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ON OSARIZAWAITE, A NEW MINERAL OF THE ALUNITE GROUP, FROM THE OSARIZAWA MINE, JAPAN*

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ABSTRACT

Osarizawaite, a new mineral, from the Osarizawa mine occurs in the oxidized zone of lead-zinc-copper veins as earthy and friable masses, associated with other secondary minerals of lead or copper. The chemical formula of osarizawaite has been determined as $Pb\,(Cu_{0.98}\,Zn_{0.02})\,(Al_{0.81}\,Fe_{0.1})_2\,(SO_4)_2\,(OH)_6$. Its physical and optical properties are: greenish-yellow in colour; specific gravity=3.89~4.02, 4.20 (calc.); mean index of refraction=1.735~1.757, birefringence strong. The unit cell dimensions for both the hexagonal cell and the corresponding rhombohedral cell are: $a_0=7.05$Å., $c_0=17.23$Å., $Z=3$; $a_{rh}=7.04$Å., $\alpha=60°06'$, $Z=1$. The data obtained demonstrate that the mineral is a new species being the aluminum analogue of beaverite and belongs to the alunite group. A new mineral name, osarizawaite, is proposed for the mineral which belongs to the alunite group and whose ideal chemical formula is $PbCuAl_2(SO_4)_2(OH)_6$ where Cu and Al may be partially replaced by Zn and Fe respectively.

Introduction

Oxidized zones fairly large scale have been found at the shallow parts of lead-zinc-copper veins among the Shôtoku and Utori vein groups which are situated in the north-eastern part of the mineralized area of the Osarizawa mine. The oxidized zone, which is lately exploited, contains various secondary minerals of lead and copper. The main constituent minerals are anglesite and limonite. They are accompanied by an unknown mineral which is greenish-yellow in colour

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and occurs in powdery or earthy masses. The writer studied the specimens of this mineral collected from the Shôtoku 6b-2 Vein, and identified it to be a new species of the composition $Pb(Cu_{0.98}Zn_{0.02})(Al_{0.81}Fe_{0.19})_2(SO_4)_2(OH)_6$.

In this paper the writer will present a brief explanation of the occurrence and the results of examinations on the new mineral, which is named "osarizawaite" after the name of the locality.

Occurrence and paragenesis

The Osarizawa mine, one of the most famous copper mines in Japan, is located in the north-eastern part of Akita Prefecture. The ore deposits consist of about four hundred veins cutting the Miocene green tuff and silicious shale complex and the augite andesite and plagio-liparite which are intruded into the complex.

The Shôtoku and Utori vein groups are situated in the north-eastern part of the Osarizawa mining area and composed of epithermal veins filling the numerous fissures of E.-W. system distributed near the two main faults "Higashi" and "Nishi", striking NE. Most of them are simple chalcopyrite-pyrite veins similar to other deposits of the Osarizawa mine, but some of them, Shôtoku 6b Vein or Utori 2 Vein in which osarizawaite occurs, are characterized by oxidized zone of considerable scale and downward they gradually pass into chalcopyrite-pyrite zone through galena-sphalerite zone. Those oxidized zones are directly bordered on the Higashi or Nishi Fault and their boundaries on other sides are controled by the accessory small faults.

The oxidized zones chiefly consist of anglesite and limonite, and the following secondary minerals have been also recognized: linarite, azurite, brochantite, malachite, chalcocite, covellite, sulphur, chalcedony, kaolinite and hydrous oxides of manganese.

Anglesite occurs forming intermittent, branch-rich veinlets or small ring ores in the limonitized vein and in some places it includes galena as nucleus.

In general, linarite, azurite, brochantite and malachite are distributed only locally, running along or somewhat standing away from the anglesite veinlets, and rarely accompanied by black manganese mineral.

Chalcocite and covellite are also found locally in limonitized vein as sweet-potato-shaped blocks of which a small quantity of galena, sphalerite, chalcopyrite and pyrite remains at the central part.

Dotty sulphur is found at times in a cavity of strongly bleached rock.

Osarizawaite occurs as a powdery or earthy crust on the surface or in the crack or cavity of the aggregate of anglesite, limonite and other associated minerals above described. It does not form a distinctive veinlet or massive aggregate, but it is clearly distinguished from the associated minerals by its characteristic colour, namely the Japanese bushwarbler colour (greenish-yellow). Although this mineral has been recognized macroscopically in small quantities only at a part of the upper second level of Shôtoku 6b-2 Vein and the upper third level of Utori 2 Vein, there is a possibility of more extensive distribution in the microscopic order.

The osarizawaite crystals collected for this study from the Shôtoku Vein were so fine that no crystal form has been recognized with the naked eye or even with a magnifying glass. Under the microscope, the mineral occurs, in some cases, on the surface of porous mother rock mainly consisting of kaolinite accompanied by quartz, limonite etc. In other cases, it occurs surrounding anglesite or along the cracks of anglesite which occurs abundantly filling the interstitial spaces of vein-quartz.

Most of osarizawaite crystals form such close masses that it was impossible to discriminate single crystals even under the microscope, but some of the scattered grains are often crystallized in distinct hexagonal outline and appear to be composed of pyramidal faces at terminal (Figs. 1∼4, Plates I and II).

Preparation of materials

The materials for the study were milled so as all the products passed through the 200 mesh screen and then osarizawaite in the +270 mesh fraction was purified by means of a super-panner and a Frantz isodynamic magnetic separator. In those processes, microscopic observation, spectrographic analysis and X-ray powder diffraction analysis were used to certify the purity of the products. As the result of those treatment, the osarizawaite concentrate free from the accompanying minerals was obtained. It was confirmed under the microscope that the concentrate contained only very small amounts of quartz which were stained partly with limonite or locked with osarizawaite and was not contaminated with any other transparent or opaque mineral at all (Fig. 4, Plate II).

Physical properties

The mineral is a greenish-yellow earthy looking material and the mass is so friable as easily crushed between fingers. The specific gravity was determined as 3.89~4.02 with a pycnometer using distilled water and removing bubbles by a vacuum pump. The specific gravity as calculated from the chemical composition and the unit-cell dimensions which are to be described later is 4.20. The discrepancy between these values is rather large, but explanation might possibly be found in the very fine-grained and closely coagurated nature of osarizawaite.

Osarizawaite is greenish-yellow or yellowish-green in thin section. The fine-grained character of the mineral precludes the measurement of any optical property other than the mean index of refraction. Measurements made on several specimens by means of immersion method yielded the mean index of refraction ranging from 1.735 to 1.757 for white light, and such tendency was perceptible that the more green-tinged grains have lower mean index. The birefringence is respectably high.

Fig. 1. Osarizawaite occurring in cavities (Cv) in kaolinized rock (pale grey). Limonite (Lm) covers the wall of cavity which in turn is covered by osarizawaite. Q=quartz.

Fig. 2. Osarizawaite (dark grey) filling interstitial space of anglesite (pale grey) crystallized around vein-quartz (Q). The grey area on the right rich in cavity is an aggregate of very fine-grained osarizawaite.

Fig. 3. Magnified figure of a part of Fig. 2.

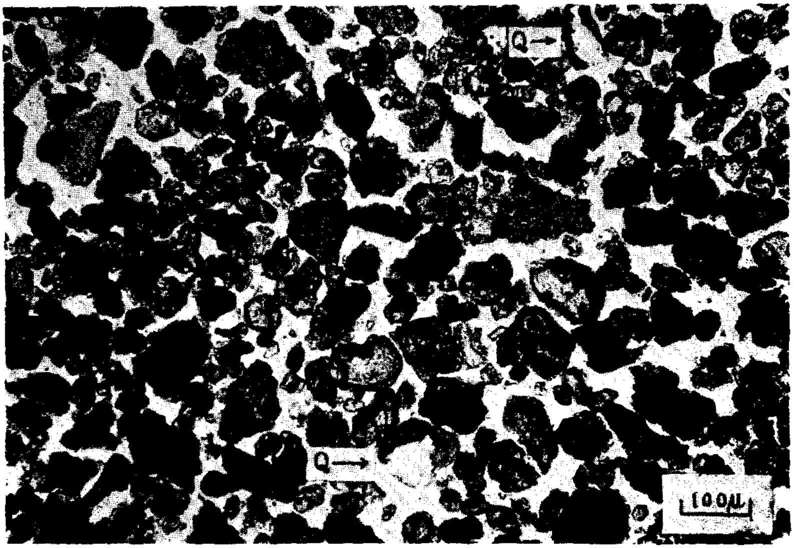

Fig. 4. Concentrate of osarizawaite.
A quartz (Q) grain at lower part is locked with osarizawaite, and one at upper part is stained partly with limonite. All the others are osarizawaite. At upper-left part or other several places, hexagonal outline of osarizawaite is recognized.

Radioactivity was not recognized.

Chemical properties

The mineral is insoluble in water and practically shows no reaction to nitric acid. Only the boiling concentrated hydrochloric or sulphuric acid disintegrates the mineral perfectly and precipitates lead chloride or lead sulphate. Also, the mineral is almost insoluble in the boiling ammonium acetate solution (Huffman's method)[3].

The standard procedures of chemical analysis were employed for each components except water. Total water was determined by the absorption method heating at 500° ± 10°C. The limitation of the temperature and the division of the total water into $H_2O(+)$ and $H_2O(-)$ were based on the dehydration test later described.

The result of the chemical analysis on the prepared concentrate is shown in Table 1. The presence of SiO_2 is caused by a small amount of quartz as were recognized under the microscope. The zinc may be a minor substituent for copper, judging from the similarity of ionic radii ($Zn^{2+}=0.83$, $Cu^{2+}=0.83$)[2], although in sulphate minerals such a illustrative instance has not yet been known as in some carbonates or phosphates, for instance, the relation between malachite and zincrosasite[7] or the substitution in veszelyite. The source of CO_2 was not ascertained, because no carbonate mineral was recognized in the concentrate under the microscope, in spite of the possibility of contamination of the accompanying carbonate minerals.

A qualitative spectrographic analysis of the mineral showed the presence of Mn and Ag in thousandths or less of one per cent.

By the result shown in Table 1, osarizawaite conforms to the formula $Pb(Cu_{0.98}Zn_{0.02})(Al_{0.81}Fe_{0.19})_2(SO_4)_2(OH)_6$. This formula resembles that of beaverite $PbCu(Fe_{0.75}Al_{0.25})_2(SO_4)_2(OH)_6$ described in "Dana's The System of Mineralogy"[5] (abbreviated to "Dana" hereafter), but there is a remarkable contrast between them in the ratio of Al to Fe.

Table 1. Chemical composition of osarizawaite.

	Wt. %	Mol. prop.	Mol. rat.		Recalc.	Ideal
PbO	32.72%	0.1466		1.02	35.41%	35.45%
CuO	11.27	0.1417	0.99	1.01	12.20	12.40
ZnO	0.22	0.0027	0.02		0.24	0.24
Fe_2O_3	4.43	0.0277	0.19	1.04	4.79	4.72
Al_2O_3	12.35	0.1211	0.85		13.36	13.18
SO_3	22.92	0.2862		2.00	24.80	25.43
SiO_2	2.18					
As	0.00					
CaO	0.00					
MgO	0.00					
CO_2	0.45					
$H_2O(+)$	8.50	0.4717		3.30	9.20	8.58
$H_2O(-)$	4.05					
Total	99.09%				100.00%	100.00%

Recalc.: Recalculated to 100% after deducting impurities.
Ideal: Ideal $Pb(Cu, Zn)(Al, Fe)_2(SO_4)_2(OH)_6$ in which $CuO/ZnO=1417/27$ and $Fe_2O_3/Al_2O_3=277/1211$.

X-ray data

X-ray powder diffraction patterns of osarizawaite were taken under the operating conditions as follows:

X-ray radiation: Cu$K\alpha$ (Ni-filtered), 35kV., 10mA.
Scale factor: 16, multiplier: 1, time constant: 4 sec.,
divergence slit: 2½°, receiving slit: 0.2 m/m, scatter slit: 2½°.
scanning speed: 1°/min.

The X-ray powder lines* are listed in Table 2. On the basis of its crystal form under the microscope and its similarities to beaverite in chemical composition, the indexing of the reflections of the mineral

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* The data obtained independently by T. Watanabe and A. Kato, on the fraction of the same material showed good agreements in *d*-spacings within the range of ±0.003 and in unit cell dimensions, $a_0=7.05$Å., $c_0=17.22$Å., with the writer's results.

Table 2. X-ray powder data for Osarizawaite.

$h\ k\ l$	I	$d_{obs.}$	$d_{calc.}$*
0 0 3 1 0 1	70	5.79Å	5.74Å 5.75
0 1 2	5	4.98	4.98
1 0 4, 1 1 0	60	3.52	3.52
0 1 5, 1 1 3	100	3.00	3.00
0 0 6 2 0 2	60	2.87	2.87 2.88
0 2 4	20	2.49	2.49
1 0 7 2 0 5, 1 2 1	60	2.28	2.28 2.29
1 1 6, 1 2 2	30	2.23	2.23
2 1 4, 0 1 8, 3 0 0	10	2.03	2.03
0 0 9 0 2 7 1 2 5 0 3 3	30	1.918	1.915 1.916 1.917 1.918
2 0 8 2 2 0	20	1.762	1.760 1.762
1 1 9 2 1 7 2 2 3, 1 3 1	20	1.683	1.682 1.683 1.685
1 0 10 0 3 6 3 1 2	5	1.660	1.658 1.660 1.661
0 1 11 3 1 5, 4 0 1	10	1.519	1.517 1.520
0 2 10 2 2 6 0 4 2	30	1.500	1.501 1.502 1.503
0 0 12 4 0 4	5	1.436	1.436 1.439
2 0 11, 0 3 9 1 3 7 0 4 5, 3 2 1	10	1.397	1.394 1.395 1.396
1 1 12 3 1 8 3 2 4, 1 4 0	5b	1.332	1.330 1.331 1.332
1 0 13 1 2 11 2 2 9, 4 0 7 2 3 5, 1 4 3	10b	1.298	1.295 1.296 1.297 1.298

* Calculated on the basis of $a_0=7.05$Å., $c_0=17.23$Å.

was carried out on the assumption that the mineral is a member of the rhombohedral system and referring to that of hidalgoite$^{6)}$. The unit cell dimensions thus obtained for both the hexagonal cell and the corresponding rhombohedral cell are: $a_0=7.05\text{Å}$., $c_0=17.23\text{Å}$., $c_0/a_0=2.44$, $Z=3$; $a_{rh}=7.04\text{Å}$., $\alpha=60°06'$, $Z=1$. Calculated d-spacings from these parameters are in good agreement with the measured values as shown in Table 2, and the indices satisfy the equation $-h+k+l=3n$, which is the prerequisite to the conventional setting of the rhombohedral cell indexed on hexagonal axes. Thus, this X-ray powder data may admit the mineral to be a member of rhombohedral system. On the other hand, the tendency that each reflection corresponds to two or three indices strongly indicates the pseudo-isometric character which is one of the common features of the alunite group.

Thermal analyses

(1) *Dehydration test*

The loss of weight of osarizawaite on heating was measured using 200 mg. of the material. The result shown in Fig. 5 was obtained after the corrections of errors which might be caused by buoyancy or convection of air on high temperature, referring to the blank test. The material was free from an absorbed or adhered water as it had been stored in a decicater for a certain time.

As shown in Fig. 5, no water is driven off upto about 400°C. in effect. At above 400°C. the losses in weight take place in three or four steps, i.e., the abrupt and distinct changes at about 400°, 600° and 850°C. and another obscure small step at 750°~800°C. This obscure step is exposed more distinctly in the differencial thermal analysis curve mentioned later.

Since the figure of loss of weight at about 400°C. approximately coincides with the content of $H_2O(+)$ measured by absorption method, it is doubtless that the first step of weight loss is the result of the dehydration of crystal water. The losses at about 600°C. and the higher temperatures are derived from expelled SO_3, that was con-

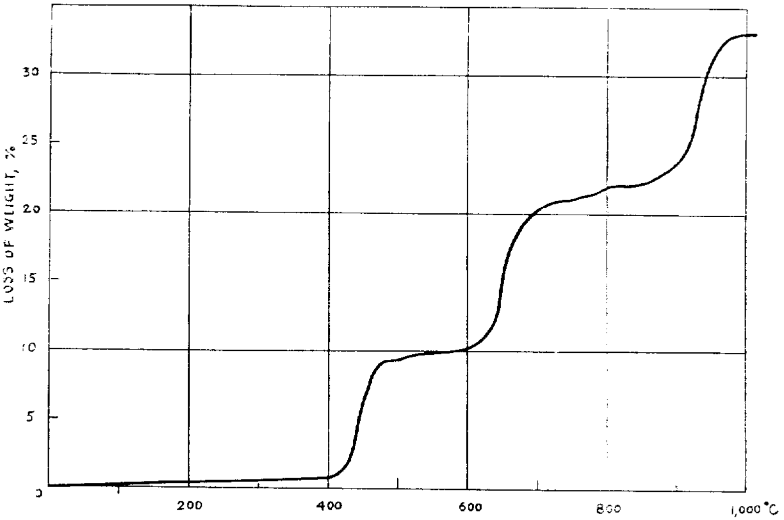

Fig. 5. Dehydration curve of osarizawaite.
Heating rate: 2°C/min. Thermo-balance: Ôshima-Fukuda M.

firmed by the rising of white smoke as well as by the detection of SO_4 ions in the distilled water after it was used to wash the dew-drops stuck on the quartz wire or the inside wall of the glass tube of thermobalance.

Therefore, the mineral is considered to decompose through the process of dehydration at about 400°C. and of expelling SO_3 at about 600° and 850°C.

(2) *Differential thermal analysis*

The differential thermogram of osarizawaite is given in Fig. 6.

The material was left as it was in room. In Fig. 6, a small endothermic peak at 100°C. may be caused by dehydration of the absorbed water, and compared with the dehydration curve, a remarkable endothermic peak at 460°C. is due to the dehydration of crystal water, while the endothermic peaks at 760° and 1,000°C. are due to vaporization of SO_3. The cause of the endothermic peak at 830°C. which may correspond with the obscure step between 750° and 800°C.

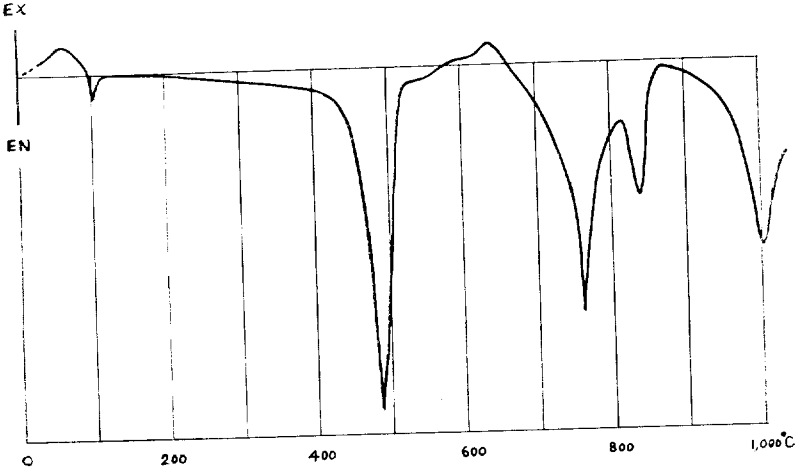

Fig. 6. Differential thermal analysis curve of osarizawaite.
Heating rate: 10°C/min.

in the dehydration curve has not been ascertained, because nothing that may invite the peak was present in the material inferring from the results of microscopic observation or chemical analysis. This insuspectable peak may be due to a previous and partial expulsion instead of whole expulsion of SO_3 at one stroke. The question will be left for further study, for instance, X-ray analysis of the product after heating at each definite temperature.

An exothermic curve below 100°C. is caused by insufficient adjustment of the apparatus, but a small exothermic peak at about 640°C. preceding the first expulsion of SO_3 is considered to be caused by transition of Al_2O_3 to α-Al_2O_3 as recognized in the d.t.a. curve of alunite[4].

Comparison of osarizawaite with beaverite

The properties of osarizawaite above described are summarized in Tables 3 and 4 comparing with those of beaverite.

There is striking resemblance between their chemical compositions, namely the molecular ratios of their components except Fe_2O_3

Table 3. Chemical compositions of osarizawaite and beaverite.

	Osarizawaite			Beaverite 1			Beaverite 2		
	Wt. %	Mol. rat.		Wt. %	Mol. rat.		Wt. %	Mol. rat.	
PbO	35.41%		1.02	33.71%		1.00	32.50%		1.00
CuO	12.20	0.99	1.01	12.02		1.00	10.74		0.92
ZnO	0.24	0.02							
Fe_2O_3	4.79	0.19	1.04	18.08	0.75	1.00	19.13	0.82	1.09
Al_2O_3	13.36	0.85		3.85	0.25		4.03	0.27	
SO_3	24.80		2.00	24.18		2.00	23.60		2.02
$H_2O(+)$	9.29		3.30	8.16		3.00	10.00		3.80
Total	100.00%			100.00%			100.00%		

Osarizawaite: Recalculated to 100 after deducting impurities.
Beaverite 1: Ideal Pb $(Cu, Fe, Al)_3 (SO_4)_2 (OH)_6$ with Cu : Fe : Al = 2 : 3 : 1 (after Dana[5]).
Beaverite 2: Beaver County, Utah. After deducting 10.05% insol. and recalculating to 100 (after Butler and Schaller[1]).

Table 4. Physical and optical properties of osarizawaite and beaverite.

	Osarizawaite	Beaverite ("Dana"[5])
Crystal system	hexagonal-R, pyramidal (?)	hexagonal-R, ditrigonal-pyramidal*
Space group	——	R3m
a_0	7.05A.	7.203Å.
c_0	17.23A.	16.94 Å.
c_0/a_0	2.444	2.351
Habit	earthy and friable masses	earthy and friable masses
Colour	greenish-yellow	canary-yellow
Specific gr.	3.89～4.02, 4.20 (calc.)	4.36, 4.31 (calc.)
Optical prop.	——	uniaxial negative
	$n=1.735\sim1.757$	ω variable, 1.85 ± 0.02
	birefringence strong	birefringence strong
Solubility	insol. in water, HNO_3, $NH_4C_2H_3O_2$,	insol. in water
	sol. in HCl or H_2SO_4 (conc, boil)	sol. in HCl (boil)

* Crystals of beaverite have not been measured. X-ray powder diffraction patterns show that it is rhombohedral and has cell dimensions close to those of other minerals of the alunite group. For this reason it is assigned to the ditrigonal-pyramidal class ("Dana"[5]).

and Al_2O_3 are much the same. The content of H_2O in beaverite will be discussed later. Only the ratio of Fe_2O_3 and Al_2O_3 is reversed between them. On the other hand, as shown in Table 4, there are respectable differences between them in the unit cell dimensions, colour, specific gravity and mean index of refraction, in spite of the resemblance of their crystallographic genealogies, modes of occurrence* or other general properties. The similar relation is found between jarosite and alunite which belong to the same group as beaverite. In regard to the unit cell dimensions, osarizawaite resembles alunite ($a_0=6.96$Å., $c_0=17.35$Å.) in contrast to the close approximation of beaverite to jarosite ($a_0=7.20$Å., $c_0=17.00$Å.). Accordingly, the differences in physical and optical properties between osarizawaite and beaverite are considered to be caused by the remarkable contrast of ratios of Fe_2O_3 to Al_2O_3.

Beaverite has been reported by B. S. Butler and W. T. Schaller[1] in 1911 as a new mineral produced from the Horn Silver mine in Beaver County, Utah, and according to their original paper, it is a name given for a mineral that have the idealized chemical formula of $CuO \cdot PbO \cdot Fe_2O_3 \cdot 2SO_3 \cdot 4H_2O$ in which the copper and lead are assumed to exist in equal molecular amounts and a little ferric iron is replaced by alumina, or the formula can be written more exactly as $4CuO \cdot 4PbO \cdot 3Fe_2O_3 \cdot Al_2O_3 \cdot 8SO_3 \cdot 16H_2O$ following to their chemical analysis. But there are some confusions regarding to the expression of the chemical formula. Namely it is described as $Pb(Cu, Fe, Al)_3(SO_4)_2(OH)_5$ in the "Dana"[5] or as $[PbCu(Fe, Al)_2(SO_4)_2(OH)_6 \cdot H_2O\,?]$ by A. N. Winchell[8], although both of them were derived from the data in the original paper.

The formula shown by original authors is also applicable to that by Winchell, and it has just one molecule of H_2O in excess compared with the formula in the "Dana". The authors gave the figure of

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* The minerals associated with osarizawaite have also been recognized with beaverite by Butler and Schaller[1].

molecular ratio 3.8 to $H_2O(+)$ of beaverite as the result of their analysis as shown in Table 3, but the accuracy of the figure seems to be still open to question, because the authors themselves noticed experimental accident in their paper. Taking the result of the writer's study on osarizawaite into consideration, $3H_2O$ (or $6OH$) may be appropriate to the crystal water of beaverite as described in the "Dana".

The components of Cu, Fe and Al in beaverite are lumped together as $(Cu, Fe, Al)_3$ in the "Dana"[5], while by Winchell[8] as $Cu(Fe, Al)_2$. The replacement between Cu^{2+} and Fe^{3+} or Al may be very difficult according to the differences between their ionic radii or their behaviors as metallic ion. In fact, such an instance has not been known. Furthermore, the lead and copper are equal in molecular ratio in osarizawaite, as well as in beaverite, while the ratios of ferric iron and aluminum are reversed. Taking those facts into consideration, it may be reasonable to express the relation of Cu, Fe and Al in the formula of beaverite as $Cu(Fe, Al)_2$ after the description by Winchell.

Referring to beaverite, the chemical formula of osarizawaite should be shown as $PbCu(Al, Fe)_2(SO_4)_2(OH)_6$ or could be written as $PbCuAl_2(SO_4)_2(OH)_6$ corresponding to the idealized formula of beaverite. The two minerals are inferred to form a subgroup in the alunite group characterized by lead and copper. The distinction between beaverite and osarizawaite is essentially made in ferric iron and aluminum contents, the former corresponding to jarosite, while the latter to alunite.

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