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Toyohaite, $Ag_2FeSn_3S_8$, a new mineral

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Abstract

Toyohaite, $Ag_2FeSn_3S_8$, tetragonal, $I4_1/a$, $a=7.464$, $c=10.80$Å, $Z=2$, is a new mineral corresponding to the Ag analogue of rhodostannite. Microprobe analyses demonstrate partial substitutions of Cu for Ag and Zn for Fe. The most Ag-rich and poor analyses are: Ag 24.39, 16.31; Cu: 0.14, 5.15; Fe 6.28, 6.18; Zn 0.37, 1.29; Cd 0.22, 0.14; Sn 41.24, 42.01; In 0.05, 0.17; totals 100.86%, 99.65%. They correspond respectively to: $(Ag_{1.95}Cu_{0.02})_{\Sigma 1.97}(Fe_{0.97}Zn_{0.05}Cd_{0.02})_{\Sigma 1.04}Sn_{2.99}S_{7.57}$, and $(Ag_{1.26}Cu_{0.68})_{\Sigma 1.94}(Fe_{0.92}Zn_{0.16}Cd_{0.01})_{\Sigma 1.09}(Sn_{2.95}In_{0.01})_{\Sigma 2.96}S_{7.39}$ (basis: total metal$=6$). Calculated density is 4.94 g/cm^3. Toyohaite has a rhodostannite-like brown reflection color with very weak dichroism and distinct to strong anisotropism. Reflectances are: 23.5–24.3% (480nm); 24.1–26.1% (546nm) 24.7–26.4% (589nm); 26.5–28.3% (650nm). X-ray powder diffraction lines and their relative intensities: 3.72(35), 3.21(100), 2.03(35) and 1.882(35). It occurs as irregular-shaped polycrystalline aggregates up to 200 μm across in a massive pyrite-sphalerite ore from the Sorachi vein of the Toyoha mine, Sapporo, Hokkaido, Japan. The intimate associates include rhodostannite, hocartite, teallite, herzenbergite, and berndtite.

Introduction

The natural occurrence of $(Ag,Cu)_2FeSn_3S_8$ corresponding to Ag-dominant analogue of rhodostannite has been known from Pirquitas deposit, Argentina (Johan and Picot, 1982), but the lack of crystallographic data has impeded the naming and complete description. We have now succeeded in characterizing the phase as a new mineral toyohaite named after the locality and in finding an extensive solid solution to rhodostannite.

The ore deposit of the Toyoha mine is situated in the southwestern part of Sapporo City, Hokkaido, and consists of more than 50 veins hosted by hydrothermally altered volcanic, pyroclastic and sedimentary rocks of Middle Miocene age, and the K-Ar dates of the veins range from 3Ma to 0.5Ma, corresponding to Pliocene to Pleistocene (Sawai *et al.*, 1989). The deposit is the most productive supplier of silver, lead and zinc in Japan, and of indium in the world. Also, it is so famous for the occurrence of such rare sulfides as canfieldite (Ohta and Yajima, 1977), hocartite and pirquitasite (Kojima *et al.*, 1979), unnamed Zn-In and Ag-In sulfides (Ohta, 1980), teallite and rhodostannite (Sugaki and Hayashi, 1986), matildite, gustavite, an unnamed Mo-Pb-Sb sulfide, herzenbergite and berndtite (Ohta *et al.*, 1987), a tin-bearing chalcopyrite (Kase, 1987), bismuth (Kanbara *et al.*, 1989), roquesite, sakuraiite, kesterite, indium-bearing sphalerite, and a chalcopyrite-stannite solid solution (Ohta, 1989). The occurrence of the present new mineral has been already reported by Ohta *et al.* (1987) under the name Ag-rhodostannite.

The mineral and name have been approved by the Commission on New Minerals and Mineral Names, IMA. Type material has been preserved at Geological Museum, Geological Survey of Japan, Hokkaido Branch, Sapporo.

Occurrence

Two mineralization stages, earlier and later, are discriminated in the veins of Toyoha deposit based on the cutting relation among the veins (Akome and Haraguchi, 1967). Yajima and Ohta (1979) indicated remarkable difference in mineral assemblages between the stages. Above-mentioned rare minerals are involved in the later-stage veins, especially in the Sorachi, Izumo and Shinano veins (Fig. 1). They are characterized by high grade zinc-lead ore containing notable amounts of silver, tin and indium.

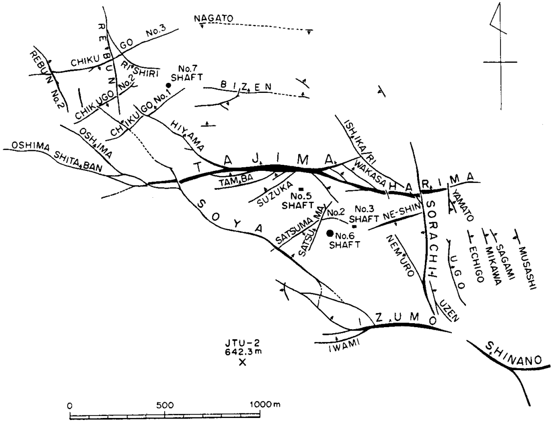

FIG. 1 Generalized vein map of the Toyoha deposit (after Kanbara *et al.*, 1989).

Kanbara *et al.* (1989) and Ohta (1989) proposed five successive sub-stages in the later stage mineralization. From earlier to later, they are represented as follows;

A. Formation of pyrrhotite and iron-rich sphalerite
B. Formation of chalcopyrite, sphalerite and galena with Sn, In, W and Bi minerals
C. Formation of sphalerite and galena with Ag-bearing sulfosalts
D. Formation of sphalerite and galena without Ag, Sn and In minerals
E. Formation of manganese carbonates

Among them, A, B and C groups are found in the veins at the southeastern part of deposit, and D and E groups are in the northwestern part, forming an obvious zonal arrangement of metals therein. Zonation of gangue minerals corresponding to this arrangement of metals is also realized in the deposit; quartz, kaolin, rutile and pyrophyllite in the southeast, and calcite, rhodochrosite and apatite to the northwest (Ohta and Marumo, 1985).

Toyohaite is found in the lower levels (300 m to 500 m level) of the central part of the Sorachi vein where basalt lava of the lower Miocene Koyanagizawa Formation is prevailing as wall rock. The vein consists of subparallel bands of A, B and C group ores and it is observed that the last one partly cut across the former two. Toyohaite has been recognized in fine-grained massive pyrite-sphalerite ore of B group.

Under the microscope, pyrite with rugged margin is cemented by sphalerite and a bit of galena. Hocartite, toyohaite and rhodostannite of irregular forms, several tens μm to 200 μm across, usually show isolated distribution in sphalerite (Fig. 2-1, 2-3). They are often situated at the margin of sphalerite grain and in druses associated with quartz and kaolin.

Toyohaite and rhodostannite are aggregate of small crystals whose individual grain size ranges from 1 to 30 μm (Fig. 2-1, 2-2). Above-mentioned ore minerals are more or less porous except hocartite and galena. Herzenbergite, berndtite and teallite are almost always in druses and the former two often replace neighboring rhodostannite and toyohaite (Fig. 2-1, 2-5). Other associated minerals are marcasite, pyrrhotite, wurtzite, cassiterite, and the unnamed Zn-In sulfide. No chalcopyrite nor stannite is observed in the toyohaite-containing specimens.

Physical and Optical Properties

Toyohaite is found only microscopically, and its megascopic color and streak are not known. Above-mentioned mode of aggregation of toyohaite impeded precise measurements of Vickers hardness, though its polishing hardness is slightly lower than that of the associated sphalerite and nearly equal to that of hocartite.

The reflection color is brownish grey, faintly more brownish than rhodostannite

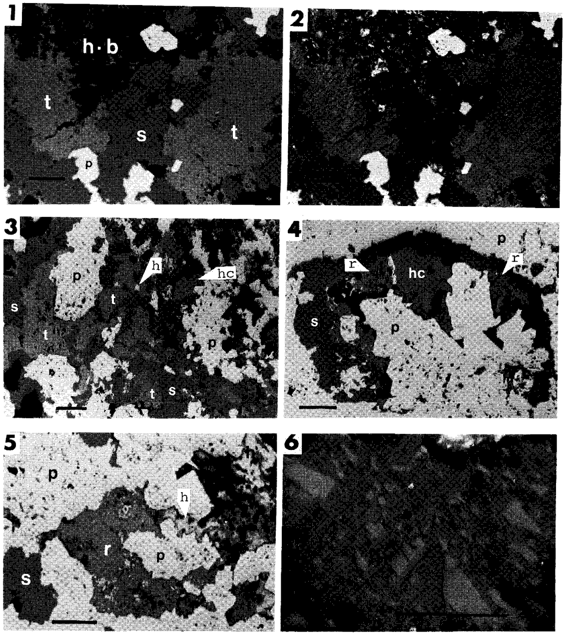

FIG. 2 Photomicrographs of toyohaite and the associated minerals.
1. Toyohaite partly replaced by fine-grained mixture of herzenbergite and berndtite. Plane reflected light.
2. Ibid. Crossed polars.
3. Toyohaite and hocartite in the matrix of sphalerite.
4. Hocartite and rhodostannite in sphalerite. Gangue minerals (black) are quartz and dickite.
5. Rhodostannite replaced by herzenbergite.
6. Checkered twins of toyohaite. Anisotropism is enhanced by Xenon-lamp illumination.

Abb: h = herzenbergite, h•b = herzenbergite mostly replaced by berndtite, hc = hocartite, p = pyrite, r = rhodostannite, s = sphalerite, t = toyohaite

Bar scale in each photograph represents 50 μm.

TABLE 1 Optical characters of toyohaite, rhodostannite and hocartite

	toyohaite	rhodostannite	hocartite
Color	brownish gray	brownish gray, less brown than toyohaite	brownish gray with violet tint, less brown than toyohaite
Birefletance	very weak	very weak	weak grayish brown to violet gray
Anisotropy	distinct to strong, greenish gray to reddish brown	weak to distinct, bluish gray to brownish gray	distinct to strong, pinkish gray to dark green
Reflectance (480nm)	23.5-24.3% 26.1-26.2%[*1]	29.4%[*2]	22.6-24.8%[*3]
Twin	checkered twin	checkered twin[*4]	polysynthetic twin

*1:Cuprian toyohaite, Johan et picot (1982) *2:Johan et picot (1982)
*3:Caye et al., (1968) *4:Hayashi and Sugaki (1986)

and hocartite. Very weak dichroism is discernible in air system. Anisotropism is distinct to strong with polarization colors changing from greenish gray to reddish brown. No internal reflection is observed. Twinning is recognized under high magnification (Fig. 2-6), and is similar to the checkered twin reported for cuprian toyohaite (Johan and Picot, 1982). The measurement of reflectance using Leitz microphotometer (SiC standard) was made on polycrystalline aggregate at four standard wavelengths in air: 23.5–24.3% (480 nm); 24.1–26.1% (546 nm); 24.7–26.4% (589 nm); 26.5–28.3% (650 nm).

Optical properties of toyohaite, rhodostannite and hocartite are summarized in Table 1.

Crystallography

Single crystal X-ray studies could not be carried out because of the small crystal size as described above. Several small fragments of toyohaite were carefully picked out from the polished sections under optical microscope. These fragments were ground together and formed into a sphere of about 100 μm in diameter with a small amount of adhesive agents. X-ray powder patterns of the specimen were measured using Cr Kα radiation and a Rigaku microdiffractometer equipped with a fine collimator of 100 μm and a PSPC (position sensitive proportional counter).

The X-ray powder data were found to correspond to those of rhodostannite (*JCPDS*, no. 33-465) after the elimination of weak reflections due to sphalerite and pyrite. The similarity of X-ray powder pattern to rhodostannite indicates that toyohaite has the same structure of tetragonal, $I4_1/a$ as that of rhodostannite, $Cu_2FeSn_3S_8$, reported by Jumas *et al.* (1979). The reflections were indexed after the reference to those of rhodostannite. The X-ray powder diffraction data are shown in Table 2. The cell dimensions were calculated by the least-squares method from 10 reflections with $2\theta > 70°$. The cell constants are tetragonal, $a=7.464(3)$, $c=10.80(2)$Å and $V=601(1)$Å^3. The density calculated from the cell dimensions and the ideal formula as $Z=2$ is 4.94 g/cm^3. The larger cell dimensions of toyohaite as compared with those of rhodostannite ($a=7.305$, $c=10.330$Å) are due to the substitution of larger Ag^+ for smaller Cu^+ ions in the tetrahedral sites of rhodostannite-type structure. The axial ratio, c/a, of toyohaite is 1.447, which is slightly shifted from $1.414(=\sqrt{2})$ of rhodostannite. If the axial ratio in the subcell corresponding to chalcopyrite is used, the ratios, c'/a' (here, $c'=c/2$ and $a'=a/\sqrt{2}$), of toyohaite and rhodostannite are 1.023 and 1.000, respectively. It indicates that the cell of the Ag-variation, toyohaite, is deformed from pseudocubic cell of the Cu-variation, rhodostannite. This kind of deformation from the pseudocubic cell is observed in the other Cu-Ag sulfides such as stannite (Cu_2FeSnS_4) – hocartite (Ag_2FeSnS_4), kesterite (Cu_2ZnSnS_4) – pirquitasite (Ag_2ZnSnS_4), and roquesite ($CuInS_2$) – $AgInS_2$, in which the ratios, c/a, are as follows;

stannite, 1.977 (Sugaki *et al.*, 1981)
hocartite, 1,909 (Caye *et al.*, 19687
kesterite, 1,999 (Schäfer and Nitsche, 1974)
pirquitasite, 2,044 (Johan and Picot, 1982)
roquesite, 2.005 (Picot and Pierrot, 1963) and
$AgInS_2$, 1.906 (Roth *et al.*, 1973)

TABLE 2 X-ray powder diffraction data for toyohaite

d_o(Å)	d_c(Å)	hkl	I/I_o
6.10	6.14	101	25
3.77	3.77	112	20
3.72	3.73	200	35
3.21	[3.24 3.19	103 211]	100
3.07	3.07	202	10
2.64	2.64	220	30
2.42	[2.42 2.40	301 114]	10
2.16	2.16	312	10
2.03	2.05 2.03	303 321	35
1.882	1.887	224	35
1.856	1.866	400	30
1.797	1.795	323	5
1.781	[1.785 1.777	411 314]	5
1.678	1.673	332	5
1.619	[1.621 1.617	206 413]	10
1.591	1.595	422	5
1.533	1.535	404	10
1.384	[1.387 1.379 1.379	415 503 433]	10
1.373	1.375	521	10
1.320	1.319	440	15
1.229	[1.228 1.228	505 435]	10

Chemistry

Microprobe analyses using Shimadzu EPMA-8705 were made. The results are given in Table 3, where three analyses of materials from the Pirquitas deposit, Argentina after Johan and Picot (1982) are tabulated. They correspond to cuprian toyohaite and argentian rhodostannite. Chemical analyses of argentian rhodostannite (R in Table 3), and hocartite (Table 4) accompanied by toyohaite also were performed.

The most Ag-rich and poor analyses give chemical formulas:

$(Ag_{1.95}Cu_{0.02})_{\Sigma 1.97}(Fe_{0.97}Zn_{0.05}Cd_{0.02})_{\Sigma 1.04}Sn_{2.99}S_{7.57}$

and

$(Ag_{1.26}Cu_{0.68})_{\Sigma 1.94}(Fe_{0.92}Zn_{0.16}Cd_{0.01})_{\Sigma 1.09}(Sn_{2.95}In_{0.01})_{\Sigma 2.96}S_{7.39}$

based on 6 total metals. These are close to the ideal formula $Ag_2FeSn_3S_8$ with minor substitutions of Cu for Ag, Zn and Cd for Fe, and In for Sn. Fig. 3 reveals a solid solution between the toyohaite and the rhodostannite from the Sorachi vein. Observed variations in Ag/(Ag + Cu) and in Zn/(Fe + Zn) for the solid solution are 0.65 to 0.99 and 0.04 to 0.22 respectively.

TABLE 3 Representative chemical compositions of toyohaite and rhodostannite from the Toyoha deposit, in comparison with those from the Pirquitas deposit, Argentina.

T: Toyohaite from the Sorachi vein –400 mL, Toyoha deposit.

J: Cuprian toyohaite (J1,J2) and argentian rhodostannite (J3) from the Pirquitas deposit, Argentina (Johan and Picot, 1982).

R: Argentian rhodostannite from the Sorachi vein –400 mL, Toyoha deposit.

Elements	T1	T2	T3	T4	T5	J1	J2	J3	R
Ag	24.39	24.39	20.01	18.79	16.31	14.86	11.77	6.51	3.73
Cu	0.14	0.20	3.24	3.67	5.15	6.75	8.23	11.69	13.14
Fe	6.28	5.82	5.66	5.87	6.18	6.50	6.42	6.80	6.08
Zn	0.37	0.47	0.59	0.87	1.29	0.00	0.00	0.00	1.96
Cd	0.22	0.29	0.00	0.00	0.14	n.a.	n:a.	n.a.	n.a.
Sn	41.24	40.49	42.51	41.90	42.01	42.00	43.46	44.21	44.96
In	0.05	0.07	0.21	0.35	0.17	n.a.	n.a.	n.a.	0.16
S	28.16	27.86	28.40	28.30	28.40	30.15	30.29	31.47	30.10
Total	100.86	99.58	100.62	99.74	99.65	100.25	100.18	100.66	100.12
Ag/(Ag+Cu) atomic ratio	0.99	0.99	0.78	0.75	0.65	0.57	0.46	0.25	0.14

Formulars based on 6 total metal:

T1 $(Ag_{1.95}Cu_{0.02})_{\Sigma 1.97}(Fe_{0.97}Zn_{0.05}Cd_{0.02})_{\Sigma 1.04}Sn_{2.99}S_{7.57}$

T2 $(Ag_{1.98}Cu_{0.03})_{\Sigma 2.01}(Fe_{0.91}Zn_{0.06}Cd_{0.02})_{\Sigma 0.99}(Sn_{2.99}In_{0.01})_{\Sigma 3.00}S_{7.62}$

T3 $(Ag_{1.57}Cu_{0.43})_{\Sigma 2.00}(Fe_{0.86}Zn_{0.08})_{\Sigma 0.94}(Sn_{3.04}In_{0.02})_{\Sigma 3.06}S_{7.51}$

T4 $(Ag_{1.47}Cu_{0.49})_{\Sigma 1.96}(Fe_{0.90}Zn_{0.12})_{\Sigma 1.02}(Sn_{3.00}In_{0.03})_{\Sigma 3.03}S_{7.49}$

T5 $(Ag_{1.26}Cu_{0.68})_{\Sigma 1.94}(Fe_{0.92}Zn_{0.16}Cd_{0.01})_{\Sigma 1.09}(Sn_{2.95}In_{0.01})_{\Sigma 2.96}S_{7.39}$

J1 $(Ag_{1.16}Cu_{0.89})_{\Sigma 2.05}Fe_{0.98}Sn_{2.97}S_{7.90}$

J2 $(Ag_{0.91}Cu_{1.08})_{\Sigma 1.99}Fe_{0.96}Sn_{3.05}S_{7.88}$

J3 $(Ag_{0.49}Cu_{1.50})_{\Sigma 1.99}Fe_{0.99}Sn_{3.03}S_{7.98}$

R $(Ag_{0.27}Cu_{1.63})_{\Sigma 1.90}(Fe_{0.86}Zn_{0.24})_{\Sigma 1.10}(Sn_{2.99}In_{0.01})_{\Sigma 3.00}S_{7.42}$

TABLE 4 Representative chemical compositions of hocartite coexisting with toyohaite at Sorachi vein -400mL of the Toyoha deposit.

Elements	1	2	3	4	5
Ag	41.56	41.13	41.43	41.53	40.88
Cu	0.28	0.38	0.39	0.49	0.52
Fe	7.48	7.93	7.34	8.17	8.02
Zn	3.32	3.13	3.20	2.22	2.30
Mn	0.00	0.40	0.00	0.00	0.28
Cd	0.00	0.44	0.00	0.00	0.46
Sn	23.59	23.01	24.06	23.93	23.23
In	0.00	0.06	0.01	0.00	0.01
S	24.31	23.81	24.07	23.92	23.52
Total	100.55	100.29	100.49	100.26	99.22
Ag/(Ag+Cu) atomic ratio	0.99	0.99	0.99	0.98	0.98

Formulars based on 8 total atoms

1 $(Ag_{2.01}Cu_{0.02})_{\Sigma 2.03}(Fe_{0.70}Zn_{0.27})_{\Sigma 0.97}Sn_{1.04}S_{3.96}$

2 $(Ag_{2.00}Cu_{0.03})_{\Sigma 2.03}(Fe_{0.74}Zn_{0.25}Mn_{0.04}Cd_{0.02})_{\Sigma 1.05}Sn_{1.02}S_{3.90}$

3 $(Ag_{2.02}Cu_{0.03})_{\Sigma 2.05}(Fe_{0.69}Zn_{0.26})_{\Sigma 0.95}Sn_{1.06}S_{3.94}$

4 $(Ag_{2.02}Cu_{0.04})_{\Sigma 2.06}(Fe_{0.77}Zn_{0.18})_{\Sigma 0.95}Sn_{1.05}S_{3.92}$

5 $(Ag_{2.02}Cu_{0.04})_{\Sigma 2.06}(Fe_{0.76}Zn_{0.19}Mn_{0.03}Cd_{0.02})_{\Sigma 2.00}Sn_{1.04}S_{3.90}$

Rhodostannite detected in the drill core sample JTU2-642.3m (MMAJ, 1990) from about 500 meters west-southwest of the Izumo vein (Fig. 1) is poor in both silver and zinc, and its compositions are not on the trend of the toyohaite-rhodostannite solid solution (Fig. 3). This presumably reflects the difference of localities. The materials from the Pirquitas deposit exhibit chemical compositions intermediate between toyohaite and the zinc-poor rhodostannite from the drill core (Table 3, Fig. 3), and can be explained as solid solutions of them. Though the highest Ag/(Ag + Cu) ratio of toyohaite is comparable to that of the associated hocartite, significant difference of the Zn/(Fe + Zn) ratios between the two is recognized (Fig. 3).

Genetic Consideration

Springer (1968) reported an association of stannite and rhodostannite, saying that the latter is an alteration product of the former and that the porous texture of the latter is explained by a shrinkage in volume during replacement. Rhodostannite and toyohaite from the Toyoha mine also have the same porous feature.

From the observation at 200 to 300 meter levels of the southern Sorachi vein, Ohta (1980) showed that hocartite and the unnamed Ag-In sulfide are considered to be replacement products after stannite and the unnamed Zn-In sulfide respectively during the sub-stage C.

As mentioned in the preceding chapter, stannite is hardly seen at the portion where

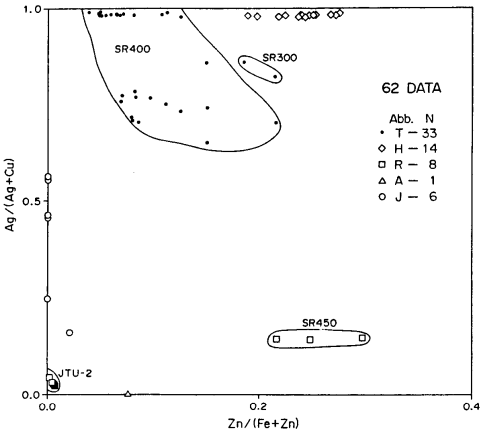

FIG. 3 Ag/(Ag + Cu) vs. Zn/(Fe + Zn) diagram for toyohaite, rhodostannite, and hocartite from the Toyoha deposit in comparison with similar phases from the Pirquitas deposit.

T: toyohaite, H: hocartite, R: rhodostannite (this study)
A: rhodostannite (Hayashi and Sugaki, 1986) J: argentian rhodostannite and cuprian toyohaite from the Pirquitas deposit (Johan and Picot, 1982)

SR300, SR400, SR450; Sorachi vein -300mL, -400mL, -450mL
JTU-2: Drill core sample JTU2-642.3m

rhodostannite, toyohaite and hocartite are observed, although it is a common mineral associated with chalcopyrite and sphalerite in the neighboring area.

It may be possible to say that toyohaite, together with rhodostannite and hocartite, is a replacement product after stannite at the successive sub-stages C and D and that total replacement took place in this case. Mineralization sequence for rhodostannite, toyohaite and hocartite are not well established yet because of their isolated occurrence. It is clear that herzenbergite, berndtite and teallite have been formed after the formation of these three minerals.

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