LETTER

Bi-bearing and REE-free zálesiite from the Fuka mine, Okayama Prefecture, Japan

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Zálesiite is found to exist as hexagonal prismatic crystals (length: up to 1 mm; width: 10 μm) and fibrous aggregates in the alteration zone in crystalline limestone near gehlenite-spurrite skarns at the Fuka mine, Okayama Prefecture, Japan. The mineral is pale green to emerald green in color with a silky to vitreous luster. Andradite, aragonite, bornite, cahnite, chalcocite, chalcopyrite, conichalcite, johnbaumite, and an unidentified Ca-Cu arsenate mineral coexist in the abovementioned limestone. From SEM-EDS analysis, the empirical formula of zálesiite is found to be $(\text{Ca}_{0.74}\text{Bi}_{0.26})_{\Sigma 1.00}(\text{Cu}_{5.80}\text{Ca}_{0.18}\text{Ni}_{0.01}\text{Zn}_{0.01})_{\Sigma 6.00}[(\text{As}_{2.86}\text{Si}_{0.12}\text{P}_{0.02})_{\Sigma 3.00}(\text{O}_{11.14}\text{OH}_{0.86})_{\Sigma 12.00}](\text{OH})_6 \cdot 3\text{H}_2\text{O}$ on the basis of the following calculation: $10(M1 + M2 + X) + 6(\text{OH}) + 3(\text{H}_2\text{O})$. Zálesiite collected from the Fuka mine contains Bi and is free of REE. The unit cell parameters of the zálesiite crystals are $a = 13.656(9)$, $c = 5.850(4)$ Å, $V = 945(1)$ Å³, and $Z = 2$. It is inferred that zálesiite is formed by the reaction between crystalline limestone, cahnite, johnbaumite, Cu sulfide, and a Bi-rich hydrothermal solution.

Keywords: Zálesiite, Mixite-group, Bi, Arsenate, Fuka mine, Hydrothermal solution

INTRODUCTION

Zálesiite, ideally represented as $\text{CaCu}_6(\text{AsO}_4)_2(\text{AsO}_3\text{OH})(\text{OH})_6 \cdot 3\text{H}_2\text{O}$, is a member of the mixite group, whose minerals have the general formula $M1M2_6(\text{XO}_4)_3(\text{OH})_6 \cdot 3\text{H}_2\text{O}$; here, $M1 = \text{Al, Bi, Ca, rare-earth elements (REE)}$, $M2 = \text{Cu}$, and $X = \text{As or P}$. In the mixite group elements, charge compensation during the substitution of a divalent cation (e.g., Ca^{2+}) with a trivalent cation (e.g., Y^{3+}) occurs by the concomitant substitution of OH^- by O^{2-} (Aruga and Nakai, 1985). Zálesiite is the Ca analog of agardite-(Y) $[\text{YCu}_6(\text{AsO}_4)_3(\text{OH})_6 \cdot 3\text{H}_2\text{O}]$ and mixite $[\text{BiCu}_6(\text{AsO}_4)_3(\text{OH})_6 \cdot 3\text{H}_2\text{O}]$. Zálesiite was first reported from Zálesí, Czech Republic by Sejkora et al. (1999). Subsequently, the mineral was found in the copper deposits at the Dolores prospect, Spain (de Baranda et al., 2003) and the Gold Hill mine, Tooele County, Utah (Adams, 2005). However, the substitution aspect in zálesiite has not yet been studied in sufficient detail.

At the Fuka mine, arsenate minerals such as cahnite (Shiraga et al., 2002) and johnbaumite (Kusachi et al.,

1996) are found to exist in the form of veins cutting through crystalline limestone near gehlenite-spurrite skarns. Zálesiite is found in the alteration zone in crystalline limestone at the fourth level of the Fuka mine. The location of the alteration zone is different from the vein reported by Shiraga et al. (2002) and Kusachi et al. (1996). This is the first report on zálesiite found in Japan. This study deals with the genesis, mode of occurrence, and mineralogical properties of zálesiite found at the Fuka mine.

OCCURRENCE AND PHYSICAL PROPERTIES

The Fuka mine is located approximately 40 km west-north-west of Okayama City, Japan (Lat. 34°46'N, Long. 133°26'E). The alteration zone (Fig. 1), which is found in crystalline limestone at the fourth level of the Fuka mine, extends vertically upwards and assumes the shape of the letter L. Cavities occur in the upper and lower portions of the alteration zone. Cahnite and pentahydroborite are present on the walls of these cavities and in the peripheral portion of the cavity in the upper portion. Bornite, chalcocite, chalcopyrite, cuprite, stringhamite, and wittichenite are sporadically disseminated in the crystalline

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Figure 1. Alteration zone in crystalline limestone at the fourth level of the Fuka mine.

limestone in the middle portion of the alteration zone. Only chalcocite, cuprite, and stringhamite are found in the euhedral crystals of calcite. Andradite, aragonite, bornite, cahnite, chalcocite, chalcopyrite, conichalcite, johnbaumite, zálesiite, and an unidentified Ca-Cu arsenate mineral occur in the cavity in the lower portion of the alteration zone. Johnbaumite is detected on the surface of the wall of the cavity. Andradite, bornite, chalcocite, and chalcopyrite are present in johnbaumite and calcite. Andradite also exists in the form of euhedral crystals.

Zálesiite occurs as hexagonal prismatic crystals (length: up to 1 mm; width: 10 μm) and fibrous aggregates (Fig. 2) in the euhedral crystals of calcite, along with conichalcite and the unidentified Ca-Cu arsenate mineral. Zálesiite is pale green to emerald green in color with a silky to vitreous luster. Pleochroism is weak, varying from pale green to pale yellowish green. The streaks are whitish to pale green in color. The calculated density of zálesiite at $Z = 2$ is 3.58 g/cm³. Moreover, zálesiite gradually dissolves in dilute hydrochloric acid.

CHEMICAL COMPOSITION

Chemical analyses of zálesiite were carried out on a scanning electron microscope (JEOL JSM-5400) equipped with an energy-dispersive spectrometer (Oxford ISIS L200) at Ehime University. Quantitative analyses were performed at an accelerating potential of 15 kV, beam current of 4.0×10^{-10} A, and a beam diameter of 3 μm . The standards used were wollastonite (for Ca and Si), InAs (for As), GaP (for P), and pure Bi, Fe, Co, Ni, Zn, and Cu. All the data were corrected using the ZAF matrix-correction program. The averaged chemical compositions of the minerals shown in Table 1 are compared with those reported by Sejkora et al. (1999) and de Baranda et

Figure 2. Photograph of zálesiite obtained from the Fuka mine. Abbreviations: Zál, zálesiite; Cal, calcite.

Table 1. Chemical composition of zálesiite

	1(n=5)		2	3
	Average(Range)			
wt%				
CaO	5.0	(4.7-5.3)	5.46	3.59
Bi ₂ O ₃	5.8	(5.5-6.2)		10.74
Y ₂ O ₃			1.50	
La ₂ O ₃			0.10	
Al ₂ O ₃			0.26	0.36
Fe ₂ O ₃	0.0	(0-0.2)		
BaO				0.23
K ₂ O				0.08
CuO	44.7	(43.9-45.7)	46.46	45.27
FeO				0.86
NiO	0.1	(0-0.3)		
ZnO	0.1	(0-0.4)		
MnO	0.0	(0-0.1)		
CoO	0.0	(0-0.1)		
PbO				0.04
MgO				<0.02
Na ₂ O				<0.01
As ₂ O ₅	31.8	(31.4-32.2)	34.27	33.36
SiO ₂	0.7	(0.6-0.8)		0.02
P ₂ O ₅	0.1	(0-0.2)	0.37	0.20
Cl				<0.01
H ₂ O	11.22	**	11.95	***
Total	99.52		100.37	94.75

* Data corresponding to five analyzed spots.

** From stoichiometry.

*** Weight loss from TG data.

1. Fuka mine (Present work).

2. Zálesi, Czech Republic (Sejkora et al., 1999).

3. Dolores prospect, Spain (de Baranda et al., 2003).

Table 2. XRD data obtained for zálesiite

1						2		1						2	
<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{calc.}	<i>d</i> _{meas.}	<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> _{meas.}	<i>I</i>	<i>d</i>	<i>I</i>
1	0	0	11.83	11.79	100	11.64	100	6	1	0	1.804	1.803	3	1.7921	6
2	0	0	5.91			5.856	3	2	1	3	1.787	1.783	3	1.7734	3
1	0	1	5.24	5.28	3	5.251	2	2	2	3	1.693			1.7164	2
1	1	1	4.44	4.46	18	4.431	41	4	4	0	1.707			1.6959	4
2	0	1	4.16	4.17	3	4.153	1	3	5	0	1.689			1.6787	4
3	0	0	3.942	3.929	4	3.911	5	4	4	1	1.639			1.6308	4
1	2	1	3.552	3.559	20	3.541	8	2	5	2	1.590			1.6152	3
2	2	0	3.414	3.405	8	3.387	17	1	7	0	1.566			1.5862	2
1	3	0	3.280	3.272	3	3.254	22	1	6	2	1.535			1.5562	4
2	2	1	2.949	2.951	17	2.9347	42	0	0	4	1.463			1.5316	2
3	1	1	2.861			2.8494	4	4	4	2	1.474			1.4703	2
2	3	0	2.713	2.709	9	2.6932	29	1	0	4	1.452	1.451	7	1.4359	5
1	4	0	2.581	2.573	9	2.5624	30	2	7	1	1.403			1.3953	1
3	2	1	2.461	2.462	23	2.4534	10	3	4	3	1.377	1.379	7	1.3758	3
2	2	2	2.221			2.2194	4	5	2	3	1.359	1.360	7	1.3567	1
1	3	2	2.183			2.1847	2	2	2	4	1.344			1.3481	2
3	3	1	2.121	2.117	3	2.1098	10	1	3	4	1.336			1.3403	1
4	0	2	2.079			2.0797	1	3	7	0	1.331			1.3225	4
3	2	2	1.989			1.9886	2								
6	0	0	1.971			1.9578	2	<i>a</i> (Å)				13.656(9)		13.571(1)	
1	0	3	1.924			1.9315	4	<i>c</i> (Å)				5.850(4)		5.880(1)	
5	0	2	1.839			1.8352	2	<i>V</i> (Å ³)				945(1)		937.8(2)	

1. Fuka mine (Present work).

2. Zálesi, Czech Republic (Sejkora et al., 1999).

al. (2003). No REE could be detected in our analyses. The empirical formula of zálesiite obtained from the Fuka mine was found to be $(\text{Ca}_{0.74}\text{Bi}_{0.26})_{\Sigma 1.00}(\text{Cu}_{5.80}\text{Ca}_{0.18}\text{Ni}_{0.01}\text{Zn}_{0.01})_{\Sigma 6.00}[(\text{As}_{2.86}\text{Si}_{0.12}\text{P}_{0.02})_{\Sigma 3.00}(\text{O}_{11.14}\text{OH}_{0.86})_{\Sigma 12.00}](\text{OH})_6 \cdot 3\text{H}_2\text{O}$ on the basis of the following calculation: $10 (M1 + M2 + X) + 6 (\text{OH}) + 3 (\text{H}_2\text{O})$. The H_2O content was estimated by stoichiometry.

CRYSTALLOGRAPHY

X-ray powder diffraction (XRD) data for zálesiite were recorded on a MAC Science M18XHF-SRA diffractometer at Ehime University using graphite-monochromatized $\text{CuK}\alpha$ radiation generated at 40 kV and 80 mA. The XRD data are shown in Table 2 and are compared with those of zálesiite obtained from the type locality (Sejkora et al., 1999). The unit cell parameters calculated from the XRD data are $a = 13.656(9)$, $c = 5.850(4)$ Å, $V = 945(1)$ Å³, and $Z = 2$.

DISCUSSION

Zálesiite from the Fuka mine contains Bi and is free of REE, similar to that obtained from the Dolores prospect (de Baranda et al., 2003). The chemical compositions at large cation sites in zálesiite and Ca-bearing mixite group

Figure 3. Ca-Bi-REE ternary diagram of the *M* site in the mixite group minerals.

minerals are plotted on a Ca-Bi-REE ternary diagram (Fig. 3). These minerals can be plotted in two distinct regions. The Agardite-zálesiite solid solutions do not contain Bi. On the other hand, the mixite-zálesiite solid solutions do not contain REE. Thus it is inferred that zálesiite has distinct solid solution properties of the agardite-zálesiite series as well as the mixite-zálesiite series.

The *a*-axis of zálesiite obtained from the Fuka mine is longer than that of zálesiite obtained from the type specimen; in addition, the cell volume of zálesiite from the Fuka mine is larger than that of zálesiite obtained from the type specimen. In zálesiite obtained from the

type locality, one-fifth of the total Ca content are substituted by Y, Al, and La. The enlargement of the unit cell in zálesiite obtained from the Fuka mine is thought to be due to the substitution of one-fourth of the Ca atoms with Bi, which is larger in size than Ca, Al, and Y.

The mineral assemblages in the upper, middle, and lower portions of the alteration zone at the Fuka mine differ to a considerable extent. B-bearing minerals are mainly present in the upper portion. From their mode of occurrence, it is likely that these minerals are formed by the reaction between a B-rich hydrothermal solution and crystalline limestone. Cu-bearing sulfides are mainly found in the middle portion. From their mode of occurrence, it is likely that these sulfides formed as primary minerals from a Cu-rich hydrothermal solution. Arsenates and conichalcite pseudomorphs after cahnite and chalcocite typically exist in the lower portion of the alteration zone. It is asserted that Ca-Cu arsenate minerals are formed later than cahnite. Moreover, conichalcite and the unidentified Ca-Cu arsenate mineral contain up to 3.1 wt% and 16.7 wt% of Bi_2O_3 , respectively. However, the alteration zone contains a very low amount of minerals that are Bi sources. A very small amount of wittichenite is present in the form of grains (diameter: $<5\text{ }\mu\text{m}$) in the middle portion of the alteration zone. These two observations indicate that the hydrothermal solution is the source of Bi. The cavity in the lower portion of the alteration zone is probably formed by the As-rich and Bi-rich hydrothermal solutions trapped in it. Kusachi et al. (1996) reported that johnbaumite from the Fuka mine is associated with arsenopyrite, löllingite, andradite and magnetite, which are formed by the reaction of fluids bearing elements such as As, Fe, and S with limestone. Shiraga et al. (2002) reported that cahnite from the Fuka mine is formed as a secondary mineral by the hydrothermal alteration of johnbaumite. Thus, the following assumptions are made: (1) andradite and johnbaumite are formed as primary minerals by the reaction between an As-rich Si-bearing solution and sulfides-bearing crystalline limestone at lower part of middle portion; (2) cahnite is formed by the hydrothermal alteration of johnbaumite; (3) conichalcite, zálesiite, and the unidentified Ca-Cu arsenate mineral are formed by the reaction between crystalline limestone, cahnite, johnbaumite, Cu-bearing sulfides, and a Bi-rich

hydrothermal solution; (4) in these minerals, Ca and Cu are derived from crystalline limestone and Cu-bearing sulfides, while As is formed from the dissociation of cahnite and johnbaumite; (5) the alteration zone is formed by the reaction of four types of hydrothermal solutions that intruded into crystalline limestone: a B-rich solution, a Cu-rich solution, an As-rich Si-bearing solution, and a Bi-rich solution.

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