).

During a mineralogical survey of gehlenite-spurrite skarns at the Fuka mine, calciborite was found as a veinlet or a mass in crystalline limestone. This is the first occurrence of calciborite in Japan and the second occurrence in the world. The present paper deals with the mineralogical properties and mode of occurrence of calciborite from the

Fuka mine.

OCCURRENCE

Calciborite 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 ($34^\circ 46'\text{N}$, $133^\circ 26'\text{E}$), which were formed as pyrometasomatic products of limestone. Calciborite occurs as aggregates, up to 1 mm in diameter, of anhedral crystals. Calciborite is formed with small amounts of calcite and bornite as a veinlet up to 5 mm width or as a mass up to 2 cm in diameter in a block of aggregates of shimazakiite, calcite and fluorite in the crystalline limestone. The other associated minerals are borate minerals such as sibirskite (Kusachi et al., 1997), nifontovite (Kusachi and Henmi, 1994), uralborite (Kusachi et al., 2000) and an undetermined hydrous calcium borate, and cuspidine (Kusachi et al., 1977) and bornite.

PHYSICAL AND OPTICAL PROPERTIES

Calciborite is milky white with a vitreous luster in hand specimens. In thin section, the mineral is colorless, transparent as shown in Figure 1. Cleavage is recognized perfect on $\{110\}$, though Petrova (1955) described no cleav-

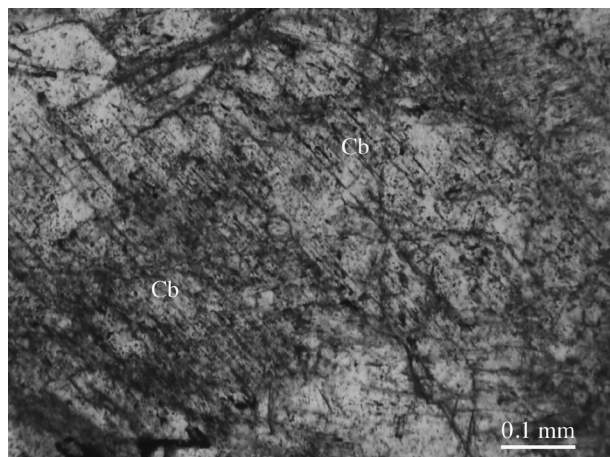


Figure 1. Photomicrograph (plane-polarized light) of calciborite. Abbreviation: Cb, calciborite.

Table 1. Optical and physical properties of calciborite from the Fuka mine

	1	2
α	1.594(2)	1.595
β	1.654(2)	1.654
γ	1.672(2)	1.67
δ	0.078	0.075
$2V$	56*	54
Sign	(-)	(-)
VHN ₅₀	177	
MHN	3.5	3.5
D (measured)	2.88(2)	2.878
D (calculated)	2.881	-
Cleavage	{110} perfect	none
Color	Milky white	-

* $2V_{\text{calc}}$.

1. Fuka, Okayama Prefecture, Japan. The present work.
2. Novofrolovo, Turinsk, Central Urals, Russia. Petrova (1955).

age. Optically, the mineral is biaxial negative with refractive indices $\alpha = 1.594(2)$, $\beta = 1.654(2)$ and $\gamma = 1.672(2)$, giving a calculated $2V = 56^\circ$. It is non-pleochroic and non-fluorescent. The density was measured as 2.88(2) using a heavy liquid (Clerichi solutions) and calculated as 2.881 g cm⁻³ based on the empirical formula and refined unit cell parameters. The mean Vickers microhardness value was 177 kg mm⁻² (ranging between 161 and 196 kg mm⁻²) on load of 50 g. In Table 1, the optical and physical properties are compared with those reported in the original description (Petrova, 1955). The data are very close to those from the type locality except cleavage. Calciborite is easily soluble in dilute hydrochloric acid.

The infrared absorption spectrum of calciborite from the Fuka mine was measured by the KBr matrix method using an infrared spectrometer (JASCO FT/IR-410) for

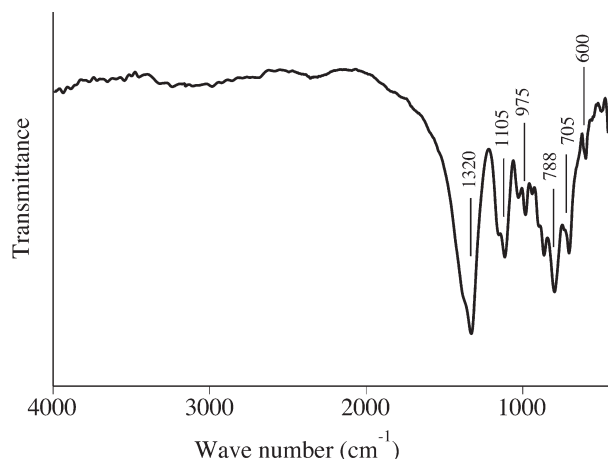


Figure 2. Infrared absorption spectra of calciborite.

the wave number range from 4000 to 400 cm⁻¹, as shown in Figure 2. The numerous absorption bands in the range from 1320 to 600 cm⁻¹ are characteristic to the borates. The spectrum of calciborite shows no absorption bands for vibrations of the H₂O, OH and CO₃.

X-RAY CRYSTALLOGRAPHY

The X-ray powder diffraction data of calciborite from the Fuka mine were obtained by using an X-ray diffractometer (Rigaku RINT-2500V) with graphite-monochromatized Cu-K α radiation generated at 40 kV and 200 mA. The cell parameters calculated from the powder data are $a = 8.373(2)$, $b = 13.811(8)$, $c = 5.012(4)$ Å. They are in close agreement with those obtained by oscillating crystal X-ray diffraction study and refining by the powder method by Shashkin et al. (1971). The data for calciborite from the Fuka mine are shown with those from the Novofrolovo mine of type locality in Table 2. The a and b -axes of calciborite from the Fuka mine were slightly shorter, whereas c -axis was slightly larger than those reported by Shashkin et al. (1971), respectively.

CHEMICAL COMPOSITION

The chemical composition was determined by means of an electron microprobe (JEOL JXA-8900R; WDS mode, 15 kV, 12 nA and 5 μ m beam diameter). A pure specimen of takedaite, nifontovite, rhodonite and CoO were used as standard materials for Ca, B, Mn and Co, respectively. The average of 10 analytical points is given in Table 3, together with the data by Malinko et al. (1963) for comparison.

Petrova (1955) first reported the chemical formula of calciborite to be Ca₅B₈O₁₇ from analytical data using picking material, which contained small amounts of dolomite, garnet and pyroxene. Subsequently, Malinko et al. (1963)

Table 2. X-ray powder diffraction data of calciborite

1						2		1						2	
<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{calc.}	<i>d</i> _{obs.}	<i>I</i>	<i>d</i>	<i>I</i>	<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{calc.}	<i>d</i> _{obs.}	<i>I</i>	<i>d</i>	<i>I</i>
1	1	0	7.160	7.17	19	7.166	68	4	2	0	2.003	2.003	5	2.005	12
0	2	0	6.906	6.91	6	6.910	10	3	4	1	1.992			1.993	<1
2	0	0	4.187			4.190	<1	1	4	2	1.971	1.972	14	1.970	55
1	1	1	4.106			4.104	8	3	5	0	1.963			1.965	9
1	3	0	4.034	4.04	16	4.037	21	2	3	2	1.948			1.947	1
1	2	1	3.650			3.649	14	4	0	1	1.932	1.931	3		
2	2	0	3.580	3.581	24	3.583	47	1	7	0	1.920	1.922	5	1.922	7
0	4	0	3.453	3.458	100	3.445	100	4	1	1	1.913			1.914	<1
1	3	1	3.143			3.142	5	2	6	1	1.871			1.872	14
2	1	1	3.129			3.130	15	3	0	2	1.865	1.865	10	1.864	47
2	2	1	2.913			2.913	35	4	2	1	1.860			1.855	23
3	1	0	2.736	2.736	4	2.738	11	0	5	2	1.856		1.858		
1	4	1	2.692			2.693	<1	3	5	1	1.828			1.829	2
2	4	0	2.664	2.665	21	2.666	37	1	7	1	1.793				
2	3	1	2.635			2.635	18	4	4	0	1.790		1.790	1.791	35
1	5	0	2.623	2.626	14	2.625	18	3	3	2	1.728			1.727	6
0	1	2	2.466	2.467	4	2.463	18	0	8	0	1.726				
2	5	0	2.402					0	6	2	1.695			1.695	<1
3	1	1	2.401			2.398	44	2	7	1	1.681			1.682	11
1	0	2	2.401	2.402	11			3	6	1	1.674			1.675	3
3	3	0	2.387	2.388	2	2.389	5	5	1	0	1.662			1.664	2
0	2	2	2.356			2.353	<1	1	6	2	1.662				
2	4	1	2.352					3	4	2	1.641	1.641	6	1.641	15
1	5	1	2.324			2.325	3	5	2	0	1.627			1.625	<1
0	6	0	2.302			2.303	14	1	1	3	1.627				
3	2	1	2.299	2.304	14			3	7	0	1.611	1.611	5	1.612	6
1	2	2	2.268	2.268	3	2.266	11	1	8	1	1.602			1.603	2
0	3	2	2.201			2.199	5	2	8	0	1.596	1.596	4	1.596	6
3	3	1	2.155			2.156	5								
2	1	2	2.125			2.123	3								
2	5	1	2.095					<i>a</i> (Å)			8.373(2)			8.380	
4	0	0	2.093	2.093	7	2.095	25	<i>b</i> (Å)			13.811(8)			13.820	
0	6	1	2.092					<i>c</i> (Å)			5.012(4)			5.006	
2	2	2	2.053			2.052	<1	α (°)			90			90	
1	6	1	2.029			2.030	8	β (°)			90			90	
0	4	2	2.028					γ (°)			90			90	
2	6	0	2.017			2.018	<1	<i>V</i> (Å ³)			579.6(5)			579.75	

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

2. Novofrolovo, Turinsk, Central Urals, Russia. Shashkin et al. (1971).

re-examined the type material, and revised the ideal formula CaB_2O_4 . The empirical formula of calciborite from the Fuka mine (based on $\text{O} = 4$ apfu), $(\text{Ca}_{0.999}\text{Mn}_{0.001}\text{Co}_{0.001})_{\Sigma 1.001}\text{B}_{1.999}\text{O}_4$, is very close to the ideal formula.

DISCUSSION

Calciborite, ideally CaB_2O_4 , shows the highest B_2O_3 content among the calcium borate minerals from the Fuka mine (Fig. 3). Shashkin et al. (1971) represented endogenic calcium metaborate group such as calciborite, korzhinskite, 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, Central Urals. The metaborate minerals are characterized by a constant molar ratio $\text{CaO}:\text{B}_2\text{O}_3 = 1:1$. Calciborite, uralborite (Kusachi et al., 2000), nifontovite (Kusachi and Henmi, 1994), frolovite (Kusachi et al., 1995a), pentahydroborite (Fujiwara et al., 1982) and hexahydroborite (Kusachi et al., 1999) were also confirmed from the Fuka mine (Fig. 3). Though there was hexahydroborite and no korzhinskite in the Fuka mine, the mineral assemblages are similar between Fuka and Novofrolovsk. Optical and physical properties of metaborate group from the Fuka mine were collectively shown in Table 4. The molecular numbers of water within

Table 3. Chemical composition of calciborite

	1			2
	n* = 10	Range	SD	
B ₂ O ₃ wt%	55.07	54.82 - 55.39	0.21	47.58
CaO	44.32	44.00 - 44.61	0.18	44.08
MgO	-			0.81
FeO	0.03	0.00 - 0.08	0.03	
Fe ₂ O ₃				0.22
SiO ₂	-			0.55
MnO	0.04	0.00 - 0.10	0.04	
Al ₂ O ₃	0.00			0.18
CoO	0.03	0.00 - 0.05	0.04	
NiO	0.02	0.00 - 0.04	0.02	
CO ₂	-			6.07
As ₂ O ₃	-			0.30
H ₂ O ⁺	-			0.17
H ₂ O ⁻	-			0.50
Total	99.51			100.46
Number of ions on the basis of O = 4				
B	1.999			1.708
Ca	0.999			0.982
Mg	-			0.025
Fe	0.000			0.003
Si	-			0.011
Mn	0.001			
Al	0.000			0.004
Co	0.001			
Ni	0.000			
C	-			0.172
As	-			0.004
H	-			0.093

* Analyzed spots.

1. Fuka, Okayama Prefecture, Japan. The present work.
2. Novofrolovo, Turinsk, Central Urals, Russia. Malinko et al. (1963).

the minerals varies from 0 (calciborite) to 6 (hexahydroborite). The refractive indices, birefringence, hardness and density of calciborite were relative high, and these values decreased with increase in water content.

Hart and Brown (1962) reported that the mineral generated at a low temperature contained much water in the system CaO-B₂O₃-H₂O. Therefore, the stabilized temperature of calciborite may be higher than another minerals in the metaborate group. Schäfer (1968b) synthesized the needle shaped single crystals of CaB₂O₄ from Ca(OH)₂ and H₃BO₃ at temperatures between 270 and 300 °C under a saturated water pressure. On the other hand, takedaite, Ca₃B₂O₆, which discovered at the Fuka mine, is anhydrous mineral as well as calciborite. Kusachi et al. (1995b) described that takedaite would appear to be formed at a temperature around 250 °C based on the result of synthetic experiment by Schäfer (1968a). In view of these results, calciborite from the Fuka mine would

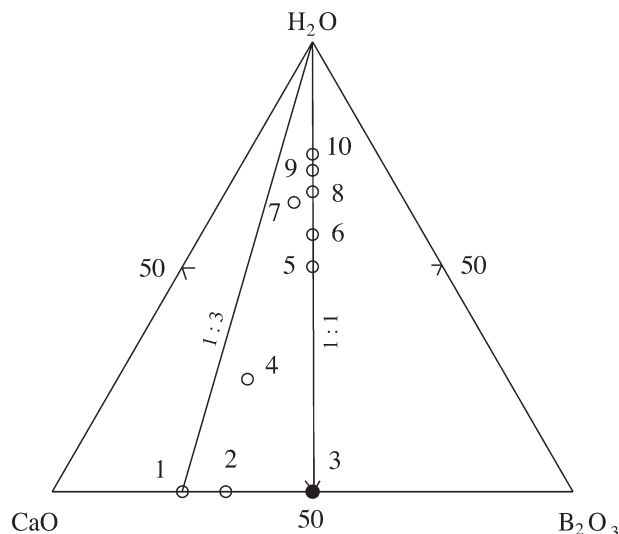


Figure 3. Minerals in the system CaO-B₂O₃-H₂O from the Fuka mine. 1, takedaite; 2, shimazakiite; 3, calciborite; 4, sibirskite; parasibirskite; 5, uralborite; 6, nifontovite; 7, olshanskyite; 8, frolovite; 9, pentahydroborite; 10, hexahydroborite.

therefore crystallized at a temperature between 250 and 300 °C. Calciborite from Fuka is formed as a veinlet and a mass in crystalline limestone. From this mode of occurrence, it is very likely that calciborite from the Fuka mine was primarily formed by a reaction of boron-bearing fluids with limestone.

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REFERENCES

- Fujiwara, T., Takada, M., Masutomi, K., Isobe, T., Okada, H., Nakai, I. and Nagashima, K. (1982) Pentahydroborite CaB₂O₄·5H₂O. *Chigaku Kenkyu*, 33, 11-20 (in Japanese).
- Hart, P.B. and Brown, C.S. (1962) The synthesis of new calcium borate compounds by hydrothermal methods. *Journal of Inorganic and Nuclear Chemistry*, 24, 1057-1065.
- Kusachi, I., Henmi, C., Saburi, S. and Henmi, K. (1977) Cuspidine from Fuka, the Town of Bitchu, Okayama Prefecture. *Mineralogical Journal*, 13, 165-170 (in Japanese).
- Kusachi, I. and Henmi, C. (1994) Nifontovite and olshanskyite from Fuka, Okayama Prefecture, Japan. *Mineralogical Magazine*, 58, 279-284.
- Kusachi, I., Henmi, C. and Kobayashi, S. (1995a) Frolovite from Fuka, Okayama Prefecture, Japan. *Mineralogical Journal*, 17,

Table 4. Optical and physical properties of calcium metaborate group from the Fuka mine

Mineral name	Calciborite ¹	Uralborite ²	Nifontovite ³	Frolovite ⁴	Penta-hydroborite ⁵	Hexa-hydroborite ⁶	
	CaB ₂ O ₄	CaB ₂ O ₂ (OH) ₄	Ca ₃ B ₆ O ₆ (OH) ₁₂ ·2H ₂ O	CaB ₂ (OH) ₈	CaB ₂ O ₄ ·5H ₂ O	CaB ₂ (OH) ₈ ·2H ₂ O	
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	
Lattice constants	<i>a</i> (Å)	8.373(2)	6.923(1)	13.12(1)	7.764(4)	7.878(5)	16.012(2)
	<i>b</i> (Å)	13.811(8)	12.326(1)	9.500(5)	5.679(4)	6.540(5)	6.689(1)
	<i>c</i> (Å)	5.012(4)	9.831(1)	13.56(1)	8.126(5)	8.066(7)	7.955(2)
	α (°)	90	90	90	113.15(1)	111.12(7)	90
	β (°)	90	97.09(1)	119.62(5)	101.604(7)	111.25(6)	103.81(1)
	γ (°)	90	90	90	107.86(1)	73.88(6)	90
Color	Milky white	Colorless	Colorless-grayish white	White-pale yellow	Colorless-pale red-brown	Colorless	
Refractive indices	ω						
	ϵ						
	α	1.594(2)	1.605	1.573	1.561	1.530	1.502(2)
	β	1.654(2)	1.611	1.577	1.573	1.536	1.505(2)
Birefringence	γ	1.672(2)	1.618	1.585	1.584	1.546	1.509(2)
	<i>d</i>	0.078	0.013	0.012	0.023	0.016	0.007
Hardness	Vickers (kg/mm ²)	177**	372**	198 - 221*	151-181*		
	Mohs	3 1/2	4 1/2	4	3 1/2	3 1/2	2 1/2
Density (g/cm ³)	Measurement	2.88(2)	2.58	2.35	2.22	2.03	1.84
	Calculation	2.881		2.37	2.26	2.058	

1. The present work. 2. Kusachi et al. (2000). 3. Kusachi and Henmi (1994). 4. Kusachi et al. (1995a). 5. Fujiwara et al. (1982). 6. Kusachi et al. (1999). * 25 g load; ** 50 g load.

- 330-337.
- Kusachi, I., Henmi, C. and Kobayashi, S. (1995b) Takedaite, a new mineral from Fuka, Okayama Prefecture, Japan. *Mineralogical Magazine*, 59, 549-552.
- Kusachi, I., Henmi, C. and Kobayashi, S. (1997) Sibirskite from Fuka, Okayama Prefecture, Japan. *Mineralogical Journal*, 19, 109-114.
- Kusachi, I., Takechi, Y., Kobayashi, S., Yamakawa, J., Nakamuta, Y., Lee, K.H. and Motomizu, F. (1999) Hexahydroborite from Fuka, Okayama Prefecture, Japan. *Mineralogical Journal*, 21, 9-14.
- Kusachi, I., Shiraga, K., Kobayashi, S., Yamakawa, Y. and Takechi, Y. (2000) Uralborite from Fuka, Okayama Prefecture, Japan. *Journal of Mineralogical and Petrological Science*, 95, 43-47.
- Kusachi, I., Kobayashi, S., Takechi, Y., Nakamuta, Y., Nagase, T., Yokoyama, K., Momma, K., Miyawaki, R., Shigeoka, M. and Matsubara, S. (2013) Shimazakiite-4M and shimazakiite-4O, Ca₂B₂O₅, two polytypes of a new mineral from Fuka, Okayama Prefecture, Japan. *Mineralogical Magazine*, 77, 93-105.
- Malinko, S.V., Kuznetsova, N.N., Pensionerova, V.M. and Rybakova, L.I. (1963) New data on calciborite. *Zapiski Vserossiiskogo Mineralogicheskogo Obshchestva*, 92, 684-690 (in Russian).
- Petrova, E.S. (1955) Calciborite, a new mineral. *Geology of Mining and Chemical Raw Materials*, 218-223 (in Russian).
- Schäfer, U.L. (1968a) Synthese und röntgenographische untersuchung der borate 3CaO·B₂O₃, 2CaO·B₂O₃ und 2CaO·B₂O₃·H₂O. *Neues Jahrbuch Mineralogie Monatshefte*, 75-80 (in German).
- Schäfer, U.L. (1968b) Untersuchungen im System CaO-Al₂O₃-B₂O₃-H₂O. *Neues Jahrbuch Mineralogie Monatshefte*, 433-440 (in German).
- Shashkin, D.P., Simonov, M.A. and Belov, N.V. (1970) Crystal structure of calciborite CaB₂O₄ = Ca₂[BO₃BO]₂. *Doklady Akademii Nauk SSSR*, 195, 345-348 (in Russian).
- Shashkin, D.P., Simonov, M.A. and Belov, N.V. (1971) X-ray diffraction studies of a group of natural calcium metaborates. *Soviet Physics-Crystallography*, 16, 186-189.

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