Au(Ag)-Sn-Sb-Pb minerals in association with placer gold from Rumoi province of Hokkaido, Japan: a description of two new minerals (rumoiite and shosanbetsuite)

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Au(Ag)-Sn-Sb-Pb minerals occurring in association with gold, rumoiite (AuSn2), shosanbetsuite (Ag3Sn), yuanjiangite (AuSn), aurostibite (AuSb2), and anyuiite (AuPb2), were found from the Shosanbetsu River (the former three), Shosanbetsu village and the Ainusawa River (the latter two), Haboro town, Rumoi province, Hokkaido, Japan. Rumoiite (IMA No. 2018-161) and shosanbetsuite (IMA No. 2018-162) have been approved as new minerals by the International Mineralogical Association, the Commission on New Minerals, Nomenclature and Classification (IMA-CNMNC) and named after the locality. Both minerals show anhedral shape at less than 5 µm and occur in close association with one another, yuanjiangite, and native lead in spherical aggregates in placer gold. The densities of rumoiite and shosanbetsuite based on their empirical formulae and powder diffraction data were calculated to be 10.1 and 11.1 g/cm³, respectively. The empirical formulae of rumoiite and shosanbetsuite were (Au0.95Ag<0.01)Σ0.96(Sn1.93Sb0.08Pb0.02Bi0.01)Σ2.04 (basis of 3 apfu) and (Ag2.46Au0.54)Σ2.99(Sn0.97Sb0.01Pb0.01Bi0.01)Σ1.01 (basis of 4 apfu), respectively. Rumoiite is orthorhombic, Pbca, with lattice parameters a = 6.9088(7) Å, b = 7.0135(17) Å, c = 11.7979(19) Å and V = 571.6(3) Å³ (Z = 8). Shosanbetsuite is orthorhombic, Pmmn, with lattice parameters a = 5.986(8) Å, b = 4.779(3) Å, c = 5.156(6) Å and V = 147.5(3) Å³ (Z = 2). Rumoiite and shosanbetsuite correspond to the synthetic AuSn2 and Ag3Sn phases, respectively. The chemical compositions for aurostibite, anyuiite, yuanjiangite, and native lead are also reported in this paper. Hydrothermal activity in ultramafic rocks after the formation of gold (electrum) grains may have been involved in the occurrence of Au(Ag)-Sn-Sb-Pb minerals.

Keywords: Rumoiite, Shosanbetsuite, Yuanjiangite, Aurostibite, Anyuiite, Placer gold

INTRODUCTION

Platinum-group minerals (PGM) are composed not only of alloys but also of a wide variety of compounds containing various elements, and the total PGM exceeds 160 species. Volatile elements such as Sn, Sb, and Pb are often associated with PGM, and at least 46 PGM species containing such elements are known. This diversity means that PGM have frequent encounters with such volatile elements at their formation site. Therefore, it is possible that gold (electrum), which often occurs simultaneously with PGM, should have a similar opportunity. Although gold is less reactive, five gold compound minerals that contain Sn, Sb, and Pb have been identified to date, and these are occasionally found in placer PGM deposits: anyuiite (AuPb2), aurostibite (AuSb2), hunchunite (Au2Pb), novodneprite (AuPb3), and yuanjiangite (AuSn) (e.g., Razin and Sidorenko, 1989; Chen et al., 1994; Sandimirova et al., 2014; Litvinenko 2017; Svetlitskaya and Nevolko, 2017). Anyuiite and novodneprite also occur as nanoscaled inclusions in peridotite olivine (Ferraris and Lorand, 2015). In addition to those minerals, some unnamed Au(Ag)-Sn minerals have been reported from placer PGM deposits in the Ol’khovaya-1 River and the Bimika River, Russia (Sandimirova et al., 2014; Litvinenko 2017). These unnamed minerals with the compositions of AuSn2 and Ag3Sn were associated with placer gold from both localities. A AuSn2 mineral associated with placer gold was also discovered from the Boiron River, Switzerland before it was found in Russia (Meisser and Brugger, 2000). However, these minerals have not
yet been formally established as mineral species.

In Japan, placer PGM deposits are known in Hokkaido and Kumamoto Prefecture (e.g., Suzuki, 1950; Nishio–Hamane et al., 2019). Although various PGM with volatile elements, including the new minerals of minakawaithe, RhSb and michitoshiite–(Cu), Rh(Cu1–xGex) 0 < x ≤ 0.5, occur in the deposits in Kumanomo (Nishio–Hamane et al., 2019; Tanaka et al., 2020), this locality is unsuitable for an investigation of the diversity of gold compounds because of the quite rare occurrence of placer gold. In contrast, the PGM placer deposits in Hokkaido are almost always accompanied by much placer gold (e.g., Suzuki, 1950). To date, placer PGM and gold in Hokkaido have been obtained mainly around the serpentinite area (Matsumoto, 1928; Aoyama, 1936; Suzuki, 1950; Mertie, 1969; Urashima et al., 1972, 1974, 1976; Nakagawa et al., 1991; Matsubara, 1992; Nakagawa and Ohta, 1993), while the author (K.S.) found that these are also available from placer deposits in the Rumoi province, Hokkaido, Japan. In this area, sedimentary rocks derived from the Teshio Mountains which consists partly of ultramafic rocks (e.g., Hata, 1961). During a mineralogical investigation for placer PGM and gold, we revealed that the PGM deposits in the Rumoi province are composed of various minerals (e.g., Nishio–Hamane and Saito, 2019). Our series of studies eventually discovered Au(Ag)–Sn–Sb–Pb minerals, including previously unidentified AuSn2 and Ag3Sn, in association with placer gold from the Rumoi province.

We have examined the AuSn2 and Ag3Sn minerals and successfully identified both to be new minerals. These two new minerals were found at the Shosanbetsu River, Minamichiyoda, Shosanbetsu Village, Rumoi province, Hokkaido, Japan. These new AuSn2 and Ag3Sn minerals have been named rumoiite (IMA No. 2018–161) and shosanbetsuite (IMA No. 2018–162), respectively after the type locality. Both the mineral and name have been approved by the International Mineralogical Association, the Commission on New Minerals, Nomenclature and Classification (IMA–CNMNC). The type specimens have been deposited in the collections of the National Museum of Nature and Science, Japan, with the specimen numbers NSM–M46178 (holotype) and M46179 (co-type). Here, we report Au(Ag)–Sn–Sb–Pb minerals in association with placer gold, including the new minerals rumoiite and shosanbetsuite, in the placer deposit from the Rumoi province, Hokkaido, Japan.

**OCCURRENCE**

The Rumoi province is composed of eight local govern-ments: Mashike town, Rumoi city, Obira town, Tomamae town, Haboro town, Shosanbetsu village, Enbetsu town, and Teshio town from south to north. Most of the area is composed of Cretaceous, Neogene, and Quaternary sedimentary rocks (e.g., Matsuno and Kino, 1960; Yamaguchi and Matsumo, 1963). Neogene sedimentary rocks from Haboro to Shosanbetsu are the most widely distributed and divided into the Haboro, Sankebetsu, Chikubetsu, Kotanbetsu, Chiepotsunai, and Enbetsu Formations from the lower to higher level, which consist of conglomerate, sandstone, and mudstone with fossils, coal, and lignite. The largest is the Kotanbetsu Formation with a thickness of several thousand meters. Although the distribution of ultramafic rocks is absent, serpentinite pebble in conglomerates and sandstones including chromite are also known, so that placer PGM and gold are considered to occur secondarily from such stratum (e.g., Suzuki, 1950; Hata, 1961). It is also suggested that they were originally derived from the Teshio Mountains (Hata, 1961).

Placer in this study were collected from Shosanbetsu river in Shosanbetsu village (44°31′21″N, 141°46′51″E) and the Ainusawa River in Haboro town (44°19′08″N, 141°54′09″E). Sand trapped in grassroots and rock crevices was passed through a sluice box to make heavy sand and then panned with a curved plate to collect samples. The heavy sand from both rivers consists mainly of chromite, magnetite, ilmenite, gold, and PGM. Small amounts of zircon, andradite, enstatite, and cassiterite can be found in heavy sand. Au(Ag)–Sn–Sb–Pb minerals occurred in association with gold. Rumoiite (AuSn2), shosanbetsuite (Ag3Sn), yuanjiangite (AuSn), aurostibite (AuSb2), and anyuiite (AuPb2) were conclusively found from the Shosanbetsu River (the former three) and the Ainusawa River (the latter two). PGM mainly occurs as alloy composed of the iridium–subgroup platinum-group elements (IPGE: Ru, Os, and Ir), and PGM that consists of the palladium–subgroup platinum-group elements (PPGE: Rh, Pd, and Pt) scarcely occur. Sn–, Sb–, and Pb–bearing minerals are also accompanied by PGM, which are currently under consideration and will be reported elsewhere.

**APPEARANCES**

**Rumoiite, shosanbetsuite, and yuanjiangite**

The placer gold from the Shosanbetsu River shows a flat elliptical to granular shape, and the maximum grain size is ~ 5 mm and 200 µm thick or less. The placer gold commonly shows an internal core–rim texture, and the rim with a thickness of several micrometers is richer in gold component than the core. One gold grain with small black spots on the surface was identified among the grains, and a spherical aggregate appeared from the cut
The spherical aggregate has a diameter of ~ 400 µm, and there is a 20–µm–thick silver–rich rim at the boundary with gold. Inside, the spherical aggregate consists of yuanjiangite, native lead, rumoiite, and shosanbetsuite. Spherical to elliptical yuanjiangite particles of 5 µm or less are scattered in the spherical aggregate, and the gaps are filled with anhedral native lead, rumoiite, and shosanbetsuite. Yuanjiangite occurs around yuanjiangite, and its distribution is concentrated in a narrow range. The thickness of shosanbetsuite is also ~ 4 µm at a maximum. Yuanjiangite and shosanbetsuite are rarely encountered together, although both come into contact with yuanjiangite and native lead. Such texture and mineral assemblage are almost entirely common with placers obtained from the Ol’khovaya–1 River, Kamchatka, Russia (Sandimirova et al., 2014), although the name of the mineral is not specified in the literature.

The physical and optical properties of yuanjiangite were obtained using synthetic AuSn2 prepared by melting the mixture and then cooling it. Yuanjiangite exhibits a metallic luster with silver white color, and the streak is gray colored. Yuanjiangite is brittle with a Mohs hardness of 2 ½. The density of yuanjiangite (10.1 g/cm³) was calculated using the empirical formula and powder XRD (pXRD) data. Yuanjiangite has a white color under the microscope in reflected light, and pleochroism is weak to very weak as a variation from white to slightly bluish white. Anisotropy is strong to moderate as blue to brownish yellow. The reflectance spectrum for yuanjiangite was measured in air relative to Al standard using the photometry system with a grating monochromator (JASCO V570; Table 1).

The physical and optical properties of yuanjiangite were also measured using Ag3Sn synthesized in the same way. Shosanbetsuite shows metallic silver white color with gray streaks and is brittle, with a Mohs hardness of 2½. The density of yuanjiangite (11.1 g/cm³) was calculated using the empirical formula and pXRD data. Shosanbetsuite has a white color under the microscope in reflected light. Pleochroism and anisotropy are weak to very weak as a variation from white to slightly bluish white. The reflectance spectrum for shosanbetsuite is shown in Table 1.

### Table 1. Reflectance of rumoiite and shosanbetsuite using Al standard in air

| λ (nm) | Rumoiite R (%) | Shosanbetsuite R (%) |
|--------|----------------|---------------------|
| 400    | 70.4           | 40.1                |
| 420    | 71.6           | 43.1                |
| 440    | 72.7           | 46.4                |
| 460    | 74.1           | 49.2                |
| 470    | 75.6           | 50.3                |
| 480    | 76.4           | 51.4                |
| 500    | 77.1           | 53.3                |
| 520    | 77.5           | 55.1                |
| 540    | 77.9           | 56.6                |
| 546    | 78.1           | 57.2                |
| 560    | 78.2           | 58.0                |
| 580    | 78.6           | 59.3                |
| 589    | 78.7           | 59.8                |
| 600    | 78.7           | 60.5                |
| 620    | 78.9           | 61.5                |
| 640    | 78.8           | 62.5                |
| 650    | 78.7           | 63.0                |
| 660    | 78.6           | 63.6                |
| 680    | 78.0           | 64.6                |
| 700    | 80.9           | 65.8                |

### Aurostibite and anyuiite

The placer gold from the Ainusawa River is also flat, elliptical to granular, with a maximum grain size of ~ 10 mm and 200 µm thick or less. It commonly has core–rim texture, with rims a few micrometers thick and richer in gold content than the core. Among the placer gold grains, grains with ash–steel–colored patches were found (Fig. 2). The maximum patch is ~ 300 µm, and multiple patches are distributed on the surface of gold placer within a range of ~ 1.5 mm. Inside, the patch consists of aurostibite and...
anyuite, both of which are irregular grains of 20 µm or less. Although the name of the mineral is not specified, minerals with chemical compositions that correspond to anyuite and aurostibite have been found on the surface of placer gold from the Of’khovaya-1 River, Kamchatka, Russia (Sandimirova et al., 2014; Svetlitskaya and Nevolko, 2017).

**CHEMICAL COMPOSITION**

Chemical analyses were conducted using scanning electron microscopy (SEM; JEOL JSM-100) equipped with energy dispersive X-ray spectroscopy (EDS; 15 kV, 0.8 nA, 1 µm beam diameter) at the Institute for Solid State Physics of the Tokyo University. The ZAF method was used for data correction, and the standards used were pure metals (Au, Ag, Sn, Sb, Pb, and Bi) and HgTe. We used AuM, AgL, SnL, SbL, PbL, BiM, and HgM lines for quantitative analysis. The chemical data for placer gold and Au(Ag)-Sn-Sb-Pb minerals in association with placer gold are summarized in Tables 2 and 3. The gold placers including Au(Ag)-Sn-Sb-Pb minerals are electrum with Au rich rim (Table 2).

**Rumoite, shosanbetsuite, yuanjiangite**

Table 3 shows the chemical data for rumoite, shosanbetsuite, yuanjiangite, and native lead. Rumoite is mainly composed of Au and Sn, with a small amount of Sb, Pb, and Bi. Ag is rarely included. The empirical formula calculated on the basis of 3 apfu is \((\text{Au}_{0.95}\text{Ag}_{0.01})_{0.96}(\text{Sn}_{1.93}\text{Sb}_{0.08}\text{Pb}_{0.02}\text{Bi}_{0.01})_{2.04}\). The simplified and ideal formulae of rumoite are common and written as \(\text{AuSn}_2\), which requires Au 45.34 wt% and Sn 54.66 wt%, a total of 100 wt%. Shosanbetsuite consists mainly of Ag and Sn.

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**Table 2.** Chemical composition of gold (electrum) grains including Au(Ag)-Sn-Sb-Pb minerals

|                  | Shosanbetsuite river | Ainusawa river |
|------------------|----------------------|---------------|
|                  | Core (n = 6)         | Rim (n = 7)   | Core (n = 5) | Rim (n = 4) |
|                  | wt% Mean (Min.-Max)  | wt% Mean (Min.-Max) | wt% Mean (Min.-Max) | wt% Mean (Min.-Max) |
| Ag               | 15.14 (14.02-16.36)  | 1.11 (0.29-2.15) | 37.95 (31.01-43.55) | 5.16 (2.06-10.53) |
| Au               | 84.44 (83.49-85.29)  | 100.58 (99.03-102.02) | 61.58 (56.00-67.28) | 95.72 (88.36-99.44) |
| Hg               | 0.59 (0.02-1.04)     | 0.39 (0-0.81)   | 0.34 (0.10-0.86)   | 0.42 (0.10-0.78)   |
| Total            | 100.17               | 102.08         | 99.88            | 101.30           |
| basis of         | Σ = 1                | Σ = 1          | Σ = 1            | Σ = 1            |
|                  | apfu                 | apfu           | apfu             | apfu             |
| Au               | 0.75                 | 0.98           | 0.47             | 0.91             |
| Ag               | 0.25                 | 0.02           | 0.53             | 0.09             |
| Hg               | 0.01                 | 0.00           | 0.00             | 0.00             |
| Σ                | 1                    | 1              | 1                | 1                |
with a substantial amount of Au, and only a few Sb, Pb and Bi are included. The empirical formula calculated on the basis of 4 apfu is (Ag₂.₄₆Au₀.₅₄)\(\Sigma\)₂.₉₉(Sn₀.₉₇Sb₀.₀₁Pb₀.₀₁Bi₀.₀₁)\(\Sigma\)₁.₀₁, and the simplified formula of shosanbetsuite is (Ag,Au)₃Sn. The ideal formula is Ag₃Sn, which requires Ag 57.68 wt% and Sn 42.32 wt%, a total of 100 wt%. Yuanjiangite is also composed of Au and Sn, while the content of other elements is low. The empirical formula calculated on the basis of 2 apfu is (Au₀.₉₅Ag₀.₀₃)\(\Sigma\)₀.₉₈(Sn₀.₉₉Pb₀.₀₁Bi₀.₀₁Sb<₀.₀₁)\(\Sigma\)₁.₀₂, and the simplified and ideal formulae are common and written as AuSn. Native lead occurred with each compound was also analyzed, the composition of which is predominantly Pb with small amounts of Sn and Sb, and Au and Ag are rarely included. The empirical formula of native lead calculated on the basis of 1 apfu is (Pb₀.₉₂Sn₀.₀₅Sb₀.₀₂Bi₀.₀₁Ag₀.₀₁Au₀.₀₁)\(\Sigma\)₂.₀₂. The compositional trend of each mineral in this study is similar to those reported earlier. Rumoiite does not readily dissolve Ag, as with the previously reported AuSn₂ mineral from the Boiron and Ol’khovaya–1 Rivers (Meisser and Brugger, 2000; Sandimirova et al., 2014). On the other hand, shosanbetsuite has some Au, which was also observed in the previously reported Ag₃Sn mineral from the Ol’khovaya–1 River (Sandimirova et al., 2014). Yuanjiangite and native lead in association with

| Table 3. Chemical compositions of Au(Ag)-Sn-Sb-Pb minerals |
|---------------------------------------------------------------|
| **Rumoiite** <br> (n = 10) | **Shosanbetsuite** <br> (n = 10) | **Yuanjiangite** <br> (n = 12) | **Lead** <br> (n = 3) |
| wt% Mean (Min.-Max) | wt% Mean (Min.-Max) | wt% Mean (Min.-Max) | wt% Mean (Min.-Max) |
| Ag | 0.08 (0.0-0.25) | 53.92 (49.09-59.30) | 0.89 (0.55-1.05) | 0.20 (0.01-0.56) |
| Sn | 52.42 (51.29-53.67) | 23.45 (20.46-27.4) | 37.79 (36.58-39.02) | 2.96 (2.07-4.50) |
| Sb | 2.12 (1.10-2.67) | 0.19 (0-0.84) | 0.16 (0-0.51) | 1.33 (0.94-1.93) |
| Au | 42.84 (41.76-44.11) | 21.44 (15.36-28.85) | 60.17 (58.45-61.28) | 0.17 (0-0.47) |
| Pb | 1.04 (0.25-2.69) | 0.62 (0.08-1.94) | 0.90 (0.46-1.28) | 93.46 (90.34-94.73) |
| Bi | 0.65 (0.04-1.32) | 0.46 (0-0.98) | 0.73 (0.23-1.47) | 0.62 (0-2.49) |
| Total | 99.14 | 100.07 | 100.63 | 98.74 |
| basis of | \(\Sigma = 3\) | \(\Sigma = 4\) | \(\Sigma = 2\) | \(\Sigma = 1\) |
| apfu | | | | |
| Ag | 0.95 | 0.54 | 0.95 | <0.01 |
| Au | <0.01 | 2.46 | 0.03 | <0.01 |
| Sb | 0.96 | 2.99 | 0.98 | 0.01 |
| Sn | 1.93 | 0.97 | 0.99 | 0.05 |
| Pb | 0.08 | 0.01 | 0.00 | 0.02 |
| Bi | 0.02 | 0.01 | 0.01 | 0.92 |
| \(\Sigma\) | 2.04 | 1.01 | 1.02 | 0.99 |

| **Ainosawa river** |
|---------------------------------------------------------------|
| **Aurostibite** <br> (n = 12) | **Anysuite** <br> (n = 6) |
| wt% Mean (Min.-Max) | wt% Mean (Min.-Max) |
| Ag | 0.31 (0-1.78) | - |
| Sn | 8.72 (1.92-12.82) | 0.23 (0-0.49) |
| Sb | 37.44 (33.72-40.15) | 9.53 (7.98-11.00) |
| Au | 43.10 (41.06-44.44) | 33.82 (27.59-37.86) |
| Pb | 8.84 (5.65-17.41) | 53.28 (49.77-59.68) |
| Bi | 0.59 (0.09-1.05) | 0.53 (0-0.86) |
| Total | 98.98 | 97.39 |
| basis of | \(\Sigma = 3\) | \(\Sigma = 3\) |
| apfu | apfu | apfu | apfu |
| Ag | 1.01 | 1.01 | - |
| \(\Sigma\) | 1.03 | 1.01 | 1.01 |
| Sn | 0.34 | 0.01 |
| Sb | 1.42 | 0.46 |
| Pb | 0.20 | 1.51 |
| Bi | 0.01 | 0.01 |
| \(\Sigma\) | 1.97 | 1.99 |
the AuSn₂ and Ag₃Sn minerals were also reported in placer gold from the Ol’khovaya–1 River (Sandimirova et al., 2014), where yuanjiangite was close to pure and the native lead also contained only a small amount of Sn.

**Aurostibite, anyuiite**

Table 3 also shows the chemical data for aurostibite and anyuiite. Aurostibite is mainly composed of Au and Sb, with a substantial amount of Sn and Pb, while the Ag and Bi content is very low. The empirical formula of aurostibite calculated on the basis of 3 apfu is \( \text{Au}_{1.01}^{\Sigma 0.01} \text{Sb}_{1.42}^{\Sigma 2.55} \text{Sn}_{0.34}^{\Sigma 0.64} \text{Pb}_{0.20}^{\Sigma 0.40} \text{Bi}_{0.01}^{\Sigma 0.02} \), and the simplified formula can be shown as \( \text{Au}^{\Sigma 1.03} \text{(Sb,Sn,Pb)}_{2} \). Aurostibite forms a partial solid solution with rumoiite (AuSn₂) and anyuiite (AuPb₂). Anyuiite consists mainly of Au and Pb, with a substantial amount of Sb, while Ag, Sn, and Bi are rarely included. The empirical formula calculated on the basis of 5 apfu is \( \text{Au}_{1.01}^{\Sigma 0.01} \text{Pb}_{1.51}^{\Sigma 2.55} \text{Sb}_{0.46}^{\Sigma 0.64} \text{Sn}_{0.01}^{\Sigma 0.02} \text{Bi}_{0.01}^{\Sigma 0.02} \), and thus the simplified formula is \( \text{Au}^{\Sigma 2.02} \text{(Pb,Sb)}_{2} \). Aurostibite and anyuiite have the same stoichiometry but different structures, which is probably why they occurred as separate phases, although they have a small solid solution to each other.

The occurrence of aurostibite and anyuiite has also been observed in placer from the Ol’khovaya–1 River, Russia (Sandimirova et al., 2014). Although both minerals showed some Sb-Pb substitution, Svetlitskaya and Nevolko (2017) suggested an immiscible gap between them and it seems to be not complete solid solution.

**CRYSTALLOGRAPHY FOR RUMOIITE AND SHOSANBETSUITE**

Single-crystal X-ray studies could not be performed due to the small grain size. Therefore, the crystallography was studied by the pXRD method. Subsequent to the previous chemical analyses, a small fragment (100 × 80 × 60 μm) consisting of polycrystalline material for pXRD was separated from a thin section. The sample was placed on Kapton tape and pXRD data were collected using a synchrotron X-ray source on the NE1 beam line at the Photon Factory Advanced Ring (PF-AR) of the High Energy Accelerator Research Organization (KEK), Japan. This source provided a 50 μm diameter collimated beam of monochromatized X-ray (\( \lambda = 0.417 \text{ Å} \)). The pXRD spectra were collected using the Debye–Scherrer method, recorded via an imaging plate detector, and then converted to conventional one-dimensional profiles using the IPAnalyzer and PIndexer software packages by Seto et al. (2010). Figure 3 shows the pXRD pattern with all diffraction data and unit cell calculations of yuanjiangite and native lead shown in the Supplemental Tables S1 and S2 (available online from https://doi.org/10.2465/jmps.210829). Although the pXRD pattern includes some unidentified peaks, rumoiite, shosanbetsuite, yuanjiangite, and native lead can be indexed.

The measurement data for rumoiite are summarized in Table 4. The seven strongest lines of rumoiite in the pXRD pattern \([d \text{ in } \text{Å} (I/I_{0}) \text{ } hkl] \) were 4.543(42) 111, 3.098(100) 210, 2.949(69) 004, 2.711(37) 104, 2.243(39) 204, 2.128(46) 115 and 1.757(51) 314. Based on these data, rumoiite can be indexed to the orthorhombic Pbca space group (No.61). The unit cell parameters, as refined from the powder data, are \( a = 6.9088(7) \text{ Å}, b = 7.0135(17) \text{ Å}, c = 11.7979(19) \text{ Å} \) and \( V = 571.6(2) \text{ Å}^{3} \) (Z = 8). The \( a:b:c \) ratio calculated from the unit cell parameters (pXRD data) is 0.985:1:1.682. Rumoiite is identical with the synthetic AuSn₂ phase. The structure consists of slightly dis-
torted AuSn₆ octahedra and a Sn–Sn dumbbell, and this is also considered as an intergrowth structure of pyrite and marcasite related slabs (Kripyakevich, 1975; Rodewald et al., 2006). Due to the similarity of the crystal structure, a partial solid solution with the pyrite-structured aurostibite may occur.

Shosanbetsuite does not have many peaks with substantial intensity due to structural restrictions, although seven peaks were observed (Table 4). The peaks of shosanbetsuite in the pXRD pattern \[d \text{ in } \text{Å}(I/I_0)\ hkl\] were observed at 2.592(11) 201, 2.576(8) 002, 2.388(29) 211, 2.275(78) 012, 1.757(70) 221 and 1.356(68) 231, 032. Based on these data, shosanbetsuite can be indexed to the orthorhombic \(Pmmn\) space group \((#59)\). The unit cell parameters as refined from the powder data are \(a = 5.986(8)\,\text{Å}, b = 4.779(3)\,\text{Å}, c = 5.156(6)\,\text{Å}\) and \(V = 147.5(3)\,\text{Å}^3\) (Z = 2). The \(a:b:c\) ratio calculated from the unit cell parameters (pXRD data) is 1.253:1:1.079. Shosanbetsuite is also identical with the synthetic Ag₃Sn phase that has the \(\beta\)-Cu₃Ti-type structure, in which Ag and Sn are ordered in relation to the \(hcp\) structure by an orthorhombic distortion of the hexagonal unit cell (e.g., Fairhurst and Cohen, 1972). This structural distortion was observed by the splitting of major peaks in the pXRD pattern (Fig. 3).

**DISCUSSION**

Pb, Sn, and Sb are constituent elements of solder and are sometimes used to join gold-plated copper electrodes in electronic devices. However, even if such contaminants are introduced, the solder never turned to placer gold after the electrodes were welded. If there were, it would be a lead grain with gold or copper inside. However, there are no factories or disposal sites along the river, and no obvious artifacts of lead (such as shotguns or fishing weights) were also found. Therefore, the Au(Ag)-Sn-Sb-Pb minerals identified are not contaminated with man-made grains but do occur by reactions in nature. Chemical reactions in low-temperature environments

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**Table 4. The pXRD data for rumoiite and shosanbetsuite**

|        | Rumoiite |        | Shosanbetsuite |
|--------|----------|--------|----------------|
| \(I/I_0^*\) | \(h k l\) | \(d_{obs}\) (Å) | \(d_{calc}\) (Å) | \(I/I_0^*\) | \(h k l\) | \(d_{obs}\) (Å) | \(d_{calc}\) (Å) |
| 42     | 111      | 4.543  | 4.542          | 11     | 201      | 2.592  | 2.589          |
| 34     | 112      | 3.775  | 3.779          | 8      | 002      | 2.576  | 2.578          |
| 2      | 200      | 3.452  | 3.454          | 29     | 020      | 2.388  | 2.390          |
| 3      | 021      | 3.364  | 3.361          | 100    | 211      | 2.275  | 2.276          |
| 100    | 210      | 3.098  | 3.099          | 78     | 012      | 2.267  | 2.269          |
| 24     | 211      | 2.998  | 2.997          | 70     | 221      | 1.757  | 2.756          |
| 69     | 004      | 2.949  | 2.950          | 68     | 231,032  | 1.356  | 1.357,1.355    |
| 26     | 122      | 2.763  | 2.763          |        |          |       |                |
| 11     | 212      | 2.744  | 2.743          |        |          |       |                |
| 37     | 104      | 2.711  | 2.713          |        |          |       |                |
| 5      | 023      | 2.619  | 2.617          |        |          |       |                |
| 4      | 114      | 2.529  | 2.530          |        |          |       |                |
| 2      | 213      | 2.433  | 2.434          |        |          |       |                |
| 29     | 221      | 2.409  | 2.409          |        |          |       |                |
| 39     | 204      | 2.243  | 2.243          |        |          |       |                |
| 32     | 214      | 2.136  | 2.137          |        |          |       |                |
| 46     | 115      | 2.128  | 2.128          |        |          |       |                |
| 25     | 223      | 2.086  | 2.086          |        |          |       |                |
| 17     | 132      | 2.074  | 2.073          |        |          |       |                |
| 24     | 312      | 2.052  | 2.051          |        |          |       |                |
| 3      | 025      | 1.958  | 1.958          |        |          |       |                |
| 4      | 133      | 1.931  | 1.930          |        |          |       |                |
| 24     | 231      | 1.912  | 1.911          |        |          |       |                |
| 4      | 224      | 1.889  | 1.890          |        |          |       |                |
| 9      | 215      | 1.876  | 1.877          |        |          |       |                |
| 4      | 232      | 1.840  | 1.830          |        |          |       |                |
| 14     | 322      | 1.827  | 1.826          |        |          |       |                |
| 2      | 304      | 1.815  | 1.815          |        |          |       |                |
| 18     | 134      | 1.771  | 1.771          |        |          |       |                |
| 51     | 314      | 1.757  | 1.757          |        |          |       |                |
| 7      | 026      | 1.715  | 1.715          |        |          |       |                |
| 16     | 225      | 1.702  | 1.703          |        |          |       |                |
| 7      | 216      | 1.660  | 1.660          |        |          |       |                |
| 1      | 331      | 1.625  | 1.625          |        |          |       |                |
| 2      | 315      | 1.604  | 1.604          |        |          |       |                |
| 1      | 117      | 1.594  | 1.595          |        |          |       |                |
| 2      | 332      | 1.581  | 1.581          |        |          |       |                |
| 5      | 240      | 1.564  | 1.564          |        |          |       |                |
| 20     | 421      | 1.537  | 1.536          |        |          |       |                |
| 10     | 027      | 1.519  | 1.519          |        |          |       |                |
| 15     | 217      | 1.481  | 1.481          |        |          |       |                |
| 11     | 136      | 1.471  | 1.470          |        |          |       |                |
| 6      | 316      | 1.463  | 1.463          |        |          |       |                |
| 14     | 423      | 1.442  | 1.442          |        |          |       |                |
| 9      | 227      | 1.391  | 1.391          |        |          |       |                |
| 10     | 244      | 1.380  | 1.381          |        |          |       |                |

* Intensities are standardized within each mineral.
such as rivers are unlikely, and sedimentary rocks containing gold grains are also rarely metamorphosed. In overseas examples, Au(Ag)-Sn-Sb-Pb minerals in placer gold are occasionally found in PGM placer deposits where ultramafic rocks are distributed (Table 5). In such cases, a large amount of PGM is typically accompanied by placer gold, such as in the Rumoi province (Nishio et al., 2017), and Sandimirova et al. (2014) suggest hydrothermal alteration in ultramafic rocks resulted in their formation. Although the placer gold and PGM found in the Rumoi area are derived from sedimentary rocks, it is considered that the sediments that were the source of the sedimentary rocks were supplied by uplift of the Teshio Mountains, where ultramafic rocks remain, even at present (e.g., Suzuki, 1950; Hata, 1961). Au(Ag)-Sn-Sb-Pb minerals including rumoite and shosanbetsuite in this study may also have been formed by hydrothermal alteration in ultramafic rocks. Although the composition of the fluid and the conditions under which hydrothermal alteration occurs are still under discussion, mineral assembly suggests that there may be at least two environments rich in Pb-Sn and Pb-Sb. It is well known that the PGM grains from worldwide including Hokkaido undergo modification after grain formation (e.g., Stumpf and Tarkian, 1976; O’Driscoll and González-Jiménez, 2016); therefore, gold (electrum) grains, which often simultaneously occur with PGM, are likely to be similarly modified.

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SUPPLEMENTARY MATERIALS

Color version of Figures 1–3 and Supplementary Tables S1 and S2 are available online from https://doi.org/10.2465/jmps.210829.

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| Mineral          | Composition | Occurrence (reference)                                      |
|------------------|-------------|-------------------------------------------------------------|
| Rumoite          | AuSn2       | PGM placer deposit (1, 2, 3), gold placer deposit (4)      |
| Shosanbetsuite   | Ag3Sn      | PGM placer deposit (1, 2, 3)                                |
| Yuanjiangite     | AuSn       | PGM placer deposit (1, 2, 3, 5), hydrothermal gold deposit (6) |
| Anyuite          | AuPb2      | PGM placer deposit (1, 2, 7, 8), peridotite (9)            |
| Novodneprite     | AuPb3      | PGM placer deposit (2, 7, 8), gold placer deposit (10), peridotite (9) |
| Hunchunite       | Au2Pb      | PGM placer deposit (2, 8), gold placer deposit (11), hydrothermal gold deposit (12) |
| Aurostibite      | AuSb2      | PGM placer deposit (1, 2), hydrothermal gold deposit (13), hydrothermal Pb-Zn deposit (14) |

1, this study; 2, Sandimirova et al. (2014); 3, Litvinenko (2017); 4, Meisser and Brugger (2000); 5, Chen et al. (1994); 6, Dunin-Barkovskaya et al. (2005); 7, Razin and Sidorenko (1989); 8, Svetlitskaya and Nevolko (2017); 9, Ferraris and Loran (2015); 10, Dyusembaeva (2006); 11, Wu et al. (1992); 12, Kalinin (2021); 13, Graham and Kaiman (1952); 14, Tarkian and Breskovska (1989).
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