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# Au-Ag-Tellurides from the Daté Mine, Hokkaido, Japan

By

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## Abstract

Mineragraphic study of gold bearing quartzose ores from the Daté mine, Hokkaido, shows the presence of krennerite, hessite and petzite as Au-Ag-telluride minerals. The paragenesis of those ores and of related massive sulphide ores of "Black Ore" type of this mine, and similar deposits of Japan are discussed. On the Au-Bi-Te mineralization, the combination of these elements are affected by the geologic environment. Namely under the volcanic hydrothermal condition Au and Te combination is common, but the plutonic hydrothermal one Te combines with Bi rather than Au. It is very interesting that the mineralization under metamorphic condition is similar to the volcanic one.

## Introduction

The Daté mine is about 70 kilometers southwest of Sapporo, near the Tôya caldera lake and the Usu active volcano of the Shikotsu-Tôya National Park. The geology of the mine has been treated by M. Watanabé and K. Yamaguchi<sup>23)</sup> and the mineralogy of the tellurium vein was reported by M. Watanabé<sup>20)</sup>. The present writer also investigated the geology of the whole mine area for several years and made recommendations as to the exploitation of the deposits. From samples collected from the deposits he obtained several dozen polished and thin sections. They were studied mineragraphically for comparison with his collections from the Té-iné, Kobetsuzawa, Mutsu-Kuzusawa and Kawazu mines that show similarities in respect to the mineralization of the deposits.

The writer would like to express his thanks to Mr. T. Tadokoro, the owner of the mine, who gave great help to the field work.

## Geology and ore deposits

Rocks of the mine area consist of rhyolitic and dacitic flows, agglomerates, tuffs and tuffbreccias of Miocene. The mineralization occurs essentially in

tuffs and tuffbreccias. The deposit is a polymetallic. The precious metals are mainly worked from the quartz veins, and base metals from the massive bodies of black and yellow ore. A strongly silicified layer of tuffbreccia form a caprock-like cover above the massive deposits, but argillitization is rather wide and distinct.

The main deposits of the massive bodies of yellow ore with brecciated structure consist of dominant pyrite, some tetrahedrite, a little chalcopyrite, sphalerite and galena, and in some portions often much argentite. Gangue minerals are quartz and sericite. Breccias are silicified and argillitized country rocks cemented by sulphides. The massive and compact black ore consists mainly of sphalerite, galena and barite, accompanied by some pyrite, tetrahedrite, chalcopyrite, quartz and sometimes argentite and pyrargyrite. In some places there are short thick lenses brecciated structure; the cements of the breccias are sericite quartz luzonite crusts enclosing fine pyrite grains and short bismuthinite needles. Supergene minerals are native silver, bornite, chalcocite, covellite, marcasite and goethite derived from weathered ore.

Numerous short gold-bearing tetrahedrite quartz veins are found scattered among the massive ore bodies. They show banded or brecciated structure which consists of fine grained quartz, a little native gold, argentite, pyrite, tetrahedrite, sphalerite, and rarely chalcopyrite and galena. Only one of these gold quartz veins a telluride bearing one, called No. 21 vein, is found at Koganezawa. The exact genetical relation between the mass and vein is not yet clear, but the vein may be younger than the mass.

It is said that vein No. 21 extends about 100 m. along the strike; the known vertical range is 30 m. It is not a simple vein, but is composed of networks of numerous thin quartz veinlets filling the brecciated fault zone which strikes to  $80^\circ$  northeast, dips  $80^\circ$  south, with a width generally less than 50 cm. Thus the main part of the vein shows brecciated structure; the brecciated fragments consist of silicified and pyritized rhyolite cemented by quartz veinlets having delicate stringers and spots of metallic minerals, but at the end part of the quartz vein grades to a thin clay vein without metallic minerals. The country rocks are widely argillitized, but in the part adjacent to the wall of the vein silicification is rather distinct, so it is hard to determine the actual boundary between the vein and country rocks. The mean tenor of hand picked ores in concentration was 200 g/t Au, 50 g/t Ag and 0.3% Cu.

The width of irregular net veinlets is less than a few centimeters. Veinlets are not uniform, but show different texture place by place. In some places they consist of compact granular quartz mass, or white unglazed porcelain microcrystalline quartz aggregate having gray or chocolate color metallic spots,

clouds, stringers or films. Those textures are very similar to that of ores from the Té-iné and Rendaiji mines. In other places veinlets show drusy or crustified texture being similar to the ores from the Kobetsuzawa and Mutsu-Kuzusawa mines. The most characteristic feature of the ore is not the texture, but the mineralogical composition; native tellurium and simple sulphides of Bi, Sb or As have not yet been found in any amount comparable to what is found in the other mines.

### Mineralogy

The primary ore of vein No. 21 consists of the following:

Metallic minerals: pyrite, sphalerite, chalcopyrite, tetrahedrite, enargite, galena, hessite, petzite, krennerite and native gold.

Gangue minerals: quartz, sericite, gypsum and barite.

Hessite—Hessite, rather rare Te-bearing mineral in the ore, occurs as small grains ( $\emptyset < 0.03$  mm). Only a few grains are found in the interstices of quartz grains, but most in krennerite with native gold and chalcopyrite.

In the polished sections hessite shows grayish-white color when it occurs as a single grain among the quartz, but shows much darker with olive green tint when it is contact with krennerite. Polish is not so good. The surface almost always scratched. Hardness is lower than that of krennerite. Reflection is lower; reflection pleochroism hardly visible. Anisotropism is weak; polarization colors dark gray and dark blue gray. Twinning lamellae are not observed.

Etch tests:

$\text{HNO}_3$  (1:1) ... (+) Slowly stains brown to black, without effervescence.

$\text{HCl}$  (1:1) ... (+) Slowly stains iridescent, some small areas are negative.

$\text{KCN}$  (20%) ... (-) Negative.

$\text{FeCl}_3$  (20%) ... (+) Instantly stains brown to iridescent, results in rough surface.

$\text{KOH}$  (40%) ... (-) Negative.

$\text{HgCl}_2$  (5%) ... (+) Stains faintly darker.

A.R. ... (+) Instantly stains brown.

As the crystals of hessite are too small, it could not take the textural etching figures by  $\text{HNO}_3$  and  $\text{HCl}$ <sup>(1),(3),(5)</sup>.

Petzite—Petzite is not so common, but it occurs in some parts of the vein. It occurs rarely as individual grains in the interstices of quartz grains, but most grains are associated with krennerite and partly replaced latter. It shows irregular form ( $\emptyset < 0.01$  mm) composed very rarely of isometric polygonal aggregate.

In the polished sections petzite show steel white and more blueish when it is in contact with krennerite. Polish is not so good. The surface has more streaks than krennerite but triangular pits are never seen. Hardness is lower than that of krennerite. Reflection is high, but lower than krennerite; reflection pleochroism could not be recognized in air nor in oil. Anisotropism is very weak in air, and faintly distinct in oil; polarization colors grayish and brownish.

Etch tests :

$\text{HNO}_3(1:1) \cdots (+)$  Instantly effervesces, then stains dark brownish violet, and takes rough surfaces.

$\text{HCl}(1:1) \cdots \cdots (-)$  Practically negative, some stains iridescent, but action is very slow and requires more than one minute.

$\text{KCN}(20\%) \cdots (-)$  Negative, sometimes stains faintly iridescent.

$\text{FeCl}_3(20\%) \cdots (+)$  Quickly stains iridescent, afterward washes and rubs clean easily.

$\text{KOH}(40\%) \cdots (-)$  Negative.

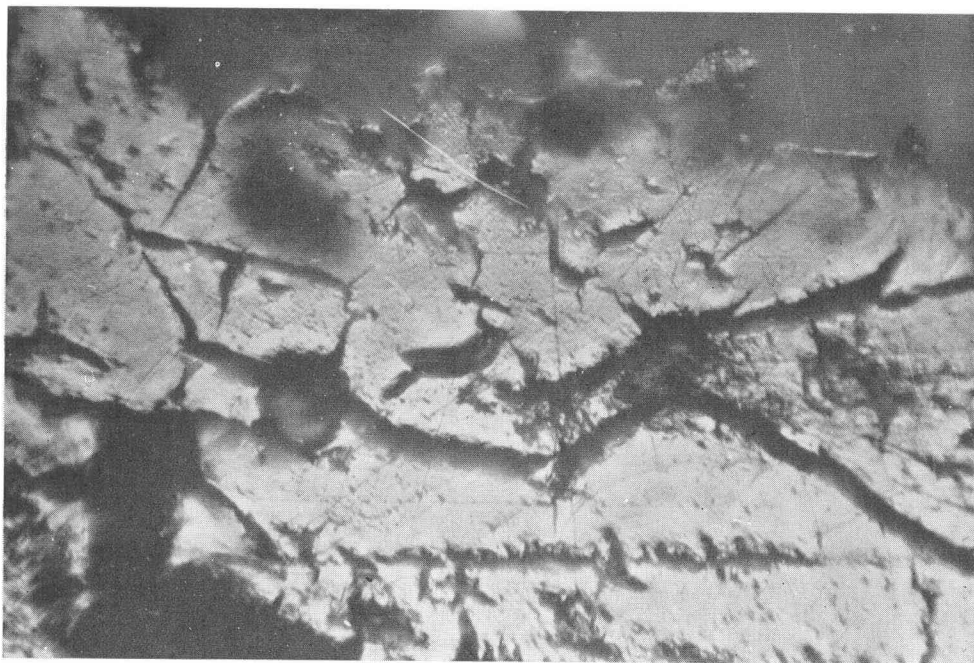


Fig. 1. Polished surface of petzite, etched with  $\text{HNO}_3(3:2)$ , from the Daté mine ( $\times 500$ ).

HgCl<sub>2</sub> (5%) ... (+) Slowly stains light brown.  
 A.R. .... (-) Almost negative.

With HNO<sub>3</sub> (conc. and 3:2) petzite displays a textural etching figure which appears suddenly when the reagent dries up. Brown tarnished wet surface changes to brown violet dry surface, and irregular alligatorskin-like etch cleavage develops<sup>1),4),5)</sup>.

Krennerite—Krennerite is an abundant mineral and stipples throughout the vein, especially concentrates near the margin of the vein. It forms xenomorphic grains ( $\varnothing < 0.2$  mm) occurring in the interstices of quartz grains. It occurs usually as simple grains associated with pyrite and sphalerite. In some places it occurs with native gold, hessite and chalcopyrite and rarely with galena, and in other places with petzite. When it encloses or is in contact with these minerals it replaces pyrite and sphalerite, but sometimes is replaced by hessite or petzite. In the polished sections krennerite shows bright silverly white color on the fresh surface, but soon tarnishes dull yellowish. Polish is not very easy. Hardness is lower than galena. Reflection is high; reflection pleochroism is not visible. Anisotropism is rather weak; polarization colors yellowish, brownish light gray to dark gray.

Etch test:

HNO<sub>3</sub> (1:1) ... (+) At the start, reaction is rather slow and differential, but after 20–30 seconds effervesces, then surface turns golden yellow, when surface dries etch cleavages appear.

HCl (1:1) ..... (-) Negative.

KCN (20%) ... (-) Practically negative, after long time surface turns yellowish light brown, and displays scratches selectively and differentially.

FeCl<sub>3</sub> (20%) ... (+) Stains slowly; after washing, surface shows brown or pale gray, and brings out scratches.

KOH (40%) ... (-) Practically negative, after long time surface turns brownish differentially, and displays scratches.

HgCl<sub>2</sub> (5%) ... (-) Negative.

A.R. .... (+) Some grains stain brown and others iridescent, and slowly effervesces.

With HNO<sub>3</sub> (conc. and 3:2) krennerite shows textural etching figures which takes the form of two etch cleavages at right angles and circular areas. These figures develop as desiccation proceeds<sup>4),13)</sup>.

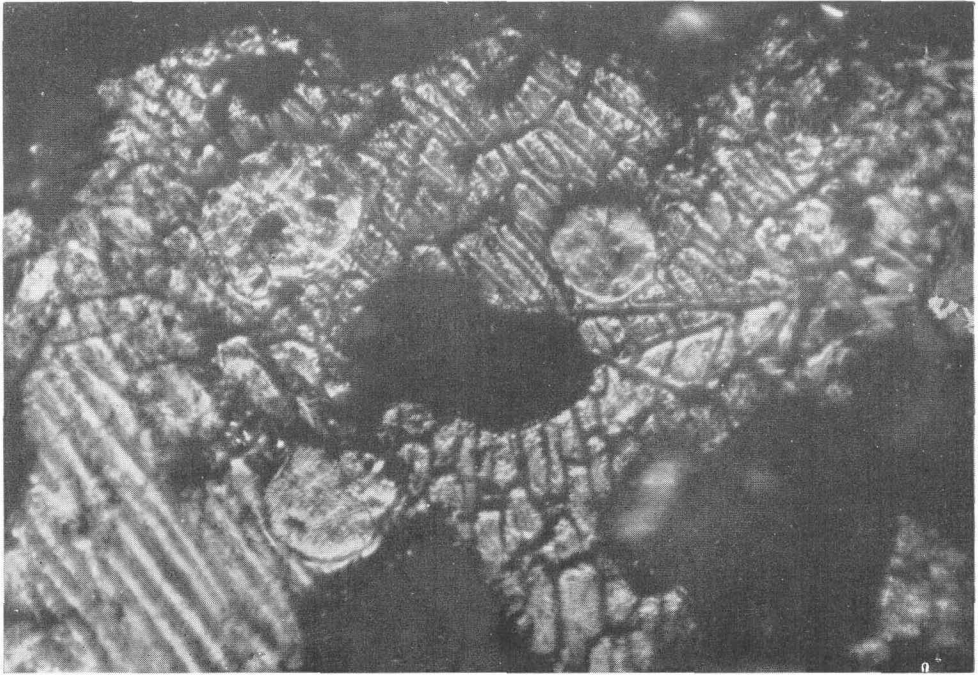


Fig. 2. Polished surface of krennerite, etched with  $\text{HNO}_3$  (3:2), from the Daté mine ( $\times 500$ )

**Sphalerite**—Sphalerite is the most abundant common sulphide in the vein, but it occurs in fine grains ( $\text{Ø} < 0.005$  mm), it is hardly recognizable to the naked eye. It aggregates into violet brown spots or stringers scattered irregularly in the vein or the boundary films along the wall of vein.

**Chalcopyrite**—Chalcopyrite is a rather rare mineral. It occurs almost always as inclusions in krennerite with hessite, native gold and often galena. As it is a very fine grain ( $\text{Ø} < 0.003$  mm), it is hardly visible to naked eye.

**Galena**—Galena is also a very rare fine mineral. It is associated with chalcopyrite and partly replaces the latter.

**Pyrite**—Pyrite is an abundant mineral scattered uniformly in the vein. It is an idiomorphic or hypidiomorphic grain ( $\text{Ø} < 0.5$  mm). It also forms stringers or clots, and almost always is in association with sphalerite.

**Tetrahedrite and enargite**—These minerals are sporadically found as small clots in the vein; they associate with pyrite and sphalerite, but do not closely with the tellurides.

**Gangue minerals**—Gangue minerals are quartz, sericite, barite and gypsum. Quartz is the most and chief constituent. It is a hypidiomorphic or micro-

granular grain. Barite takes the form of tabular crystals scattered uniformly in the quartz mass and often is closely associated with sphalerite. Small gypsum flake is rarely found in the quartz mass.

From the modes of occurrence of the minerals of the ore under study, the sequence of mineralization began with the deposition of quartz, sericite and pyrite, followed next by barite and sphalerite. Krennerite deposited after sphalerite. But at a later stage krennerite crystallized with petzite in some places, and with hessite, native gold and chalcopyrite in others. The association of tetrahedrite and enargite is very rare and uncommon. They may be accidental minerals captured from some other tetrahedrite quartz vein or massive ore body that already had been deposited.

### Other localities and modes of occurrence of Au-Ag-tellurides of Japan

A review of the literature and the writer's investigations reveal that although the number of known localities is very few, yet the localities and modes of occurrence of Au-Ag-tellurides are restricted by geologic environments in Japan.

At the Té-iné mine, sylvanite occurs from one of the veins of the upper portion of the Mitsuyama deposits. Sylvanite is intimately associated with native tellurium and is accompanied by a slight amount of pyrite, tetrahedrite, and gray anisotropic unknown mineral<sup>24</sup>). As the oxidation products of tetrahedrite and native tellurium, tellurite and téinéite are found<sup>26</sup>). Hessite occurs from another vein of the middle portion of the same deposits, and is intermixed with native gold, native tellurium and richardite<sup>17</sup>). These two veins are baritic quartz veins cutting the silicified andesitic breccias. The other veins of the same deposits are gold tetrahedrite barite quartz veins. They are very poor in common sulphides, such as chalcopyrite, sphalerite and galena, but rich in tetrahedrite, enargite, luzonite and bismuthinite. When bismuthinite is enclosed by luzonite, there is a characteristic reaction zone in the succession of bismuthinite, emplectite, klaprothite, Bi-bearing tetrahedrite, goldfieldite and luzonite<sup>25</sup>).

At the Kobetsuzawa mine, Au-Ag-tellurides occur from the net work veins of sericitic quartz veins occurring in strongly silicified dacitic breccias. Hessite, petzite and sylvanite are closely associated with altaite and pyrite. Small amounts of pyrrhotite, marcasite, chalcopyrite, sphalerite, galena, stibnite, dyscrasite, hematite, realgar and zeolite are also found. Often altaite encloses pale pinkish anisotropic unknown minerals and is replaced by supergene richardite.



Native tellurium and barite are not yet found<sup>5)</sup>.

At the Mutsu-Kuzusawa mine, Au-Ag-tellurides occur from a baritic pyrite quartz vein, called "Hom-pi", cutting the silicified and pyritized plagioclase liparitic breccia. Krennerite are associated with some petzite and hessite is intermixed with native tellurium. They are almost always associated with very small amounts of sphalerite, galena, tetrahedrite, argentite, native gold, tetradymite, goldfieldite, klaprothite, bismuthinite and calcite<sup>4),21)</sup>.

The Rendaiji mine is one of the Kawazu mines. In it are found several groups of manganiferous gold quartz veins cutting the andesitic propylite and its tuffs. But Au-Ag-tellurides occur from a quartz vein, named "Hinokizawa", having an appearance of unglazed white porcelain. It is composed essentially of fine quartz and leverierite, and is poor in common sulphides and carbonates which are richly found in other groups of the veins of this mine<sup>7),11)</sup>. Slight amounts of sylvanite and hessite intimately associate with native tellurium having been identified under the microscope by the writer. Other minerals are native gold, richardite, tetradymite, sphalerite, pyrite and chalcopyrite<sup>22)</sup>.

The Suzaki mine is also one of the Kawazu mines. The deposit is a replacement deposit of the black ore type. It forms two or more chimney-like bodies which consist chiefly of barite, quartz and pyrite. They show brecciated and crustified structure. Au-Ag-tellurides are found from one of these ore bodies, called "New Otake", composed of ring ores. Calaverite occurs with pyrite and in intimate association with hessite, native tellurium and chalcopyrite in the inner ore crust. This is fractured by hessite-sylvanite veinlets partly replaced by acanthite. The outer crust consists of pyrite, small amounts of chalcopyrite and sphalerite, and rarely marcasite and tetrahedrite<sup>18),22)</sup>.

The Chûgû mine was worked for gold in some quartz veins cutting the liparite. Hessite and tellurite were found in the interstices of quartz grains. Rarely spongy gold was also found; it has been assumed that the gold was a decomposition product of telluride<sup>10),22)</sup>.

From the Takéno mine it was recorded that very minute grains of altaite and native tellurium were found from a vein. But Au-Ag-tellurides were not found. The veins of this mine consist of quartz, adularia, chlorite and some pyrite and chalcopyrite. They traverse tuffs, liparite and andesite of Tertiary and the foundation of granodioritic rocks of older age<sup>12),19)</sup>.

At the Yamada mine, telluride occurs from a quartz vein cutting the propylite. The vein consists of an aggregate of quartz, traversed by later veinlets which are made of prismatic quartz with some pyrite, chalcopyrite and hessite<sup>8),9)</sup>. From the Iriki mine, near by the Yamada mine, weissite is found in a chimney-like ore body occurring in the brecciated liparite<sup>8)</sup>.

Above mentioned tellurium-bearing ore deposits, with the exception of those of the Yamada and Iriki, have the same nature and are found in the areas of the so-called green tuff regions composed of green colored and propylitized volcanics and sediments of Miocene. Although the Takéno mine is in the same region, the ore deposits consisting of several veins are formed not only in the Tertiary volcanics but in the granodioritic rocks of older age. Then the mineralogical composition and texture of ores are somewhat different from others. Black ore type of deposits are also limited in these regions. Recently some one has noted that in the southern part of the islands of Japan green tuffs are seen. Almost all of the ore deposits formed in the Tertiary volcanics of the green tuff regions are subvolcanic epithermal or xenothermal deposits.

The ore deposits of the Suwa mine are a bedded cupriferous pyritic deposit and have developed concordantly with the major tectonic structure of country rocks composed of green schists of the Abukuma mountain region. The ore consists mainly of pyrite with small amounts of chalcopyrite. Barren or sulphide-poor secretion veinlets of quartz often occur in the gangue rocks and both walls of the pyrite ore. Some Au-Ag-tellurides were found in one of these veinlets. They consist of quartz, calcite, pyrite, chalcopyrite, tellurobismuthite, altaite, and Te-bearing galena, with small amounts of petzite, sylvanite, native gold, sphalerite and galena. Minute grains of petzite and sylvanite are rarely enclosed in tellurobismuthite and altaite filling the interstices of grains of quartz and calcite<sup>15)</sup>.

It was reported that sylvanite and petzite occurred at the Nojiri mine which is located in the Kitakami mountain region. Au-Ag-tellurides were said to occur in minute grains with native gold and argentite in a milk-white quartz. But no microscopic observation had been made, and the existence of these minerals was later doubted. The ore deposits of this mine are plutonic hypothermal gold quartz veins<sup>6)</sup>.

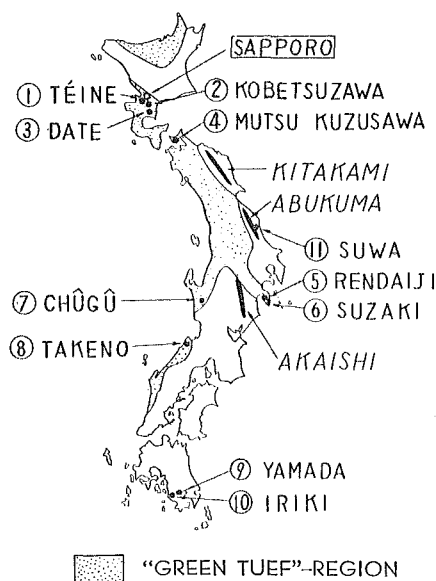


Fig. 3. A map showing the localities of the deposits of Au-Ag telluride minerals.

### Conclusion

In Japan economically important gold ores are divided into two groups. One is the acidic or siliceous ore and the other is the basic or sulphidic ore. Siliceous ores are chiefly mined from the deposits of gold quartz vein of subvolcanic hydrothermal type; and these also belong to the silver-gold deposit of Nolan's classification in which the content of silver weighs much higher than that of gold. Basic ores are mainly mined from the deposits of sulphide-rich veins or masses belonging to the black ore type.

Tellurium-bearing gold deposits belong to the gold-silver of Nolan's classification, since the content of silver is rather poor in comparison with that of gold. Moreover tellurium-bearing gold deposits are classified into three genetical types: the first is plutonic hydrothermal type and shows a simple gold quartz vein filling the fissures of Palaeozoic or Mesozoic sediments or granitic plutonics at the Kitakami and Akaishi mountain regions, such as the Nojiri, Imadeyama, Ooya, Ayukawa, Kinkéi and others. The second is subvolcanic hydrothermal type and is found in the areas of so-called green tuff regions. The deposits of the Suzaki mine massive replacement deposits of the black ore type. At the Daté mine massive ore deposits and veins occur in the same limited area, but tellurides occurs from the vein not from masses. All of the other deposits are complex net veins composed of minute baritic quartz veins; they seem also to have genetical relationships with the deposition of black ore. The third is the metamorphic type of the Suwa mine. The original nature of the country rocks of this last type is very alike to that of green tuffs.

In the tellurium-bearing gold deposits of plutonic hydrothermal sort, Au-Bi-Te mineralization is very common; Au crystallizes as native gold, Te combines with Bi to form tetradyomite or tellurobismuthite, but Au-tellurides and native tellurium are not mineralized. As accessory minerals, Cu and As crystallize as simple sulphides such as chalcopyrite and arsenopyrite. On the other hand, as a subvolcanic hydrothermal deposit, Au combines with Te to form Au-tellurides. Although Bi is a rather rare element, if present it combines with Te forming tetradyomite or tellurobismuthite, with Cu forming klaprothite, or simply deposits as bismuthinite. Cu-As-Sb combination is common; tetrahedrite is in association within the Au-telluride deposits or occurs as important economic Cu-minerals of the other ore bodies of the same mine area. It is interesting that a mineralogical assemblage of secretion veins of metamorphic deposit is closely similar to a subvolcanic hydrothermal Au-Te-Bi mineralization.

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