Watanabeite, $Cu_4(As,Sb)_2S_5$, a new mineral from the Teine mine, Sapporo, Hokkaido, Japan

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Abstract

Watanabeite $Cu_4(As,Sb)_2S_5$, in which As>Sb, is a new copper sulphosalt that occurs with quartz in a hydrothermal vein at the Teine mine, Sapporo, Hokkaido, Japan. It is silvery lead–grey in colour with lead–grey streak. VHN_{100} = 253–306 kg/mm^2, brittle. It has no cleavage and the fracture is uneven. The measured density = 4.66(2) g/cm^3. The mean of six microprobe analyses gave Cu 41.1, Ag 0.1, Mn 0.3, As 15.4, Sb 14.3, Bi 2.4, S 26.2, a total of 99.8 wt.%, corresponding to: $(Cu_{3.94}Mn_{0.03}Ag_{0.01})_{\Sigma 3.98}(As_{1.25}Sb_{0.72}Bi_{0.07})_{\Sigma 2.04}S_{4.98}$ (basis: total atoms = 11), or ideally, $Cu_4(As,Sb)_2S_5$, with As > Sb. The X-ray powder pattern resembles that of tetrahedrite but has subsidiary diffractions and is similar to that of synthetic $Cu_{24}As_{12}S_{31}$ (Maske and Skinner, 1971). It is indexed on an orthorhombic cell with a = 14.51 Å, b = 13.30 Å, c = 17.96 Å (all ±0.01 Å), and Z = 16. Calculated density is 4.66 g/cm^3. It is optically similar to tetrahedrite but is grey and weakly bireflectant. No internal reflections were observed. The maximum and minimum reflectance values in air and in oil (n_D = 1.515) for the COM wavelengths are: 470 nm—32.5, 31.5; 17.7, 17.0, 546 nm—32.0, 31.1; 17.0, 16.3, 589 nm—31.1, 30.3; 16.1 m 15.5, 650 nm—30.0, 29.3; 15.0, 14.5%, respectively. Watanabeite forms masses composed of aggregates of minute grains up to 50 μm in diameter. Apart from some minute inclusions of emplectite, native bismuth and tennantite, it is almost monomineralic.

KEYWORDS: watanabeite, new mineral, Teine mine, Japan, copper sulphosalt.

Introduction

DURING the examination of Cu-bearing sulphosalts by the first author at the Natural History Museum, London, in 1990–91, it was found that a specimen labelled as tetrahedrite from the Teine mine, Sapporo, Hokkaido, Japan, supplied by the National Science Museum, Tokyo, was weakly anisotropic under the ore microscope. Microprobe analysis indicated the ideal formula to be $Cu_4(As,Sb)_2S_5$ with As>Sb. The X-ray powder pattern proved to be very similar to those of the tetrahedrite group, but involved many subsidiary diffractions, which are not indexable on the cubic cell of the tetrahedrite group, although all of the strongest diffractions correspond well with those of tetrahedrite, thus suggesting the existence of a subcell structure.

The mineral is named watanabeite in honour of the late Professor Takeo Watanabe (1907–1986), the former President of IAGOD (1972–1976), who first reported the occurrence of native tellurium and sylvanite from the Teine mine. The mineral and the name have been approved by the Commission on New Minerals and Mineral Names, International Mineralogical Association.

Type material is preserved at the National Science Museum, Tokyo, under the catalogue number NSM-M26138, University Museum, University of Tokyo, and at the Natural History Museum, London, as E.1400, BM 1992, 238.

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Occurrence

The specimen on which this characterisation is based is from a piece of massive silvery lead–grey ore preserved at the National Science Museum, Tokyo. Macroscopically, watanabeite is indistinguishable from tetrahedrite group minerals. The hand specimen appears to consist only of the metallic mineral and quartz (except for a very minor amount of the secondary copper mineral, devilline). Recently, two specimens containing watanabeite or its Sb-dominant analogue were collected from one of the dumps of the Takinosawa deposit of the mine, where it is embedded within quartz grains in aggregates of tetrahedrite group minerals.

Under the ore microscope, the watanabeite specimen is nearly monomineralic. Watanabeite is grey in plane-polarised light and resembles tetrahedrite. It is not noticeably bireflectant or pleochroic but is weakly anisotropic between crossed polars. This anisotropy revealed that the sample examined, though apparently massive, consisted of a mosaic of generally elongated (up to 50 μm long) or near-rectangular grains with linear grain boundaries (Fig. 1). Twinning was not observed. The electron microprobe survey identified inclusions of small grains of emplectite, native bismuth and tennantite–tetrahedrite. In this assemblage, the tennantite–tetrahedrite is slightly darker than watanabeite.

Chemical analysis

In Table 1, the results of the electron microprobe analysis are given together with the ranges of elements detected. The empirical formula for the average of six analyses calculated on the basis of total atoms = 11 is: $(Cu_{3.94}Mn_{0.03}Ag_{0.01})_{\Sigma 3.98}(As_{1.25}Sb_{0.72}Bi_{0.07})_{\Sigma 2.04}S_{4.98}$, or ideally $Cu_4(As,Sb)_2S_5$ where As>Sb. The principal compositional variation given by six analyses is represented by the substitution of Sb for As with As:Sb ≈ 12:8 to 11:9. Another specimen collected recently from the Takinosawa deposit has As:Sb ≈ 41:59 which may represent a possible Sb-rich member of a solid-solution series.

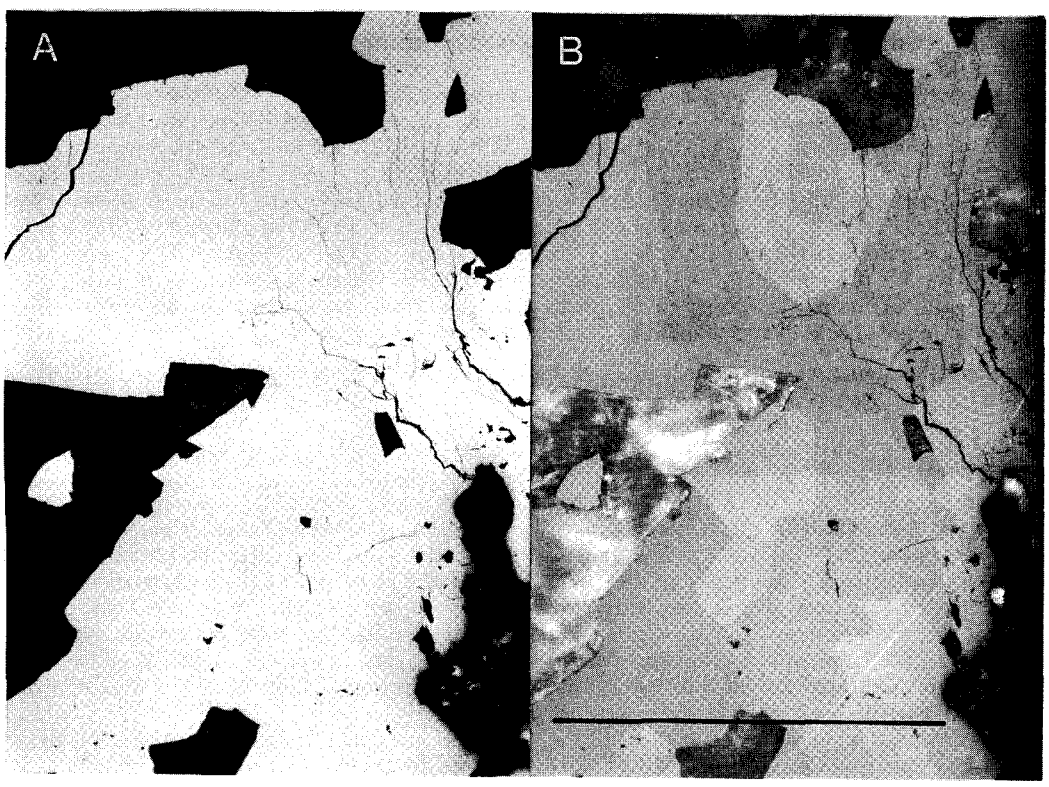

FIG. 1. Photomicrograph of grain aggregate of watanabeite to demonstrate the outline of grains and anisotropy; A in plane polarised light, B with crossed polars; Scale bar—0.5 mm.

Table 1. Chemical analyses of watanabeite

	1	2	3	4	5	6	1a	1b
Cu	41.1	40.91	42.23	41.21	41.12	40.78	3.94	
Ag	0.1	0.09	0.09	0.09	0.08	0.06	0.01	
Fe	0.0	0.00	0.01	0.13	0.12	0.18	0.00	4
Zn	0.0	0.00	0.01	0.00	0.01	0.00	0.00	
Mn	0.3	0.03	0.06	0.18	0.17	0.60	0.03	
As	15.4	15.70	13.27	16.45	14.64	15.79	1.25	
Sb	14.3	16.37	17.26	14.09	15.08	14.13	0.72	2
Bi	2.4	1.02	1.25	1.69	1.93	1.90	0.07	
S	26.2	26.24	25.92	26.28	26.37	26.25	4.98	5
Total	99.8	100.36	100.10	100.12	99.52	99.70		

1. Mean of six analyses including 2 and 3 (in wt %)
2. Most As-rich analysis (in wt%). As:Sb:Bi = 60:39:1
3. Most Sb-rich analysis (in wt%). As:Sb:Bi = 54:44:2
4-6. Compositional variation in a single grain (in wt%) 4(core) to 6(rim).
1a. Mole ratio of 1. Calculated on the basis of total atoms = 11.
1b. Theoretical figures.

Analytical conditions:
Instrument: JCMA-733 mk II
Accelerating voltage: 20 kV
Beam current: 2.00 x 10^{-8} amps on Faraday cage
Standards: analysed chalcopyrite (Cu), synthetic MnS (Mn), $AgBiS_2$ (Ag,Bi), Ag_3AsS_3 (As), $Cu_{10}Zn_2Sb_{1.4}As_{2.4}S_{13}$ (Sb), $Zn_{0.6}Fe_{0.4}S$ (S)

Crystallography

The minute grain size of the mineral impeded a single crystal study. Therefore, the unit cell data were obtained after indexing the X-ray powder diffraction pattern, which is composed of stronger lines indexed on a tetrahedrite-like cubic cell with a' = 10.37 Å and subsidiary lines of weaker intensity. The unit cell obtained is orthorhomibic with a = 14.51(1), b = 13.30(1) and c = 17.96(1) Å (Table 2). The cell includes 16 molecules of $Cu_4(As,Sb)_2S_5$. The diffraction pattern in Table 2 is indexed on this cell. Also, the strongest diffractions indexable on a tetrahedrite cell are indicated, though some of them have indices violating the space group requirement of tetrahedrite. The powder pattern of synthetic $Cu_{24}As_{12}S_{31}$ (Maske and Skinner, 1971) is also very similar to that of watanabeite (Table 3) and cannot be indexed on any cubic cell. It involves some weaker subsidiary diffractions, suggesting non-cubic symmetry, and it is optically anisotropic. But the stronger diffractions in the powder pattern of synthetic $Cu_{24}As_{12}S_{31}$ deviate slightly from a cubic subcell. In watanabeite, these deviations are smaller still. Therefore, it is still uncertain whether their material corresponds to the synthetic analogue of watanabeite or not. However, the formula, when calculated on the same basis as that of the watanabeite, gives $Cu_{3.94}As_{1.97}S_{5.09}$ which is virtually indentical to $Cu_4As_2S_5$, or Sb-free watanabeite.

Reflectance measurement

Reflectance spectra in air and in oil (Zeiss n_D = 1.515) for watanabeite were measured relative to an SiC reflectance standard (Zeiss, No. 314) using the equipment and procedures reported by Criddle *et al.* (1983). The data are given in Table 4 and

Table 2. X-ray powder pattern of watanabeite

I	$d_{obs.}$	$d_{cal.}$	hkl	(***)	I	$d_{obs.}$	$d_{cal.}$	hkl	(***)
1	11.2	11.3	101		1	2.382	2.383	425*	(331)
1	7.61	7.64	102		3	2.344	2.347	236	
2	7.36	7.44	012	(110)			2.344	532	
2	6.74	6.73	201		1	2.324	2.331	350	(420)
		6.65	020		5	2.238	2.242	603	
1	6.23	6.24	021				2.234	317	
1	6.12	6.04	120	(111)	3	2.210	2.214	018*	(332)
2	5.19	5.19	212	(200)	1	2.194	2.199	146*	
2	4.63	4.67	301	(210)	1	2.171	2.175	161*	
1	4.57	4.54	310		2	2.132	2.136	534*	
4	4.43	4.45	023		2	2.115	2.117	218	(422)
1	4.12	4.13	131				2.115	155	
2	3.96	3.97	032		1	2.074	2.069	417	(500)
3	3.78	3.78	230		2	2.054	2.058	516*	
		3.76	303		2b	2.037	2.036	308*	(510)+
3	3.68	3.67	214	(220)		~2.018	2.018	337*	
7	3.36	3.37	115		5	1.975	1.979	720*	
		3.36	402		1	1.959	1.961	550*	(520)+
2	3.31	3.32	040		1	1.925	1.924	209	
		3.31	224				1.922	507	
1	3.22	3.22	025		1	1.896	1.896	446*	(521)
		3.21	331		40	1.833	1.835	428	(440)
100	2.999	3.001	422	(222)	4	1.794	1.796	0.0.10*	
		2.993	006		4	1.778	1.777	0.1.10*	(530)+
1	2.966	2.976	241		2	1.740	1.742	821*	
2	2.828	2.835	510		1	1.705	1.705	706*	(610)
		2.828	404		1	1.693	1.692	429*	
1	2.777	2.774	431	(321)	2	1.680	1.680	075*	(611)
		2.767	206		2	1.650	1.650	832*	
2	2.746	2.741	135		1	1.647	1.648	538*	
2	2.735	2.740	340		1	1.608	1.609	752*	
		2.730	026		1	1.584	1.586	841*	
1	2.622	2.624	144*		15b	1.564	1.564	4.2.10*	(622)
20	2.594	2.598	424	(400)	1	1.550	1.550	184*	
		2.589	151		1	1.541	1.541	816*	
3	2.514	2.519	017*	(410)	5	1.497	1.497	0.0.12*	(444)
1	2.481	2.482	117		1	1.469	1.469	933*	
		2.482	036						
2	2.441	2.445	136*	(330)+					

Diffractometer method. Co/Fe radiation. b = broad.

* attached to hkl indices means the presence of more than two additive indices.

(***) means that the indices in this column are for a cubic subcell with a = 10.37Å. As to the indexing, the extinction rule required by the body-centered cell of tennantite-tetrahedrite or galkhaite is not considered, allowing the survival of h+k+l = odd.

+ means the presence of additive indices.

Fig. 2. As seen in the latter, watanabeite is very weakly bireflectant (although, in the sample found recently at Takinosawa with $Cu_4(Sb_{1.18}As_{0.82})_{\Sigma 2}S_5$, and Sb>As, the anisotropy and bireflectance are stronger).

Similar minerals

It is obvious that the mineral has a tetrahedrite-like structure, with a cubic subcell with $a' = 10.37$ Å, close to a of tetrahedrite, and that it has similar

Table 3. Comparison of X-ray powder pattern of watanabeite with with synthetic "$Cu_{24}As_{12}S_{31}$"(=$Cu_{3.94}As_{1.97}S_{5.09}$)

1		2		1		2		1		2	
I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)
3	3.68			1	2.382			40	1.833	80	1.842
		10	3.469	2	2.344	5	2.336	4	1.794		
7	3.36			5	2.238			2	1.740	5	1.735
2	3.31	10	3.314	3	2.210	5	2.213	1	1.705		
1	3.22			1	2.194			1	1.693		
100	2.999	100	2.991	1	2.171			2	1.680		
1	2.966			2	2.132			2	1.650		
2	2.828			2	2.115			1	1.647		
1	2.777			1	2.074	10	2.071			5	1.628
2	2.746			2	2.054			1	1.608		
2	2.735			2b	2.037	10	2.035	1	1.584		
1	2.622				~2.018			15b	1.564	70	1.571
20	2.594	50	2.595	5	1.975			1	1.550		
3	2.514			1	1.959			1	1.541		
1	2.481			1	1.925	5	1.938	5	1.497	10	1.505
2	2.441	4	2.443	1	1.896						

1. Watanabeite (partial pattern d<3.7Å). Co/Fe radiation. Diffractometer method. b = broad.
2. $Cu_{24}As_{12}S_{31}$. Cu/Ni radiation. Diffractometer method. After Maske and Skinner (1971).

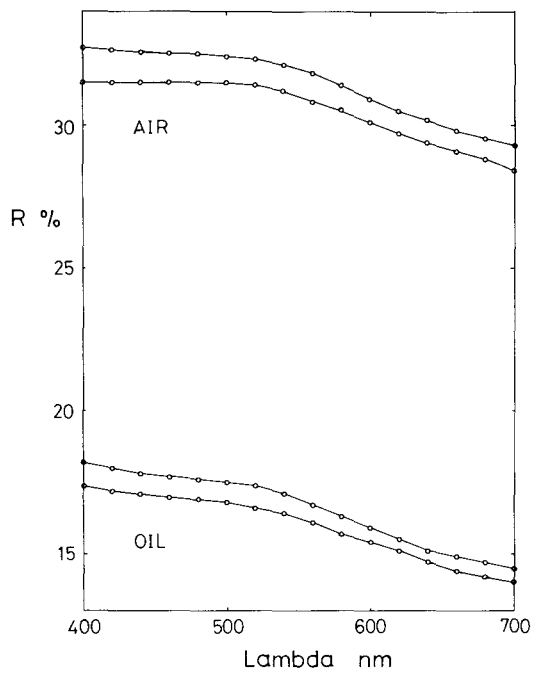

FIG. 2. Reflectance spectra of watanabeite in air and oil.

diffraction intensities. Watanabeite is not unique in this; both nowackiite (Marumo, 1967) and sinnerite (Marumo and Nowacki, 1964) have similar powder patterns to that of tetrahedrite.

Table 4. Reflectance values for watanabeite

λ (nm)	Air R_1	Air R_2	Oil R_1	Oil R_2
470	31.5	32.5	17.0	17.7
546	31.1	32.0	16.3	17.0
589	30.3	31.2	15.5	16.1
650	29.3	30.0	14.5	15.0
400	31.5	32.8	17.4	18.2
420	31.5	32.7	17.2	18.0
440	31.5	32.6	17.1	17.8
460	31.5	32.5	17.0	17.7
480	31.5	32.5	16.9	17.6
500	31.5	32.4	16.8	17.5
520	31.4	32.3	16.6	17.4
540	31.2	32.1	16.4	17.1
560	30.8	31.8	16.1	16.7
580	30.5	31.4	15.7	16.3
600	30.1	30.9	15.4	15.9
620	29.7	30.5	15.1	15.5
640	29.4	30.2	14.7	15.1
660	29.1	29.8	14.4	14.9
680	28.8	29.5	14.2	14.7
700	28.4	29.3	14.0	14.5

Colour values

	Air R_1	Air R_2	Oil R_1	Oil R_2	Illuminant
x	.305	.305	.300	.299	
y	.315	.314	.311	.311	
Y %	30.8	31.7	16.0	16.7	C
λ_d	487	486	484	485	
P_e %	2.0	2.1	4.3	4.6	
x	.442	.441	.436	.435	
y	.409	.409	.408	.409	
Y %	30.6	31.5	15.8	16.4	A
λ_d	498	498	496	496	
P_e %	1.4	1.5	2.7	2.9	

Table 5. Comparison of chemical compositions of sulphosalts with similar X-ray powder pattern to tetrahedrite group.

	metals	As+Sb	S	ideal formulae*
Tennantite	12	4	13	$Cu_{10}(Fe,Zn)_2As_4S_{13}$
Nowackiite	9	4	12	$Cu_6Zn_3As_4S_{12}$
Watanabeite	8	4	10	$Cu_8(As,Sb)_4S_{10}$
Galkhaite	6.5	4	12	$(Hg,Cu,Zn)_6(Tl,Cs)_{0.5}As_4S_{12}$
Sinnerite	6	4	9	$Cu_6As_4S_9$

(* normalized to (As,Sb) = 4)

The metal : semi-metal : sulphur ratios in these are compared with those of tennantite, watanabeite and galkhaite in Table 5.

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References

Criddle, A. J., Stanley, C. J., Chisholm, J. E., and Fejer, E. E. (1983). *Bull. Minér.*, **106**, 511–518.

Marumo, F. (1967) *Z. Krist.*, **124**, 352–368.

Marumo, F. and Nowacki, W. (1964). *Schweiz. min. petr. Mitt.*, **44**, 439–454.

Maske, F. and Skinner, B. J. (1971). *Econ. Geol.*, **66**, 901–918.

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