Platinum-group minerals in the placer deposit in northwestern Hokkaido, Japan: description of a new mineral, tomamaeite

Daisuke Nishio-Hamane* and Katsuyuki Saito**

*Institute for Solid State Physics, the University of Tokyo, Kashiwa 277-8581, Japan
**Minatomachi, Rumoi, Hokkaido 077-0046, Japan

Mineralogical investigation of platinum-group minerals (PGM) from the placer deposit in northwestern Hokkaido, Japan, was conducted at six rivers and two coasts covering an area of 70 km north-south and 30 km east-west: the Moshosanbetsu River (M), the Shosanbetsu River (S), the Ainusawa River (A), the Tomamae coast (T), the Obira coast (OC), the Kamikinenbetsu River (K), the Obirashibe River (OR), and the Numatapon River (N) from north to south. Details of the major PGM grain and the occurrence of small but diverse PGM inclusions were revealed in this study. Among diverse PGM inclusions, Cu₃Pt mineral was discovered in PGM placer from the coast of Tomamae town, and it has been approved as a new mineral, tomamaeite, named after the type locality, by the International Mineralogical Association, the Commission on New Minerals, Nomenclature and Classification (IMA-CNMC). Later, tomamaeite was also discovered in five localities. Tomamaeite occurs in Pt-Fe(Cu) alloys such as tulameenite, ferronickelplatinum, tetraferroplatinum, and hongshiite as an anhedral particle with a size of less than 20 µm. Tomamaeite is an opaque mineral and has metallic luster with a pale mist white color in reflected light. The hardness of tomamaeite has yet to be determined, although it is estimated to be ~ 3½ from comparison with compositionally related minerals and the calculated density is 12.4 g·cm⁻³ using the empirical formula and powder X-ray diffraction data. The empirical formula of tomamaeite calculated on the basis of 4 apfu is (Cu₃.01Fe₀.06Ni₀.01)Σ₃.08(Pt₀.90Ru₀.01Rh<₀.01Pd<₀.01Os<₀.01Ir<₀.01)Σ₀.93, (Cu₂.92Fe₀.05Ni₀.04)Σ₃.01(Pt₀.97Pd₀.01Rh₀.01)Σ₀.99, (Cu₂.86Sb₀.13Fe₀.03Ni₀.02)Σ₃.03(Pt₁.02Ir₀.02Pd₀.01Os₀.01)Σ₁.07, (Cu₂.71Sb₀.19Fe₀.02Ni₀.02)Σ₂.94(Pt₁.06Ir₀.02)Σ₁.10 from the Tomamae coast, the Moshosanbetsu River, the Shosanbetsu River, the Ainusawa River, the Kamikinenbetsu-sawa River, and the Numatapon River, respectively. Crystal chemistry was investigated using tomamaeite from the Tomamae coast. Tomamaeite is cubic, Pm₃m, with lattice parameters a = 3.683(2) Å and V = 49.97(7) Å³ (Z = 1) of Cu₃Au-type structure, in which Pt occupies the position of origin, and Cu occupies the face-centered positions on a face-centered cubic lattice. PGM from northwestern Hokkaido probably have a mostly common origin and are characterized by depleted ultramafic rocks, and tomamaeite is a non-unique mineral that is formed during the universal post-magmatic process with alteration of such ultramafic rocks to serpentinite.

Keywords: Tomamaeite, Platinum-group mineral, Placer PGM, Northwestern Hokkaido

INTRODUCTION

The platinum-group minerals (PGM) are a diversified collection of minerals that include platinum-group elements (PGE: Os, Ir, Ru, Pt, and Pd), and the International Mineralogical Association database currently contains more than 160 distinct species. PGM are known to be derived from maﬁc and ultramaﬁc rocks (e.g., O’Driscoll and González-Jiménez, 2016), and placer PGM deposits have been formed in Hokkaido and Kumamoto Prefecture, Japan (e.g., Suzuki, 1950; Nishio–Hamane et al., 2019). In Hokkaido, only the deposits surrounding current ultramafic rocks distributed along the Kamui-Kotan belt have been studied to date (Matsumoto, 1928; Aoyama, 1936; Mertie, 1969; Urashima et al., 1972, 1974, 1976; Urashima and Nedachi, 1978; Urashima et al., 1982; Ohta and Nakagawa, 1990; Nakagawa et al., 1991; Matsubara, 1992; Nakagawa and Ohta, 1993), while PGM are also available from placer deposits in northwestern Hokkaido, Japan (e.g., Suzuki, 1950; Tsushima et al., 1954; Hata, 1961; Nishio–Hamane and Saito, 2021). However, no modern research has been done on northwestern Hokkai-
do, where even the species of PGM, for example, are completely unknown to date. Therefore, the present study was practically the first investigation for PGM in this area, by which an unnamed Cu$_3$Pt mineral was discovered in PGM placer from the coast of Tomamae town.

Cu$_3$Pt mineral was originally discovered in replacement rims composed of tulameenite on an isoferraplatinum core as a fine inclusion with diameters up to several tens of micrometers (Distler et al., 1986) and was subsequently reported to have similar occurrence in various localities (e.g., Orsoev et al., 2001; Grokhovskaya et al., 2005, 2009; Kozlov et al., 2011; Tolstykh et al., 2015; Grokhovskaya et al., 2019; Kuzmin et al., 2020). Grokhovskaya et al. (2018) reported the occurrence of 10 µm intergrowth grains consisting of orcelite, laurite, and Cu$_3$Pt mineral in chromitite. On the other hand, none have been established as mineral species due to their microscopic grain size. The Cu$_3$Pt mineral in the present work was also of a similar size; however, after close inspection, it was successfully established that this is a new mineral with Cu$_3$Au-type structure. This new mineral was named tomamaeite after the type locality, Tomamae town, Hokkaido, Japan. The meaning of Tomamae is the place where there are many of Toma’s flowers (Corydalis ambigua) in the language of the Ainu, the indigenous people of Hokkaido. Both the mineral and name have been approved as No. 2019–129 by IMA–CNMNC. The type specimens have been deposited in the collections of the National Museum of Nature and Science, Japan, specimen number NSM–M47328. After the approval of tomamaeite, we have conducted further investigation and discovered that it occurs in five additional localities in northwestern Hokkaido. This paper describes the new mineral tomamaeite in detail and reports the occurrence of PGM in northwestern Hokkaido.

OCCURRENCE

Figure 1 shows the geological setting and distribution of the PGM placer deposit in the studied area, northwestern Hokkaido. The geological setting in this area is divided into the Rebun-Kabato terrane, Sorachi–Yezo terrane, Kamuipton unit, and Idonappu terrane from west to east (e.g., Wallis et al., 2020), and ultramafic rocks are associated in the Kamuipton unit along the Teshio Mountains. The survey area is ~ 70 km from north to south and ~ 30 km from west to east, covering six rivers and two coasts. The sampling sites are the Moshosanbetsu River, the Shosanbetsu River, the Ainusawa River, the Tomamae coast, the Obira coast, the Kamikinenbetsusawa River, the Obirashibe River, and the Numatapon River from north to south. All rivers are located in the Sorachi–Yezo terrane, which consists mainly of sedimentary rocks of the Late Cretaceous to Neogene age. The Tomamae and Obira coasts are sandy beaches located at the foot of coastal terraces composed mainly of sediments of the Late Pleistocene. Only the Numatapon River passes through the peridotite bodies, while other localities have no contact with current ultramafic rocks. However, serpentinite pebbles in conglomerates and chromite-bearing sandstones have been observed in sedimental rocks; therefore, placer PGM are considered to occur secondly from such strata (e.g., Suzuki, 1950; Hata, 1961). Sediments containing ultramafic materials are considered to have been supplied from past Teshio Mountains, which rise to the east of the sampling site (e.g., Hata, 1961).

The type locality of tomamaeite is located at the coast, Tomamae town, Hokkaido, Japan (44°17′09″N 141°38′58″E). Coastal terraces with a height of ~ 30 m have been developed at the sampling site. The bottom of the terraces consists of conglomeratic sandstone that corresponds to the Chepotsunai formation of the middle to late Miocene (Matsumo and Kino, 1960). The upper layer is Late Pleistocene sediments that consist of sand and lignite-bearing clay involved with granules and pebbles. The terrace is eroded by the sea, wind and rain, and the heavy sand is naturally dense on the bedrock. Although this heavy sand has been known to contain fine gold and...
PGM placer (e.g., Tsushima et al., 1954), they have never been studied to date.

PGM placer was collected along with the heavy sand by specific gravity sorting. Sediments were run through a sluice box lined with riffles to capture heavy sand, and then it was panned with a curved plate to collect PGM placer. The heavy sand was formed mainly of chromite, magnetite, and titanite, the proportions of which in each locality are shown in Figure 2. In the Numatapon River and the Kamikinenbetsusawa Rivers, chromite is dominant, while magnetite or titanite are dominant in other localities. The particle size of the PGM placer is distinctly different between the river PGM and coastal PGM (Fig. 3). River PGM placer is frequently larger than 1 mm and occasionally reaches 5 mm in length. On the other hand, coastal PGM placer grains are mostly less than 0.5 mm in length. Placer gold was always present in all localities, and intermetallic alloys including gold and silver accompanied by placer gold were obtained from the Shosanbetsu and Ainusawa Rivers (Nishio–Hamane and Saito, 2021).

In a rare case, the Ainusawa River yielded quongite (Supplementary Fig. S1; available online from https://doi.org/10.2465/jmps.220309), which was firstly described from Luobusha ophiolite (Fang et al., 2009).

APPEARANCE

PGM placer grains

Representative appearances of PGM placer grains from northwestern Hokkaido are shown in Figure 4. PGM placer can be broadly divided into Os–Ir–Ru alloys and Pt–Fe(Cu) alloys, where the former is dominant over the latter. Rutheniridosmine, ruthenium, osmium, and iridium are the most commonly occurring PGM, and the other PGM are less common. Rutheniridosmine and ruthenium are both silvery–white metals that often occur as single-phase grains. They are often in irregular masses with sharp edges, but rarely with triangular to hexagonal symmetry (Figs. 4a–4d). Osmium also often occurs monophaseic grains that are a bluish–silver color. The irregularly shaped grains have rounded edges and are rarely hexagonal crystals (Figs. 4e and 4f). Iridium is a yellowish–silver metal that is occasionally associated with other grains, such as rutheniridosmine, and is not often obtained as single–phase grains, and cubic crystals are very rarely found (Figs. 4g and 4h). Pt–Fe(Cu) alloys are platinum, isoferrroplatinum, tulameenite, ferronickelplatinum, and tetraferroplatinum. Platinum has a brownish silver color, is extremely rare as a single–phase grain, and has only been obtained from the Obira coast to date (Fig. 4i); however, it occurs in Pt–Fe(Cu) alloys such as tulameenite as fine fragment. Isoferroplatinum occurs as brownish silver round tablets and the accessories of other PGM (Figs. 4j and 4k). The appearance of isoferrroplatinum is common to platinum; however, in almost all cases, the metal with this appearance was isoferrroplatinum, not platinum. Tulameenite and ferronickelplatinum are also brownish silver metals, similar to isoferrroplatinum. They are not obtained as single–phase grains but are accompanied by the periphery and interior of other PGM, such as rutheniridosmine and osmium (Figs. 4i and 4m). Tetraferroplatinum is an ochre–colored metal that occurs as grains with a core of isoferrroplatinum. As for other PGM, chengdeite is a rare grayish–black metal that is only slightly associated with some iridium grains. Erlichmanite, irarsite, and tolovkite are sulfi de PGM with a steel black metallic luster that covers part or all of the surface of Os–Ir–Ru alloys (Figs. 4p–4r). PGM other than those described so far occur as inclusions.

PGM inclusions

Table 1 shows a list of the localities and PGM. Most inclusions are anhedral fine particles; therefore, mineral
Figure 4. Representative appearances of PGM placer from Northwestern Hokkaido. Abbreviations of the localities are the same as Figure 1. See Table 1 for abbreviations of mineral names.
| Mineral (symbol)         | Composition | Locality |
|-------------------------|-------------|----------|
| **PGM alloys (intermetallic alloys)** |             |          |
| Ruthenium (Ru)          | Ru          | M S T A K OC OR N |
| Osmium (Os)             | Os          | M S T A K OC OR N |
| Iridium (Ir)            | Ir          | M S T A K OC OR N |
| Rutheniridosmine (Rir)  | (Ir,Os,Ru)  | M S T A K OC OR N |
| Platinum (Pt)           | Pt          | M S T A K OC OR N |
| Garutitite (Gar)        | (Ni,Fe,Ir)  | M S T A K OC OR N |
| Hexaferrum (Hfe)        | (Fe,Os,Ru,Ir)| M S T A K OC OR N |
| Kitagohaité (Kgh)       | Pt₁Cu₁₋ₓ  | M S T A K OC OR N |
| Isoferroplatinum (Ifpt) | Pt₃Feₓ     | M S T A K OC OR N |
| Orthocuproplatinum (Ocpt)| Pt₃Cuₓ²₋ₓ  | M S T A K OC OR N |
| Chengdeite (Cgd)        | Ir₁Feₓ     | M S T A K OC OR N |
| Tulameenite (Tul)       | Pt₁CuFeₓ  | M S T A K OC OR N |
| Ferronickelplatinum (Fnpt) | Pt₁FeNiₓ  | M S T A K OC OR N |
| Tetraferroplatinum (Tfpt) | Pt₁Feₓ   | M S T A K OC OR N |
| Hongshiite (Hng)        | Pt₁Cu₁₋ₓ  | M S T A K OC OR N |
| Skargaardite (Skg)      | Pd₁Cuₓ     | M S T A K OC OR N |
| Tomamaeite (Tmm)        | Cu₃Ptₓ     | M S T A K OC OR N |
| **PGM sulﬁdes (sulfosalts, arsenides, antimonides, tellurides)** |             |          |
| Laurite (Lrt)           | RuS₂       | M S T A K OC OR N |
| Erlichmanite (Erl)      | OsS₂       | M S T A K OC OR N |
| Braggite (Bg)           | Pt₁Sₓ      | M S T A K OC OR N |
| Cooperite (Cpe)         | Pt₁₃ₓ       | M S T A K OC OR N |
| Cuproprondiste (Crh)    | (Cu₁₋ₓFeₓ₁₋ₓ)Rh₂S₄ | M S T A K OC OR N |
| Vysotskite (Vsk)        | (Pd,Ni)Sₓ | M S T A K OC OR N |
| Bowieite (Bow)          | Rh₂S₃ₓ      | M S T A K OC OR N |
| Kashinite (Ksh)         | Ir₁S₃ₓ     | M S T A K OC OR N |
| Cherepanovite (Cpv)     | Rh₁₂As₇ₓ   | M S T A K OC OR N |
| Rhodarsenide (Rda)      | Rh₂Asₓ     | M S T A K OC OR N |
| Polkanovite (Pkv)       | Rh₂₁₂As₇ₓ | M S T A K OC OR N |
| Palladoarsenide (Pda)   | Pd₂As       | M S T A K OC OR N |
| Palladodymite (Pdd)     | Pd₂As       | M S T A K OC OR N |
| Sperrylite (Spy)        | Pt₃Asₓ      | M S T A K OC OR N |
| Iridarsenite (Ird)      | IrAs₂       | M S T A K OC OR N |
| Merteite-I (Met-I)      | Pd₅₋ₓ(Sb,As)₂₋ₓ (x = 0.1-0.2) | M S T A K OC OR N |
| Merteite-II (Met-II)    | Pd₅₋ₓSb₂₋ₓAs₀.₅ | M S T A K OC OR N |
| Minakawaite (Mka)       | RhSb        | M S T A K OC OR N |
| Zaccariniite (Zcr)      | Rh₃Asₓ     | M S T A K OC OR N |
| Hollingworthite (Hlw)   | Rh₃Asₓ     | M S T A K OC OR N |
| Irsarsite (Irs)         | Ir₃Asₓ     | M S T A K OC OR N |
| Tolovkite (Tol)         | Ir₃Sbₓ     | M S T A K OC OR N |
| Stibiopalladinite (Sptdn)| Pd₁₁Sb₂ₓ | M S T A K OC OR N |
| Keithonite (Kei)        | Pd₁₁Teₓ    | M S T A K OC OR N |
| Törnroosite (Trs)       | Pd₁₁₃As₇Te₂ | M S T A K OC OR N |
| Cu₂Pd₃S₃          | Cu₂Pd₃S₃     | M S T A K OC OR N |
| Ni₂RhS₃           | Ni₂RhS₃     | M S T A K OC OR N |
| (Rh,Cu)S₄         | (Rh,Cu)S₄     | M S T A K OC OR N |

M, the Moshosanbetsu River; S, the Shosanbetsu River; T, the Tomamae coast; A, the Ainusawa River; K, the Kamikinenbetsusawa River; OC, the Obirashibe coast; N, the Numatapon River.
names were assigned based on the results of chemical analysis. There is no significant difference in occurrence of PGM inclusions between the localities; therefore, the Tomamae coast is described here as a representative example. Figure 5 shows representative occurrences of PGM inclusions from the Tomamae coast. Ruthenium often forms eutectic crystals with isoferroplatinum (Fig. 5a). Garutite is found just below the surface of rutheniridosmine grains, and irarsite is also scattered near the surface of osmium grains (Figs. 5b and 5c). Isoferroplatinum is often accompanied by a rim that consists of tulameenite, ferronickelplatinum and tetraferroplatinum (Fig. 5d), all of which are accompanied by various inclusions inside. Hongshiite occurs in isoferroplatinum with eutectic texture (Fig. 5e). Irarsite, laurite, mertieite–I, mertieite–II, braggite (cooperite), hollingworthite, cuprorhodsite, bowieite, and palladoarsenide (palladodymite) are found in isoferroplatinum (Figs. 5f–5j), and sperrylite and rhodarsenide are also accompanied with isoferroplatinum (Fig. 5k). There are also small inclusions in tulameenite, ferronickelplatinum, and tetraferroplatinum that occur around isoferroplatinum. Zaccariniite, cherepanovite, minakawite, and an unnamed Rh₃As₂ mineral were found in such occurrences (Figs. 5l–5n). Tomamaeite and kitagohaite are also included in tulameenite (Fig. 5o).

PGM occurred in localities other than Tomamae coast are summarized in Supplementary Figure S2 (Fig. S2 is available online from https://doi.org/10.2465/jmps.220309). Orthocuproplatinum occurs in an aggregate with hongshiite, rhodarsenide, sperrylite, and cherepanovite in rutheniridosmine grains present in the Moshosanbetsu River (Fig. S2a) and was also found from the Numatapon River. Hexaferrum is uniquely found from the Shosanbetsu River and occurs as small particles together with tomamaeite in the chengdeite rim developed on the outer edge of iridium grains (Fig. S2b). Polkanovite was found at the Shosanbetsu and Numatapon Rivers, and in the former locality, it occurs in rutheniridosmine grains with sperrylite (Fig. S2c). An aggregate consisting of lead and antimony is associated with rutheniridosmine grains at the Ainusawa River (Fig. S2d). Lead was also found in placer gold in the Shosanbetsu River (Nishio–Hamane and Saito, 2021). Stibiopalladinite was only found at the Obirahibire River and occurs as an inclusion of rutheniridosmine with isoferroplatinum (Fig. S2e). Kashinite, keithconite, and törnroosite are uniquely found in isoferroplatinum and iridium from the Obira coast, where they are accompanied by unnamed minerals with Cu₂Pd₆S₃, Ni₂RhS₃, and (Rh,Cu)₅S₄ compositions (Figs. S2f–S2h). Platinum is not obtained as a single-phase grain but occurs as an inclusion in rutheniridosmine grains at the Numatapon River, (Fig. S2i). Iridarsenite, which has not been found from the Tomamae coast, has been found to occur from the Showanbetsu River and the Ainusawa River and was accompanied by tomamaeite in the former locality (Fig. 6s). The details of the intermetallic alloy minerals including new minerals (rumoiite and shosanbetsuite) from the Shosanbetsu River and Ainusawa River have been reported by Nishio–Hamane and Saito (2021).

### Tomamaeite

The new mineral tomamaeite is a common mineral in the PGM placer deposit of northwestern Hokkaido and has been found in localities except the Obirahibire River and the Obira coast (Table 1). Figure 6 shows the representative occurrence of tomamaeite from each locality. Toma-
Figure 5. Representative occurrence of PGM inclusions from the Tomamae coast by back-scattered electron images. See Table 1 for abbreviations of mineral names.
Tomamaeite occurs always as fine anhedral inclusions up to 20 µm in length in tulameenite, tetraferroplatinum, ferro-nickelplatinum, and hongshiite. Similar inclusions of zaccharinite, rhodarsenide, iridarsenite, and platinum occur around tomamaeite, and fragments of rutheniridosmine were rarely found. Due to such occurrence, most physical and optical properties of tomamaeite could not be measured. Tomamaeite is an opaque mineral and has metallic luster with a pale mist white color in reflected light. Its hardness has not been determined, although it is estimated to be ~3½ by comparison with compositionally related minerals; hongshiite (4), orthocuproplatinum (4), auricupride (3½), and native copper (2½–3). The calculated density is 12.4 g·cm⁻³ from the empirical formula and powder X-ray diffraction (XRD) data. Streak, cleavage, parting, tenacity, and fracture could not be measured.

CHEMICAL COMPOSITION

Chemical analyses were conducted using a scanning electron microscope (JEOL IT-100) equipped with an energy dispersive X-ray spectroscope (15 kV, 0.8 nA, 1 µm beam diameter) at the Institute for Solid State Physics, the University of Tokyo, and the ZAF method was used for data correction. The standards used were pure materials (C, Fe, Ni, Cu, Sn, Sb, Te, W, Re, Ph, and PGE), pyrite (S), and indium arsenide (As). Tables 2 and 3 summarize the chemical compositions of tomamaeite and PGM from the Tomamae coast, respectively. The compositions of PGM from other localities are summarized in Supplementary Tables S1–S7 (Tables S1–S7 are available online from https://doi.org/10.2465/jmps.220309).

Tomamaeite

Tomamaeite from the Tomamae coast is characterized by a homogeneous composition, dominated by Cu and Pt with few other elements, while a small amount of Sb is occasionally contained in tomamaeite from the Shosanbetsu River and Ainusawa River (Table 2, Tables S1–S4, and...
The empirical formula of tomamaeite calculated on the basis of 4 apfu is $(\text{Cu}_{3.01}\text{Fe}_{0.06}\text{Ni}_{0.01})\Sigma_{3.08}(\text{Pt}_{0.90}\text{Ru}_{0.01}\text{Rh}<0.01\text{Pd}<0.01\text{Os}<0.01\text{Ir}<0.01)\Sigma_{0.93}$, $(\text{Cu}_{2.92}\text{Fe}_{0.05}\text{Ni}_{0.04})\Sigma_{3.01}(\text{Pt}_{0.97}\text{Pd}_{0.01}\text{Rh}_{0.01})\Sigma_{0.99}$, $(\text{Cu}_{2.86}\text{Sb}_{0.13}\text{Fe}_{0.03}\text{Ni}_{0.02})\Sigma_{3.03}(\text{Pt}_{0.92}\text{Ir}_{0.02}\text{Pd}_{0.01}\text{Os}_{0.01})\Sigma_{1.06}$, $(\text{Cu}_{2.71}\text{Sb}_{0.19}\text{Fe}_{0.02}\text{Ni}_{0.01})\Sigma_{2.91}(\text{Pt}_{1.01}\text{Ir}_{0.05})\Sigma_{1.06}$, and $(\text{Cu}_{2.93}\text{Fe}_{0.02})\Sigma_{2.94}(\text{Pt}_{1.04}\text{Rh}_{0.01})\Sigma_{1.06}$ from the Tomamae coast, the Moshosanbetsu River, the Shosanbetsu River, the Ainusawa River, the Kamikinenbetsusawa River, and the Numatapon River, respectively. The ideal formula is $\text{Cu}_3\text{Pt}$, which requires 49.42 wt% Cu and 50.58 wt% Pt, a total of 100 wt%.

Table 2. Chemical composition of tomamaeite from the Tomamae coast

| Mineral         | Fe | Ni | Cu | Ru | Rh | Pd | Os | Ir | Pt | Total |
|-----------------|----|----|----|----|----|----|----|----|----|-------|
| Avg             | 0.86 | 0.12 | 51.64 | 0.33 | 0.11 | 0.06 | 0.09 | 0.08 | 47.63 | 100.91 |
| Min.            | 0.47 | nd  | 50.93 | 0.02 | nd  | nd  | nd  | nd  | 46.75 |
| Max             | 1.08 | 0.23 | 52.61 | 0.87 | 0.29 | 0.20 | 0.55 | 0.50 | 48.12 |

Formula (basis of) $(\text{Cu}_{3.01}\text{Fe}_{0.06}\text{Ni}_{0.01})\Sigma_{3.08}(\text{Pt}_{0.90}\text{Ru}_{0.01}\text{Rh}<0.01\text{Pd}<0.01\text{Os}<0.01\text{Ir}<0.01)\Sigma_{0.93}$ ($\Sigma = 4$)

Table 3. Representative chemical composition of PGM excluding tomamaeite from the Tomamae coast

| PGM alloys (intermetallic alloys) | Fe | Ni | Cu | Ru | Rh | Pd | Sb | Os | Ir | Pt | Total (wt%) |
|----------------------------------|----|----|----|----|----|----|----|----|----|----|-------------|
| Ruthenium                        | -  | -  | -  | 61.11 | 6.97 | 0.30 | -  | 9.41 | 15.99 | 4.70 | 98.49 |
| Osmium                           | -  | -  | -  | 0.02 | 0.88 | 0.14 | -  | 78.35 | 21.42 |     | 100.82 |
| Iridium                          | -  | -  | -  | 7.04 | 0.82 | 0.24 | -  | 23.94 | 70.39 |     | 102.43 |
| Rutheniridosmine                 | -  | -  | -  | 17.89 | 1.17 | -  | -  | 36.93 | 44.40 |     | 100.39 |
| Garutite                         | 8.29 | 30.65 | -  | 0.13 | 0.09 | -  | -  | 60.82 |     |     | 99.98 |
| Kitagohaitie                     | 1.17 | 0.14 | 2.49 | 0.66 | -  | -  | -  | 3.18 | 91.48 |     | 99.12 |
| Isoferroplatinum                 | 8.45 | -  | 0.37 | 0.11 | 0.33 | -  | -  | 4.49 | 86.88 |     | 100.63 |
| Tulameenite                      | 12.84 | 3.28 | 5.11 | 0.56 | -  | -  | -  | 3.03 | 76.73 |     | 101.56 |
| Ferronickelplatinum              | 12.37 | 7.52 | 0.35 | 0.11 | 0.33 | -  | -  | 1.95 | 78.42 |     | 101.79 |
| Tetraferroplatinum               | 20.34 | 0.35 | 0.33 | 0.80 | 0.41 | -  | -  | 0.19 | 79.36 |     | 101.80 |
| Hongshiite                       | 1.97 | 0.52 | 16.24 | -  | 0.37 | 8.36 | -  | 1.13 | 73.28 |     | 101.86 |

| PGM sulfo-areno-tellurides       | S  | Fe | Ni | Cu | As | Ru | Rh | Pd | Sb | Os | Ir | Pt | Total (wt%) |
|----------------------------------|----|----|----|----|----|----|----|----|----|----|----|----|-------------|
| Laurite                          | 31.69 | -  | -  | 2.68 | 33.83 | 1.10 | -  | -  | 18.07 | 11.19 | -  | 98.56 |
| Erlichmanite                     | 27.34 | -  | -  | 1.42 | 10.35 | 0.03 | -  | -  | 43.03 | 16.53 | -  | 98.70 |
| Braggite                         | 13.50 | -  | -  | -  | -  | -  | -  | -  | 85.47 |     |     | 98.97 |
| Cooperite                        | 32.64 | 0.65 | 1.35 | 11.34 | -  | -  | -  | 26.48 | -  | -  | 100.63 |
| Cuprorhodsite                    | 27.58 | 0.65 | 1.35 | 11.34 | -  | -  | -  | 26.48 | -  | -  | 100.63 |
| Bowiwiite                        | 32.64 | 0.65 | 1.35 | 11.34 | -  | -  | -  | 26.48 | -  | -  | 100.63 |
| Cherepanovite                    | 0.17 | -  | -  | -  | -  | -  | -  | 42.62 | 16.31 | 39.00 | 1.28 | -  | 101.06 |
| Rhodarsenide                     | 0.11 | -  | -  | -  | 26.09 | -  | 68.13 | 3.18 | -  | -  | -  | 99.54 |
| Palladoarsenide                  | -  | -  | -  | -  | -  | -  | -  | -  | 2.76 | 62.78 | -  | 101.92 |
| Palladodymite                    | -  | -  | -  | -  | -  | -  | -  | -  | 2.76 | 62.78 | -  | 101.92 |
Other PGM

Platinum-group elements can be broadly classified into iridium-subgroup platinum-group elements (IPGE; Ru, Os, and Ir) and palladium-subgroup platinum-group elements (PPGE; Rh, Pd, and Pt) based on their relative compatible behavior (e.g., Leblanc, 1991), and the principal components of PGM also tend to be biased one way or the other (Tables 3 and S1–S7). On the other hand, cherepanovite and hollingworthite are mainly composed of Rh of PPGE but often have Ru and Ir of IPGE as secondary components, respectively (Tables 3, S1–S3, and S7). As for IPGE-based PGM, small amounts of Rh are infrequently found in iridarsenite, irarsite, and kashinite, while sperrylite also contains small amounts of Ir (Tables 3, S2, S4, and S5). However, with the exception of a few such examples, the majority of PGM are made up of IPGE or PPGE-based alloys.

Figure 7 shows the chemical variations of IPGE-based alloy grains. In almost all localities, rutheniridosmine is the most common. However, there are slight differences among the localities; for example, in the Shosanbetsu River, the composition of rutheniridosmine is clearly biased toward a low Ru content. The next most common species is osmium, the composition of which is often borderline with rutheniridosmine, but occasionally a near end-member component is observed. The composition on the Os–Ir line is occasionally found, but the composition along the Os–Ru line is almost unobserved.

Iridium and ruthenium appear with equal frequency. The composition of iridium was biased toward the Os content close to the immiscibility gap and with low Ru content.
and no composition close to the end-member components was observed. Iridium with composition on the Ir–Ru line is rarely observed. For ruthenium, the composition is usually triple point to slightly Ru-rich, but rarely Ru-rich on the Ru–Ir line. There are only a few analysis points on the immiscibility gap, and iridium with rhenium as a third component has also been obtained from the Aimusawa River (Table S3). These compositions may reflect anomalous formation conditions.

Figure 8 shows compositional variations of PPGE–based (intermetallic) alloys. Although there are not many analysis points, platinum includes a little copper and is occasionally close to kitagohaite. Platinum as grain from the Obira coast is described, while its composition is close to the border with isoferroplatinum. The situation is the same for kitagohaite. Although kitagohaite of the Tomamae coast crosses the boundary, it is quite close to the boundary with platinum. Isoferroplatinum exhibits a wide range of compositions. The composition expands in the direction of platinum, tulameenite (ferronickelplatinum), and orthocuproplatinum, and continue slightly to platinum and orthocuproplatinum. On the other hand, extension in the tetraferroplatinum direction is limited. Orthocuproplatinum appears to have a tendency to divide into those close to the end-member direction and those close to the boundary with isoferroplatinum. Among tetraferroplatinum, tulameenite (ferronickelplatinum), and hongshiite, there seem to be a small gap between the first two and a somewhat clearer gap between the latter two. The composition of hongshiite is slightly extended toward
orthocuproplatinum in the Tomamae coast and the Numa-
tapon River. There is little variation in the composition
of tomamaeite.

CRYSTALLOGRAPHY FOR TOMAMAEITE

The micro–XRD measurement technique was applied to
powder XRD measurements for tomamaeite, which was
conducted using a diffractometer (Rigaku Ultrax18, CrKα
radiation, 40 kV, 200 mA, 100 µm collimator) equipped
with a curved position sensitive proportional counter and
an oscillation sample stage at the Institute for Solid State
Physics, the University of Tokyo. The powder XRD pat-
tern for tomamaeite was successfully obtained using the
sample shown in Figures 6a and 6b. Figure 9 shows the
XRD pattern, and the resulting data are summarized in
Table 4. Although tulameenite and ruthenium were con-
tained in the diffractogram pattern due to the close relation-
ship of occurrence, the peaks of tomamaeite could be
identified sufficiently. The five strongest lines of toma-
maeite in the powder XRD pattern \[d \text{ in Å} \] (\(I/I_0\) \(hkl\)) are
2.596(35) 110, 2.123(100) 111, 1.843(96) 200, 1.646(28)
210, and 1.303(42) 220. Based on these data, tomamaeite
can be indexed to the cubic \(Pm\overline{3}m\) space group (#221).

The unit cell parameters, as re-fi-ne from the powder XRD
data, are \(a = 3.683(2) \) Å and \(V = 49.97(7) \) Å³ (\(Z = 1\)).

The crystal structure was also investigated using
transmission electron microscopy (TEM; JEOL–2010F,
operated at 200 kV), and the sample in Figure 6c was thinned by Ar milling using an ion-slicer (JEOL EM-09100IS) at the Institute for Solid State Physics, the University of Tokyo. Figure 10 shows TEM images, selected area electron diffraction patterns (SAED), and the crystal structure of tomamaeite. Submicron-sized tomamaeite is found in tetraferroplatinum (Fig. 10a), and the HRTEM image from [110] is completely consistent with the simulated image (Fig. 10b). SAED images were obtained from the [100], [110], [111], [210], and [310] directions, and no extinction rule was observed in any direction (Figs. 10c–10g). The images and chemical composition indicate that tomamaeite has a $Pm\overline{3}m$ space group with Cu-Pt ordered structure (Fig. 10h). This structure is modeled by $Cu_{3}Au$ (e.g., Kubiak and Janczak, 1991), and all atoms are located on the sites of a face-centered cubic lattice in which Pt occupies the position of origin, and Cu occupies the face-centered positions (Fig. 10h). No crystallographic orientation relationship was also observed between tomamaeite and tetraferroplatinum.

Cu$_3$Au as a substance has been known for a long time, Ogawa et al. (1973) reported a phase diagram of Pt content and synthesis temperature. According to the phase diagram, the Cu$_3$Au-type phase is more stable at lower Pt content and lower temperature. Tomamaeite used for TEM observations showed no traces of long-period structures, which is consistent with the Pt content being slightly lower than the ideal Cu$_3$Pt (Table 2) and with the low-temperature reaction such as serpentinization, as discussed later.

**DISCUSSION**

The amount of IPGE-based alloys is dominant over PPGE-based alloys in all localities. It is well known that PGM that originate from depleted ultramafic rocks tend to be rich in IPGE and poor in PPGE because of the relative incompatible behavior of PGGE (e.g., Leblanc, 1991). Considering the north–south continuity of the Kamuikotan unit and occurrence of PGM (e.g., Nakagawa et al.,
PGM in this studied area is also considered to originate from depleted ultramafic rocks in ophiolite. Figure 11 shows the chemical variation of chromite, which is simultaneously obtained with PGM. The composition of chromite from the Numatapon River originated by the Takadomari peridotite is close to that from the Obirashibe River and Kamikinenbetsusawa River. On the other hand, the distribution of chromite compositions from other localities is somewhat weighted towards a lower Cr content. This trend may reflect the degree of depletion, and slightly fertile (or primitive) ultramafic rocks were probably distributed in the past. Nevertheless, it does not have a strong effect on the species and amount of PGM, because there was no significant regional maldistribution in the occurrence and composition of PGM (Table 1, Fig. 7, and Fig. 8). Therefore, a majority of PGM in northwestern Hokkaido was probably caused by an almost common petrogenesis, although there may be small exceptions.

The chemical compositions of IPGE-based alloys were often close to an almost equal Os/Ir ratio and formed a trend directed toward Ru on the Os–Ir–Ru diagram (Fig. 7). This trend is also well known in the IPGE-based alloys derived from ophiolites and is considered to be the result of alloy crystallization when the immiscibility gap is vertically deformed under high pressure (Bird and Bassett, 1980). It has also been suggested that the Ru content may be related to the timing of crystallization, and alloys formed at a later stage in magmatic processes tend to be richer in Ru and PPGE (e.g., Tolstykh et al., 2015; Airiyants et al., 2022). After Os–Ir alloy crystallizes, the residual system is rich in Ru and PPGE and may occasionally form a eutectic crystal consisting of ruthenium and isoferroplatinum, such as shown in Figure 5a. On the other hand, Pt–Fe(Cu) alloy minerals such as tulameenite, ferronickelplatinum, and tetraferroplatinum are further later minerals than that of ruthenium and isoferroplatinum. These Pt–Fe(Cu) alloys do not occur alone but are
very often developed on the periphery of isosterroplatinum or IPGE-based alloys because they are typical secondary minerals occurred to post-magmatic (hydrothermal to metasomatic) processes in association with serpentinization (e.g., Tolstykh et al., 2015).

Tomamaeite in Hokkaido is found only as minute particles in Pt-Fe(Cu) alloys (Fig. 7), and its occurrence is common in many localities (e.g., Orsoev et al., 2001; Grokhovskaya et al., 2005, 2009; Kozlov et al., 2011; Tolstykh et al., 2015; Grokhovskaya et al., 2019; Kuzmin et al., 2020). Based on these occurrences, tomamaeite is thought to occur by decomposition of Pt-Fe(Cu) alloys such as tulameenite, and its counterpart, the Pt-rich phase, should also occur. It is rarely observed as native (e.g., Tolstykh et al., 2015). Based on these occurrences, tomamaeite is missing. This implies that a reaction has proceeded in which the Pt-rich phase is quickly consumed, which may be accommodated into isoferroplatinum and host Pt-group minerals. Indeed, it is common for those to be richer in Pt than the ideal compositions (Fig. 8). The involvement of metasomatic fluids with volatile elements has also been considered to form tomamaeite (e.g., Tolstykh et al., 2015). In Hokkaido, the presence of various sulfide, arsenide, and telluride inclusions implies the intervention of metasomatic fluids with volatile elements (Table 1). The details of such activity are a subject to be clarified in the future. However, the wide occurrence of tomamaeite in PGM originated from ophiolite indicates that tomamaeite is a non-unique mineral in the universal post-magmatic processes associated with serpentinization.

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SUPPLEMENTARY MATERIALS

Supplementary Tables S1–S7 and Figures S1–S2 are available online from https://doi.org/10.2465/jmps.220309.

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