

# Chemistry and Occurrences of Native Tellurium from Epithermal Gold Deposits in Japan

Masataka NAKATA<sup>1</sup> and Kosei KOMURO<sup>2</sup>

<sup>1</sup>Department of Astronomy and Earth Sciences, Tokyo Gakugei University, Koganei, Tokyo, Japan and <sup>2</sup>Graduate School of Life and Environmental Sciences, University of Tsukuba, Tsukuba, Ibaraki, Japan

## Abstract

The chemistry and mode of occurrences of native tellurium in the epithermal gold ores from Teine, Kobetsuzawa, Mutsu, Kawazu, Suzaki and Iriki in Japan are examined. Mineral assemblages in contact with native tellurium are: quartz-sylvanite at Teine, quartz-hessite-sylvanite-telluriantimony at Kobetsuzawa, quartz at Mutsu, quartz-stutzite-hessite-sylvanite-tetradymite at Kawazu, quartz at Suzaki, and quartz-goldfieldite at Iriki. The peak patterns of XRD for native tellurium from these six ores are nearly identical to that of JCPDS 4-554. Their chemical compositions of Te range from 98.16 to 100.73 wt.%, showing nearly pure tellurium. Other elements detected are: Se of 0-0.85 and Cu of 0-0.74 at Teine, Sb of 0.45-0.47 and Se of 0.19-0.27 at Kawazu, Se of 0.22-1.11 and Sb of 0-0.49 at Suzaki, and Cu of 0.69-0.98, As of 0.22-0.28 and Bi of 0-0.22 wt.% at Iriki. No other elements are detected in the ores of Kobetsuzawa and Mutsu. The ranges of associated minor compositions are consistent with those of the experimental phase. The differences would be related to associate minerals.

The mineral assemblages in these ores agree well with the previously proposed experimental phase relations in Au-Ag-Te ternary system for 120-280°C. The Suzaki ore has high Te-Au assemblage: from calaverite-sylvanite-krennerite via native tellurium to petzite, with changing mineralization stage, whereas the Kobetsuzawa and the Kawazu ores have high Te-Ag assemblage of tellurium-hessite, and native tellurium-stutzite-hessite-sylvanite, respectively. The Teine ore has intermediate assemblage of native tellurium-sylvanite. The mineral assemblages in Au-Ag-Te system are related to the hydrothermal environment especially to the pH condition, i.e., Au rich assemblages under acidic and Ag rich assemblages under intermediate pH conditions, being supported by alteration mineral species. The other telluriferous epithermal gold deposits not in association with native tellurium such as Agawa, Date, Takeno, Chugu, Chitose, Sado and Kushikino are estimated to have been formed under higher pH

condition as adularia and calcite occur in these deposits. The pH-Eh diagram for aqueous tellurium species and tellurium minerals at 250°C indicates that the region of native tellurium occurs between those of aqueous telluride and tellurous species at lower pH, being consistent with their mineral assemblages in ores and alteration envelopes.

Keywords: native tellurium, epithermal gold deposit, Teine, Kobetsuzawa, Mutsu, Kawazu, Suzaki, Iriki, EPMA

Corresponding Author: Masataka NAKATA, Department of Astronomy and Earth Sciences, Tokyo Gakugei University, 4-1-1 Nukuikita, Koganei, Tokyo 184-8501, Japan, E-mail: nakata@u-gakugei.ac.jp

## 1. Introduction

Telluriferous minerals found in some epithermal gold deposits of the Japanese Islands are native tellurium, tellurides and telluriferous sulfosalts in the original ores and tellurite in the secondary oxide ores. Tellurides are calaverite ( $\text{AuTe}_2$ ), sylvanite ( $\text{AuAgTe}_4$ ), krennerite ( $(\text{Au,Ag})\text{Te}_2$ ), petzite ( $\text{Ag}_3\text{AuTe}_2$ ), hessite ( $\text{Ag}_2\text{Te}$ ), stutzite ( $\text{Ag}_5\text{Te}_3$ ), empressite ( $\text{AgTe}$ ), kostovite ( $\text{CuAuTe}_4$ ), rickardite ( $\text{Cu}_7\text{Te}_5$ ), coloradoite ( $\text{HgTe}$ ), tellurantimony ( $\text{Sb}_2\text{Te}_3$ ), altaite ( $\text{PbTe}$ ), frobergite ( $\text{FeTe}_2$ ), tellurobismuthite ( $\text{Bi}_2\text{Te}_3$ ), kawazulite ( $\text{Bi}_2\text{Te}_2\text{Se}$ ), tetradymite ( $\text{Bi}_2\text{Te}_2\text{S}$ ) and poubaite ( $\text{PbBi}_2\text{Se}_2\text{Te}_2$ ). Goldfieldite ( $\text{Cu}_{12}(\text{Te,Sb,As})_4\text{S}_{13}$ ) occurs as telluriferous sulfosalts. Shikazono et al. (1990) pointed out that the Te-type deposits with tellurium minerals are generally poor in sulfides except for pyrite and marcasite and have low Ag/Au ratio (less than 10), and proposed a model that Te-type formed in the volcanic rocks at sites closer to the volcanic center under lower pH conditions.

Among these telluriferous minerals, native tellurium is known to be found in the following five deposits in Japan: Teine (Watanabe, 1934, 1952; Watanabe, 1935, 1936), Kobetsuzawa (Nakata et al., 1985, 1989), Mutsu (Kinoshita, 1945; Ishibashi and Ohmachi, 1949), Kawazu (Watanabe, 1934, 1952), and Suzaki (Watanabe, 1932, 1933, 1952; Endo, 1964; Honma et al., 1979). In addition, we found native tellurium newly in the gold veins at Iriki. The mode of occurrences and mineral chemistry of native tellurium from these Japanese telluriferous ores have, however, not well been described in these studies. In the course of understanding of the tellurium mineralization in the epithermal gold deposits in the Japanese Islands, chemistry and mode of occurrences of native tellurium in these ores are examined. Here we describe the analytical results and discuss the hydrothermal conditions for native tellurium formation.

## 2. Outline of Geology and Ore Deposits

The epithermal gold deposits with telluriferous minerals are distributed widely in Cretaceous to the present volcanic terranes in the Japanese Islands (Fig. 1). The occurrences of native tellurium are limited in the following six deposits: Teine and Kobetsuzawa in the western Hokkaido, Mutsu in the Shimokita Peninsula of the northern Honshu, Kawazu and Suzaki in the Izu Peninsula of the central Honshu, and Iriki in the southern Kyushu. Their mineralizations are considered to have been related to the activities of the host volcanoes (e.g., Watanabe, 2002). Their ore-geological features are summarized in Table 1. Their mineral compositions reported in the previous literatures are tabulated in Table 2.

The Teine deposits are epithermal telluriferous gold-silver-copper bearing quartz

veins. According to Sugimoto (1952), they occur in altered andesite and greenish tuffs of the Teine Formation in the Zenibako Group of Middle Miocene in age. On the basis of the distribution of these veins and their mineralogy, the veins are divided into three groups: Mitsuyama, Koganezawa and Ban'nozawa. In these groups, Mitsuyama veins are characterized by the occurrences of native tellurium and tellurides in some restricted bands (Watanabe, 1934, 1952; Watanabe, 1935, 1936; Sugimoto, 1952). The veins are composed of a series of micro-bands mainly of microcrystalline quartz and barite, with minor amount of tetrahedrite, energite, luzonite, electrum, native tellurium, sylvanite, petzite, hessite, rickardite and goldfieldite. The veins in association with native tellurium are classified into the high sulfidation type (Watanabe, 2002). Homogenization temperature of fluid inclusions in quartz ranges from 206 to 243°C (Watanabe, 1979). Silicification, sericitization, kaolinitization and dissemination of pyrite are extensively found in the host rocks. The K-Ar ages for sericite in veins are in the range of 4.0 and 5.0 Ma (Sawai and Itaya, 1996; MMAJ, 1996), which are related to the volcanic activity of the Pliocene Teine volcano of about 4.0 Ma (Watanabe, 2002).

The Kobetsuzawa epithermal telluriferous gold-bearing quartz deposit occurs as network veinlets in altered andesite and tuffs of middle Miocene to Pliocene in Age. The veinlets are composed mainly of fine quartz, calcite, sericite and clays with minor amount of pyrite, sphalerite, chalcopryrite, native tellurium, altaite, hessite, tellurantimony and frohbergite (Ishibashi, 1956; Nakata et al., 1985, 1989). Silicification, sericitization, and kaolinitization are found in the host rocks (Osanai et al., 1956). Watanabe (2002) classified the deposit into the high sulfidation type. The K-Ar ages for sericite in veinlets are 3.6 Ma (Sawai and Itaya, 1996; MMAJ, 1996), which are related to the volcanic activity of the Pliocene volcano (Watanabe, 2002).

The Mutsu deposit, which is also called as Kuzusawa deposit occurs as epithermal telluriferous gold-bearing quartz veins. They are hosted in the greenish tuffs, tuffaceous sands and shales of the Hinokigawa Formation of Middle Miocene in Age, which are cut by dykes of rhyolite, two-pyroxene quartz andesite, biotite hornblende dacite. The veins are composed of microcrystalline quartz, with minor amount of pyrite, chalcopryrite, sphalerite, galena, tetrahedrite, electrum, native tellurium and tellurobismuthite (Kinoshita, 1945; Ishibashi and Ohmachi, 1949). Silicification and sericitization are found in the vicinity of the host rocks. In the vicinity of the deposit, volcanic activity of the Osore-zan was reported between 0.01-0.1 Ma (Togashi, 1977).

The Kawazu area consists of Subara andesites of Pliocene in Age, which is greenish to grayish altered andesitic lavas with andesitic pyroclastics and sedimentary rocks (MMAJ, 1987). The Kawazu epithermal telluriferous gold-silver bearing quartz veins

occur in the Subara andesite. In these veins, the Hinokizawa telluriferous veins are characterized by milky fine quartz with microbands of aggregates of native tellurium and tellurobismuthite grains (Watanabe, 1934, 1952; Endo, 1964). Rickardite, empressite, hessite and pyrite are also found in the Te-bearing microbands (Watanabe, 1952; Takasu, 1965; Shikazono et al., 1990). Homogenization temperature of fluid inclusions in quartz ranges from 206 to 281 °C (MMAJ, 1987). Silicification, sericitization, kaolinitization and chloritization are extensive in the host rocks. The K-Ar ages for sericite in veins are  $1.4\sim 1.5\pm 0.3$  Ma (MMAJ, 1987).

The Suzaki deposits occur as breccia pipes in altered auriferous silicified stock in andesitic lavas and pyroclastics of the Yugashima Group of early Oligocene to middle Miocene in age (MMAJ, 1987). The ore consists mainly of pyrite and marcasite with minor amounts of chalcopyrite, sphalerite, tetrahedrite, electrum and barite (Watanabe, 1932, 1933, 1952; Endo, 1964). The telluriferous crusts of microcrystalline quartz, native tellurium, calaverite and sylvanite with 3 cm in thickness occur on pipes and are covered by sulfides mainly of pyrite and marcasite (Honma et al., 1979). Alunitization and kaolinitization are extensively found in the host rocks (MMAJ, 1987).

The Iriki epithermal gold-silver bearing quartz veins occur as breccia pipes and are hosted in the acidic tuffs of Kokubu Group in Pleistocene age (Fujii et al., 1989). The veins consist mainly of white fine quartz and chalcedonic quartz with pyrite. The tellurium rich ores cover as ring ore directly on the host rocks and are composed of tetrahedrite, famatinite, luzonite, chalcopyrite, argentite, galena and sphalerite (Uetani et al., 1966). Native tellurium is newly found in the ore. The host rocks are hydrothermally altered to kaolinite (Fujii et al., 1989). Watanabe (2005) classified the deposit into the low sulfidation type. The K-Ar ages for sericite in veins are  $0.453\pm 0.018$  Ma (Matsumoto and Fujii, 1989), which are related with the activities of Imuta volcano of 0.3-0.4 Ma (Matsumoto and Fujii, 1989).

### 3. Samples

The samples used in this study are employed from the Sakurai collection, except for the Kawazu sample (No. MI-01452) which is collected in the University Museum in the University of Tokyo. They cover all of the known localities for native tellurium in the Japanese Islands. Their structural, textural and mineralogical features are examined by a binocular stereoscopic microscope and an ore microscope.

The Teine sample consists of fine and coarse parts (Fig. 2 ①). The fine part is composed of quartz with metallic portions mainly of native tellurium associated with barite of up to 2 mm in size. The coarse part cuts the fine part and is composed of large

barite laths and coarse tetrahedrite grains. Under the ore microscope, native tellurium grains of 200-300  $\mu\text{m}$  in diameter are dispersed in quartz in the fine part (Fig. 3 ①). Aggregates of native tellurium crystals include sylvanite. In part, native tellurium is replaced by goldfieldite.

The Kobetsuzawa sample consists of the white part and the metallic part which cut the white part as micronetwork veinlets (Fig. 2 ②). Under the ore microscope, native tellurium is found in quartz with hessite and corroded pyrite (Fig. 3 ②), and also with sylvanite and tellurantimony in the white part. The metallic part consists mainly of pyrite and sphalerite.

The sample from Mutsu mine is a vein rock composed mainly of needle quartz with marcasite, pyrite and arsenopyrite (Fig. 2 ③). Under the ore microscope, native tellurium grains occur in quartz (Fig. 3 ③).

The Kawazu sample shows banded growth texture of the milky fine quartz part and the coarser gray quartz part (Fig. 2 ④). Native tellurium with metallic luster occurs in the coarser gray quartz part. Under the ore microscope, aggregates of native tellurium grains of 1-2 mm are arranged in the growth lines in the coarser gray quartz part (Fig. 3 ④). Stutzite, hessite, sylvanite and tetradymite are found in closer association with native tellurium.

The Suzaki sample was already described briefly by Honma et al. (1979). It is divided into three parts: microband part, massive aggregate part and drusy quartz part, in growth order (Fig. 2 ⑤). The microband part is composed of the tellurides band and the fine quartz band. The tellurides band consists mainly of calaverite, with sylvanite, kostovite, poubaite and krennerite. The massive aggregate part is mainly of aggregates of needle crystals of native tellurium and quartz (Fig. 3 ⑤). The massive aggregate part is cut by microveinlets of petzite. The drusy quartz part consists of quartz and the larger euhedral marcasite and pyrite crystals.

The sample from Iriki is characterized by growth banding ore vein on the altered trachytic host rock. The ore vein is divided into three bands: goldfieldite band, fine tetrahedrite band and coarse famatinite-quartz band (Fig. 2 ⑥). The goldfieldite band covers directly on the host rock. The fine tetrahedrite bands and coarse famatinite-quartz bands are piled alternately on the goldfieldite band. Under the ore microscope, the goldfieldite band is composed mainly of goldfieldite and quartz (Fig. 3 ⑥). In the aggregates of goldfieldite, native tellurium is found as grains and inclusions. The fine tetrahedrite bands are composed mainly of quartz, tetrahedrite and pyrite. The coarse famatinite-quartz bands consist of quartz, famatinite, pyrite, marcasite, chalcopyrite, pyrrotite, argentite and luzonite.

#### 4. Native tellurium

The properties of native tellurium from the above six samples are examined by ore microscopy, X-ray diffraction (XRD) and electron probe microanalysis (EPMA). The XRD was carried out with a Rigaku Rint-1200 system for drilled and pulverized powder specimen for native tellurium aggregates. The peak patterns of XRD for six samples are almost identical to that of JCPDS 4-554. It has hexagonal system with a rhombohedral lattice. The EPMA analyses were made for the polished specimen using a JEOL Model JCSA-733 electron microprobe analyzer of the Ocean Research Institute in the University of Tokyo under operating conditions of acceleration voltage 25 kV, probe current of  $2.0 \times 10^{-8}$  A, and a beam diameter of smaller than 2  $\mu\text{m}$ . The results of qualitative analysis of the native tellurium revealed the presence of Te, Cu, As, Sb, Bi and Se. Standards used are: pure Te metal for Te, synthetic  $\text{Ag}_3\text{AsS}_3$  for As, synthetic  $\text{Cu}_{10}\text{Fe}_{1.8}\text{Zn}_{0.2}\text{Sb}_4\text{S}_{13}$  for Sb, synthetic  $\text{AgBiS}_2$  for Bi, pure Se metal for Se, natural chalcopyrite of known composition for Cu and synthetic  $\text{Zn}_{0.6}\text{Fe}_{0.4}\text{S}$  for S. Data for quantitative analysis were processed by the ZAF method with the corrections for atomic number, absorption and fluorescence effects of Sweatman and Long (1969).

The ore microscopic features of native tellurium are almost identical throughout the examined samples, having the same characteristics as was in Uytendogaardt and Burke (1971). It is white in color with very high reflectivity. Bireflectance is distinct with white to light gray in color, and anisotropy is strong in bluish and brownish gray tints. The hardness is greater than that of sylvanite. Except for the Iriki sample, native tellurium occurs as needle-like crystals under a binocular stereoscopic microscope, but as irregular aggregates under the ore microscope. Contact mineral assemblages described in the previous section are summarized as follows: native tellurium-quartz at the Mutsu and the Suzaki, native tellurium-stutzite-hessite-sylvanite-tetradymite-quartz at Kawazu, native tellurium-hessite-sylvanite-telluriantimony-quartz at the Kobetsuzawa, native tellurium-sylvanite-quartz at the Teine and native tellurium-goldfieldite at Iriki.

The chemical compositions of native tellurium grains for six samples are tabulated in Table 3. The composition of Te for 48 analytical points for six localities ranges from 98.16 to 100.73 wt.%. No other elements are detected in the ores of Kobetsuzawa and Mutsu, showing nearly pure compositions. Native tellurium from the Teine has Se of 0 to 0.85 and Cu of 0 to 0.74 wt.%. Native tellurium from the Kawazu contains Sb of 0.45 to 0.47 and Se of 0.19 to 0.27 wt.%, and that from Suzaki contains Se of 0.22 to 1.11 and Sb of 0 to 0.49 wt.%. The Iriki native tellurium has Cu of 0.69 to 0.98, As of 0.22 to 0.28, Bi of 0 to 0.22 wt.% and S under the detection limit, the signal of which may not be

significantly derived from the X-ray fluorescence of the surrounding goldfieldite.

## 5. Discussion

### 5-1. Chemical Composition of Native Tellurium

The native tellurium from the Japanese epithermal gold deposits has nearly pure chemical composition with some trace elements such as Se, Cu, Sb, Bi and As of 0-1.2 wt.%. The compositions are quite similar to those from the other localities in the previous literatures (Table 4), except for that from the Late Paleozoic Kairagach deposit, Uzbekistan, which contains the high content of Se up to 10.25 wt.% (Plotinskaya et al., 2006). This tendency is well explained by the experimental works for phase relations of alloys, in which the region of solid solution around the Te phase cannot be found in Au-Te, Ag-Te, As-Te, Bi-Te, Cu-Te, Fe-Te, Pb-Te and Sb-Te systems, whereas Te-Se system has perfectly continuous region of solid solution between Te and Se having the same crystal structure (Okamoto, 2000).

Trace element compositions of native tellurium from each locality would be explained by the associated minerals, except for Sb. In the Suzaki ore containing selenides such as clausthalite, native tellurium has selenium of 0.22-1.11 wt.%. The native tellurium aggregates of Iriki and Teine which are associated with goldfieldite contain constituent elements of goldfieldite, i.e., Cu-As-Bi and Cu-Se, respectively. The Kawazu native tellurium grains with Se of 0.19-0.27 wt.% are associated with selenium-bearing hessite. The Kobetsuzawa ore with pyrite and hessite, and the Mutsu ore with no contact associated sulfide or sulfosalt minerals have native tellurium with almost pure composition. On the other hand, Sb compositions are not well explained: native tellurium with Sb under the detection limit from the Kobetsuzawa ore with tellurantimony, and native tellurium with Sb of 0-0.5 wt.% from the Kawazu and the Suzaki ores without any antimony-bearing minerals.

### 5-2. Mineral Assemblages

The contact mineral assemblages for the ores with native tellurium examined in this study are plotted in the Au-Ag-Te ternary system for 120-280°C with the tie lines by Afifi et al. (1988) (Fig. 4). The assemblages agree well with the previously proposed experimental phase relations. The Suzaki ore has high Te-Au assemblages: from calaverite-sylvanite-krennerite via native tellurium to petzite in order of mineralization stage, whereas the Kobetsuzawa and the Kawazu ores have high Te-Ag assemblages of tellurium-hessite-sylvanite, and native tellurium-stutzite-hessite-sylvanite, respectively. The Teine ore has intermediate assemblage of native tellurium-sylvanite.



Taking the assemblage of alteration minerals into consideration (Table 1), the Suzaki ore with kaolinite has Au rich assemblages, whereas the ores in association with sericite such as Kobetsuzawa and Kawazu tend to have Ag rich assemblages. Teine ore with both sericitization and kaolinitization tends to be intermediate. This relationship suggests that the mineral assemblages in Au-Ag-Te system would be related to the hydrothermal environment especially on the pH condition, i.e., Au rich assemblages under acidic and Ag rich assemblages under intermediate pH conditions. This relationship would also be supported by the  $\log f_{O_2}$ -pH diagram by Zhang and Spry (1994), where calaverite occupies lower to intermediate pH region and hessite covers intermediate to higher pH region. Empressite in the Kawazu sample might be formed by phase transition during the cooling stage.

The mineral assemblages for other telluriferous epithermal gold deposits not in association with native tellurium in the Japanese Islands are also shown in the Au-Ag-Te ternary system of Figure 4 (⑧-⑪). The mineral assemblages for these ores are plotted in the lower regions with lower tellurium contents in these diagrams. The Agawa and the Date ores have calaverite-electrum lines, suggesting higher Au and lower Te-Ag environment. Chemical compositions of electrum from these ores (Soeda, 1978; Shikazono et al., 1990) are concordant with the tie line in the diagram, suggesting that the Ag/Au ratio of electrum have been controlled by mineral equilibria in Au-Ag-Te system, although the detailed experimental works with changing temperature are necessary. The Takeno ores are plotted in the petzite-hessite-electrum region, and the Chugu ores are on the hessite-electrum line. The chemical compositions of electrum from Takeno and Chugu ores (Shikazono et al., 1990) are also quite consistent with the tie line. Considering that these telluriferous gold deposits not in association with native tellurium such as Agawa, Date, Takeno, Chugu, Chitose, Sado and Kushikino contain carbonate minerals and adularia (Shikazono et al., 1990), they are estimated to have been formed under higher pH conditions.

The other minerals in closer association with native tellurium are tellurobismuthite and tetradymite which are also with hessite and stutzite in the Kawazu ore. The assemblage of native tellurium-tellurobismuthite-stutzite is stable equilibrium relation in Ag-Bi-Te ternary system for 137°C of Babanly et al. (2007), although the mutual phase relationship among hessite, stutzite and  $\gamma$ -phase during cooling has not been clear in detail. In the Iriki sample, native tellurium occurs in the aggregates of goldfieldite as dispersed inclusions. This occurrence might be originated from a kind of exsolution with cooling, however, the detailed mechanism remains unsolved and would be clarified by further study.

### 5-3. Hydrothermal Conditions for Native Tellurium Formation

Tellurium is known to have some valences and to change its geochemical behavior with the difference of redox conditions. On the basis of thermodynamic data from McPhail (1995) for tellurium species, and from SUPCRT92 (Johnson et al., 1992) and its update (Shock, 1998) for other species, the pH-Eh diagram for aqueous tellurium species at 250°C that is estimated typical and general temperature of epithermal gold deposits with native tellurium in Japan, is shown in Figure 5. The predominant species are oxoacidic tellurous species under oxidizing condition and telluride species under reducing condition. It is noted that the tellurium dimer ( $\text{Te}_2^{2-}$ ) is predominant under higher pH condition between the regions of telluride and tellurous species at the conditions of high total tellurium concentrations.

The pH-Eh diagram for aqueous tellurium species and tellurium minerals at 250°C are shown in Figure 6. The region of native tellurium occurs between those of tellurides and tellurous species at lower pH, matching approximately with the stability of native tellurium in the log  $f_{\text{O}_2}$ -pH diagrams by Zhang and Spry (1994) and McPhail (1995). It is emphasized here that the solubility of native tellurium is very low, indicating that native tellurium deposits from dilute Te solution of over 1.28 ppt at the appropriate conditions.

In the pH-Eh diagram for aqueous Se, S and Te species at 250°C (Fig. 7), the selenide species oxidize at higher Eh conditions than sulfide and telluride species, regardless of pH. On the other hand, the relative oxidation of sulfide and telluride species depends on pH: sulfides oxidize at higher Eh than tellurides under pH less than 6, and vice versa under pH greater than 6. This suggests that the oxidation states of Te, Se and S are key factor in understanding of the environment of epithermal gold deposits, which was already demonstrated by a series of geochemical and mineralogical work for seleniferous minerals by Shikazono (1978), Shikazono and Takeuchi (1984) and Shikazono et al. (1990). Combined with the diagram for native tellurium of Figure 6, the region of native tellurium with the total Te contour less than  $10^{-14}$  mol/l is included in the aqueous selenides ( $\text{H}_2\text{Se}$ ,  $\text{HSe}^-$ ) and also in  $\text{H}_2\text{S}$  region, which agrees with the mineral assemblages basically with sulfides and sulfosalts in these ores.

It is concluded to say that native tellurium mineralization in the epithermal gold deposits would have been formed under middle Eh and acidic to intermediate pH conditions. The chemical condition would be estimated to be intermediate between the high sulfidation (acid-sulfate) type and the low sulfidation (adularia-sericite) type by Heald et al. (1987) and Hedenquist et al. (1996), as was already estimated by Shikazono

et al. (1990). Mineral assemblages of tellurous minerals in Au-Ag-Te system are strongly related to their alteration mineral, i.e., high Te-Au assemblages of native tellurium-calaverite-krennerite-sylvanite are associated with the kaolinite, high Te-Ag assemblages of native tellurium-sylvanite-hessite-stutzite are with sericite, and low Te assemblages not with native tellurium but with petzite and/or electrum are associated with adularia and calcite, suggesting that mineral assemblages of tellurous minerals are controlled by pH conditions. Thus, the mineral assemblages of tellurous minerals are useful in understanding the formative environment of epithermal gold deposits in the volcanic terranes.

Acknowledgements: We are very grateful to Prof. Naotatsu Shikazono and Dr. Yasushi Watanabe for careful reviews and valuable comments. We thank Drs. Kiminori Sato and Jin-Yeon Hwang for valuable discussion. This work was partially supported by a Grant-in-Aid of the Japanese Ministry of Education, Science, Sports and Culture (Grant No. 21540317).

#### References

- Afifi, A. M., Kelly, W. C. and Essene, E. J. (1988) Phase relations among tellurides, sulfides, and oxides: I. Thermochemical data and calculated equilibria. *Econ. Geol.*, 83, 377-394.
- Anthony, J. W., Bideaux, R. A., Bladh, K. W. and Nichols, M. C. (1990) *Handbook of Mineralogy: 1, Elements, Sulfide, Sulfosalts*. Mineral Data Publishing, Tucson, Arizona, 588p.
- Babanly, M. B., Shykhyev, Yu. M., Babanly, N. B. and Yusibov, Yu. A. (2007) Phase equilibria in the Ag-Bi-Te system. *Russian Jour. Inorg. Chem.* 52, 434-440.
- Endo, M. (1964) On some tellur minerals and their textures from Okuyama and neighboring mines, Izu Peninsula. *Jour. Assoc. Petrol. Mineral. Econ. Geol. Japan*, 51, 98-107 (in Japanese with English abstr.).
- Fadda, S., Fiori, M., Grillo, S. M., Matzuzzi, C. (2005) Polymetallic assemblages with precious metal tellurides and sulfosalts from the Furtei epithermal Au deposit, Sardinia, Italy: paragenesis and genetic significance. In Mao, I. and Bierlein, F. P. (eds.), *Mineral Deposit Research: Meeting the Global Challenge*, 1395-1398, Springer, Berlin.
- Fujii, N., Tsukimura, K. and Julio, J. M. (1989) Mode of occurrence and genetic processes of the Iriki kaolin deposit, southern Kyushu. *Bull. Geol. Surv. Japan*, 40, 299-322 (in Japanese with English abstr.).

- Heald, P., Foley, N. K. and Hayba, D. O. (1987) Comparative anatomy of volcanic-hosted epithermal deposits: acid-sulfate and adularia-sericite types. *Econ. Geol.*, 82, 1-26.
- Hedenquist, J. W., Izawa, E., Arribas, A. and White, N. C. (1996) Epithermal gold deposits: styles, characteristics, and exploration. *Resource Geol. Spec. Publ. No.1*, Society of Resource Geology, Tokyo, 17p.
- Honma, H., Nakata, M. and Fujii, T. (1979) New data of (Au,Ag)Te<sub>2</sub> type minerals from the Susaki mine and the Cripple Creek District. *Jour. Mineral. Soc. Japan*, 14, 175-187 (in Japanese).
- Ishibashi, M. (1956) Some tellurium-bearing minerals from the Kobetsuzawa mine, Sapporo, Hokkaido. *Jour. Mineral. Soc. Japan*, 2, 447-457 (in Japanese).
- Ishibashi, M. and Ohmachi, K. (1949) On some tellurium minerals from the Mutsu gold mine, Aomori Prefecture. *Hokkaido Chishitsu Yoho*, 12, 1-5 (in Japanese).
- Johnson, J. W., Oelkers, E. H. and Helgeson, H. C. (1992) SUPCRT92: A software package for calculating the standard modal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bar and 0 to 1000°C. *Computers and Geosciences*, 18, 899-947.
- Kinoshita, K. (1945) Tellurium-bearing gold ore from the Kuzuzawa mine, Aomori Prefecture. *Bull. Fac. Eng. Kyushu Univ.*, 19, 111-114 (in Japanese).
- Matsumoto, A. and Fujii, N. (1989) K-Ar age of two lavas from the Imuta volcano, Kagoshima Prefecture, southern Kyushu: with reference to the formation of Iriki kaolin deposit. *Jour. Assoc. Petrol. Mineral. Econ. Geol. Japan*, 84, 398-402 (in Japanese with English abstr.).
- McPhail, D. C. (1995) Thermodynamic properties of aqueous tellurium species between 25°C and 350°C. *Geochim. Cosmochim. Acta*, 59, 851-866.
- MMAJ (1987) Report on the Regional Exploration Researches of the Izu Region. Metal Mining Agency of Japan, 152p. (in Japanese).
- MMAJ (1996) Report on Detailed Geological Structure Survey during the Fiscal Year Heisei 7: Jozankei-Harukayama Area. Metal Mining Agency of Japan, 90p. (in Japanese).
- Nakata, M., Chung, J. I., Honma, H. and Sakurai, K. (1985) On tellurantimony from the Kobetsuzawa Mine, Sapporo, Hokkaido. *Jour. Mineral. Soc. Japan*, 17, 79-83 (in Japanese).
- Nakata, M., Honma, H., Chung, J. I. and Sakurai, K. (1989) Frobergite from the Kobetsuzawa mine, Sapporo, Hokkaido, Japan. *Mineral. Mag.*, 53, 387-388.
- Okamoto, H. (2000) Desk Handbook: Phase Diagrams for Binary Alloys. MSM International, 827p.

- Osanai, H., Sugimoto, R. and Kitagawa, Y. (1956) Explanatory Text of the Geological Map of Japan, Scale 1:50,000, Sapporo. Geol. Surv. Hokkaido, 64p. (in Japanese with English abstr.).
- Pals, D. W. and Spry, P. G. (2003) Telluride mineralogy of the low-sulfidation epithermal Emperor gold deposits, Vatukoula, Fiji. *Mineral. and Petrol.*, 79, 285-307.
- Plotinskaya, O. Yu., Kovalenker, V. A., Seltmann, R. and Stanley, C. J. (2006) Te and Se mineralogy of the high-sulfidation Kochbulak and Kairagach epithermal gold telluride deposits (Kurama Ridge, Middle Tien Shan, Uzbekistan). *Mineral. and Petrol.*, 87, 187-207.
- Sawai, O. and Itaya, T. (1996) K-Ar ages of vein-type deposits in the Otaru-Shikotsu district, southwest Hokkaido, Japan. *Resource Geol.*, 46, 33-42 (in Japanese with English abstr.).
- Shikazono, N. (1978) Selenium content of acanthite and the chemical environments of Japanese vein-type deposits. *Econ. Geol.*, 73, 524-533.
- Shikazono, N. and Takeuchi, K. (1984) Estimates of selenium and sulfur fugacities and formation temperature for selenium-rich gold-silver vein-type deposits. *Geochem. Jour.*, 18, 263-268.
- Shikazono, N., Nakata, M. and Shimizu, M. (1990) Geochemical, mineralogic and geologic characteristics of Se- and Te-bearing epithermal gold deposits in Japan. *Mining Geol.*, 40, 337-352.
- Shock, E. L. (1998) Slop98.dat (computer data file). <http://www.cohnosz.net/download/slop98.edit.dat> accessed on 2010-12-23.
- Soeda, A. (1978) Gold-silver deposits in Chugoku district. In *Mining Metal. Inst. Japan* (ed.) *Gold-Silver Ore in Japan, Part II*, 1-24 (in Japanese).
- Sugimoto, R. (1952) On the geology of the Teine mine, with some remarks on the mineral composition and paragenesis of the Mitsuyama, Koganesawa ore deposits. *Jour. Assoc. Petrol. Mineral. Econ. Geol. Japan*, 36, 72-84 (in Japanese with English abstr.).
- Sweatman, T. R. and Long, J. V. P. (1969) Quantitative electron probe micro analysis of rock-forming minerals. *Jour. Petrol.*, 10, 332-379.
- Takasu, S. (1965) Silver tellurides from the Kawazu mine, Shizuoka Prefecture. *Jour. Miner. Soc. Japan*, 7, 350-355 (in Japanese with English abstr.).
- Togashi, S. (1977) Petrology of Osore-Yama Volcano, Japan. *Jour. Assoc. Petrol. Mineral. Econ. Geol. Japan*, 72, 45-60 (in Japanese with English abstr.).
- Uetani, K., Sakurai, K. and Kato, A. (1966) The occurrence of selenian stibioluzonite from the Iriki Mine, Kagoshima Prefecture, Japan. *Bull. Nat. Sci. Mus. Tokyo*, 9,

609-613.

- Uytenbogaardt, W. and Burke, E. A. J. (1971) Tables for Microscopic Identification of Ore Minerals, 2nd ed., Elsevier, New York, 430p.
- Watanabe, M. (1932) On the telluride gold ore and native tellurium from the Suzaki Mine, Shizuoka Pref. (1). Jour. Assoc. Petrol. Mineral. Econ. Geol. Japan, 8, 73-84 (in Japanese).
- Watanabe, M. (1933) On the telluride gold ore and native tellurium from the Suzaki Mine, Shizuoka Pref. (2). Jour. Assoc. Petrol. Mineral. Econ. Geol. Japan, 10, 147-156 (in Japanese).
- Watanabe, M. (1934) Study of Telluride Gold-Silver Ores. Shinko-sha, Tokyo, 231p. (in Japanese).
- Watanabe, M. (1952) Mode of occurrence of tellurium bearing minerals in Japan. Sci. Rep. Tohoku Univ., Ser. III, No. 4, 45-80.
- Watanabe, M. (1979) Fluid inclusions in some Neogene ore deposits in the Green Tuff Region. Mining Geol., 29, 307-321.
- Watanabe, T. (1935) On the native tellurium from the Teine mine, Hokkaido. Jour. Assoc. Petrol. Mineral. Econ. Geol. Japan, 13, 171-175 (in Japanese).
- Watanabe, T. (1936) Microscopic study of the tellurium-bearing gold-silver ore from the Takinosawa vein, Teine mine, Hokkaido. Jour. Geol. Soc. Japan, 43, 787-799 (in Japanese).
- Watanabe, Y. (2002) Late Cenozoic metallogeny of southwest Hokkaido, Japan. Resource Geol., 52, 191-210.
- Watanabe, Y. (2005) Late Cenozoic evolution of epithermal gold metallogenic provinces in Kyushu, Japan. Mineral. Deposita, 40, 307-323.
- Zhang, X. and Spry, P. G. (1994) Calculated stability of aqueous tellurium species, calaverite, and hessite at elevated temperatures. Econ. Geol., 89, 1152-1166.

#### Caption

Fig. 1 Distribution of epithermal gold deposits with telluriferous minerals and locations of deposits with native tellurium in the Japanese Islands. ★: deposit with native tellurium, ●: deposit not with native tellurium but with other telluriferous minerals, and ○: other large epithermal gold deposit. The dashed lines indicate the present volcanic front.

Fig. 2 Photographs of polished sections under a binocular stereoscopic microscope. ① Teine, ②Kobetsuzawa, ③Mutsu, ④Kawazu, ⑤Suzaki and ⑥Iriki.

Fig. 3 Photomicrographs for occurrences of native tellurium under a ore microscope

(open nicol). ①Teine, ②Kobetsuzawa, ③Mutsu, ④Kawazu, ⑤Suzaki and ⑥Iriki. Abbreviations are: Te: native tellurium, Cv: calaverite, Sv: sylvanite, Sz: stutzite, He: hessite, gf: goldfieldite, py: pyrite and qt: quartz.

Fig. 4 ①Au-Ag-Te ternary system for 120-280°C. The phases and tie lines are from Afifi et al. (1988). Plots of contact mineral assemblages for ②Teine, ③Kobetsuzawa, ④Mutsu, ⑤Kawazu, ⑥Suzaki, ⑦Iriki, ⑧Date (Shikazono et al., 1990), ⑨Agawa (Soeda, 1978), ⑩Takeno (Shikazono et al., 1990) and ⑪Chugu (Shikazono et al., 1990). Abbreviations are: te: native tellurium, cv: calaverite, kn: krennerite, sv: sylvanite, em: empressite, sz: stutzite, he: hessite, pz: petzite, au: native gold, ag: native silver, el: electrum, ■: identified mineral phase and ★: composition of electrum.

Fig. 5 The pH-Eh diagram for aqueous tellurium species at 250°C. Dashed lines indicate the contours of  $\text{Te}_2^{2-}$  with the condition of total Te concentration of  $10^{-8}$ ,  $10^{-10}$  and  $10^{-12}$  (mol/l).

Fig. 6 The pH-Eh diagram for aqueous tellurium species and tellurium minerals at 250°C. Hatched areas indicate the fields of native tellurium with the condition of the condition of total Te concentration of  $10^{-8}$ ,  $10^{-10}$ ,  $10^{-12}$  and  $10^{-14}$  (mol/l). Dashed lines indicate the contours of  $\text{Te}_2^{2-}$  as same as in Figure 5.

Fig. 7 The pH-Eh diagram for aqueous Se and S species at 250°C. The fields for Te species of  $10^{-12}$  mol/l total Te contents are shown with dashed lines.

Table 1 Summary of ore-geological features of the epithermal gold deposits with native tellurium.

Table 2 Mineral compositions of the ore deposits with native tellurium reported in the previous literatures.

Table 3 Chemical compositions of native tellurium by EPMA for six localities.

Table 4 Chemical compositions of native tellurium from other localities.

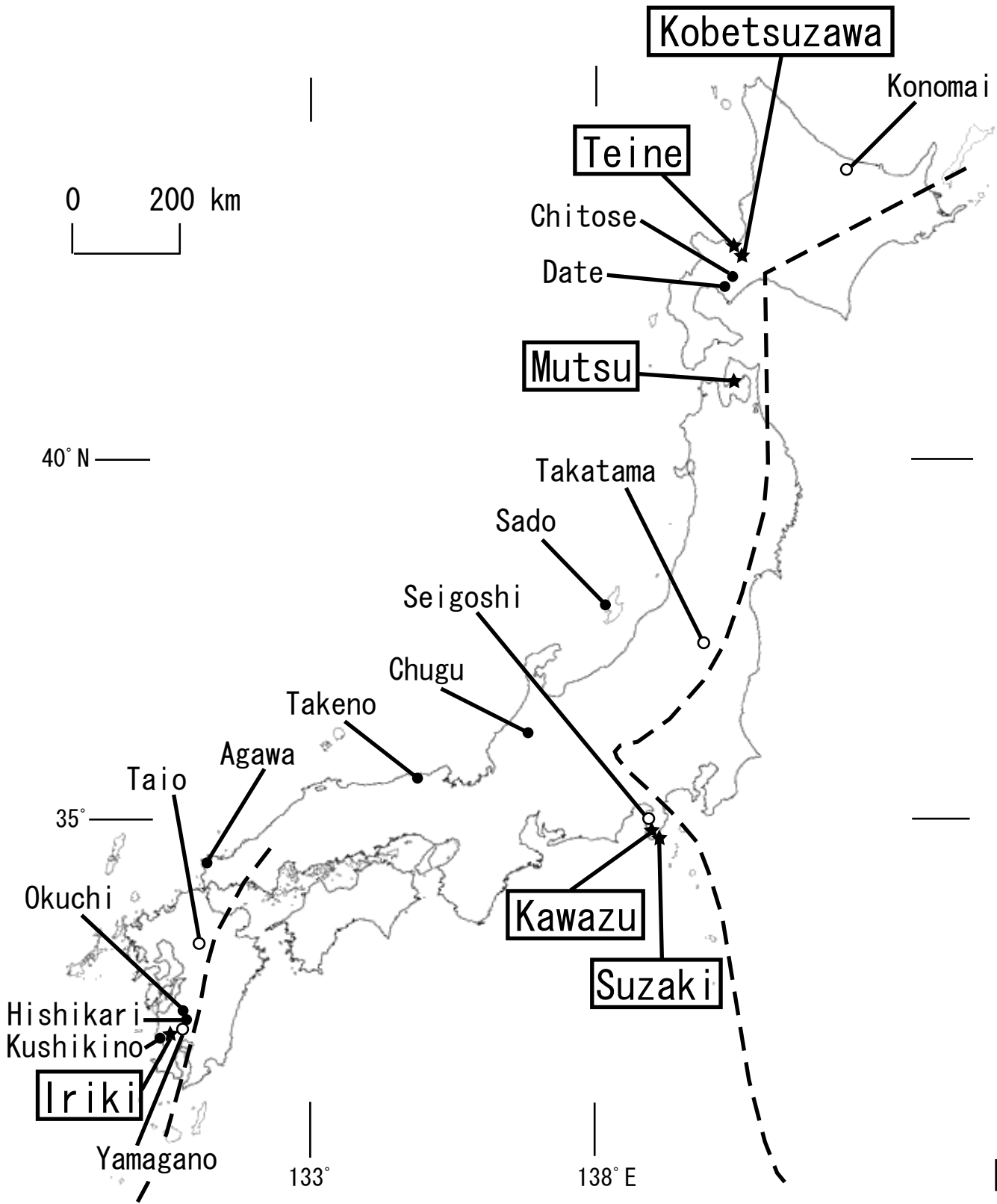


Fig. 1



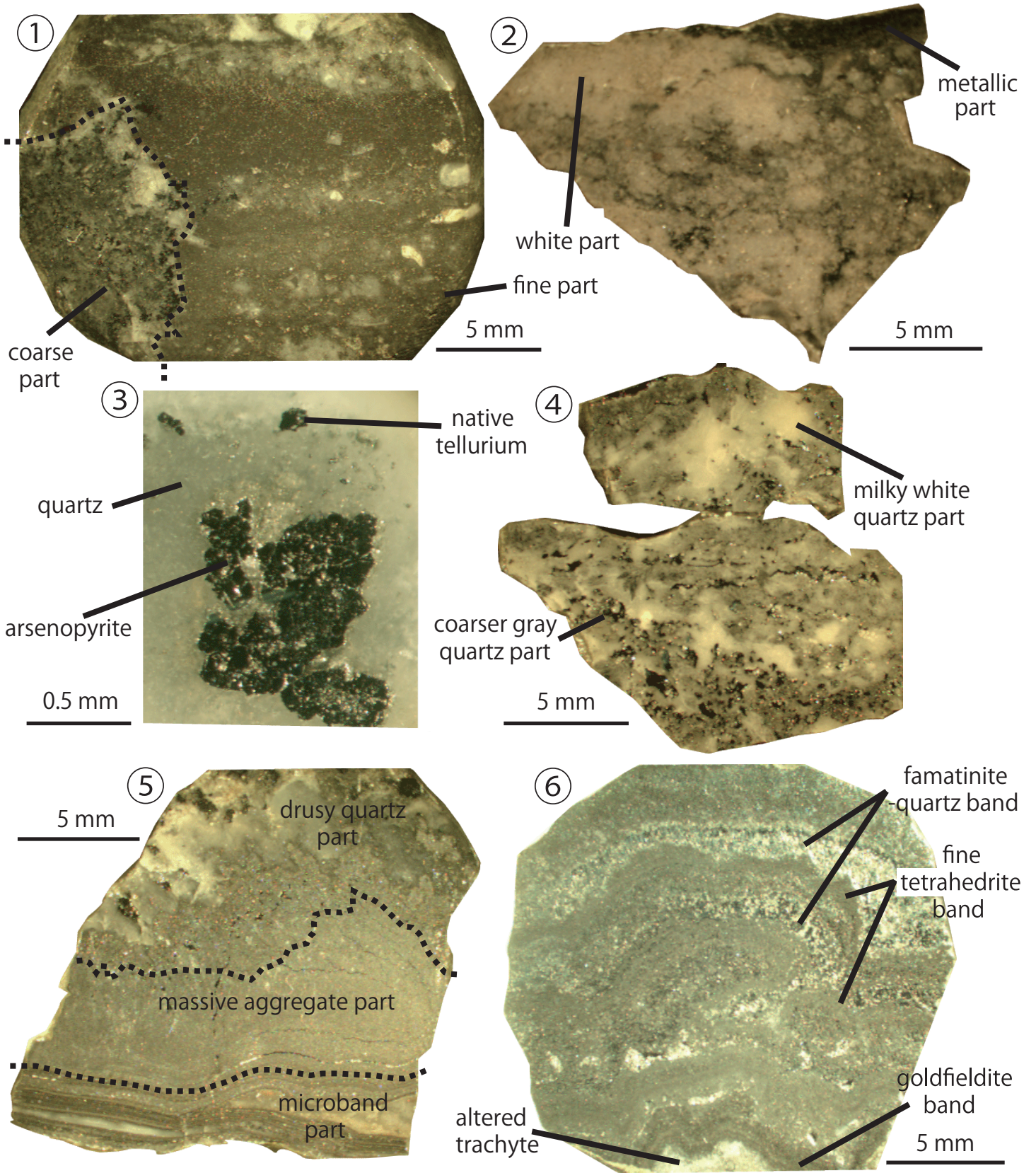


Fig. 2

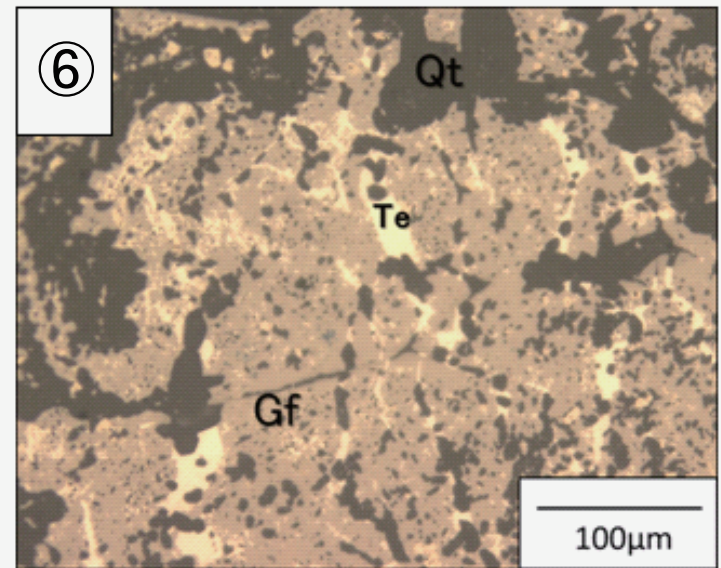
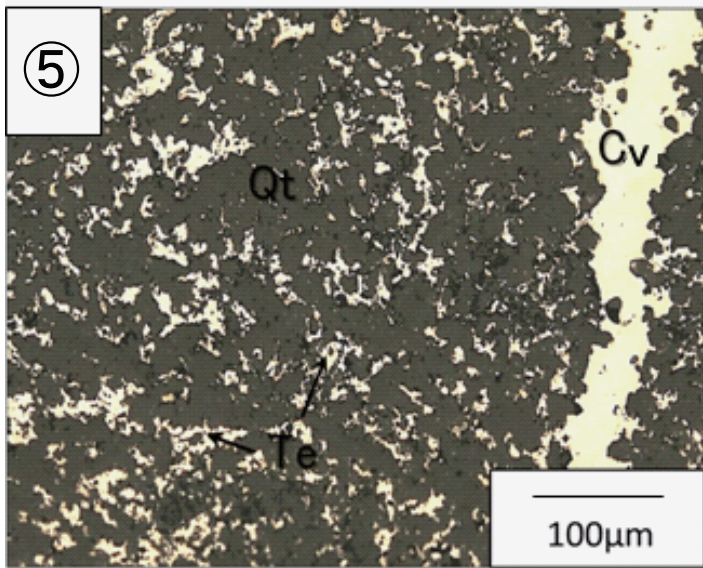
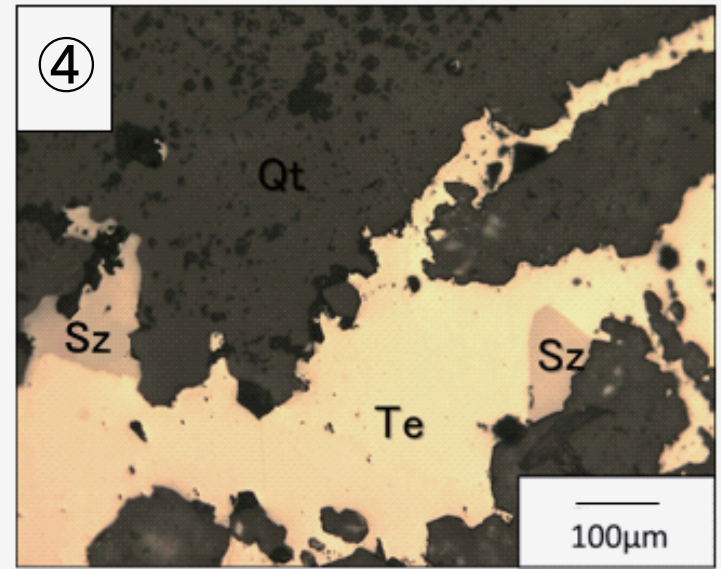
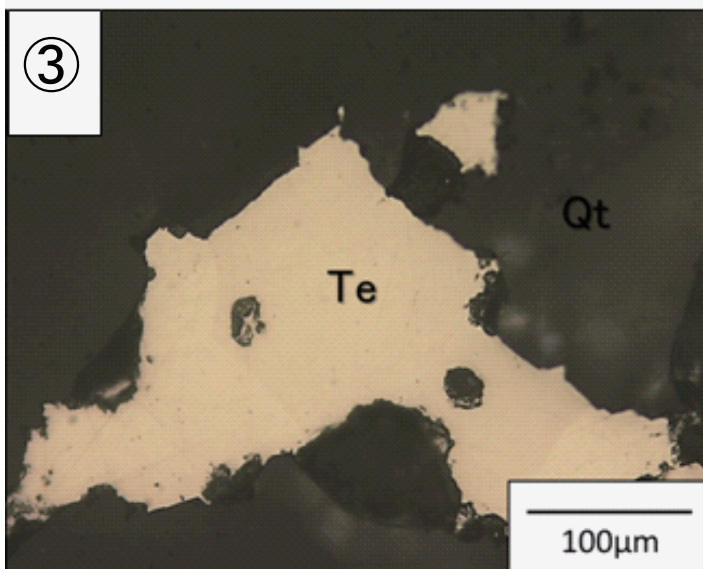
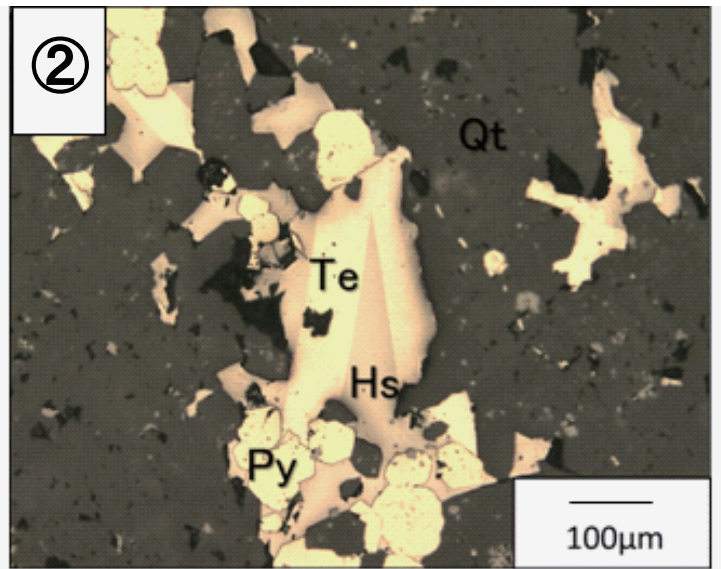
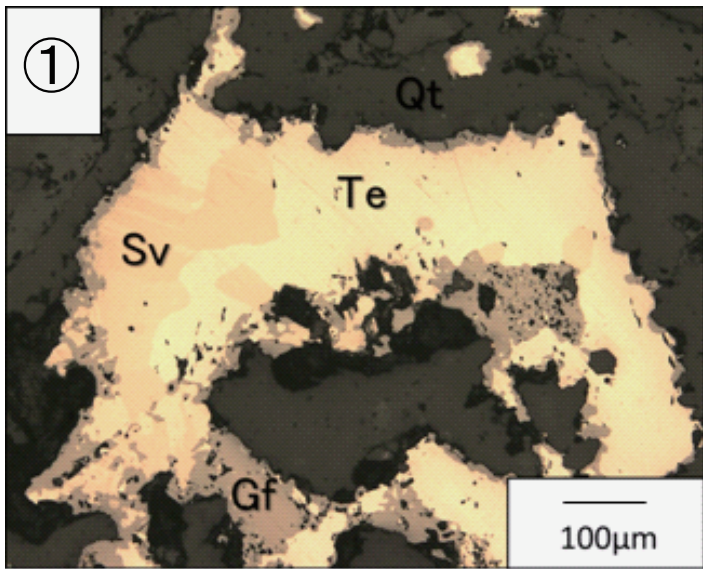


Fig. 3

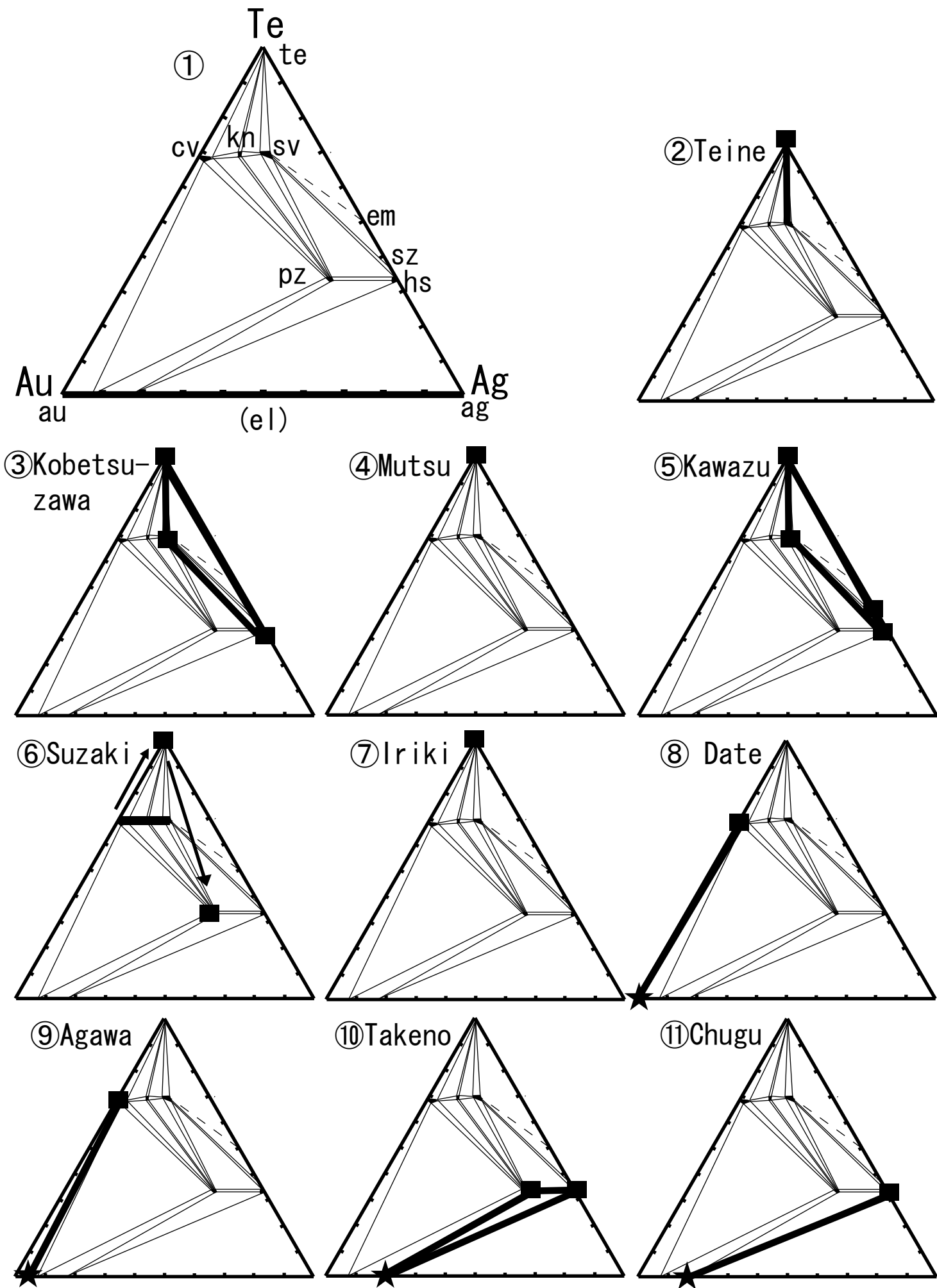


Fig. 4

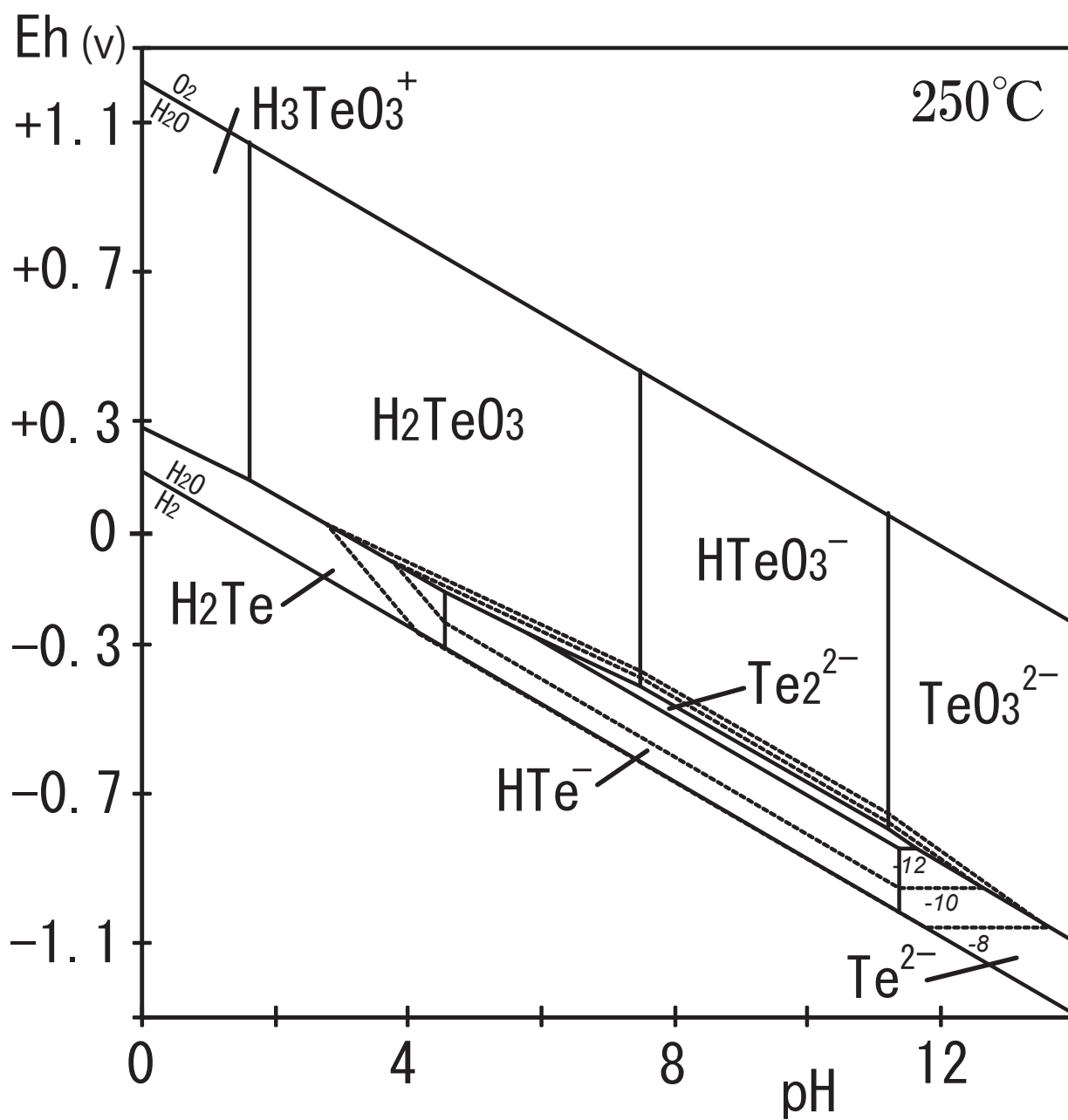


Fig. 5

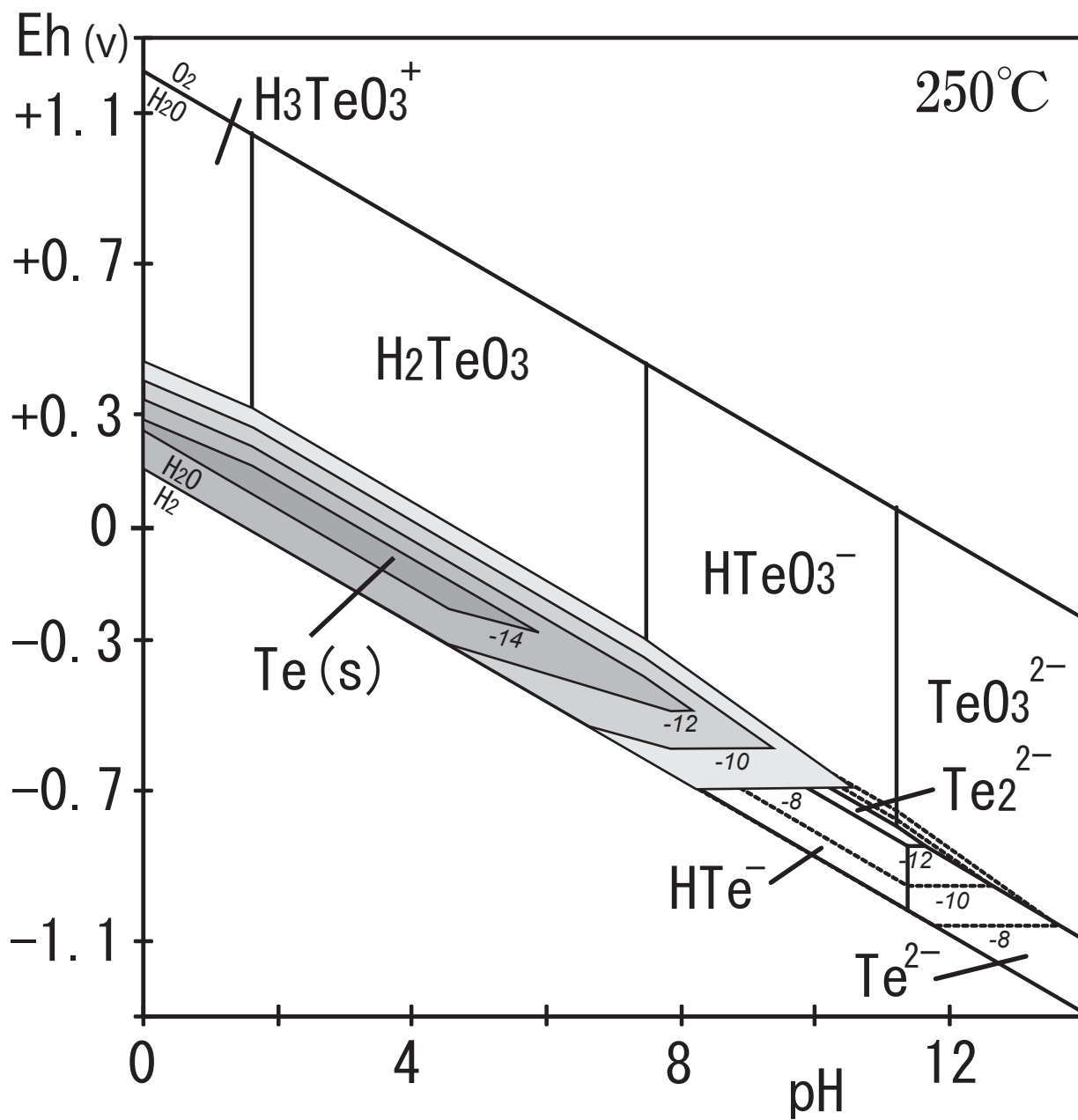


Fig. 6

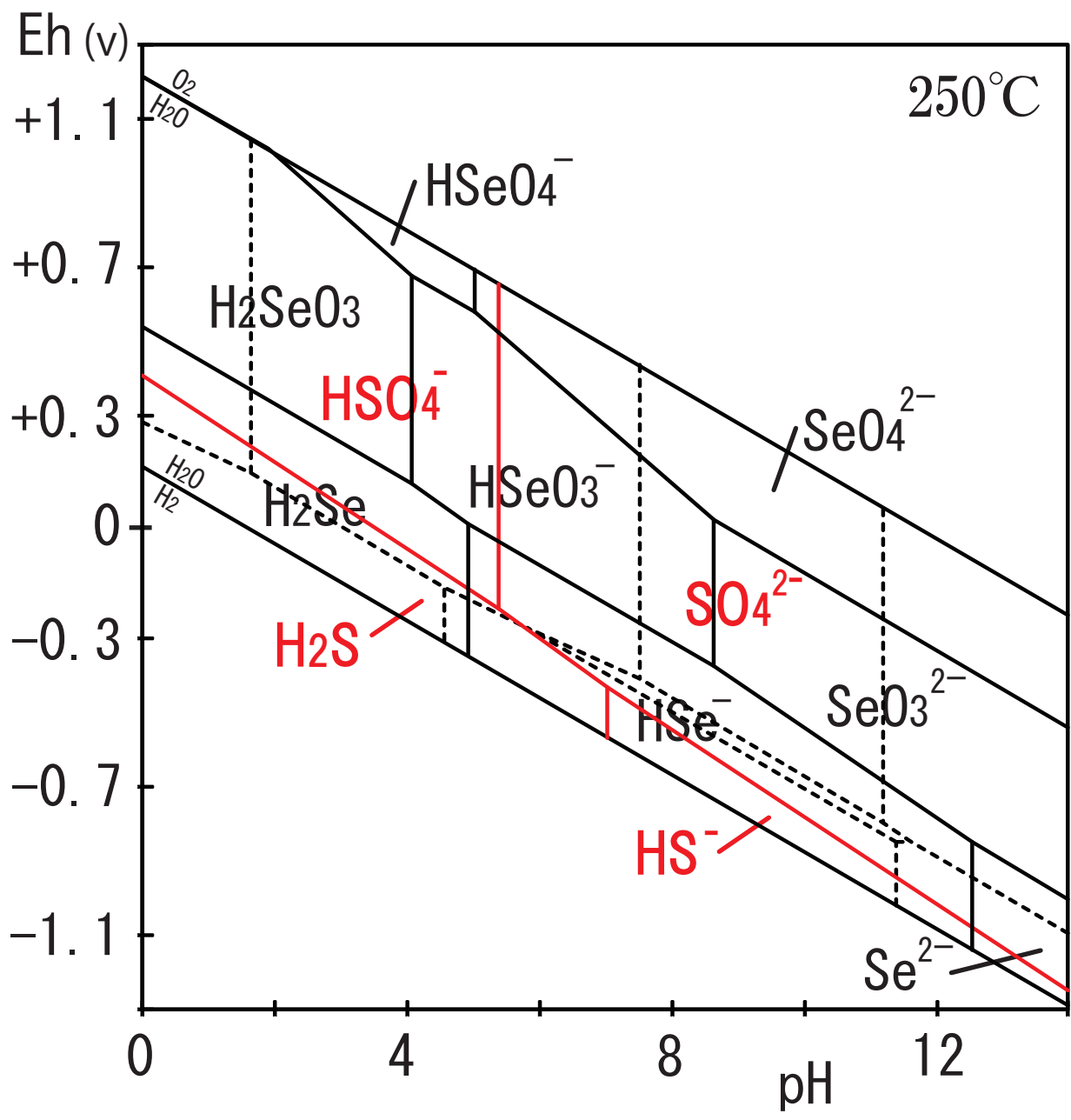


Fig. 7

Deposit	Ag/Au (ratio)*	Geology			Ore Deposits		
		Host rocks	Alternation minerals		Mode of occurrence	K-Ar ages (Ma)	Homogeni- zation (°C)
			Sericite	Kaolinite			
Teine (Mitsuyama group)	6	andesite, greenish tuffs	○	○	vein	4.0–5.0	206–243
Kobetsuzawa	48.1	andesite, tuffs	○		network veinlet	3.6	
Mutsu	0.1	greenish tuffs, tuffaceous sand, tuffaceous shale,	○		vein		
Kawazu (Hinokizawa)	1–5	andesite, tuffs	○		vein	1.4–1.5±0.3	206–281
Suzaki	0.1	andesite, pyroclastics		○	breccia pipe		
Iriki	10–12	acidic tuffs		○	breccia pipe	0.453±0.018	

\*Shikazono et al. (1990)

Table 1

Deposit	Telluriferous minerals															Gangue minerals											
	native tellurium	calaverite	krennerite	sylvanite	petzite	empelessite	stutzite	hessite	kostovite	frohbergite	altaite	tellurantimony	tellurobismuthite	tetradymite	kawazulite	poubaite	rickardite	goldfieldite	quartz	anatase	calcite	rhodochrosite	barite	zeolite	sericite	kaolinite	
Teine (Mitsuyama group)	○			○	○											○	○	○		○	○	○		○	○	○	
Kobetsuzawa	○			○					○		○	○					○	○	○	○	○			○	○	○	○
Mutsu	○											○	○						○	○	○				○	○	○
Kawazu (Hinokizawa)	○			○		○	○					○	○	○	○	○	○	○	○	○			○		○	○	○
Suzaki	○	○	○	○	○			○											○	○	○			○	○	○	○
Iriki	○																	○	○	○						○	○

Deposit	Opaque minerals																									
	electrum	pyrite	pyrrhotite	marcasite	arsenopyrite	bornite	chalcocite	chalcopyrite	luzonite	enargite	famatinite	tetrahedrite	hakite	stannoidite	emlectite	hemusite	argentite	galena	sphalerite	realgar	orpiment	stibnite	bismuthinite	clausthalite	hematite	
Teine (Mitsuyama group)	○	○				○	○					○	○		○			○	○	○	○	○	○			○
Kobetsuzawa		○	○															○	○	○	○					○
Mutsu	○	○			○									○		○		○	○	○	○			○		○
Kawazu (Hinokizawa)		○	○		○													○	○	○	○			○		○
Suzaki	○	○	○	○	○													○	○	○	○			○		○
Iriki		○	○	○	○												○	○	○	○				○		○

modified after Shikazono et al. (1990).

Table 2





Locality	Au	Ag	Bi	Te	Se	S	Fe	Cu	Pb	Sb	Total (wt%)	Ref.
Emperor deposit, Fiji	0.00	0.00	0.05	99.87	0.00	0.00					99.92	1
Gunnison Co., Colorado, USA				99.45	0.40		0.11				99.96	2
Kochbulak deposit, Uzbekistan	0.03	0.09	0.00	98.62	0.15	0.01	0.01	0.07	0.01	0.70	99.69	3
Kairagach deposit, Uzbekistan		0.05		90.31	10.25	0.09	0.01	0.01	0.08	0.39	101.19	3
Furtei deposit, Italy				100.00							100.00	4

Ref.: 1) Pals and Spry (2003), 2) Anthony et al. (1990), 3) Plotinskaya et al. (2006), 4) Fadda et al. (2005).

Table 4