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# Pararsenolamprite, a new polymorph of native As, from the Mukuno mine, Oita Prefecture, Japan

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**ABSTRACT**

Pararsenolamprite, the third polymorph of native As, is found at the Mukuno mine, Oita Prefecture, Japan. It is orthorhombic, $Pmn2_1$ or $P2_1nm$, $a$ = 3.633(2), $b$ = 10.196(2), $c$ = 10.314(2) Å, $Z$ = 18. The seven strongest lines in the X-ray powder diffraction pattern are: 5.17 (100) (002), 4.60 (24) (012), 3.259 (58) (013), 2.840 (27) (032), 2.580 (22) (004), 2.299 (23) (024), and 1.794 (26) (105). Electron microprobe analysis gives As 91.89, Sb 7.25, S 0.48, total 99.62 wt.% (mean of 8), and lead to the empirical formula, $As_{0.96}Sb_{0.03}S_{0.01}$. It is lead grey in colour and opaque with metallic lustre and black streak. It is sectile and brittle with perfect cleavage on {001}. The $VHN_{25}$ is 66–91 kg/mm$^2$, corresponding to 2–2.5 in Mohs' hardness scale. The measured and calculated densities are 5.88(5) g/cm$^3$ and 6.01 g/cm$^3$, respectively. In reflected plane-polarized light in air, it is white with a slightly greenish blue tint. Anisotoropy is strong, dark brown to dark greenish grey. Bireflectance is distinct; parallel to elongation it is creamy; perpendicular to elongation it is brown, grey and green. Internal reflections are absent. The reflectance spectra are tabulated in the text.

Pararsenolamprite occurs as euhedral crystals in close association with arsenic, stibnite and quartz in a Sb-As-Ag-Au-bearing quartz vein cutting altered Neogene andesite from the Mukuno mine. It forms radial or parallel aggregates of bladed cystals up to 0.8 mm in length.

**Keywords:** pararsenolamprite, arsenic, polymorph, new mineral, Mukuno mine, X-ray, chemistry, optical data.

## Introduction

The Mukuno mine is a well known locality for native arsenic in Japan. A lead-grey mineral with metallic lustre that resembled arsenolamprite (Hintze, 1886) was collected from the mine. X-ray diffraction (XRD) analysis revealed that the powder diffraction data are quite different from those of arsenolamprite or native arsenic.

The mineral is named as a new polymorph of native As, related to arsenolamprite. The mineral and the mineral name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association (no. 99-047). The type specimen is deposited at the National Science Museum, Tokyo, under catalogue number NSM M-28015.

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## Occurrence

Pararsenolamprite is found on the dump of hydrothermal Sb-As-Ag-Au ore deposits of the Mukuno mine (Lat. 33°28′47″N, Long. 131°26′15″E), Yamaga-cho, Oita Prefecture, Kyushu, Japan. The ore deposit comprises two major quartz veins ranging 0.2–2 m in thickness with a N60°W strike and 60°S dip (Kinoshita, 1961). They are developed in altered Neogene andesite, and their constituents are quartz, pyrite, stibnite, miargyrite, Ag-bearing tetrahedrite and native arsenic with minor native gold, löllingite and pararsenolamprite. The lower part of the ore

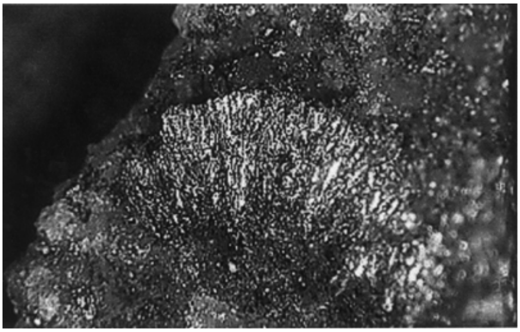


FIG. 1. Pararsenolamprite comprising minute bladed crystals in a quartz vug. Field of view: ~3.4 × 2.2 mm.

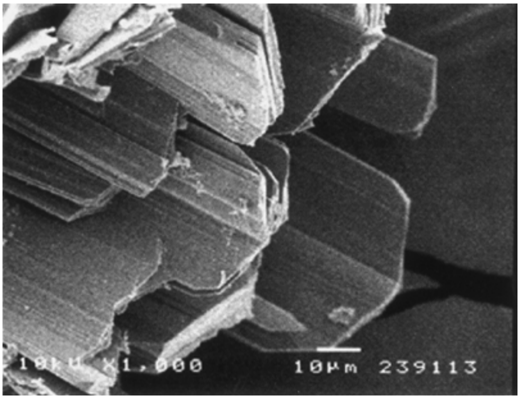

FIG. 2. SEM image of pararsenolamprite. Scale bar: 10 μm.

vein is rich in Au, Ag and As, but Sb increases upwards with a decrease of Au, Ag and As. Pararsenolamprite coexists with quartz, native arsenic and stibnite, especially growing over colloform aggregates of native arsenic. The mineral forms radial or parallel aggregates of minute bladed crystals up to 0.8 mm in length (Fig. 1). Rare euhedral crystals elongated on [100] and flattened on (001) are observed in vugs of the quartz vein (Fig. 2). Pararsenolamprite strongly is resistant to alteration, in contrast to native arsenic which is easily altered to claudetite (Fig. 3) or the source of secondary arsenates such as kankite.

## Physical and optical properties

Pararsenolamprite is lead grey in colour and opaque with metallic lustre and black streak. It is sectile and brittle with perfect cleavage on {001}. The appearance resembles that of arsenolamprite (Johan, 1959). The density measured by Berman balance is 5.88 (5) g/cm$^3$ and the calculated density is 6.01 g/cm$^3$. It has microhardness $VHN_{25}$ in the range 66−91 kg/mm$^2$ based on five indentations. The Mohs' hardness is ~2−2.5.

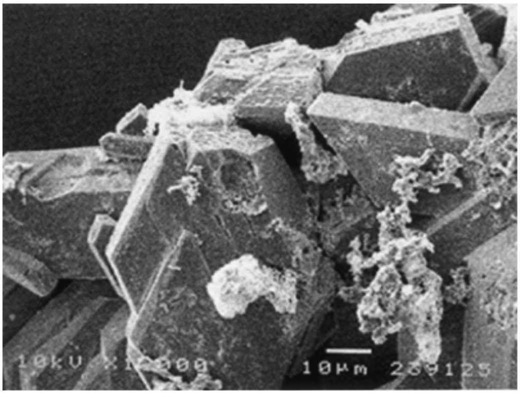


FIG. 3. SEM image of claudetite altered from the associated native As with pararsenolamprite. Scale bar: 10 μm.

TABLE 1. Reflectance values for pararsenolamprite from the Mukuno mine, Japan.

| | Air | | Oil | |
|---|---|---|---|---|
| nm | $R_1$ | $R_2$ | $R_1$ | $R_2$ |
| 470 | 49.0 | 44.0 | 33.6 | 29.3 |
| 546 | 47.0 | 42.1 | 31.5 | 28.0 |
| 589 | 44.8 | 39.9 | 29.7 | 26.9 |
| 650 | 44.9 | 40.3 | 29.2 | 26.0 |
| 400 | 57.6 | 49.6 | 37.9 | 30.9 |
| 420 | 53.7 | 47.1 | 36.3 | 30.2 |
| 440 | 51.0 | 45.5 | 35.0 | 29.9 |
| 460 | 49.6 | 44.5 | 34.1 | 29.6 |
| 480 | 48.7 | 43.7 | 33.2 | 29.2 |
| 500 | 47.7 | 42.9 | 32.2 | 28.8 |
| 520 | 47.8 | 42.9 | 32.1 | 28.4 |
| 540 | 47.4 | 42.5 | 31.8 | 28.1 |
| 560 | 45.9 | 40.9 | 30.6 | 27.6 |
| 580 | 44.8 | 39.9 | 29.8 | 27.1 |
| 600 | 44.8 | 39.8 | 29.5 | 26.7 |
| 620 | 45.9 | 40.9 | 30.1 | 26.3 |
| 640 | 45.7 | 40.9 | 30.1 | 26.1 |
| 660 | 44.7 | 40.3 | 29.1 | 26.1 |
| 680 | 44.4 | 40.3 | 28.8 | 25.9 |
| 700 | 43.3 | 39.5 | 28.2 | 25.9 |

TABLE 2. X-ray powder diffraction data for native As-minerals.

| | 1 | | | | 2 | | | 3 | |
|---|---|---|---|---|---|---|---|---|---|
| *h k l* | $d_{calc.}$ | $d_{obs.}$ | *I* | *h k l* | *d* | *I* | *h k l* | *d* | *I* |
| 0 0 2 | 5.16 | 5.17 | 10 | 0 0 2 | 5.494 | 11 | 0 0 3 | 3.52 | 26 |
| 0 1 2 | 4.60 | 4.60 | 24 | 0 1 2 | 3.469 | 23 | 1 0 1 | 3.112 | 6 |
| 0 2 2 | 3.63 | 3.61 | 4 | 1 1 1 | 2.738 | 100 | 0 1 2 | 2.771 | 100 |
| 0 1 3 | 3.258 | 3.259 | 58 | 0 1 4 | 2.3423 | 1 | 1 0 4 | 2.050 | 24 |
| 0 3 2 | 2.838 | 2.840 | 27 | 0 2 0 | 2.2351 | 24 | 1 1 0 | 1.879 | 26 |
| 0 0 4 | 2.579 | 2.580 | 22 | 0 2 2 | 2.0706 | 1 | 0 1 5 | 1.768 | 10 |
| 1 2 2 | 2.566 | 2.562 | 16 | 1 2 1 | 1.8777 | 9 | 0 0 6 | 1.757 | 7 |
| 0 1 4 | 2.500 | 2.501 | 15 | 0 0 6 | 1.8330 | 4 | 1 1 3 | 1.658 | 6 |
| 1 1 3 | 2.425 | 2.426 | 9 | 2 0 0 | 1.8247 | 11 | 2 0 2 | 1.556 | 11 |
| 0 2 4 | 2.301 | 2.299 | 23 | 1 1 5 | 1.7361 | 32 | 0 2 4 | 1.386 | 6 |
| 1 4 1 | 2.045 | 2.044 | 4 | 1 2 3 | 1.6909 | 12 | 1 0 7 | 1.367 | 4 |
| 0 2 5 | 1.912 | 1.913 | 5 | 2 1 2 | 1.6149 | 3 | 2 0 5 | 1.289 | 5 |
| 2 0 0 | 1.817 | 1.817 | 8 | 2 0 4 | 1.5204 | 9 | 1 1 6 | 1.284 | 5 |
| 1 0 5 | 1.794 | 1.794 | 26 | 0 3 2 | 1.4380 | 7 | 0 1 8 | 1.222 | 1 |
| 1 1 5 | 1.767 | 1.767 | 15 | 0 2 6 | 1.4174 | 2 | 1 2 2 | 1.1987 | 7 |
| 0 3 5 | 1.763 | 1.763 | 13 | 2 2 0 | 1.4136 | 5 | 0 0 9 | 1.1722 | 1 |
| 0 2 6 | 1.629 | 1.627 | 7 | 0 0 8 | 1.3750 | 2 | 2 1 4 | 1.1158 | 4 |
| 2 2 2 | 1.624 | | | 1 3 1 | 1.3687 | 2 | 0 2 7 | 1.1062 | 2 |
| 2 2 3 | 1.532 | 1.530 | 4 | 0 3 4 | 1.3102 | 1 | 3 0 0 | 1.0857 | 3 |
| 2 3 2 | 1.530 | | | 2 0 6 | 1.2935 | 2 | 1 2 5 | 1.0631 | 3 |
| 2 3 3 | 1.452 | 1.451 | 5 | 2 2 4 | 1.2571 | 4 | 3 0 3 | 1.0374 | 2 |
| 0 5 5 | 1.450 | | | 2 1 6 | 1.2423 | 1 | 1 1 9 | 0.9948 | 2 |
| 0 2 7 | 1.415 | 1.416 | 7 | 1 2 7 | 1.2126 | 4 | 2 1 7 | 0.9531 | 2 |

1: Pararsenolamprite from the Mukuno mine, Oita, Japan. $a$ = 3.633, $b$ = 10.196, $c$ = 10.314 Å
2: Arsenolamprite, ICDD 30-100. $a$ = 3.65, $b$ = 4.47, $c$ = 11.0 Å
3: Arsenic, ICDD 5-632. $a$ = 3.760, $c$ = 10.548 Å

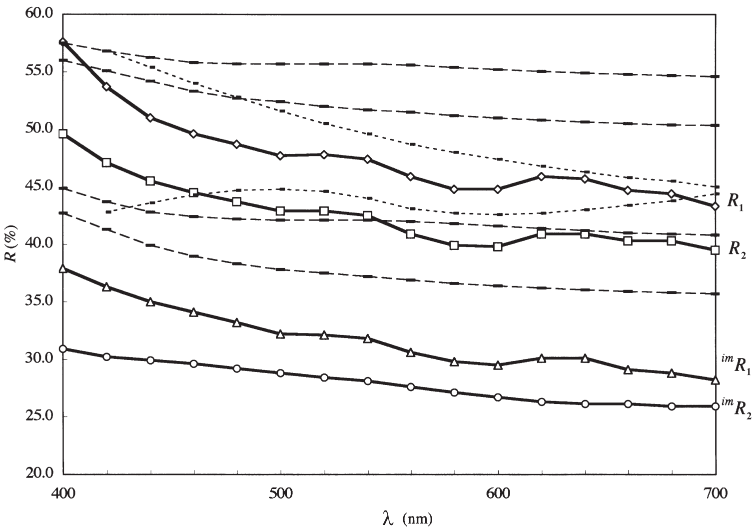


FIG. 4. Reflectance spectra of pararsenolamprite (lines), arsenolamprite (dotted lines), and arsenic (dashed lines) in air ($R$) and oil (${}^{im}R$). (No data for arsenolamprite in oil.)

TABLE 3. Chemical compositions of pararsenolamprite and associated arsenic from the Mukuno mine, Japan.

| Constituent | Pararsenolamprite Wt.% (average of 8 analyses) | Pararsenolamprite Range | Arsenic Wt.% (average of 8 analyses) | Arsenic Range |
|---|---|---|---|---|
| As | 91.89 | ~90.50–92.79 | 96.80 | ~96.15–97.28 |
| Sb | 7.25 | ~6.27–8.19 | 2.54 | ~2.16–3.25 |
| S | 0.48 | ~0.34–0.71 | 0.30 | ~0.16–0.66 |
| Total | 99.62 | | 99.64 | |

Pararsenolamprite is white with a slightly greenish blue tint in plane-polarized light. Internal reflections are not observed in plane-polarized light or between crossed polars. It is distinctly bireflectant; cream-coloured parallel to elongation; brown, grey, green perpendicular to elongation. It is strongly anisotropic between crossed polars; dark brown, greenish grey, and more anisotropic than arsenolamprite.

Reflectance spectra in air and in oil (Nikon $n_D$ = 1.515) for pararsenolamprite were measured relative to a WC standard. The equipment used was a Nikon photometry system P100 including an Optiphot-2 microscope photometer with photometer-controller P101, monochromater G-70 and two-light-flux interference examination. The reflectance data are summarized in Table 1 and Fig. 4. These are distinctly lower than those of arsenic (Criddle and Stanley, 1993) and very similar to those of arsenolamprite (Picot and Johan, 1982).

## Crystallography

The powder XRD pattern for pararsenolamprite was obtained using a diffractometer (Rigaku LINT 2100), employing monochromatized Cu-$K\alpha$ radiation. There are many differences between the patterns of arsenolamprite and those of native As (Table 2). The cell parameters refined from the data are: $a$ = 3.633(2), $b$ = 10.196(2), $c$ = 10.314(2) Å, $V$ = 382.1(1) $Å^3$, $Z$ = 18.

As described above, pararsenolamprite occurs as aggregates of minute bladed crystals, which show parallel growth along the $b$ axis (Fig. 2), but no single crystals could be separated for structural analysis. However, one of the aggregate samples investigated using a Weissenberg camera gave crystallographic data. The oscillation photograph of the aggregate shows that the directions of the $b$ axes of crystal fragments are almost parallel to each other. The ($h0l$) and ($h1l$) Weissenberg photographs show that the aggregate consists of two groups of crystals, which are related to the rotation around the $b$ axis. The ($hk0$), ($0kl$), ($1kl$) and ($2kl$) precession photographs were obtained with the same aggregate for one of the two crystal groups. The Weissenberg and precession photographs suggest that pararsenolamprite is orthorhombic and that the possible space group is $Pmn2_1$ or $P2_1nm$, unlike that of arsenolamprite, *Bmab* (Smith *et al*., 1975).

## Chemical composition

The chemical compositions of pararsenolamprite and native As in the Mukuno mine were determined using a JEOL 733 Mark II electron microprobe analyser at the Earth and Planetary Sciences Institute of the University of Tokyo, using the methods of Shimizu *et al*. (1986). The accelerating voltage was 20 kV, and the beam current was $2.00 \times 10^{-8}$ A on a Faraday cage. The standards used were synthetic $Cu_3AsS_4$ (As), synthetic $Cu_{10}Zn_2Sb_{1.4}As_{2.6}S_{13}$ (Sb), and synthetic ZnS (S). No other element with atomic number >10 was detected. The mean analytical results and ranges in parentheses for eight analyses are: As 91.89 (90.50–92.79), Sb 7.25 (6.27–8.19), S 0.48 (0.34–0.71), total 99.62 wt.% (Table 3). The empirical formula is $As_{0.94}Sb_{0.05}S_{0.01}$ on the basis of total atoms = 1. The chemical compositions of the associated As are also given in Table 3 for comparison.

## Conclusions

Table 4 demonstrates the comparison of crystal data, physical properties and optical properties of three native As minerals. Pararsenolamprite is more resistant to alteration by weathering or oxidation than native As. This may be due to the

TABLE 4. Comparison of crystal data, physical properties and optical properties of native As minerals.

| | Pararsenolamprite | Arsenolamprite | Arsenic |
|---|---|---|---|
| Occurrence | In hydrothermal quartz vein in association with arsenic and stibnite | In carbonate rocks and in calcite veins | In hydrothermal veins |
| Crystal system | Orthorhombic | Orthorhombic | Trigonal |
| Space group | $Pmn2_1$ or $P2_1nm$ | *Bmab* | $R\bar{3}m$ |
| Cell parameters | | | |
| $a$ (Å) | 3.633 | 3.65 | 3.760 |
| $b$ | 10.196 | 4.47 | |
| $c$ | 10.314 | 11.0 | 10.548 |
| $V$ (Å$^3$) | 382.1 | 179.5 | 129.1 |
| $Z$ | 18 | 8 | 6 |
| Colour | Lead grey | Grey-white, tarnishes to black | Tin-white, tarnishes to dark grey |
| VHN (kg/mm$^2$) | 66–91 (25 g load) | not determined | 72–173 (100 g load) |
| Mohs hardness | 2–2½ | 2 | 3½ |
| $D_{meas.}$ (g/cm$^3$) | 5.88(5) | ~5.63–5.78 | ~5.3–5.5 |
| $D_{calc.}$ (g/cm3) | 6.01 | 5.78 | 5.58 |
| Optical properties | | | |
| colour | white with greenish blue tint | white | white |
| anisotropy | strong, dark brown to dark greenish grey | weak in air, strong in oil | distinct, yellowish brown and light grey to yellowish grey |
| bireflectance | distinct, ‖ elongation: creamy, ⊥ elongation: brown, grey, green | distinct, ‖ (001): similar to arsenic, ⊥ (001): darker | feeble in air, distinct in oil |
| reflectance | | | |
| $R_{max}$ (%) | ~57.6 (400 nm)–43.3 (700 nm) | ~56.8 (420 nm)–45.0 (700 nm) | ~57.5 (400 nm)–54.6 (700 nm) |
| $R_{min}$ (%) | ~49.6 (400 nm)–39.5 (700 nm) | ~42.8 (420 nm)–44.4 (700 nm) | ~56.0 (400 nm)–50.4 (700 nm) |
| $^{im}R_{max}$ (%) | ~37.9 (400 nm)–28.2 (700 nm) | n.d. | ~44.85 (400 nm)–40.8 (700 nm) |
| $^{im}R_{min}$ (%) | ~30.9 (400 nm)–25.9 (700 nm) | n.d. | ~42.7 (400 nm)–35.7 (700 nm) |

stronger bonding in the crystal structure which is consistent with a higher density than that of arsenic. Pararsenolamprite is also characterized by a considerable amount of Sb, and there is a significant difference in the Sb content compared to coexisting As. It could be the Sb content that causes the resistance to weathering. Although some occurrences of arsenolamprite are known (e.g. Johan, 1959; Clark, 1970), detailed chemical data have not been reported. Thus comparisons between arsenolamprite and pararsenolamprite could not be made. The phase corresponding to pararsenolamprite has not been synthesized from pure As as a starting material.

## Acknowledgements

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