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Tsugaruite, $Pb_4As_2S_7$, a new mineral species from the Yunosawa mine, Aomori Prefecture, Japan

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ABSTRACT

Tsugaruite, $Pb_4As_2S_7$, is a new Pb-As sulphosalt from the Yunosawa mine, Aomori Prefecture, northern Japan. X-ray studies indicated it to be orthorhombic *Pnn*2 or *Pnnm*, *a* 15.179(1), *b* 38.195(1), *c* 8.0745(1) Å, Z = 16 [$Pb_4As_2S_7$] with a subcell with $c' = 1/2c$. The six strongest diffractions in the X-ray powder pattern [d (in Å), (*I*), (*hkl*)] are: 4.47 (30) (340), 3.705 (34) (1.10.0), 3.395 (100) (450), 2.870 (34) (192), 2.819 (53) (550), and 2.739 (48) (560, 2.13.0). The average of seven electron microprobe analyses gave Pb 68.70, Tl 0.13, As 12.45, S 18.64, total 99.92 wt.%. The empirical formula calculated on the basis of total atoms = 13 is $Pb_{3.99}Tl_{0.01}As_{2.00}S_{7.00}$, corresponding to the ideal formula $Pb_4As_2S_7$. The calculated density is 6.83 g/cm^3 for the ideal formula.

Tsugaruite is opaque with a metallic lustre and lead-grey streak. No cleavage was observed. It is brittle with uneven fracture. VHN_{25} is 75.4–94.9 kg/mm^2, mean 86.4 (n = 4), corresponding to 2.5–3 in Mohs' hardness scale. In reflected plane-polarised light in air, it is white with a greenish tint, more greenish than jordanite. Bireflectance and pleochroism are weak, weaker than those of jordanite; and anisotropism is weak to moderate, weaker than that of jordanite. No internal reflections. The reflectance spectra are tabulated in the text.

Tsugaruite was found in a thin baryte veinlet exposed in the wall of a small open cut of the Yunosawa mine. It forms radiating groups of long tabular tapering crystals elongated along *c* and tabular to *b*, up to 0.04 mm wide and 2 mm long. The associated minerals are jordanite, which formed earlier than tsugaruite, and galena. The chemical similarity of tsugaruite and jordanite and their intergrown character indicates that earlier jordanite analyses may also include analyses of tsugarite.

KEYWORDS: tsugaruite, jordante, new mineral, Yunosawa mine, Aomori Prefecture, Japan, X-ray, chemical, and optical data.

Introduction

TSUGARUITE, ideally $Pb_4As_2S_7$, is a new mineral from the Yunosawa mine, Aomori Prefecture, Japan. The mineral is named for the old province, Tsugaru, which is in current usage as a part of composite name of 'gun', a Japanese provincial unit next to prefecture. The mineral and the mineral name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association. Type materials are deposited both at the University Museum, University of Tokyo and the National Science Museum, Tokyo, under catalogue number NSM M-27594.

Occurrence

Tsugaruite occurs at the Yunosawa mine, Ikarigaseki-mura, Minami-Tsugaru-gun, Aomori Prefecture, Japan (Lat. 40°25′45"N, Long. 140°36′54"E). In the mining area, the Tobe Formation of Miocene age is widely distributed, and is chiefly composed of altered pumiceous pyroclastic rocks (e.g. Inoue and Mituhasi, 1962); several hot springs of Na^{+}-Cl^{-}-HCO_3^{-} type (Matsubaya *et al.*, 1975) and fumaroles are observed (Honda, 1982). Veinlets and/or networks of *c.* 2 cm or less in width in the wall of a small open cut of the mine consist of wurtzite, marcasite, galena, baryte, jordanite and small amounts of tsugaruite, gratonite, canfieldite, Ag-bearing tennantite-tetrahedrite series minerals and secondary mimetite. The coexisted minerals are jordanite, wurtzite, marcasite, galena and baryte, and gratonite is not in direct contact with tsugaruite. Tsugaruite is a rare constituent of the veinlets, and a product of low-temperature hydrothermal mineralization, formed later than jordanite.

Appearance and physical properties

Tsugaruite occurs as radiating groups of tabular crystals, elongate to {001} and tabular on {010}, up to 0.04 mm wide and 2 mm long (Figs. 1 and 2). It has microhardness VHN_{25} in the range 75.4–94.9 kg/mm^2 based on four indentations. The mean is 86.7 which corresponds to Mohs' hardness of 2.5–3. The mineral is opaque with metallic lustre and lead-grey streak. The megascopic colour is silvery lead-grey. No cleavage was observed. The fracture is uneven and the tenacity is brittle. The paucity of material and the small grain size precluded a Berman balance specific gravity determination. The calculated density is 6.83 g/cm^3, which is the largest among Pb-As sulphosalts, using the formula $Pb_4As_2S_7$ and $Z = 16$.

Optical properties

In polished sections, in plane-polarised light, tsugaruite is weakly bireflectant and weakly pleochroic from white with a greenish tint to grey white with a greenish tint (Figs. 1 and 2).

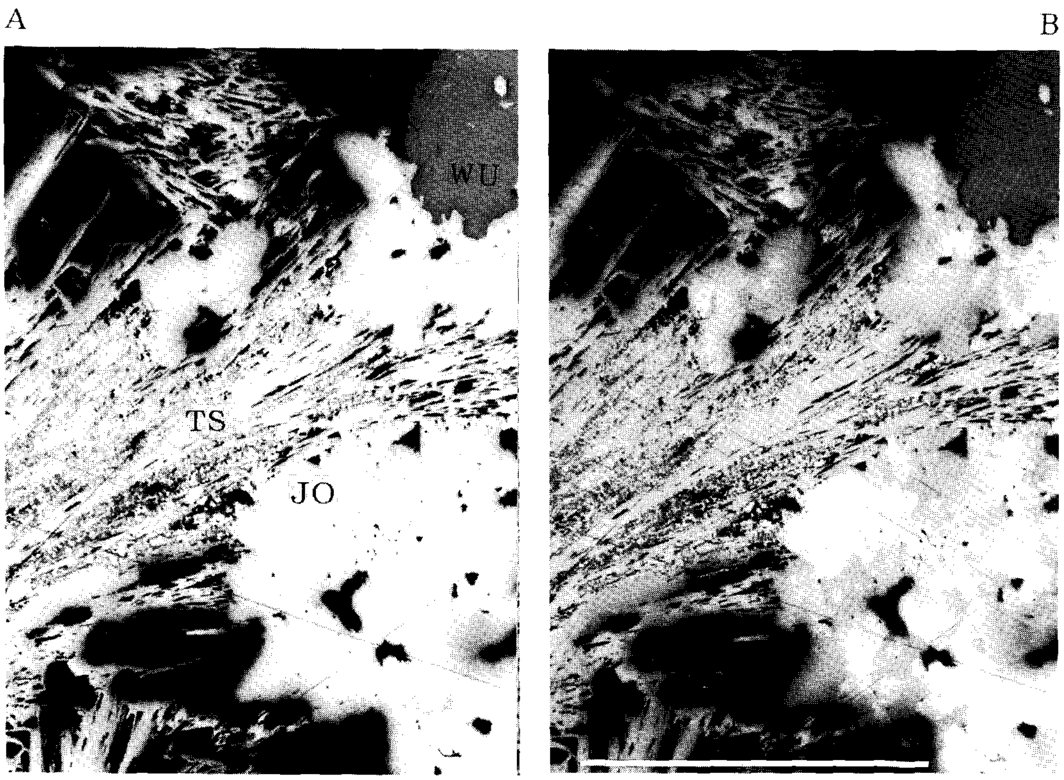

FIG. 1. Photomicrograph of tabular tsugaruite (TS) on massive jordanite (JO). (A) in plane polarised light, (B) with crossed polars; scale bar 500 μm.

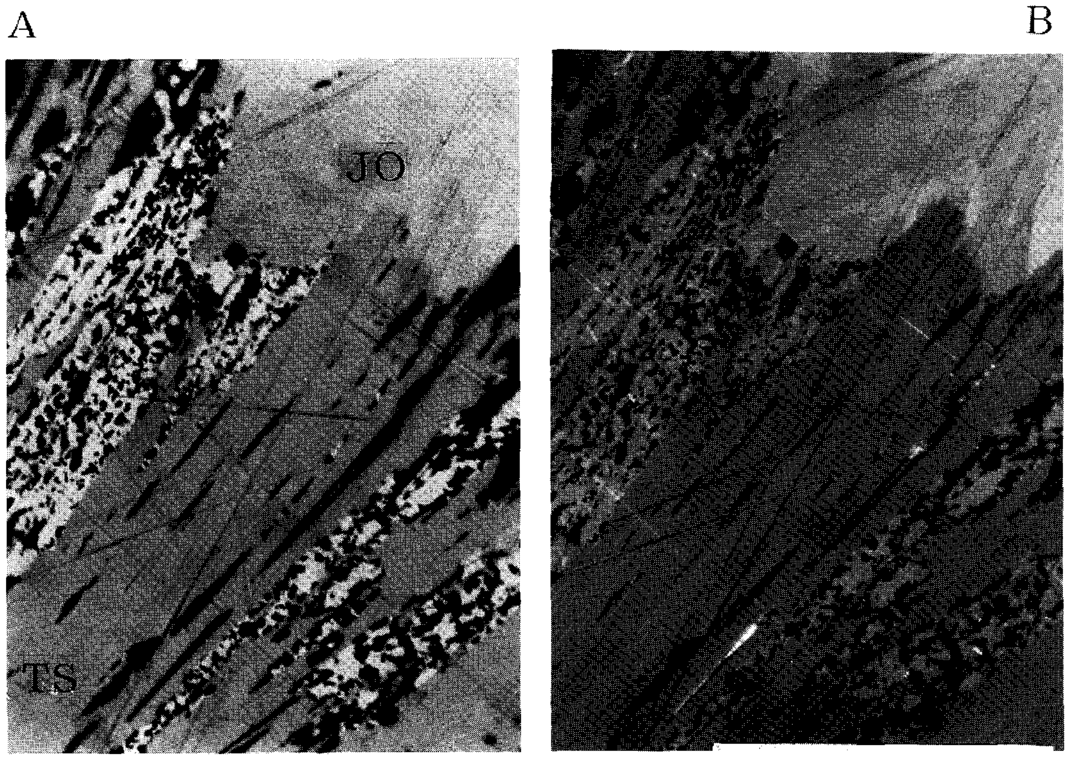

FIG. 2. Photomicrograph of tabular tsugaruite (TS) on massive jordanite (JO). (A) in plane polarised light, (B) with crossed polars; scale bar 100 μm. Oil immersion.

When immersed in oil (N_D 1.515), the bireflectance and reflectance pleochroism are not enhanced. Internal reflections were not observed in plane-polarised light and between crossed polars. The mineral is weakly to moderately anisotropic, with characteristic rotation tints. The sequence of rotation tints are from nearly straight extinction, dark brownish grey; dark yellowish grey; and dark greenish grey.

In comparison with jordanite, tsugaruite is slightly softer, slightly darker, slightly more greenish, less pleochroic and less anisotropic than jordanite.

Reflectance data

Reflectance measurements were made against a SiC standard (Zeiss No. 851). Immersion measurements were made with Nikon oil, N_D 1.515 at a room temperature of 20°C. The equipment is a Nikon Optiphot-2 microscope photometer with a Nikon photometer-head-measurement-finder, a Nikon photometer-controller P101, a Nikon monochrometer G-70 and a Nikon two-light-flux interference examination. The reflectance data are summarised in Table 1 and Fig. 3. The values (R_{min} and R_{max} in air and R_{min} and R_{max} in oil) for the COM wavelengths are: (33.8, 34.0; 19.2, 19.4%) 470 nm, (31.8, 31.9; 18.2, 19.6%) 546 nm, (31.2, 31.3; 17.4, 19.3%) 589 nm, (30.4, 30.4; 16.3, 18.4%) 650 nm.

Chemical data

Seven chemical analyses were carried out by means of an electron microprobe using the following standards: synthetic PbS (Pb-$M\alpha$), Cu_3AsS_4 (As-$L\alpha$), ZnS (S-$K\alpha$) and lorandite (Tl-$L\alpha$) (Table 2). The mean analytical results (and ranges) are: Pb 68.70 (68.30–68.81), Tl 0.13 (0.07–0.20), As 12.45 (12.37–12.50), S 18.64

TABLE 1. Reflectance values for tsugaruite from the Yunosawa mine, Japan

	Air		Oil	
nm	R_1	R_2	R_1	R_2
470	33.8	34.0	19.2	19.4
546	31.8	31.9	19.6	18.2
589	31.2	31.3	19.3	17.4
650	30.4	30.4	18.4	16.3
400	38.4	43.5	17.9	18.5
420	37.2	39.2	17.7	18.9
440	35.4	36.1	18.5	19.7
460	34.4	34.5	19.1	19.5
480	33.2	33.4	19.3	19.3
500	32.6	32.8	19.6	19.1
520	32.2	32.3	19.6	18.7
540	31.9	32.0	19.6	18.3
560	31.6	31.7	19.5	18.0
580	31.3	31.4	19.4	17.6
600	30.9	31.1	19.2	17.2
620	30.7	30.7	18.9	16.7
640	30.5	30.5	18.5	16.4
660	30.2	30.3	18.3	16.1
680	30.0	30.0	17.8	15.7
700	29.6	29.7	17.4	15.4

(18.54–18.77), total 99.92 wt.%. Ag, Cu, Fe and Sb are less than the limit of detection. The empirical formula based on total atoms = 13, is: $(Pb_{3.99}\ Tl_{0.01})_{\Sigma 4.00}As_{2.00}S_{7.00}$. The simplified formula is $Pb_4As_2S_7$.

X-ray crystallography

Several fragments of the tsugaruite sample with lath shape (approximate dimension: 100 × 30 × 5 μm) were used for the preliminary study for X-ray crystallography with a RIGAKU RASA-7R four-circle diffractometer. The Mo-*Kα* radiation used for the measurement was generated by a rotation target-type cathode with a operation condition of 56 kV and 270 mA, and monochromatized with a graphite monochrometer. Some of the samples gave X-ray diffraction peaks which can be indexed on an orthorhombic cell. Oscillation and Weissenberg photographs of one of the fragments (110 × 30 × 5 μm) indicated that the true cell has a doubled *c* dimension, and this was confirmed by the reinvestigation with the diffractometer. The possible space groups are *Pnn*2 or *Pnnm*. The diffraction spots of the films were diffuse and the profiles of the diffraction peaks measured on the diffractometer were extremely broad. The fragment was not suitable for obtaining the correct intensity collection for crystal structure analysis.

X-ray powder diffraction data (Table 3) were obtained using a RIGAKU RAD-IIA X-ray diffractometer, Ni-filtered Cu-*Kα* radiation, a scan rate of ½° per min. The data were also measured by means of a Gandolfi camera (diameter of 114.6 mm) with Ni-filtered Cu-*Kα* radiation for the crystal fragments selected under a microscope. The refined cell parameters from the data obtained by the diffractometer with internal standards, NBS No. 640b (silicon) and

TABLE 2. Representative chemical compositions of tsugaruite and jordanite from the Yunosawa mine, Japan

	Tsugaruite								Jordanite
	1	2	3	4	5	6	7	8	9
								Mean (1–7)	
Pb (wt.%)	68.34	68.59	68.81	68.30	69.17	68.77	68.94	68.70	70.23
Tl	0.07	0.10	0.11	0.12	0.15	0.15	0.20	0.13	0.20
As	12.42	12.47	12.43	12.37	12.50	12.48	12.50	12.45	10.92
S	18.56	18.63	18.64	18.52	18.74	18.67	18.71	18.64	17.90
Total	99.39	99.79	99.99	99.31	100.56	100.07	100.35	99.92	99.25
Atomic proportions based on total atoms = 13									Total atoms = 43
Pb	3.990	3.988	3.998	3.994	3.996	3.990	3.990	3.993	13.963
Tl	0.004	0.006	0.006	0.007	0.009	0.009	0.012	0.008	0.040
As	2.006	2.006	1.998	2.001	1.998	2.003	2.001	2.001	6.006
S	7.000	7.000	6.998	6.998	6.997	6.999	6.997	6.998	22.991

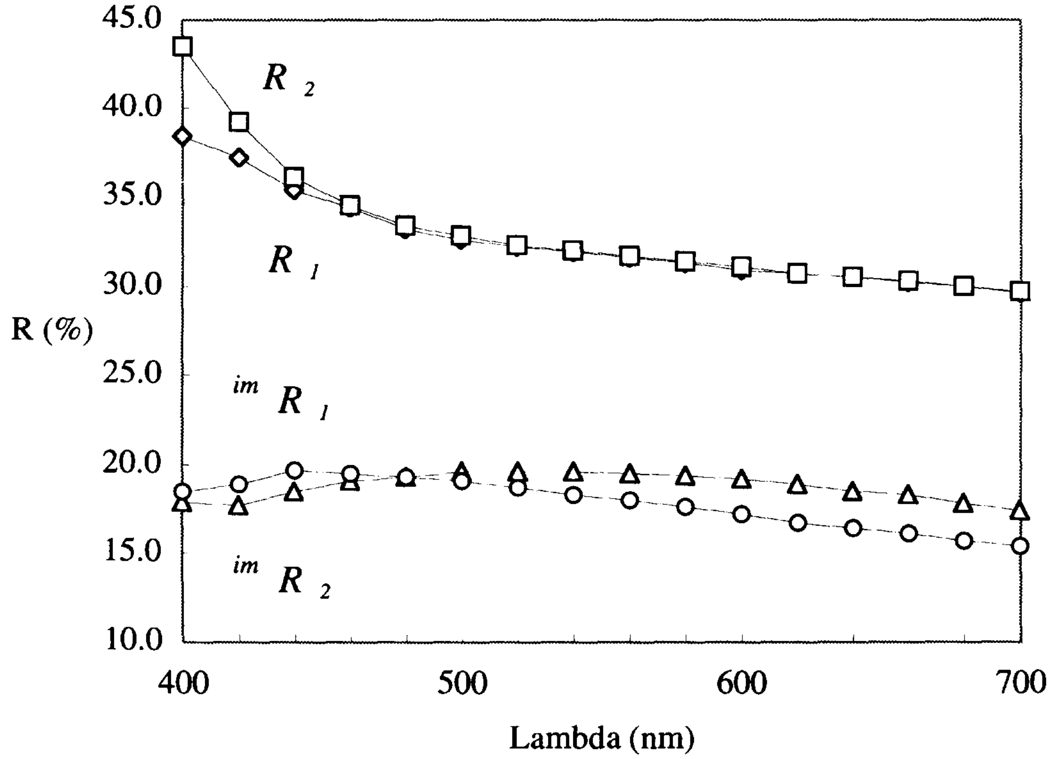

FIG. 3. Reflectance spectra of tsugaruite in air and oil.

No. 645 (synthetic equivalent of mica) are: a = 15.179(1), b = 38.195(1), c = 8.0745(5) Å.

Relationship to known species

According to both the chemical composition, and X-ray powder data, the mineral has no analogues among minerals or synthetic compounds. Compositionally, (Ag,Cu) → Pb substitution and charge balance in lengenbachite ($Pb_6(Ag,Cu)_2As_4S_{13}$) gives tsugaruite ($Pb_4As_2S_7$). Gratonite and jordanite have the following relationships to tsugaruite (Fig. 4):

$Pb_9As_4S_{15}$ (gratonite) = $2Pb_4As_2S_7$ (tsugaruite) + PbS (galena) and

$Pb_{14}As_6S_{23}$ (jordanite) = $3Pb_4As_2S_7$ (tsugaruite) + 2PbS (galena).

Because of the obsevation that jordanite was formed earlier than tsugaruite and gratonite and that tsugaruite does not coexist with gratonite, the following reactions can be suggested at the Yunosawa mine.

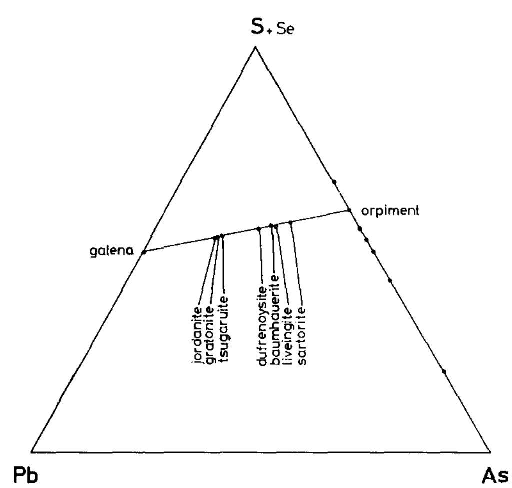

FIG. 4. Compositional plots of sulphide and Pb-As sulphosalt minerals between PbS (galena) and As_2S_3 (orpiment) in the Pb–As–S system.

TABLE 3. X-ray powder data for tsugaruite from the Yunosawa mine, Japan

I	*d* obs.	*d* calc.	*h*	*k*	*l*	*I*	*d* obs.	*d* calc.	*h*	*k*	*l*
<1	14.17	14.11	1	1	0	11	2.018	2.018	3	10	3
5	7.10	7.05	2	2	0	12	1.995	1.995	6	7	2
3	6.54	6.52	2	3	0	6	1.988	1.984	2	12	3
1	5.22	5.21	1	5	1	1	1.962	1.961	3	11	3
1	4.79	4.79	2	4	1	5	1.949	1.950	4	9	3
7	4.70	4.70	3	3	0			1.948	2	1	4
30	4.47	4.47	3	4	0	5	1.943	1.941	2	2	4
3	4.31	4.33	1	7	1	3	1.932	1.931	7	9	0
3	4.28	4.29	3	0	1			1.928	2	3	4
5	4.22	4.22	3	5	0	15	1.915	1.917	6	13	0
3	4.11	4.17	2	6	1			1.913	6	9	2
5	4.10	4.09	1	9	0	17	1.908	1.908	7	1	2
5	4.05	4.06	3	3	1			1.904	3	16	2
		4.04	2	8	0	16	1.903	1.901	7	2	2
		4.04	0	0	2	19	1.898	1.897	8	0	0
1	3.962	3.961	3	6	0	17	1.873	1.873	4	15	2
4	3.880	3.881	1	1	2	2	1.858	1.855	3	3	4
6	3.824	3.823	1	2	2	4	1.841	1.840	3	4	4
34	3.705	3.704	1	10	0	4	1.834	1.837	2	7	4
3	3.565	3.564	2	0	2	3	1.823	1.821	3	5	4
9	3.548	3.549	2	1	2	2	1.813	1.810	1	9	4
11	3.504	3.504	2	2	2	2	1.808	1.806	2	8	4
100	3.395	3.399	4	5	0	4	1.770	1.773	1	10	4
5	3.260	3.260	4	6	0	4	1.764	1.763	8	8	0
3	3.230	3.230	2	5	2	6	1.741	1.742	5	11	3
6	3.184	3.183	0	12	0			1.742	7	9	2
9	3.119	3.115	1	12	0	9	1.738	1.736	4	5	4
		3.114	3	2	2	13	1.733	1.734	1	11	4
15	3.060	3.063	3	3	2	10	1.731	1.732	6	13	2
18	3.016	3.021	1	8	2			1.732	8	9	0
26	2.981	2.984	2	7	2	2	1.700	1.699	8	10	0
14	2.890	2.893	5	4	0	4	1.692	1.694	1	12	4
34	2.870	2.872	1	9	2	4	1.689	1.686	6	14	2
25	2.858	2.856	2	8	2	1	1.668	1.670	4	8	4
53	2.819	2.821	5	5	0	2	1.664	1.665	8	11	0
18	2.772	2.775	0	10	2	3	1.643	1.643	4	9	4
48	2.739	2.740	2	13	0	3	1.640	1.642	5	5	4
		2.740	5	6	0	3	1.631	1.632	7	6	3
2	2.652	2.656	4	4	2	3	1.628	1.630	8	12	0
		2.653	5	7	0	4	1.625	1.625	5	6	4
1	2.629	2.633	3	8	2			1.625	2	13	4
9	2.599	2.600	4	5	2	1	1.614	1.613	7	7	3
<1	2.564	2.562	5	8	0	<1	1.595	1.592	8	9	2
1	2.505	2.504	1	5	3			1.592	7	8	3
5	2.489	2.487	2	11	2	1	1.589	1.590	9	8	0
4	2.481	2.481	6	3	0	1	1.569	1.567	9	9	0
6	2.399	2.401	3	14	0			1.566	6	3	4
19	2.374	2.376	3	0	3	1	1.559	1.561	6	13	3
		2.374	2	12	2	1	1.549	1.549	2	15	4
15	2.352	2.352	5	4	2	3	1.543	1.545	3	14	4
5	2.313	2.313	5	5	2			1.543	9	10	0
4	2.296	2.295	6	7	0	4	1.541	1.539	8	11	2
8	2.269	2.267	5	6	2	3	1.538	1.537	3	1	5
		2.267	2	13	2	1	1.532	1.533	3	2	5

TABLE 3. *Contd*

I	*d* obs.	*d* calc.	*h*	*k*	*l*	*I*	*d* obs.	*d* calc.	*h*	*k*	*l*
9	2.241	2.241	3	12	2	2	1.522	1.524	4	13	4
10	2.234	2.236	1	14	2	7	1.515	1.516	6	7	4
		2.235	6	8	0	6	1.513	1.513	10	2	0
3	2.218	2.215	4	14	0	2	1.495	1.498	6	8	4
22	2.160	2.159	3	16	0	2	1.492	1.492	4	14	4
27	2.150	2.150	3	13	2	1	1.486	1.485	4	1	5
5	2.138	2.138	7	3	0	3	1.476	1.476	7	1	4
13	2.113	2.114	4	15	0	5	1.472	1.473	7	2	4
		2.114	6	3	2	5	1.469	1.468	7	3	4
3	2.101	2.098	6	9	1	3	1.460	1.460	4	15	4
2	2.069	2.072	2	15	2	3	1.445	1.446	3	9	5
8	2.051	2.053	7	6	0	8	1.439	1.441	9	10	2
		2.048	2	11	3	7	1.418	1.420	9	11	2
10	2.033	2.037	1	12	3	1	1.417	1.417	10	2	2
		2.032	6	6	2	1	1.404	1.403	5	15	4
10	2.027	2.029	5	14	0	3	1.388	1.390	6	13	4
11	2.022	2.019	0	0	4	3	1.379	1.379	8	2	4

Unit cell parameters: *a* 15.179(1), *b* 38.195(1), *c* 8.0745(5) Å.

$Pb_{14}As_6S_{23}$ (jordanite) → $3Pb_4As_2S_7$ (tsugaruite) + 2PbS (galena)

$2Pb_{14}As_6S_{23}$ (jordanite) → $3Pb_9As_4S_{15}$ (gratonite) + PbS (galena).

The chemical formula for tsugaruite had been formerly applied to jordanite. However, this was revised to $Pb_{14}As_7S_{24}$ in Dana's System of Mineralogy (Palache *et al.*, 1944), but this does not balance. The actual formula has been proposed by Ito and Nowacki (1974) as $Pb_{14}As_6S_{23}$, to which the material involved in our examination is very close, verifying the compositional similarity between the two.

The chemical similarity between jordanite and tsugaruite has caused confusion in the past. For example, Watanabe and Nakano (1936) described the latter mineral as jordanite. Under favourable conditions the minerals can be distinguished in mine exposures and subsequently from their chemical compositions and optics. We believe that published jordanite analyses also contain some examples of tsugaruite.

Acknowledgements

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