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OSAKAITE, $Zn_4SO_4(OH)_6{\bullet}5H_2O$, A NEW MINERAL SPECIES FROM THE HIRAO MINE, OSAKA, JAPAN

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ABSTRACT

Osakaite, ideally $Zn_4SO_4(OH)_6{\bullet}5H_2O$, is a new mineral species that occurs on the gallery wall and in cracks in altered shale at the Hirao mine, Minoo City, Osaka Prefecture, Japan. The mineral is found as stalactitic aggregates of hexagonal platy crystals up to 0.5 mm across and 0.01 mm in thickness. The associated minerals are hydrozincite, smithsonite, "chlorite" and "limonite". Osakaite is either pale blue to colorless or white, and is transparent with a pearly luster. It has a perfect {001} cleavage. The mineral is triclinic, and the most probable space-group is $P\bar{1}$, with *a* 8.358(5), *b* 8.337(4), *c* 11.027(2) Å, α 94.79(2), β 83.16(2), γ 119.61(4)°, *V* 663.0(4) Å^3 and *Z* = 2. The strongest lines in the X-ray powder-diffraction pattern [*d* in Å(*I*)(*hkl*)] are: 10.96(100)(001), 2.717(21)(3$\bar{1}$1), 1.574(18)(5$\bar{3}$3,2$\bar{4}$5,5$\bar{2}$3), 3.642(17)(003), and 5.47(16)(002). Inductively coupled plasma – atomic emission spectrometry and thermogravimetric analysis gave ZnO 55.30, CuO 3.44, SO_3 14.66, H_2O 26.01, for a total of 99.41 wt%. The empirical formula is $(Zn_{3.75}Cu_{0.24})_{\Sigma 3.99}(SO_4)_{1.01}(OH)_{5.96}{\bullet}4.99H_2O$ on the basis of O = 15. The mineral is optically biaxial negative with α 1.532(2), β 1.565(2), γ 1.567(2), and $2V_{calc}$ = 27.2°. The density is 2.70(2) g/cm^3 (meas.) and 2.75 g/cm^3 (calc.). The Vickers microhardness is 20.3 (16.5–22.8) kg/mm^2 (10 g load), corresponding to a Mohs hardness of 1. It is likely that at the Hirao mine, osakaite was formed in Zn-, Cu- and SO_4-bearing groundwater derived from sphalerite and chalcopyrite in the host rock at around 20°C.

Keywords: osakaite, basic zinc sulfate, namuwite, Hirao mine, Osaka, Japan.

SOMMAIRE

La nouvelle espèce osakaïte, de composition idéale $Zn_4SO_4(OH)_6{\bullet}5H_2O$, a été découverte sur la paroi d'une gallerie et dans les fissures d'un shale altéré à la mine Hirao, près de la ville de Minoo, préfecture d'Osaka, au Japon. Le minéral se présente en agrégats stalactitiques de cristaux hexagonaux en plaquettes atteignant un diamètre de 0.5 mm et une épaisseur de 0.01 mm. Lui sont associées hydrozincite, smithsonite, "chlorite" et "limonite". Les cristaux d'osakaïte sont soit bleu pâle à incolores ou blancs, et transparents avec un éclat nacré. Le clivage {001} est parfait. Il s'agit d'un minéral triclinique, avec le groupe spatial probable $P\bar{1}$, et les paramètres *a* 8.358(5), *b* 8.337(4), *c* 11.027(2) Å, α 94.79(2), β 83.16(2), γ 119.61(4)°, *V* 663.0(4) Å^3 et *Z* = 2. Les cinq raies les plus intenses du spectre de diffraction, méthode des poudres [*d* en Å(*I*)(*hkl*)] sont: 10.96(100)(001), 2.717(21)(3$\bar{1}$1), 1.574(18)(5$\bar{3}$3,2$\bar{4}$5,5$\bar{2}$3), 3.642(17)(003), et 5.47(16)(002). Une analyse avec un plasma à couplage inductif et spectrométrie de masse, et une analyse thermogravimétrique, ont donné ZnO 55.30, CuO 3.44, SO_3 14.66, H_2O 26.01, pour un total de 99.41% (poids). La formule empirique est $(Zn_{3.75}Cu_{0.24})_{\Sigma 3.99}(SO_4)_{1.01}(OH)_{5.96}{\bullet}4.99H_2O$ sur une base de 15 atomes d'oxygène. Le minéral est biaxe négatif, avec α 1.532(2), β 1.565(2), γ 1.567(2), et $2V_{calc}$ = 27.2°. La densité est 2.70(2) g/cm^3 (mes.) et 2.75 g/cm^3 (calc.). La microdureté de Vickers est 20.3 (16.5–22.8) kg/mm^2 (avec une charge de 10 g), ce qui correspond à une dureté de Mohs de 1. Il semble tout probable que l'osakaïte se soit formée à partir d'eau souterraine porteuse de Zn, Cu, et SO_4, dérivés de la sphalérite et la chalcopyrite dans la roche hôte, à environ 20°C.

(Traduit par la Rédaction)

Mots-clés: osakaïte, sulfate basique de zinc, namuwite, mine Hirao, Osaka, Japon.

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Introduction

Rare copper zinc sulfate minerals such as ktenasite (Ohnishi *et al*. 2002), ramsbeckite (Ohnishi *et al*. 2004), schulenbergite and the Zn-dominant analogue of schulenbergite (Ohnishi *et al*. 2007) have been identified on the gallery wall and in cracks in altered shale at the Hirao mine, Osaka Prefecture, Japan. During a survey of secondary minerals in the same mine, one of the authors (M.O.) collected pale blue to colorless platy crystals in June 2, 1999. Subsequent X-ray powder-diffraction and chemical analyses confirmed it to be the natural analogue of synthetic basic zinc sulfate pentahydrate, $Zn_4SO_4(OH)_6 \bullet 5H_2O$, reported by Bear *et al*. (1986, 1987).

The new basic zinc sulfate mineral was named osakaite after the type locality, in Osaka Prefecture. The mineral data and the name were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA No. 2006–049). The holotype specimen of osakaite is deposited at the National Science Museum, Tokyo, under the registration number NSM–M28983.

Occurrence

Small deposits of Cu, Zn, Pb, Fe and Mn can be found in the Tamba and Ultra–Tamba terranes around Minoo (Minoh) City, but all the mines exploiting those deposits are now closed. The Hirao mine (lat. 34°50'N, long. 135°28'E) is developed in shale belonging to the Minoo complex of the Tamba terrane, of Jurassic age (Matsuura *et al*. 1995), and located about 17 km north of Osaka City (Fig. 1). The primary ore-minerals are sphalerite, chalcopyrite, pyrite and galena. Among them, sphalerite is predominant, and the mineral is disseminated through the host rock, which consists of "chlorite" altered during a hydrothermal alteration process. In the mine, many secondary minerals such as smithsonite, hydrozincite, schulenbergite, the Zn-dominant analogue of schulenbergite, brianyoungite, hemimorphite, brochantite, ramsbeckite, aurichalcite, malachite, azurite, posnjakite and ktenasite occur on the gallery wall and in cracks in the altered shale (Ohnishi *et al*. 2001, 2002, 2004, 2007).

Osakaite is one of the secondary minerals. The mineral occurs in two different aspects. The first type

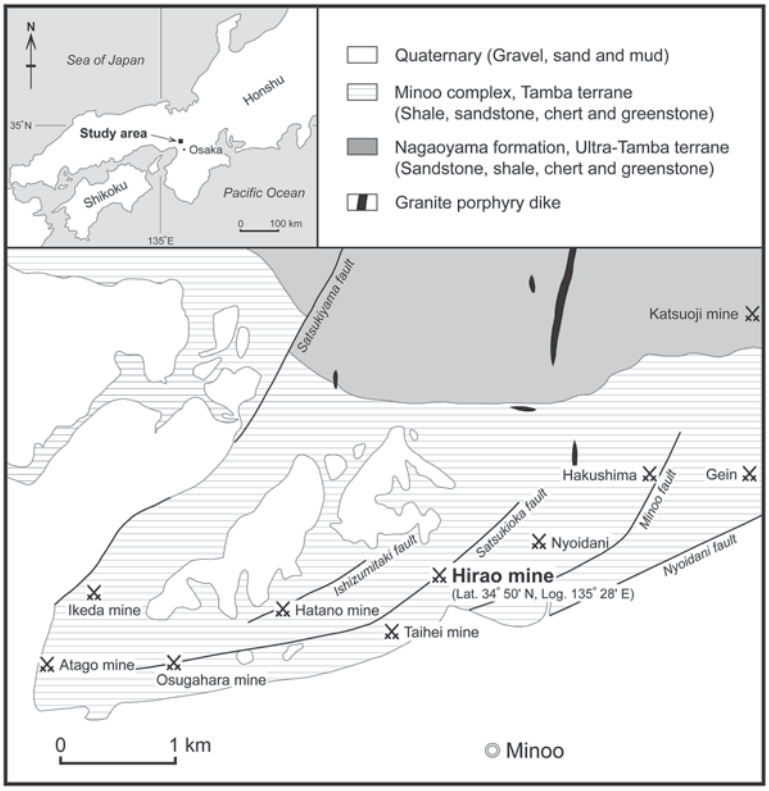

FIG. 1. Geological map around the Hirao mine at Minoo City, Osaka Prefecture, Japan (modified from Matsuura *et al*. 1995, Fujita & Kasama 1982).

occurs as hexagonal platy crystals up to 0.5 mm across and 0.01 mm in thickness in the form of stalactitic aggregates up to 2 cm long (Fig. 2). The second type occurs in cracks in the altered shale. The associated minerals are hydrozincite, smithsonite, "chlorite" and "limonite". Secondary electron (SE) and back-scattered electron (BSE) images of osakaite are shown in Figure 3.

Physical and Optical Properties

Osakaite is either pale blue to colorless or white, and is transparent with a pearly luster. The streak is white to pale blue. In thin sections, the mineral is colorless to pale blue. The crystals of osakaite are somewhat flexible, and have a perfect {001} cleavage. Optically, the mineral is biaxial negative, α 1.532(2), β 1.565(2), γ 1.567(2) and $2V_{calc}$ = 27.2°. The elongation is positive. The density measured using a Clerici solution is 2.70(1) g/cm^3, and the calculated density is 2.75 g/cm^3 based on the empirical formula and the refined unit-cell parameters. The Vickers microhardness is 20.3 (16.5–22.8) kg/mm^2 (10 g load), corresponding to a Mohs hardness of 1. No fluorescence effect is observed under short- or long-wave ultraviolet light. Osakaite is easily soluble in dilute HCl and HNO_3.

X-Ray Crystallography

X-ray powder-diffraction (XRD) data for osakaite were obtained at 16°C using a Rigaku RAD–1B diffractometer at Okayama University with Ni-filtered Cu*K*α radiation generated at 30 kV and 15 mA (Table 1). The XRD data were indexed on the basis of the unit cell reported for synthetic $Zn_4SO_4(OH)_6{\bullet}5H_2O$ by Bear *et al*. (1987). The unit-cell parameters refined by least squares from the XRD data are *a* 8.358(5), *b* 8.337(4), *c* 11.027(2) Å, α 94.79(2), β 83.16(2), γ119.61(4)°, *V* = 663.0(4) Å^3 and *Z* = 2. The space group is inferred to be $P\bar{1}$, by analogy with synthetic $Zn_4SO_4(OH)_6{\bullet}5H_2O$. A preferred orientation effect owing to the perfect {001} cleavage may be present. The single-crystal X-ray studies could not be carried out owing to the lack of suitable crystals.

Infrared Spectroscopy

The infrared absorption spectrum of osakaite was measured with a HITACHI 270–50 infrared spectrophotometer at Okayama University of Science; we used a KBr pellet method to scan the wavenumber region 4000 to 250 cm^{-1} (Fig. 4). The strong absorption band at 3420 cm^{-1} is attributed to O–H stretching vibrations, and the weak absorption band at 1620 cm^{-1} is attributed to H–O–H bending vibrations. The absorption bands at 1120, 1070 and 960 cm^{-1} are attributed to ν_3 and ν_1 SO_4-stretching vibrations, and 650 and 460 cm^{-1} are attributed to ν_4 and ν_2 SO_4-bending vibrations, respectively. Several absorption bands in the low-frequency

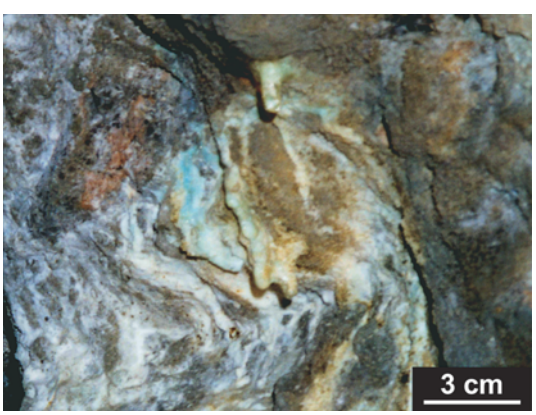

FIG. 2. Stalactitic mode of occurrence of osakaite at the Hirao mine.

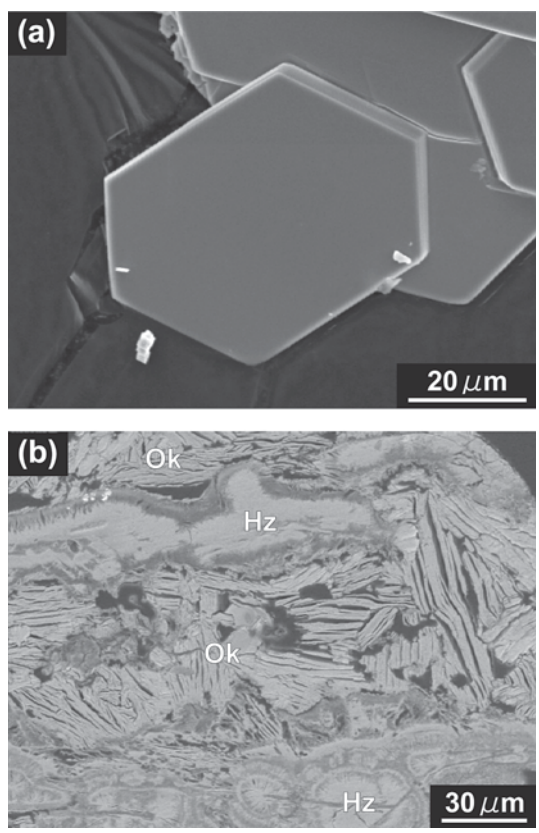

FIG. 3. Secondary electron (a) and back-scattered electron (b) images of osakaite. Abbreviations: Ok, osakaite; Hz, hydrozincite.

TABLE 1. REPRESENTATIVE X-RAY POWDER-DIFFRACTION DATA FOR OSAKAITE

			1			2					1			2	
h	*k*	*l*	d_{calc}	d_{meas}	*I*	*d*	*I*	*h*	*k*	*l*	d_{calc}	d_{meas}		*d*	*I*
0	0	1	10.94	10.96	100	10.95	100	0	3	2	2.187			2.184	3
1	0	0	7.24	7.21	1	7.23	5	1	$\bar{1}$	5	2.165			2.160	4
1	0	1	6.30	6.30	2	6.34	5	$\bar{1}$	3	3	2.118			2.121	2
0	$\bar{1}$	1	6.12			6.08	5	2	$\bar{4}$	1	2.073	2.071	3	2.064	5
0	1	1	5.96			6.00	6	$\bar{1}$	1	5	2.028			2.025	5
$\bar{1}$	0	1	5.80			5.76	5	$\bar{4}$	1	0	2.000	2.000	2	1.999	3
0	0	2	5.47	5.47	16	5.46	100	4	$\bar{3}$	1	2.000				
0	1	2	4.31	4.29	2	4.32	5	1	1	5	1.970			1.969	3
$\bar{1}$	2	0	4.15	4.16	7	4.17	8	$\bar{1}$	4	1	1.951	1.950	1	1.955	4
2	1	1	4.04			4.05	2	1	2	4	1.951				
$\bar{1}$	$\bar{1}$	1	3.872			3.85	2	$\bar{3}$	3	3	1.899	1.899	2	1.897	3
$\bar{1}$	2	1	3.779			3.80	3	$\bar{4}$	2	2	1.867	1.866	2	1.865	4
$\bar{2}$	1	1	3.734			3.73	3	4	$\bar{3}$	3	1.843	1.844	1	1.844	4
0	0	3	3.648	3.642	17	3.64	77	1	$\bar{1}$	6	1.819	1.819	4	1.819	12
2	$\bar{1}$	2	3.514	3.512	3	3.52	11	$\bar{2}$	0	5	1.802	1.803	2	1.808	6
1	$\bar{2}$	2	3.451	3.450	2	3.44	8	4	$\bar{4}$	1	1.802				
1	$\bar{1}$	3	3.417	3.414	4	3.41	18	0	3	4	1.786	1.786	2	1.788	6
0	1	3	3.222	3.229	8	3.23	27	0	4	1	1.779	1.779	1	1.772	4
$\bar{1}$	2	2	3.182	3.200	7	3.20	15	4	$\bar{2}$	4	1.757			1.757	3
$\bar{2}$	1	2	3.131	3.131	5	3.13	22	0	1	6	1.757				
0	$\bar{2}$	2	3.061	3.064	2	3.05	3	1	$\bar{2}$	6	1.724	1.723	2	1.726	6
0	2	2	2.982			3.00	2	1	2	5	1.722				
2	$\bar{1}$	3	2.918			2.919	3	4	$\bar{4}$	3	1.688			1.688	5
$\bar{2}$	2	2	2.848	2.852	2	2.853	6	3	1	4	1.676			1.678	2
1	1	3	2.803	2.803	1	2.810	4	$\bar{4}$	3	3	1.662			1.662	3
3	$\bar{1}$	1	2.715	2.717	21	2.726	14	1	$\bar{4}$	4	1.662				
1	$\bar{1}$	4	2.662	2.663	8	2.665	11	5	$\bar{3}$	1	1.658	1.658	2	1.655	3
$\bar{3}$	1	1	2.575			2.578	7	$\bar{3}$	2	5	1.609	1.609	2	1.612	6
$\bar{3}$	2	1	2.559	2.562	9	2.567	16	$\bar{5}$	3	1	1.600			1.600	6
2	$\bar{3}$	2	2.533	2.532	7	2.535	17	5	$\bar{3}$	3	1.574	1.574	18	1.577	12
1	$\bar{3}$	2	2.507			2.507	4	2	$\bar{4}$	5	1.574				
1	2	2	2.467	2.465	4	2.470	11	5	$\bar{2}$	3	1.574				
$\bar{1}$	$\bar{2}$	2	2.442			2.449	4	3	$\bar{4}$	5	1.556	1.556	3	1.559	8
$\bar{2}$	2	3	2.418			2.419	6	2	2	5	1.542			1.543	3
3	0	1	2.402	2.404	4	2.400	4	$\bar{3}$	3	5	1.527	1.527	2	1.531	5
0	$\bar{3}$	1	2.373			2.368	3	2	$\bar{2}$	7	1.499	1.499	2		
1	1	4	2.330	2.327	4	2.325	10	2	4	1	1.364	1.364	3		
2	$\bar{2}$	4	2.309			2.306	4	2	6	1	1.364				
2	0	4	2.284	2.283	3	2.286	7	$\bar{1}$	$\bar{2}$	7	1.351	1.351	2		
0	$\bar{3}$	2	2.233			2.237	4	0	$\bar{1}$	8	1.351				
1	2	3	2.207	2.205	3	2.211	7	$\bar{1}$	$\bar{3}$	6	1.351				

1. Osakaite (present work).
2. Synthetic $Zn_4SO_4(OH)_6 \cdot 5H_2O$ (Bear *et al.* 1987).

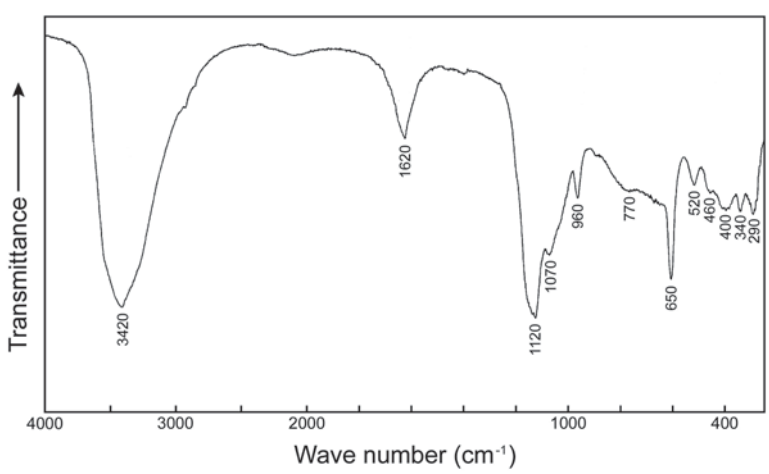

FIG. 4. Infrared absorption spectrum of osakaite.

region may be attributed to vibrations involving (Zn,Cu) O_6 octahedra and lattice modes.

THERMAL ANALYSIS

Thermogravimetry (TG) and differential thermal analysis (DTA) curves of osakaite were collected with a Rigaku TG–8120 thermal analyzer at Okayama University using a 20.5 mg sample in air from room temperature to 1000°C at a rate of 10°C/min (Fig. 5). Two endothermic peaks at 55° and 101°C correspond to the loss of H_2O molecules, and an endothermic peak at 296°C corresponds to the loss of the hydroxyl group. The losses are 14.83 and 11.18 wt.%, respectively. The XRD data and the electron-microprobe analyses of products heated to 500°C revealed the presence of ZnO and $ZnSO_4$. On the other hand, the product was entirely transformed into ZnO at 1000°C. From these results, the endothermic peak at 834°C suggests the loss of SO_3. The loss amounts to 14.66 wt.%.

CHEMICAL COMPOSITION

Chemical analyses were carried out using a JEOL JXA–8900R electron-microprobe analyzer at Okayama University of Science, with wavelength-dispersive spectrometry (15 kV and 12 nA). They revealed the presence of Zn, Cu, S and O. The Zn, S and O are principal constituents of osakaite, whereas the amount of Cu is minor. However, the electron-microprobe results are not reliable owing to the loss of H_2O molecules under vacuum conditions, and the mineral is unstable under the electron beam. The Zn and Cu contents were therefore determined with a Perkin–Elmer Optima 5300 DV inductively coupled plasma – atomic emission spectrometer (ICP–AES) at the Chiba Institute of Science. The 3.55 mg sample was dissolved in dilute HNO_3 before the analyses. The H_2O and SO_3 contents were determined by TG analysis from the weight loss between room temperature and 500°C, and between 600° and 1000°C, respectively. The average results of three ICP–AES analyses and the TG analysis are given in Table 2, along with the expected values for stoichiometric $Zn_4SO_4(OH)_6{\bullet}5H_2O$. The empirical formula of osakaite calculated on the basis of 15 atoms of oxygen is $(Zn_{3.75}Cu_{0.24})_{\Sigma 3.99}(SO_4)_{1.01}(OH)_{5.96}{\bullet}4.99H_2O$, which gives the ideal formula $Zn_4SO_4(OH)_6{\bullet}5H_2O$.

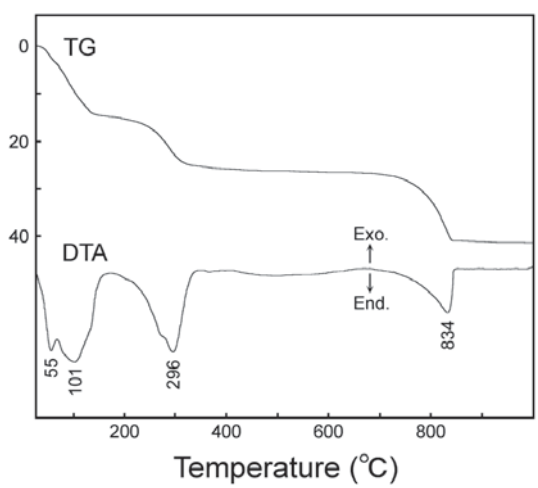

FIG. 5. Thermogravimetric and differential thermal analysis curves for osakaite.

DISCUSSION

Basic zinc sulfates having the general formula $Zn_4SO_4(OH)_6{\bullet}mH_2O$ with $m = 0, 0.5, 1, 3, 4$ and 5 have been reported (*e.g.*, Iitaka *et al.* 1962, Glibert 1977, Bear *et al.* 1986, 1987). In nature, the only tetrahydrate to have been found is namuwite, for which $m = 4$ (Bevins *et al.* 1982). The lower hydrates than namuwite may also occur in nature. Osakaite is a natural analogue of synthetic $Zn_4SO_4(OH)_6{\bullet}5H_2O$ and a higher hydrated analogue of namuwite. The XRD data for osakaite and synthetic $Zn_4SO_4(OH)_6{\bullet}5H_2O$ show close agreement. The crystal structures of synthetic $Zn_4SO_4(OH)_6{\bullet}5H_2O$ and namuwite were determined by single-crystal X-ray techniques by Bear *et al.* (1986) and Groat (1996), respectively. According to the results, the symmetry of synthetic $Zn_4SO_4(OH)_6{\bullet}5H_2O$ (triclinic, $P\bar{1}$) is different from that of namuwite (trigonal, $P\bar{3}$). The crystallographic data, physical and optical properties for osakaite, synthetic $Zn_4SO_4(OH)_6{\bullet}5H_2O$ and namuwite are compared in Table 3. Osakaite is the most H_2O-rich of the basic zinc copper sulfate minerals of the system (ZnO + CuO) – SO_3 – H_2O (Fig. 6).

Osakaite dehydrates to namuwite by the loss of a molecule of H_2O in a dry atmosphere, heating around 35°C, or X-ray irradiation (approximately 10 h at 30 kV and 15 mA, or 0.5 to 1 h at 40 kV and 200 mA). The basal spacing decreases from 11.0 to 10.5 Å. Rehydration occurs by immersion in water at around 20°C. The XRD pattern of the rehydrated material shows

TABLE 2. CHEMICAL COMPOSITION OF OSAKAITE

	1	range	2		1		2
ZnO wt.%	55.30	54.31–56.08	59.22	Zn *apfu*	3.75	3.99	4
CuO	3.44	3.39–3.48		Cu	0.24		
SO_3	14.66		14.56	S	1.01		1
H_2O	26.01		26.22	H	15.95		16
Total	99.41		100.00				

Columns: 1. osakaite (present work). 2. theoretical values for $Zn_4SO_4(OH)_6{\bullet}5H_2O$. The compositions are reported in atoms per formula unit (*apfu*) calculated on the basis of 15 atoms of oxygen.

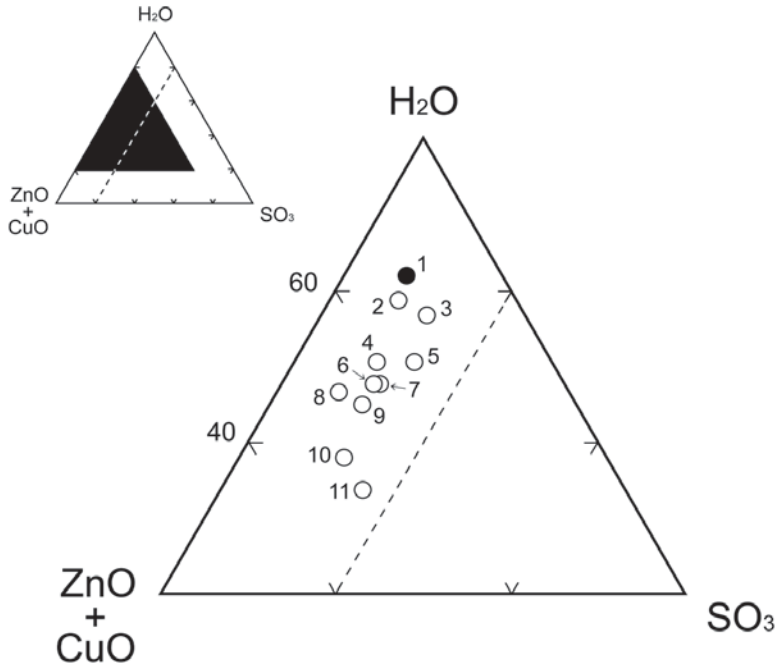

FIG. 6. The basic zinc copper sulfate minerals displayed in term of the diagram (ZnO + CuO) – SO_3 – H_2O. Minerals plotted: 1: osakaite, 2: namuwite, 3: ktenasite, 4: langite and wroewolfeite, 5: christelite, 6: ramsbeckite, 7: schulenbergite, 8: redgillite, 9: posnjakite, 10: brochantite, and 11: antlerite.

TABLE 3. COMPARISON OF CRYSTALLOGRAPHIC DATA, PHYSICAL AND OPTICAL PROPERTIES OF OSAKAITE, SYNTHETIC $Zn_4SO_4(OH)_6{\bullet}5H_2O$ AND NAMUWITE

	1	2	3
Formula	$Zn_4SO_4(OH)_6{\bullet}5H_2O$	$Zn_4SO_4(OH)_6{\bullet}5H_2O$	$(Zn,Cu)_4SO_4(OH)_6{\bullet}4H_2O$
System	Triclinic	Triclinic	Trigonal
Space group	probably $P\bar{1}$	$P\bar{1}$	$P3$
Unit-cell parameters			
a (Å)	8.358(5)	8.354(2)	8.331(6)
b (Å)	8.337(4)	8.350(2)	
c (Å)	11.027(2)	11.001(2)	10.54(1)
α (°)	94.79(2)	94.41(2)	
β (°)	83.16(2)	82.95(2)	
γ (°)	119.61(4)	119.93(2)	
V (Å^3)	663.0(4)	659.9(3)	634(1)
Z	2	2	2
Color	pale blue to colorless and white	n.g.*	pale sea-green
Streak	white to pale blue	n.g.	pale green
Luster	pearly	n.g.	pearly
Indices of refraction	α 1.532, β 1.565, γ 1.567	n.g.	1.577
Sign	biaxial (–)	n.g.	uniaxial
D_{meas} (g/cm^3)	2.70	2.79	2.77
D_{calc} (g/cm^3)	2.75	2.77	n.g.
Hardness (Mohs)	1	n.g.	2

Columns: 1. osakaite (present work), 2. synthetic $Zn_4SO_4(OH)_6{\bullet}5H_2O$ (Bear *et al.* 1986, 1987). 3. namuwite (Bevins *et al.* 1982, Groat 1996). * n.g.: not given.

broader X-ray reflections than the original osakaite. The dehydration–rehydration transition of osakaite has also been reported for the material synthesized by Bear *et al.* (1986, 1987).

The chemical analysis of osakaite by ICP–AES (Table 2) shows 6 atom % Cu at the Zn site, which is unlike the synthetic $Zn_4SO_4(OH)_6{\bullet}5H_2O$ (Bear *et al.* 1986, 1987), which does not incorporate Cu. The structure of $Zn_4SO_4(OH)_6{\bullet}5H_2O$ has Zn in two sites, one octahedral and the other tetrahedral in coordination. Eby & Hawthorne (1993) pointed out that the tetrahedrally coordinated Zn sites must be completely occupied by Zn, because Cu in zinc–copper oxysalts does not occur in tetrahedral coordination. The octahedral sites will, therefore, be filled by Cu, with the remaining sites being filled by Zn atoms. On the basis of the structure model (Bear *et al.* 1986), the chemical composition of osakaite from the Hirao mine can be rewritten as $[^{[VI]}(Zn_{5.51}Cu_{0.48})_{\Sigma 5.99}(OH)_{5.92}{}^{[IV]}Zn_{2.00}(OH)_{6.00}(H_2O)_{2.00}(SO_4)_{2.02}](H_2O)_{7.98}$ (30 O *apfu*). Osakaite contains 8 atom % Cu at the octahedrally coordinated Zn site.

Osakaite from the Hirao mine occurs as stalactites (Fig. 2). In the gallery where osakaite was found, the temperature of the groundwater is around 20°C. Bear

et al. (1986, 1987) synthesized $Zn_4SO_4(OH)_6 \bullet 5H_2O$ at room temperature by a chemical reaction using a $ZnSO_4$ solution and powdered zinc metal or zinc oxide. Therefore, it is likely that osakaite crystallized at around 20°C from Zn-, Cu- and SO_4-bearing groundwater derived from sphalerite and chalcopyrite in the host rock, and the gallery at the Hirao mine maintained the temperature and humidity conditions favorable to the existence of the osakaite.

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