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Conditions of Bi-telluride formation in Vyghorlat-Huta volcanic ridge, Transcarpathian region, Ukraine

Volodymir S. Melnikov[1], Sergiy Bondarenko[1], Oleksandr Grinchenko[2]

[1] Institute of Geochemistry, Mineralogy and Ore Formation, NAS of Ukraine; [2] Geological Department, Kiev National Taras Shevchenko University, Kiev Ukraine; E-mail: alexgrin@univ.kiev.ua

Abstract. Bismuth-telluride mineralization is confined to metasomatic fields of the Vyghorlat-Huta volcanic ridge, Transcarpathians. Tsumoite (BiTe), pilsenite (Bi_4Te_3), non-stoichiometric Bi_2Te and native bismuth are located within different high-temperature metasomatic rocks. Formation of tsumoite is connected with minerals of quartz-tourmaline facies. Pilsenite and Bi_2Te are typical minerals for montmorillonite-bearing rocks. It is suggested that an increase in the Bi-content in tellurides is accompanied by a decrease in temperature stability.

Keywords: Bi-tellurides, metasomatites, Ukrainian Transcarpathians

Introduction

Bismuth telluride formation in the Transcarpathian area is associated with metasomatic alteration of volcanic rocks of the Vyghorlat-Huta ridge, Ukrainian Carpathian Mountains. Fields of metasomatically altered rocks (a type of secondary quartzite) with manifestation of Bi-Te mineralization are known around the village of Il'kovtsy, Podulki area, and on the Siniak River, the Smerekov Kamin' area (Lazarenko, 1960; Lazarenko et al., 1960). A prominent feature of the metasomatites is the presence of tourmaline, topaz and fluorite. Alteration is a result of the influence of volcanic solfatars on primary andesites and their related tuffs. Ore mineralization in the metasomatites of the Vyghorlat-Huta ridge differs essentially from the gold-polymetallic mineralization of Beregovo area in that the equivalent metasomatic rocks in the Muzhievo gold deposit (Beregovo area) do not contain any Bi-tellurides at all and the secondary quartzites of Vyghorlat-Huta ridge, containing Bi-tellurides, generally do not contain visible gold. High concentrations of gold are established only in the Il'kovtsy area.

The first findings of bismuth tellurides are reported as the mineral “wehrlite” (Lesnjak and Giller, 1959). Study of wehrlite separates from the Il'kovtsy-Podulki area by X-ray and electron probe microanalysis showed that they represent different minerals: pilsenite, tsumoite and a phase with composition close to Bi_2Te. Spheroidal inclusions of native bismuth, intergrown with joseite and Bi-tellurides of complex composition were found in montmorillonite from metasomatites of the Smerekov Kamin' area.

Mineralogy

Variation in Bi:Te ratio is typical of Bi-tellurides from the Transcarpathians. It is manifested in disturbances of stoichiometry between metals and (Te+Se+S). Melnikov et al. (2004) have shown, by X-ray analysis, that non-stoichiometry of tsumoite (BiTe), pilsenite (Bi_4Te_3) and the unnamed phase Bi_2Te is the result of their disordered mixed-layered structure. It is possible to assume that, among Bi-tellurides, there is homologous series of structures constructed from different numbers of layers of Bi_2 and Bi_2Te_3 (Melnikov, 2004). Their composition is thus described by the general formula $m Bi_2Te_3 \cdot n Bi_2 = Bi_2(m+n)Te_3 m$, where m and n are integers. With the help of m and n coefficients it is possible to describe the composition of all layered Bi-tellurides - for example: 1) Bi_2 (bismuth), m=0, n=1; 2); Bi_2Te_3 (tellurobismuthite), m=1, n=0; 3); Bi_4Te_3 (pilsenite), m=1, m=2, n=5; 4) BiTe (tsumoite), m=2, n=1; 5); Bi_2Te, m=1, n=2; 6) Bi_7Te_3 (hedleyite), m=2, n=5; 7) Bi_3Te_2, m=4, n=5. From the above list, stable phases have n values ≤ 1. Phases with $n \geq 2$ contain pair layers of Bi_2 which destabilize the structure. Probably, minerals with such structures are formed at low temperatures and high bismuth contents. If the coefficients m and n are not integers, the structures will be disordered mixed-layered ones.

The predominant phase of the high-temperature quartz-tourmaline facies in the Podulka area is tsumoite, with both ordered and disordered structures. In the latter, more widespread variety, tsumoite composition is described by the formula with abundant bismuth $BiTe_{1-x}$ (x = 0.2-0.3). Pilsenite is not found in quartz-tourmaline metasomatites of the Podulka area, but it is present in lower-temperature montmorillonite rocks. Pilsenite with ordered structure is the typical Bi-telluride of the montmorillonite metasomatites in the Il'kovtsy area. The unnamed phase also occurs here. This displays abundant disordering and can be written Bi_2Te_{1+x} (x = 0.2-0.3). Native bismuth is intergrown with Bi-tellurides enriched in sulphur and selenium within montmorillonite metasomatites of the Smerekov Kamin' area. Tetradymite with excess tellurium, sulpho-selenium tsumoite, stoichiometric joseite (Bi_4TeS_2) and a phase with the composition Bi_4TeS were also found there. The highest Se content was found in tsumoite; lower concentrations were determined in the later joseite. The S:Se ratio reflects the evolution of the parent solution composition as temperature falls.

Investigation of phase relations in the Bi-Te system (Abrikosov and Bankina, 1958) shows that Bi-tellurides are stable over a temperature interval from 580 to 270°C. Their temperature stability decreases with increase in Bi contents, and increases if Se and S enter into the structure. At crystallization from melt, depending on the rate of cooling, either solid solutions or stoichiometric phases are formed. However, the data obtained for synthetic Bi-tellurides are not applicable to natural mineral-forming systems because of the fact that their crystallization occurs from water-bearing fluid. The formation of the disordered variety of tsumoite and pilsenite points to their growth by a “layer by layer” mechanism. In this case, any variations in the solution parameters (Bi:Te ratio, temperature, pH) may result in the formation of layers different in structure which will be alternated irregularly. Probably, the formation of ordered structures is caused by more stable growth conditions.

Formation conditions

At present, there are no data on the formation conditions of Bi-tellurides in the Transcarpathian metasomatites. Some data can be obtained by analyzing mineral parageneses in which “wehrlite” has been found. In the Il'kovtsy-Podulki area, the greatest number of reports of tsumoite is from quartz-tourmaline metasomatites. These rocks may be related to secondary quartzites with tourmaline contents of 20-30% (Lazarenko, 1960). Sericite, kaolinite, hydromica and beidellite (montmorillonite) are distributed extremely inhomogeneously. The gradual character of initial rock transformation is shown by the successive replacement of such minerals as: sericite → hydromica (= mixed-layered structure mica-beidellite) → beidellite (montmorillonite) → amorphous substance (allophane?). Kaolinite is formed at conditions of low K activity, in an acidic environment.

Quartz-tourmaline rocks are the most high-temperature metasomatites of the Vyghorlat-Huta volcanic ridge. The presence of tourmaline, a mineral typical of greisens and pegmatites, and large amounts of sericite testifies to this conclusion. Unlike the hydromica that relates to polytype 1*Md*, sericite has a polytypy of 2*M1*. In spite of the fact that the temperature of quartz, determined by homogenization of fluid inclusions, appeared to be above 250°C (Sobolev et al., 1955), tourmaline rocks are typically formed at mesothermal conditions. Conditions of formation of metasomatites with dumortierite and topaz are close to those in which lamellae of "wehrlite" were also found. It is possible, that the spherolitic form of tourmaline, topaz and dumortierite segregation is caused not only by crystallization in the solid environment, but also by moderate temperature of hydrothermal solution. Small amounts of Bi-tellurides were found in lower-temperature associations: alunitized rocks with opal (Il'kovtsy) and rocks intensively replaced by montmorillonite (Smerekov Kamin'). Hydromicaceous metasomatites also contain small amounts of Bi-tellurides.

The composition of the hydrothermal solution from which Bi- tellurides were crystallized is not known. However, "wehrlite" was found both in alunite bearing opalites, and in association with siderite. It testifies to the possibility of crystallization from both acid and alkaline solutions.

Tellurobismuthite from tourmaline metasomatites were never found together with native bismuth, but the joint occurrence of "wehrlite" and native bismuth was observed in later monoquartzites and quartz, "kaolinite metasomatites" (Lesnjak and Giller, 1959; Lazarenko, 1960). In this association, bismuth appears to be the predominant mineral. Such a relationship is probably caused by later crystallization of bismuth from a solution depleted in tellurium. However, in a montmorillonite from the Smerekov Kamin' area, spheroidal segregations of bismuth are overgrown by joseite and contains intergrowths of other bismuth tellurides, including Se-tsumoite). Selenious tsumoite is observed as intergrowths within a bismuth globule.

According to the data of Dobbe (1993), tsumoite can exist with native bismuth only below 226ºC. However, this fact does not contradict an earlier crystallization of tsumoite. Overgrowth of tsumoite by droplets of bismuth can occur at lower temperature. The joseite crystallized later since it forms selvages on spheroids of bismuth.

The highest Se content is observed in tsumoite, whereas the later joseite shows only small amounts of the element. Detailed examination of all available Bi-telluride specimens makes it possible to note that the S:Se ratio increases with the Bi:(Te+Se+S) ratio. It is possible to propose that such behaviour reflects an evolution of the composition of solution as the temperature falls. Plates of "wehrlite" are very often found within dehydration cracks of smectitic material (beidellite, montmorillonite, nontronite) which is formed by intense metasomatic alteration of volcanic rocks. As a result, an erroneous interpretation has arisen concerning the low-temperature genesis of Bi-tellurides in metasomatic rocks of the Transcarpathian region. It is clear that dehydration of smectites might not precede the deposition of "wehrlite" from hydrothermal solution. Smectites do not crack in a water-rich environment.

Confinement of "wehrlite" lamellae to these cracks might be interpreted by the rheological properties of water-saturated smectite in which formation of cracks is initiated by the presence of other phases. Frequent confinement of Bi-tellurides to smectitic segregations is caused, apparently, by other reasons. We note that, in the majority of metasomatites, smectites are formed at the final stage of rock alteration. Their presence can be considered as an indicator of the duration of the process. The longer the process, the greater the amount of solution containing ore components will be infiltrated into the rock. Therefore, if this is true, the largest concentration of Bi-tellurides should be expected in the most intensively altered rocks.

The relationship between Bi-Te-mineralization in the Il'kovtsy-Podulki area and the increased concentrations of Au and Ag has been known for a long time. Elevated Ag concentration (up to 1 wt.% and more) is frequently established in tsumoite. This has a crystallochemical basis since the mineral volynskite ($AgBiTe_2$) is isostructural to tsumoite (Bayliss, 1991). Isomorphic admixtures of Ag, Sb and Pb were also found in pilsenite. Therefore, Bi-tellurides may be good indicators of Au-Ag-mineralization when concentration of these elements in the rock is insignificant. The similarity of geochemical behaviour and fluid paths of Au, Ag and Bi is substantially determined by the products of the solfataric processes. Their transfer is carried out by a fluid phase enriched not only in B and F, but also in S, Se and Te.

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