

LETTER

Study of Zn-bearing beaverite $\text{Pb}(\text{Fe}_2\text{Zn})(\text{SO}_4)_2(\text{OH})_6$ obtained from Mikawa mine, Niigata Prefecture, Japan

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Zn-bearing beaverite occurs as a secondary mineral in an oxidized zone of a quartz vein in the hydrothermal Cu–Zn–Pb ore deposit of the Mikawa mine, Niigata Prefecture, Japan. The Zn-bearing beaverite is dark brown in color with streaks and the associated minerals are quartz, galena, sphalerite, pyrite, anglesite, beaverite, orthoclase, and osarizawaite. The empirical formula of the mineral based on EPMA is $\text{Pb}_{0.95}(\text{Fe}_{1.88}\text{Al}_{0.10})_{\Sigma 1.98}(\text{Zn}_{0.83}\text{Cu}_{0.30})_{\Sigma 1.13}(\text{SO}_4)_2[\text{O}_{0.38}(\text{OH})_{5.36}]_{\Sigma 5.74}$ for $S = 2$, which leads to the ideal formula $\text{Pb}(\text{Fe}_2\text{Zn})(\text{SO}_4)_2(\text{OH})_6$. The crystal structure is refined by Rietveld analysis in the space group $R\bar{3}m$. Using powder XRD data obtained by the combined use of a Gandolfi camera and monochromatic synchrotron radiation, the following values are obtained: $a = 7.3028(2)$, $c = 17.0517(4)$ Å, $V = 787.56(4)$ Å³, and $D_{\text{calc}} = 4.25$ g/cm³.

Keywords: Alunite group, Beaverite, Rietveld analysis, Zinc

INTRODUCTION

Beaverite, ideally $\text{Pb}(\text{Fe}_2\text{Cu})(\text{SO}_4)_2(\text{OH})_6$, is a lead sulfate member of the alunite group minerals. The formula of the alunite group minerals is generally represented by $AM_3(\text{XO}_4)_2(\text{OH})_6$ (where, $A = \text{K}^+$, Na^+ , NH_4^+ , Ca^{2+} , Pb^{2+} ; $M = \text{Al}^{3+}$, Fe^{3+} , ... and minor Cu^{2+} , Zn^{2+} , $X = \text{S}^{6+}$, As^{5+} , P^{5+} and minor Si^{4+}) and the crystal systems are rhombohedral with the space group $R\bar{3}m$. With regard to the chemical characteristics, beaverite contains divalent Pb^{2+} instead of the monovalent cation in the A site and divalent Cu^{2+} replacing a part of the trivalent Fe^{3+} in the M^{3+} site. The chemical properties show coupled substitutions with a charge compensation mechanism at the A and M sites toward the ordinal members of the alunite group minerals. Zinc is usually detected in a copper-containing beaverite substituting for the Cu^{2+} ion. Dutrizac et al. (1983) have reported that the synthetic Zn analogue of beaverite can be precipitated from a solution containing PbSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, and ZnSO_4 at 130 °C. During the mineralogical investigation of beaverite obtained from the Mikawa

mine, crystals of beaverite containing a large amount of Zn have been found. This is the first report of the occurrence of Zn-bearing beaverite with $\text{Zn} > \text{Cu}$.

OCCURRENCE

The Mikawa mine is located at Mikawa, Aga-machi, Higashikanbara-gun, Niigata Prefecture, Japan (37.47° N, 139.27°E). The hydrothermal Cu–Pb–Zn ore deposits were formed during volcanic activities in the mid Miocene age (Nagasawa, 1951). Zn-bearing beaverite occurs as a powdery or earthy crust with ordinary Zn-poor beaverite on the surface or in the crack or cavity of the aggregate of anglesite, galena, pyrite, sphalerite, and quartz. The mineral is often found on quartz crystals. Zn-bearing beaverite is a secondary mineral in the oxidized zone of the hydrothermal Cu–Zn–Pb ore deposit. It is brownish yellow in color. Figure 1 shows the aggregation of minute rhombohedral and hexagonal crystals.

CHEMICAL COMPOSITION

A preliminary chemical analysis using an SEM–EDS (JEOL JSM-5400) indicated that the mineral consisted

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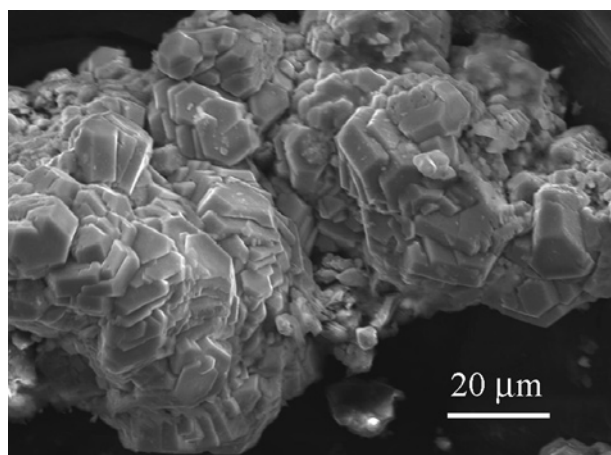


Figure 1. SEM micrograph of Zn-bearing beaverite from Mikawa mine showing hexagonal plates.

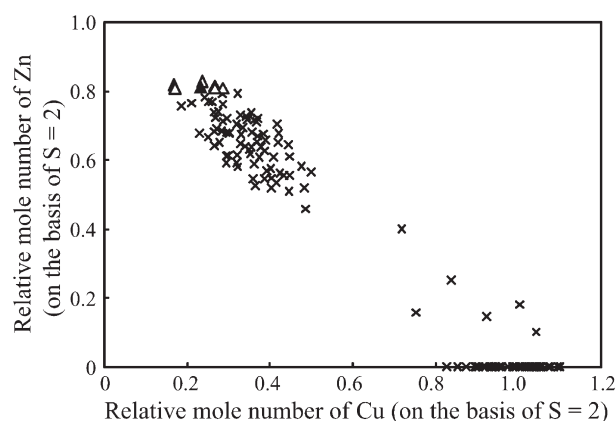


Figure 2. Correlation between Cu and Zn contents in Zn-bearing beaverite from Mikawa mine. The relative mole numbers represent the contents of Zn and Cu for each sample, calculated for $S = 2$ defined by the chemical formula of beaverite $\text{PbFe}_2(\text{Cu,Zn})(\text{SO}_4)_2(\text{OH})_6$. Open triangles indicate the samples that were used in the X-ray diffraction analysis. Their average composition is indicated by a solid triangle.

of Pb, S, and Fe, with small amounts of Zn, Cu, and Al. Quantitative analyses were carried out using a JEOL JXA-8800M WDS electron microprobe analyzer. The accelerating voltage, beam current, beam diameter, and duration for the intensity measurement were 15 kV, 10 nA, 1 μm , and 100 s, respectively. The water content could not be directly determined due to the limited amount of the available sample. The water content was, therefore, calculated from the difference between 100% and the weight percent of the unhydrated component. The results of this calculation are given in Table 1. The empirical formula of the Zn-bearing beaverite is $\text{Pb}_{0.95}(\text{Fe}_{1.88}\text{Al}_{0.10})_{\Sigma 1.98}(\text{Zn}_{0.83}\text{Cu}_{0.30})_{\Sigma 1.13}(\text{SO}_4)_2[\text{O}_{0.38}(\text{OH})_{5.36}]_{\Sigma 5.74}$ for $S = 2$, which is consistent with the ideal formula $\text{Pb}(\text{Fe}_2\text{Zn})(\text{SO}_4)_2(\text{OH})_6$. More than 100 electron microprobe analyses were carried

Table 1. The chemical composition of Zn-bearing beaverite used for the X-ray diffraction analysis

	wt%				No. cations
	Average	Range	SD		
PbO	31.94	31.68-32.19	0.22	Pb	0.95
Fe_2O_3	22.46	21.81-23.10	0.07	Fe	1.88
ZnO	10.15	8.57-11.01	0.61	Zn	0.83
CuO	3.59	2.65-5.14	1.08	Cu	0.30
Al_2O_3	0.78	0.67-0.84	1.09	Al	0.10
SO_3	23.95	23.38-24.49	0.55	S	2
H_2O	7.22			H	5.36
Total	100				

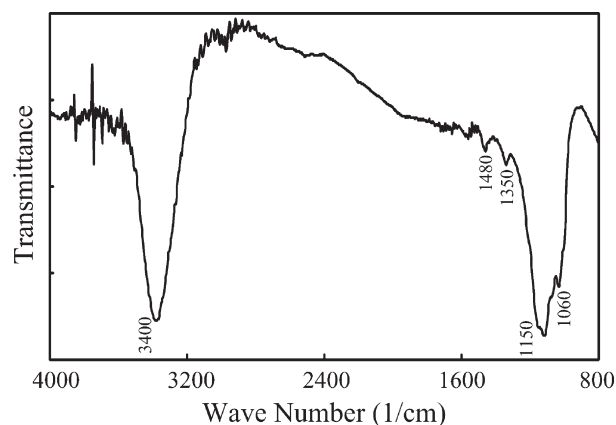


Figure 3. Infrared absorption spectrum of Zn-bearing beaverite from Mikawa mine.

out for 12 grains of the Zn-bearing beaverite and beaverite from the same locality. The analytical results of the Zn and Cu contents are plotted in Figure 2, which shows a negative correlation between the two components.

INFRARED SPECTRA

The infrared absorption spectrum of the Zn-bearing beaverite was obtained using a microscopic FT-IR spectrometer (HORIBA FT/IR-730) in the reflection mode for the region from 800 cm^{-1} to 4000 cm^{-1} (Fig. 3). The spectrum exhibits absorption bands at 3400 cm^{-1} due to the OH group and at 1060 cm^{-1} and 1100 cm^{-1} due to the sulphate group. Weak absorption bands due to H-O-H bending are also observed at 1350 cm^{-1} and 1480 cm^{-1} .

X-RAY DIFFRACTION STUDY

An X-ray diffraction study was carried out using a fragment from a thin section containing a large amount of Zn that was analyzed by the electron microprobe. One specimen ($\sim 20 \mu\text{m}$ in diameter) selected out of 12 grains analyzed by a WDS electron microprobe analyzer exhibited

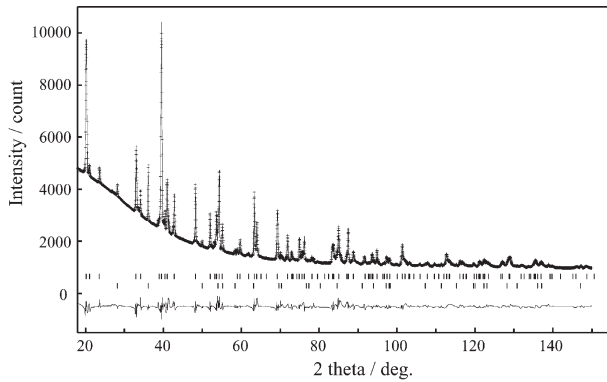


Figure 4. Rietveld analysis of Zn-bearing beaverite. The observed and calculated diffraction profiles (top) are indicated by plus signs and a line, respectively. The short bars indicate the Bragg angles (up: Zn-bearing beaverite, down: quartz) and the difference diffraction pattern at the bottom.

highest Zn concentrations, which are indicated by open triangles in Figure 2. No single-crystal work could be carried out because of the occurrence mode, a small aggregation of crystals. The X-ray powder diffraction pattern for the Rietveld analysis of the Zn-bearing beaverite was

Table 2. Final atomic parameters for Zn-bearing beaverite

	x	y	z	$B(\text{\AA}^2)^{**}$
Pb	0	0	0	2.75(7)
M^*	0.5	0	0.5	0.18(8)
S	0	0	0.3137(4)	2.7(2)
O1	0	0	0.4070(7)	0.3(2)
O2	0.2207(5)	-0.2207(5)	-0.0485(4)	0.3(2)
OH	0.1308(5)	-0.1308(5)	0.1296(5)	1.3(2)

* The occupancy parameter for the M site was fixed based on the chemical analysis data: $0.66\text{Fe} + 0.25\text{Zn} + 0.09\text{Cu} + 0.03\text{Al}$.

** The equivalent isotopic temperature factor B is in the form $B_j = 8\pi^2 U_j$.

obtained using a Gandolfi camera, because the specimen showed an extremely limited size of a chemically homogeneous part ($\sim 20 \mu\text{m}$); otherwise, a specimen having a complex solid solution should be used in the analysis. The diffraction data were collected by the camera with a diameter of 114.6 mm, utilizing monochromatized synchrotron radiation ($\lambda = 2.0765 \text{\AA}$) at the BL37XU beamline of SPring-8, Japan Synchrotron Radiation Research Institute (JASRI), Hyogo Prefecture, Japan. A Si(111) double crys-

Table 3. X-ray powder diffraction data for Zn-bearing beaverite

h	k	l	I/I_0	$d_{\text{obs}}/\text{\AA}$	$d_{\text{calc}}^*/\text{\AA}$	h	k	l	I/I_0	$d_{\text{obs}}/\text{\AA}$	$d_{\text{calc}}^*/\text{\AA}$	h	k	l	I/I_0	$d_{\text{obs}}/\text{\AA}$	$d_{\text{calc}}^*/\text{\AA}$
1	0	1	100	5.930	5.947	1	0	10	3	1.646	1.648	2	3	7	7	1.247	1.246
0	0	3	6	5.684	5.701	1	3	4	1	1.622	1.624	1	4	6	1	1.242	1.242
0	1	2	8	5.079	5.094	1	2	8	1	1.591	1.593	1	3	10	3	1.223	1.224
1	1	0	39	3.651	3.660	4	0	1	1	1.574	1.575	3	3	0	6	1.217	1.218
1	0	4	9	3.535	3.542	3	1	5	7	1.560	1.561	0	5	4	1	1.213	1.213
0	2	1	43	3.110	3.119	0	4	2	12	1.555	1.556	2	3	8	1	1.200	1.200
1	1	3	61	3.072	3.077	2	2	6	14	1.536	1.538	0	1	14	1	1.196	1.197
0	1	5	7	3.002	3.007	0	1	11	2	1.506	1.507	2	4	1	1	1.192	1.191
2	0	2	31	2.965	2.964	0	2	10	26	1.501	1.502	3	3	3	4	1.190	1.191
0	0	6	23	2.842	2.842	4	0	4	11	1.482	1.484	5	0	5	2	1.186	1.187
0	2	4	30	2.540	2.540	3	2	1	3	1.446	1.447	4	2	2	6	1.184	1.184
2	1	1	10	2.367	2.367	0	4	5	1	1.434	1.436	3	0	12	3	1.179	1.179
2	0	5	4	2.319	2.311	2	3	2	1	1.430	1.432	3	1	11	1	1.162	1.162
1	2	2	11	2.302	2.305	1	3	7	4	1.423	1.425	4	0	10	7	1.159	1.160
1	0	7	39	2.273	2.276	0	0	12	1	1.421	1.421	2	4	4	6	1.151	1.152
1	1	6	5	2.243	2.246	3	0	9	8	1.409	1.410	2	1	13	4	1.151	1.151
3	0	0	3	2.108	2.111	2	0	11	1	1.392	1.393	0	0	15	1	1.137	1.137
2	1	4	4	2.085	2.088	2	1	10	1	1.389	1.389	2	0	14	4	1.137	1.136
0	1	8	1	2.020	2.022	4	1	0	2	1.380	1.381	5	1	1	1	1.133	1.134
3	0	3	33	1.977	1.979	3	2	4	1	1.375	1.375	4	2	5	1	1.128	1.129
1	2	5	9	1.957	1.960	3	1	8	1	1.354	1.356	1	5	2	1	1.126	1.126
0	2	7	1	1.930	1.932	4	1	3	6	1.341	1.342	0	5	7	3	1.123	1.122
0	0	9	1	1.895	1.897	2	3	5	1	1.335	1.336	2	2	12	6	1.121	1.122
2	2	0	33	1.826	1.828	4	0	7	1	1.326	1.326	3	3	6	1	1.119	1.119
2	0	8	12	1.767	1.769	1	1	12	1	1.324	1.325	4	1	9	3	1.116	1.116
1	3	1	3	1.745	1.747	2	2	9	1	1.315	1.316	0	4	11	1	1.107	1.108
2	2	3	1	1.738	1.740	1	2	11	2	1.301	1.302	3	2	10	1	1.105	1.106
1	3	2	1	1.718	1.720	1	0	13	3	1.284	1.285	5	1	4	1	1.098	1.098
2	1	7	7	1.706	1.708	0	4	8	3	1.270	1.271	5	0	8	1	1.088	1.087
3	0	6	3	1.693	1.695	0	5	1	2	1.261	1.262	1	1	15	4	1.085	1.086
1	1	9	7	1.682	1.683	5	0	2	2	1.251	1.252	1	2	14	1	1.085	1.084

$a = 7.3028(2) \text{\AA}$ and $c = 17.0517(4) \text{\AA}$.

tal was employed to monochromatize the radiation. The diffraction data were recorded on an imaging plate and processed by a Fuji BAS-2500 bio-imaging analyzer and a computer program written by Nakamuta (1999). Since the sample used was an aggregate of fine crystals, a good powder diffraction pattern suitable for Rietveld analysis was obtained by using a small single grain. However, the powder diffraction pattern showed that the sample contained significant quantities of quartz, in addition to Zn-bearing beaverite. Rietveld analysis was carried out using these two phases. The occupancy parameters of the Zn-bearing beaverite were fixed on the basis of the empirical formula. The refinement provided lattice parameters in a hexagonal system with $a = 7.3028(2)$, $c = 17.0517(4)$ Å, and $V = 787.56(4)$ Å³. The structure of beaverite $[(R\bar{3}m)]$ (Breidenstein et al., 1992) was taken as an initial model for the Rietveld analysis using the program RIETAN (Izumi 1993). The structure was successfully refined and the refinement converged to $R_{wp} = 3.07$, $R_p = 1.99$, $Re = 2.35$, $S = 1.31$, $R_I = 5.06$, and $R_F = 3.12$ (Fig. 4). The final atomic coordinates with displacement parameters are given in Table 2. The powder diffraction data and refined lattice parameters are listed in Table 3.

RELATIONSHIP TO BEAVERITE

A substantial solid solution between Al and Fe in the M site of the general formula of the alunite group $AM_3(XO_4)_2(OH)_6$ is also poorly documented, although intermediate compositions between alunite, $KAl_3(SO_4)_2(OH)_6$ and jarosite, $KFe_3(SO_4)_2(OH)_6$, exist (Brophy et al., 1962). Similarly, a series between osarizawaite, $Pb(Al_2Cu)(SO_4)_2(OH)_6$, and beaverite, $Pb(Fe_2Cu)(SO_4)_2(OH)_6$, is known, where the additional incorporation of other divalent ions such as Zn into the M site is possible. The present mineral $Pb(Fe_2Zn)(SO_4)_2(OH)_6$ corresponds to this case and can be expressed as an end-member of a substitution of Zn for Cu at the octahedral M site in $Pb(Fe_2Cu)(SO_4)_2(OH)_6$. Two substitution mechanisms are observed for the introduction of divalent cations into the A site of the alunite group minerals, namely $(A'^{2+})_x(A^+)^{1-2x}$ and $(A'^{2+}M'^{2+})_x(A^+M^{3+})^{1-x}$. An example of the former ($x = 0.5$) is plumbojarosite $Pb_{0.5}Fe_3(SO_4)_2(OH)_6$ ($x = 0.5$) with a superlattice of double cells, $c = \sim 34$ Å. On the contrary, beaverite shows the latter type of substitution for jarosite, $(Pb^{2+}Cu^{2+})_x(K^+Fe^{3+})^{1-x}$. The substitution of divalent Cu for 1/3 of the trivalent Fe in the octahedral M site can compensate for the change in the charge balance accompanied with the substitution of Pb^{2+} for K^+ at the A site. Consequently, Cu is not a mere partial substituent,

but is an essential element in beaverite as the end-member ($x = 1$) of the substitution in $(Pb^{2+}Cu^{2+})_x(K^+Fe^{3+})^{1-x}$. Zn in this mineral without the superlattice is, therefore, a key element for the solid solutions in the members of the alunite group minerals with a full occupancy of Pb^{2+} in the A site.

As can be seen in Figure 2, a linear negative correlation is observed between the contents of Cu and Zn. The specimens from the Mikawa mine can be compositionally classified into two groups — Zn-bearing beaverite ($Zn > Cu$) and Zn-poor ($Cu > Zn$) or Zn-free beaverite. The analytical data show that no continuous solid solution is observed between the Zn- and Cu-end-members of beaverite.

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