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Second Occurrence of Arsendescloizite and Implications for Mineralization in the Oxidized Zone of the Kamegai Mine, Toyama Prefecture, Japan

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Abstract This study investigates secondary minerals taken from the oxidation zone of the Hokora deposit at the Kamegai mine in Toyama Prefecture, Japan. Smithsonite, hydrozincite, hemimorphite, aurichalcite, mimetite, adamite, zincolivenite, legrandite, and the rare arsenate mineral arsendescloizite are identified as secondary minerals. This is the second occurrence of arsendescloizite in Japan. It forms yellow spherical crystals 200–500 μm in size, and is associated with hydrozincite and smithsonite within gaps in veinlets which cut limonite. The empirical formula of arsendescloizite is $(Pb_{0.93}Cd_{0.05})_{\Sigma 0.98}Zn_{1.03}As_{1.00}O_4(OH)$, which is close to the end member composition. X-ray diffraction patterns were indexed as orthorhombic, of space group $P2_12_12_1$, with unit cell parameters of $a = 7.6218(7)$ Å, $b = 9.3153(8)$ Å, $c = 6.0491(6)$ Å, and $V = 429.47(7)$ Å^3. The secondary minerals were likely formed in groundwater conditions of approximately Eh $\approx$ 0.5 V and pH $>$ 5. The neutral to basic groundwater conditions could be affected by surrounding limestone or siliceous limestone.

Key words: arsendescloizite, Hokora deposit, Kamegai mine, oxidized zone, secondary minerals, Pb-Zn deposit

Introduction

The oxidation zone of a primary sulfide deposit is formed by chemical weathering under an oxidizing environment near the surface, where primary sulfide minerals are altered into various secondary minerals. In the case of zinc, oxidation of sulfide minerals gives rise to supergene non-sulfide zinc deposits. Common secondary zinc minerals are smithsonite ($ZnCO_3$), hemimorphite [$Zn_4Si_2O_7(OH)_2 \cdot H_2O$)], hydrozincite [$Zn_5(CO_3)_2(OH)_6$], and sauconite [$Na_{0.3}Zn_3(Si,Al)_4O_{10}(OH)_2 \cdot 4H_2O$] (e.g., Hitzman *et al.*, 2003). Additionally, various arsenate minerals can be formed where arsenic, copper and lead are present (e.g., Bowell, 2014). The species of secondary minerals in an oxidation zone are due to multiple factors, such as the composition of primary minerals and the geochemistry of the groundwater. These minerals are important indicators of the formation conditions of the oxidation zone.

This study aims to characterize the mineralogy of secondary minerals taken from the oxidation zone of the Kamegai mine in Toyama Prefecture, and to reconstruct the geochemical conditions under which they were formed. In addition, a rare arsenate mineral, arsendescloizite [$PbZn(AsO_4)(OH)$], a member of the descloizite subgroup in the adelite-descloizite group, was identified in this study. Arsendescloizite is an arsenate-analogue of descloizite [$PbZn(VO_4)$ (OH)], the vanadate. It typically occurs in oxidized Pb-Zn deposits, and was first discovered at the Tsumeb mine in Namibia (Keller and Dunn, 1982). In Japan it had previously been reported only from the Toroku mine in Miyazaki Prefecture (Kato and Matsubara, 1993). Descloizite is also rare in Japan, with known localities including the Miyoshino mine in Fukuoka Prefecture (Okamoto *et al.*, 1959) and the Yasaka mine in Yamaguchi Prefecture (Inoue *et al.*, 1959). In this paper we describe the mineralogical characteristics, especially the chemical composition of arsendescloizite from the Kamegai mine.

Occurrence

The Kamegai mine is a Pb–Zn deposit located in the southeastern part of Toyama Prefecture, hosted in the Hida metamorphic rocks of the Hida belt (Suwa *et al.*, 1981). This belt is subdivided into the Western, Central, and Eastern massifs. The Kamegai mine and the Kamioka mine are in the Central massif (Akiyama, 1980a). While the igneous rocks related to mineralization at the Kamegai and Kamioka mines remain poorly understood (Sato *et al.*, 1990), Inishi syenitic rock is distributed around high-temperature metasomatic deposits associated with hedenbergite skarn in the area (Akiyama, 1980b).

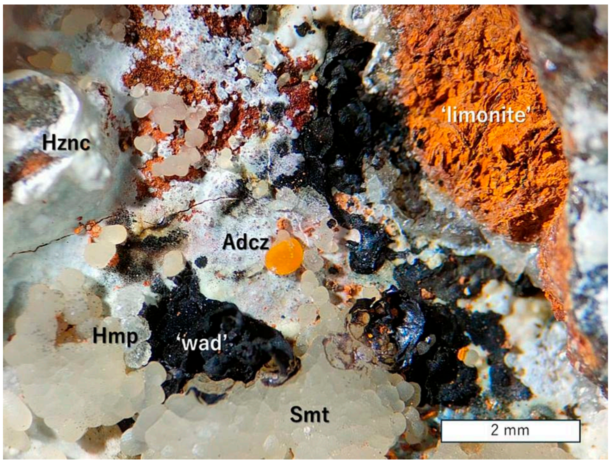

Fig. 1. A representative occurrence of arsendescloizite (NSM-M49061). Arsendescloizite (Adcz), smithsonite (Smt), hemimorphite (Hmp), hydrozincite (Hznc).

This study concentrates on the Hokora deposit at the Kamegai mine. This deposit is a vein-type replacement orebody that formed along both walls of a porphyritic dike intruding limestone or siliceous limestone. The main ore mineral is galena, and the outcrop is characterized by abundant non-sulfide zinc minerals referred to as “calamine” (Iwao *et al.*, 1953).

Fig. 2. A representative occurrence of legrandite (NSM-M53644).

Although no outcrops are observable today, rocks derived from the Hokora deposit remain in a mine dump. This mine dump contains gneiss, marble, and limonite. The following mineral species were identified in this study:

- Arsenate minerals: arsendescloizite, mimetite, adamite, legrandite, zincolivenite and pharmacosiderite.
- Secondary zinc minerals: smithsonite, hydrozincite, hemimorphite and aurichalcite.
- Other secondary minerals: malachite, brochantite and linarite.
- Primary sulfide minerals: pyrite, sphalerite, arsenopyrite, chalcopyrite and galena.

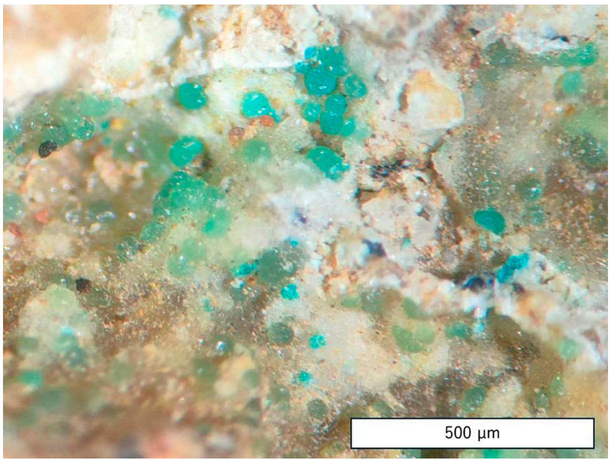

Fig. 3. A representative occurrence of zincolivenite (NSM-M53645). The color variation in the green spherical crystals of zincolivenite is due to the closely associated brochantite.

Arsendescloizite occurs in limonite and is found in gaps between veinlets of white (hydrozincite) to translucent (smithsonite) secondary minerals. It is associated with hydrozincite, smithsonite, hemimorphite, and Zn-, Pb-, Mn-, Co-, and Si-bearing “wad”. It forms yellow spherical crystals (200–500 µm in diameter) on the surfaces of hydrozincite or smithsonite that cover gaps of veinlets (Fig. 1). The fractured surface of the spherical crystal exhibits a radial texture. The specimen of arsendescloizite has been deposited at the National Museum of Nature and Science, Tsukuba, Japan (specimen number NSM-M 49061).

Mimetite occurs in a veinlet with a similar mineral assemblage to that of arsendescloizite on the same specimen, appearing as yellow spherical crystals. Adamite was identified on a separate specimen, forming yellow to white prismatic crystals or green radial aggregates in limonite cavities. Legrandite mineralized as yellow prismatic crystals in limonite cavities (Fig. 2), which is a similar occurrence to adamite. Adamite or legrandite crystals may grow in a cavity of arsenopyrite-rich limonite. Zincolivenite forms green spherical crystals of about 100 µm size and is closely associated with hemimorphite, smithsonite, brochantite, and malachite in limonite cavities (Fig. 3).

Chemical composition

A quantitative analysis of arsendescloizite was conducted using energy dispersive X-ray spectroscopy attached to a scanning electron microscope, SEM-EDS, (JEOL JSM-5600, at the Institute for Solid State Physics, The University of Tokyo) and semi-quantitative analysis for identification of mineral species was carried out with SEM-EDS, (JEOL JSM-6610, at the National Museum of Nature and Science). The analytical conditions of quantitative analysis were an accelerating voltage of 15 kV and a beam current of 0.4 nA with a beam diameter of 1 µm. The following standards were used. Zn: Zn metal; As: InAs; Cd: Cd metal; Pb: PbTe. The analytical result is shown in Table 1. The empirical formula of arsendescloizite on the basis of O = 5 and H = 1 atoms per formula unit (*apfu*) is $(Pb_{0.93}Cd_{0.05})_{\Sigma 0.98}Zn_{1.03}As_{1.00}O_4(OH)$. This is close to the end-member composition $[PbZn(AsO_4)(OH)]$, and differs from that of Toroku mine as reported by Kato and Matsubara (1993) in that it contains large amounts of calcium and copper.

Table 1. Chemical composition of arsendescloizite (wt%).

	This study			Kato and Matsubara (1993)
	weight %	*apfu*		weight %
PbO	51.91	Pb	0.93	40.60
CaO	n.d.	Cd	0.05	4.49
ZnO	20.98	Σ	0.98	13.72
CdO	1.69			2.77
CuO	n.d.	Zn	1.03	8.81
As_2O_5	28.86			28.78
P_2O_5	n.d.	As	1.00	0.79
H_2O^*	2.26	H	1	
Total	105.70	O	5	99.42

n.d. = not detected. * Calculated value based on stoichiometry.

X-ray crystallography

X-ray powder diffraction data of arsendescloizite was obtained using a single-crystal X-ray micro-diffractometer (Rigaku Synergy Custom with MicroMax-007HF, at the National Museum of Nature and Science), applying a Gandolfi-like motion on the φ and ω axes to randomize the sample orientation. Cu$K\alpha$ radiation was used (40 kV, 30 nA), monochromatized by Varimax multilayer optics. The scanning range was 12–75° in 2θ. Diffraction peak intensities were extracted by QualX2 software (Altomare *et al.*, 2015) after subtraction of background, and unit cell parameters were refined by RIETAN-FP (Izumi and Momma, 2007). Diffraction line positions were calibrated using an internal Si standard (NIST 640b), while diffraction peak intensities were extracted from measurement without an internal standard, to avoid peak overlap. The diffraction pattern and a list of the peaks of arsendescloizite are shown in Fig. 4 and Table 2. The diffraction peaks were indexed as orthorhombic, of space group $P2_12_12_1$. The refined unit cell parameters are a = 7.6218(7) Å, b = 9.3153(8) Å, c = 6.0491(6) Å, and V = 429.47(7) Å^3.

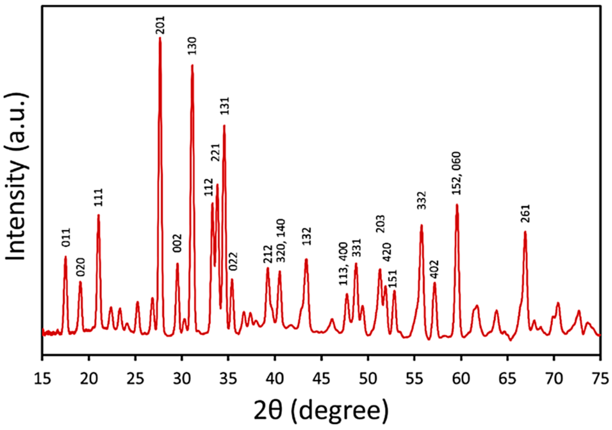

Fig. 4. X-ray diffraction pattern of arsendescloizite. A baseline correction was performed on the original data. a.u. = arbitrary unit.

Table 2. X-ray diffraction peaks (d in Å) of arsendescloizite.

I_{meas}	d_{meas}	d_{calc}	*hkl*	I_{meas}	d_{meas}	d_{calc}	*hkl*
27	5.06	5.073	011	24	2.085	2.084	132
18	4.65	4.658	020	14	1.904	1.908	113
38	4.22	4.223	111			1.905	400
100	3.22	3.224	201	24	1.867	1.870	331
24	3.02	3.025	002	22	1.780	1.782	203
90	2.87	2.876	130	16	1.761	1.764	420
43	2.69	2.691	112	15	1.731	1.734	151
50	2.65	2.651	221	39	1.647	1.649	332
70	2.59	2.597	131	19	1.610	1.612	402
17	2.53	2.537	022	44	1.550	1.553	152
20	2.29	2.296	212			1.553	060
19	2.22	2.230	320	35	1.397	1.399	261
		2.227	140				

Raman spectroscopy

Raman spectra of the arsenate minerals (arsendescloizite, mimetite, adamite, zincolivenite and legrandite) were obtained with a confocal micro Raman spectrometer (Thermo Fisher Scientific DXR3, at the Department of Earth and Planetary Science, The University of Tokyo). All Raman spectra were obtained using a 532.3 nm excitation line from a Nd:YVO_4 laser. The laser power was 10.0 mW. The background was measured 10 times for each measurement. Each acquisition consisted of six cycles with an exposure time of 10 seconds. A 50 μm aperture and a high-resolution grating with 1800 lines/mm were used. Spectral acquisition ranged from 26 to 1856 cm^{-1} with a resolution of 3.2–3.9 cm^{-1}. Calibration was carried out using Ne lamp. The obtained spectra are shown in Fig. 5. Mineral species were identified by comparing the measured Raman spectra with those listed in the RRUFF database (https://rruff.info/).

Discussion

Mineralogical studies of arsenic behavior have been conducted in the oxidation zones of Cu–Pb–Zn deposits at the Tsumeb mine in Namibia, a classic site known for its diverse arsenate minerals (e.g., Bowell and Mocke, 2018; Bowell, 2014). The key geochemical parameters controlling the speciation of arsenic in natural waters are Eh and pH (Smedley *et al.*, 2002). Mimetite is stable in conditions where Eh $\approx$ 0.5 V and pH $\approx$ 5, while adamite and legrandite are stable at pH $>$ 6 under similar redox conditions (Bowell, 2014). Mimetite, adamite and legrandite are present in the Hokora deposit at the Kamegai mine, suggesting groundwater conditions of Eh $\approx$ 0.5 V and pH $>$ 5.

In the Cu–Zn–As–CO_3 system, adamite becomes stable near a neutral pH of 7, when copper activity is low. Its stability field narrows under lower As and Zn activities (Bowell, 2014). At higher pH values, smithsonite becomes the stable phase. The occurrence of both adamite and smithsonite in the Hokora deposit at the Kamegai mine indicates neutral to basic groundwater conditions. This aligns with the observation that smithsonite is associated with hydrozincite, which is known to be stable under basic conditions (Takahashi, 1960).

The association of arsendescloizite and mimetite with smithsonite-bearing veinlets suggests that these arsenates formed under more basic conditions than those of adamite, likely in neutral to basic groundwater. The neutral to basic condition of the groundwater may have been affected by limestone or siliceous limestone, both of which are abundant in the area.

Conclusion

This study documents the secondary minerals taken from the oxidized zone of the Hokora deposit at the Kamegai mine. Based on mineralogical evidence, secondary zinc minerals likely formed from groundwater conditions of Eh $\approx$ 0.5 V and pH $>$ 5. We also report the second occurrence of arsendescloizite in Japan, which was likely crystallized under similar neutral to basic groundwater conditions.

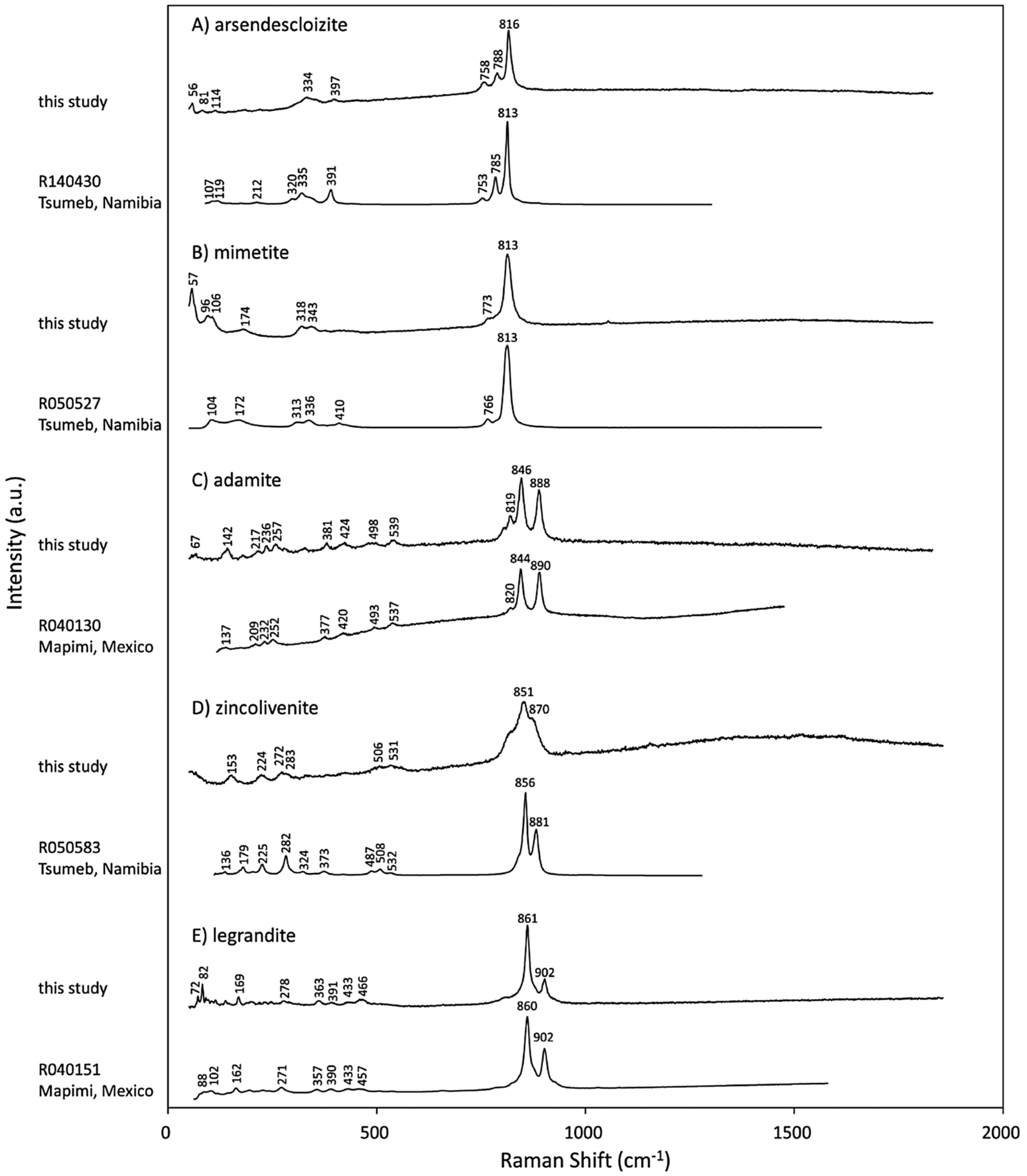

Fig. 5. Raman spectra of each arsenate mineral in this study, and references in the RRUFF database (https://rruff.info/). A: arsendescloizite, B: mimetite, C: adamite, D: zincolivenite, E: legrandite.

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