Germanium-bearing Colusite from the Yanahara Mine, Japan, and Its Significance to Ore Genesis

Katsuo KASE*, Masahiro YAMAMOTO* and Chiharu MITSUNO*

Abstract: Colusite, Cu$_{26}$V$_2$(As,Ge)$_6$S$_{32}$, containing up to 4.3 wt.% Ge occurs with pyrite, chalcopyrite and bornite in sphalerite-barite-rich ores of the volcanogenic massive sulfide orebody at Hinotani L-1, the Yanahara mine. Electron microprobe analysis reveals that As and V are pentavalent and Ge is tetravalent in the mineral the same as in germanite and renierite, suggesting that the Ge-bearing colusite was precipitated under high $f_2$ and $f_0_2$ conditions. These Ge-bearing minerals sometimes occur in the Kuroko deposits related with felsic volcanism, associated with pyrite, chalcopyrite and bornite as at Hinotani, while practically no Ge-bearing minerals occur in the Besshi-type deposits related with mafic volcanism. It is concluded that the ore solutions responsible for the Hinotani L-1 orebody and possibly for whole orebodies at Yanahara are related with felsic volcanism.

1. Introduction

There are two major types of volcanogenic massive sulfide deposits in Japan: Kuroko deposits and Besshi-type deposits. The Kuroko deposits are genetically related with Miocene dacitic-rhyolitic volcanism, and characterized by high Zn, Pb and Ag contents and an abundance of sulfate minerals. The Besshi-type cupriferous iron sulfide deposits, equivalent to Kieslager, occur in the sequence consisting of basalts and sediments, or their metamorphic equivalents, and are very low in the Pb content and poor in sulfate minerals.

The volcanogenic massive pyritic deposit of the Yanahara mine, located about 40 km northeast of Okayama, Southwest Japan, is hosted by felsic pyroclastic rocks, up to 30 m thick, in the Paleozoic black slate. The large Main orebody is accompanied by several smaller orebodies at Yanahara (Fig. 1). The mine has produced more than 37 million tons of pyrite ores with an average grade of 44% Fe, 47% S, 0.2% Cu, 0.3% Zn and 0.02% Pb (MITI, 1980). Although felsic volcanic rocks are closely associated with the deposit at Yanahara, it is very low in the Pb content, and the ore mineralogy is similar to that of the typical Besshi-type deposits. The deposit is thus ambiguous in the classification, and sometimes called...
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RESOURCE GEOLOGY:

the Yanahara-type Kieslager (MITSUNO, 1963; MITI, 1980).

Germanium-bearing colusite is present in a small amount in the Hinotani L-1 orebody of the Yanahara mine. Germanium-bearing sulfide minerals such as germanite, colusite and renierite have been found in small amounts at many Cu-Zn-Pb deposits of various types throughout the world (e.g., BERNSTEIN, 1986), including the classical examples at Tsumeb, Namibia and Kipushi, Zaire. The knowledge on the meaning in ore genesis of Ge-bearing minerals is, however, incomplete. We describe in this paper the mode of occurrence and chemistry of the Ge-bearing colusite at Yanahara, and discuss its significance to ore genesis.

2. Geology and Ore Deposit in the Yanahara Mine

Rocks exposed in the Yanahara mining area are composed of weakly metamorphosed Paleozoic formations called the Maizuru Group. The group is divided into the lowermost, lower, middle and upper formations. The middle formation, in which the orebodies at Yanahara are embedded, is 700 m thick, and mainly consists of black slate, with some intercalations of felsic pyroclastic rock in the lower horizons, and with sandstone and limestone containing fossil coral of Middle Permian in the upper horizons (MITSUNO, 1988).

A weakly metamorphosed sheeted complex consisting of diabase, quartz diorite and granodiorite is conformably present in the strata of the Maizuru Group. A lack of contact aureole leads to an idea that the complex might have intruded with consolidated state. An alternative is that the complex is a fault-bounded, dismembered ophiolite derived from the oceanic crust and upper mantle (ISHIWATARI, 1985). At late Cretaceous time, granitoid masses intruded into the Maizuru Group, and thermally metamorphosed the surrounding slates to cordierite-biotite or biotite hornfels, and pyrite to pyrrhotite and/or magnetite in the marginal parts of the orebodies.

Most of the orebodies at Yanahara occur in the felsic pyroclastic rocks of a definite stratigraphic horizon underlain by diabasic complex, and are dominantly composed of pyrite with small amounts of chalcopyrite and sphalerite. The Hinotani L-1 orebody in which the Ge-bearing colusite occurs, situated about 100 m beneath the Hinotani orebody to the east of the Main orebody, is conformably underlain by felsic pyroclastic rocks and overlain by diabasic complex (Fig. 2). Geologic data are insufficient to determine whether the L-1 orebody occupies the identical ore horizon with the other orebodies or not, because an extent of gallery is very limited in the L-1 orebody. The L-1 orebody is very Zn-rich, and composed of sphalerite, barite, pyrite, chalcopyrite, bornite, tennantite and galena in the order of decreasing amount, being markedly different in mineralogy from most orebodies at Yanahara. In the marginal parts of the orebody, pyrrhotite appears by the thermal effects of granitoid intrusion.

3. Ge-bearing Colusite in the Hinotani L-1 Orebody

The Ge-bearing colusite occurs sporadically in sphalerite and chalcopyrite, and rarely in pyrite with a granular form, smaller than 0.1 mm across
Germanium-bearing colusite from the Yanahara mine

Fig. 3 Photomicrographs of Ge-bearing colusite (col) from the Hinotani L-1 orebody. Open nicol. Reflected light. Field width is 0.6 mm. A. Colusite associated with pyrite (py), chalcopyrite (cp) and bornite (bn) assemblage. The dark domains are mostly barite. sp: sphalerite, gn: galena, and tn: tennantite. B. Colusite in sphalerite. Abbreviations and dark domains as in A.

(Fig. 3). The association with pyrite, chalcopyrite and bornite assemblage and barite is characteristic (Fig. 3-A). The Ge-bearing colusite is isotropic, pale brown yellow, and less brownish compared with the associated bornite under reflected light.

The powder diffraction data of the Ge-bearing colusite were obtained by using an X-ray microdiffractometer on the polished surface because of its small grain size. Three strong reflections were detected at 3.05, 1.87 and 1.60°, which can be indexed as (222), (044) and (226), respectively, based on a cubic unit cell with a 10.6Å (MURDOCH, 1953).

The chemical compositions of the Ge-bearing colusite and related minerals were determined on a JEOL electron microprobe analyzer operating at 25 kV and 0.02 µA specimen currents measured on Cu metal. The correction procedure was that of SWEATMAN and LONG (1969). Chemical compositions of the Ge-bearing colusite are listed in Table 1, with number of atoms calculated on the basis of 66 total atoms per formula unit according to ORLANDI et al. (1981). The formulae obtained from the number of atoms are very analogous to

Table 1 Chemical compositions* and number of atoms based on 66 total atoms per unit formula of Ge-bearing colusite in the Hinotani L-1 orebody of the Yanahara mine.

<table>
<thead>
<tr>
<th>Weight percent</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
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<tr>
<td>Cu</td>
<td>50.3</td>
<td>50.9</td>
<td>51.0</td>
<td>50.5</td>
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<td>Fe</td>
<td>0.6</td>
<td>0.6</td>
<td>0.9</td>
<td>0.1</td>
<td>0.7</td>
<td>1.0</td>
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<tr>
<td>Zn</td>
<td>0.8</td>
<td>0.1</td>
<td>0.3</td>
<td>1.7</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>As</td>
<td>11.3</td>
<td>11.2</td>
<td>10.6</td>
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<td>Sb</td>
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<td>0.4</td>
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<td>0.3</td>
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<tr>
<td>Ge</td>
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<td>2.1</td>
<td>2.5</td>
<td>3.5</td>
<td>3.9</td>
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<td>3.3</td>
<td>3.2</td>
<td>3.2</td>
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<tr>
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<td>32.1</td>
<td>32.0</td>
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<td>101.1</td>
<td>101.0</td>
<td>100.6</td>
<td>100.8</td>
</tr>
</tbody>
</table>

* Results of electron microprobe analyses.

Listed in the order of increasing Ge contents.

Fig. 4 Relationships between number of As (NAs: solid circles) and As+Sb+V (NAs+Sb+V: open circles) to number of Ge (NGe) in Ge-bearing colusite, based on formulae calculated on the basis of 66 total atoms per formula unit. The equations are obtained by the least squares regression.

SWEATMAN and LONG (1969).
Table 2 Chemical composition* of sulfide-sulfate fraction of sphalerite-barite-rich ore with Ge-bearing colusite.

<table>
<thead>
<tr>
<th>weight percent</th>
<th>ppm</th>
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<tr>
<td>Cu</td>
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<td>Zn</td>
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<tr>
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<td>Fe</td>
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<td>Ba</td>
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<td>S</td>
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<td>V</td>
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</tr>
<tr>
<td>As</td>
<td>500</td>
</tr>
<tr>
<td>Sb</td>
<td>60</td>
</tr>
</tbody>
</table>

*Ba and S: gravimetry as BaSO₄, Fe: titration using potassium dichromate, other elements: inductively coupled plasma-atomic emission spectroscopy.

The ideal one proposed by ORLANDI et al. (1981): Cu₂₆V₂(As,Sn)₆S₃₂ with substitution of Ge for Sr. The Fe, Zn and Sb contents are very low, and Cu and V contents are uniform for the L-1 colusite. The Ge content shows a good negative linear correlation with As and As + Sb + V (Fig. 4), which implies the substitution of Ge for As. The mineral with this compositional range may belong to a member of colusite (PSCHENICHNYI et al., 1974). The associated sphalerite is close to ZnS in composition with less than 0.4 mol% FeS, less than 0.1 mol% CuS and MnS. The associated tennantite is Zn-rich with a mean composition of 8 analyses: Cu₁₀.₅(Zn₁₉.₆Fe₀.₀₄)₂₂.₀₀(As₃.₁₇Sb₀.₇₃)₂₃.₉₀S₃.₁₀ based on 29 total atoms per formula unit.

One of the sphalerite- and barite-rich ores containing Ge-bearing colusite in a small amount was chemically analyzed for its sulfide-sulfate fraction, with a result of 40 ppm Ge (Table 2). Microscopic observation indicates that ores with such a Ge content are widespread in the L-1 orebody. Sulfur isotope ratios of sphalerite, pyrite and barite from the same ore specimen as the analyzed one are available in YAMAMOTO et al. (1984), the ratios being 1.9, 1.2 and 15.1%, respectively. The ratios being 1.9, 1.2 and 15.1%, respectively. The isotope ratio of sulfur is close to the inferred ratio of the Permian seawater sulfate sulfur (YAMAMOTO et al., 1984), indicating the L-1 orebody to be submarine volcanic-sedimentary type.

4. Discussion

NAKAI et al. (1976) studied the valence state of Cu by X-ray photoelectron spectroscopy in 21 sulfide and sulfosalts minerals including germanite, and found that all Cu are monovalent. Colusite and germanite have analogous crystal structures (p43n) and chemical formulae with 66 atoms per formula unit (ORLANDI et al., 1981; TETTENHORST and CORBATO, 1984; SPIRIDONOV, 1987). It is likely that Cu in colusite is monovalent. The valence states of other constituent elements can be assessed based on the balance of the charges in colusite. The Ge-bearing colusite at Hinotani L-1 is simple in composition to assess the charges of constituent elements, and the balance of charges is most reasonably maintained by pentavalent As, Sb and V, tetravalent Ge, trivalent Fe, and divalent Zn. The present data, however, show no correlations between constituent elements except for the negative linear correlation between Ge and As. Therefore, the substitution relationship is not understood to maintain the balance of charges in the mineral.

The valence states of As and Sb are different from their valence states in tetrahedrite-tennantite in which these elements are trivalent, suggesting that the Ge-bearing colusite was precipitated under higher fO₂ conditions. In fact, the fO₂ of pyrite, bornite and chalcopyrite assemblage is higher than that of bornite-free chalcopyrite and pyrite assemblage at a given T and total dissolved sulfur. The latter assemblage with or without tetrahedrite-tennantite is ubiquitous in the Ge-bearing colusite-free ores.

The Ge-bearing sulfosalts minerals hitherto described in the volcanogenic massive sulfide deposits of Japan are mostly from Kuroko deposits. They include germanite from Kamikita (TAKEUCHI et al., 1956), germanite, renierite and Sn-, Ge-bearing colusite from Shakanai (URASHIMA et al., 1968; MIYAZAKI et al., 1978; MATSUOKA and YUI, 1979), and renierite from Furutobe (HAYASHI et al., 1985). In the Besshi-type deposits related with mafic volcanism, only colusite with a very small amount of Ge occurs very rarely at Ikadazu, central Shikoku (KASE and YAMAMOTO, 1988). These Ge-bearing minerals are all associated with pyrite, chalcopyrite and bornite the same as at Hinotani L-1. The association with minerals being stable under high fO₂ conditions, mainly with pyrite, chalcopyrite and bornite, seems to be common to the Ge-bearing sulfide minerals hitherto described in the world (e.g., BERNSTEIN, 1986). The balance of the electrostatic charges of these Ge-bearing minerals is
most reasonably maintained by pentavalent As, Sb and V, tetravalent Ge and trivalent Fe as shown by Bernstein (1986) for renierite from Ruby Creek, Alaska, though it is sometimes difficult to assess the charges because of their complicated chemical compositions. Therefore, it is concluded that not only high fo2 conditions but also high fs2 conditions are needed for the precipitation of Ge-bearing minerals including Ge-bearing colusite. It is believed that the bulk of Ge is dispersed in the outer Earth’s crust, in substitution for Si4+ in the tetrahedral framework of silicate minerals (Frondel and Ito, 1957). According to Hoermann (1970), the abundance of Ge is a little larger in felsic igneous rocks than in mafic ones. Germanium appears to concentrate in some degree in late differentiates (Mason and Moore, 1982). Thus, it is likely that ore solutions with affinity to felsic volcanic rocks are generally more enriched in Ge than those with affinity to mafic volcanic rocks. The Ge contents in ore solutions may be reflected in the sulfide ores derived from them. In fact, the Ge contents of 122 ores from the Besshi-type deposits in Japan are all below the value of the detection limit (5ppm). On the other hand, in one third of total 139 analyses of Kuroko ores the Ge contents are over 10ppm up to 120ppm (MITI, 1992). In the Besshi-type deposits in Japan are all below the value of the detection limit (5ppm). On the other hand, in one third of total 139 analyses of Kuroko ores the Ge contents are over 10ppm up to 120ppm (MITI, 1992). In the Besshi-type deposits in Japan are all below the value of the detection limit (5ppm). On the other hand, in one third of total 139 analyses of Kuroko ores the Ge contents are over 10ppm up to 120ppm (MITI, 1992).

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References


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柾原鉱山におけるGeを含むコルース鉱の産出とその鉱床成因論的意義

加瀬克雄・山本雅弘・光野千春

要旨：隕亀鉱物、重晶石に富む柾原鉱山火の谷 L-1 鉱体にはGeを含む約4.3 wt % 含むコルース鉱が発見され、隕亀鉱と併せて産出する。コルース鉱のEPMAによる分析結果は、As および V は45ppm、Ge は44ppmで含まれ、この鉱物は高さf20 f2O3 の環境で沈殿したことを示唆する。Geを含む硫化鉱物であるゲルマン鉱とレニエル鉱の既存の化学組成データと鉱物共生は、両鉱物ともコルース鉱と類似した環境で沈殿することを示す。これらのGeを含む鉱物はフェルシックな火山活動と成因的関連を有する黒鉛鉱床では、黄鉄鉱、黄銅鉱、スピリドーン鉱と共生して時々産出する。マフィックな火山活動と成因的関連を有する別型鉱床の鉱体の一部には、高いf2O3環境で生成されたと考えられる部分もあるが、Geを含む礦物をほとんど見ない。柾原火の谷 L-1 鉱体のコルース鉱はフェルシックな火山活動に関係して生成された熱水溶液から沈殿したものと結論される。