### Au-Ag-Te-Se deposits

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## Te- and Bi-bearing assemblages in the Elshitsa and Radka epithermal deposits, Central Srednogorie, Bulgaria: Mineralogy and genetical features

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**Abstract.** The Late Cretaceous Elshitsa and Radka epithermal Cu-Au deposits, located in the southern part of the Panagyurishte district, Bulgaria, are closely related to porphyry-copper deposits and were formed by high-to intermediate-sulphidation hydrothermal systems. Rare bismuth, copper, bismuth-copper, gold, and gold-silver tellurides, sulphotellurides (buckhornite), and bismuth sulphosalts are typomorphic for the main economic stage of mineralisation. This paper summarises the particularities of the Te- and Bi-bearing assemblages in the two epithermal deposits and their genetical features.

Key words: tellurides, bismuth sulphosalts, goldfieldite, buckhornite, epithermal, Elshitsa, Radka, Panagyurishte

#### Introduction

Bismuth- and tellurium-bearing minerals are a common feature in many high- and intermediate-sulphidation epithermal deposits with dominantly magmatic signatures of the mineralising fluids. In such hydrothermal systems, these minerals are usually typomorphic for the early stages of mineralisation. They are commonly present in minor amounts and rarely have an economic value (as gold carrier for instance; Arribas, 1995). This contribution describes and reviews the peculiarities of Te- and Bi-bearing mineral assemblages in the Late Cretaceous Elshitsa and Radka epithermal Cu-Au deposits from the southern part of the Panagyurishte district, Central Srednogorie in Bulgaria. Rare tellurides, sulphotellurides and bismuth sulphosalts occur in association with the main economic minerals such as chalcopyrite, bornite and tennantite and some trace minerals of Ga, Ge, In, Sn, As and Se. The genetical features of the studied assemblages and their metallogenic significance are also discussed.

#### **Geological setting**

The Late Cretaceous calc-alkaline magmatism in the central part of the Srednogorie zone in Bulgaria was focused within NNW-SSE oriented corridor, known as the Panagyurishte mineral district. The later hosts the main Cu and Au-Cu deposits in Bulgaria, including from north to south: the producing Chelopech, and the past-producing Krassen, Radka and



Fig. 1. Geological map of the southern part of Panagyurishte district, showing the location of Elshitsa and Radka epithermal deposits (modified after Cheshitev et al., 1995)

Elshitsa epithermal Cu-Au deposits, and the producing Elatsite and Assarel porphyry Cu-Au, and past-producing Medet, Tsar Assen and Vlaykov Vruh porphyry copper deposits. The northern zone stands out as the more fertile part of the district, whereas the southern porphyrycopper deposits are much smaller and correlate with lesser economic Elshitsa, Radka and Krassen epithermal deposits.

The geology of the southern part of the district is summarised in Figure 1. The Cu-Au deposit of Elshitsa is located about 1 km to the NW of the Vlaykov Vruh porphyry-Cu deposit. These two neighbouring deposits constitute the best example for the tight spatial association of high-sulphidation epithermal and porphyry-Cu deposits in the Panagyurishte district. Recently, Kouzmanov (2001) and Moritz et al. (2004) presented some new results concerning the stable and radiogenic isotope geochemistry of the studied deposits, thus supporting the idea of the genetic link between the epithermal Cu-Au deposits and spatially associated porphyry Cu-Au systems.

The Elshitsa and Radka deposits are hosted by dacitic volcanic and subvolcanic rocks (Fig. 1). The deposits consist of several lenticular, columnar and lens-like steeply dipping ore bodies (Bogdanov and Popov, 2003). At Elshitsa, disseminated ore bodies are also developed as a halo around the massive ones. Two compositionally distinct types of ores have been recognised: ore consisting dominantly of massive pyrite, and Cu-Au sulphide ore, consisting of pyrite-chalcopyrite (at Elshitsa) or pyrite-chalcopyrite-bornitetennantite (at Radka) with minor polymetallic mineralisation. Alteration (Pb-Zn) and mineralisation processes in both deposits are similar, despite some minor differences in mineral assemblages and the character of the main ore minerals. The two deposits share a number of paragenetic features including: (1) an early massive to disseminated pyrite stage, followed by (2) an intermediate Au-bearing Cu-As-S stage and (3) a late base-metal stage (predominantly Zn, Pb, Ba ± Au). A last sulphate (anhydrite) stage ends the mineral paragenesis.

# Mineralogy of the Te- and Bi-bearing assemblages at Elshitsa and Radka

The geology and mineralisation processes of the Elshitsa and Radka deposits have been studied extensively for the last 80 years, but

very detailed mineralogical and geochemical investigations were only possible in last 20 years, with the application of modern microscale mineralogical characterisation techniques. Bismuth- and tellurium-bearing minerals in the Elshitsa and Radka deposits form usually small  $(<100 \ \mu m)$  inclusions or aggregates within the main ore-forming minerals of the economic Cu-As-S stage - chalcopyrite, bornite and/or tennantite or precipitate in the interstices of the early massive fine-grained and colloform pyrite (Fig. 2). Kovalenker et al. (1986) reported a well defined Bi- and Te-bearing mineral assemblage at Elshitsa for the first time. This consisted of native tellurium, altaite [PbTe], goldfieldite [Cu<sub>12</sub>(Te, As)<sub>4</sub>S<sub>13</sub>], sylvanite [(Au,  $Ag_{2}Te_{4}$ , tellurobismuthite  $[Bi_{2}Te_{3}]$ , and tetradymite [Bi<sub>2</sub>Te<sub>2</sub>S], in association with chalcopyrite and tennantite. Popov et al. (2000) completed the list of Bi- and Te-minerals from Elshitsa with native bismuth, bismuthinite [Bi<sub>2</sub>S<sub>3</sub>], emplectite [CuBiS<sub>2</sub>], hessite [Ag<sub>2</sub>Te], krennerite [AuTe<sub>2</sub>], kawazulite [Bi<sub>2</sub>Te<sub>2</sub>Se], and weissite [Cu<sub>1.9</sub>Te]. Tsonev et al. (2000) reported the presence of bismuthinite,  $[Ag_3Pb_3Bi_9S_{18}],$ schirmerite tetradymite, wittichenite [Cu<sub>3</sub>BiS<sub>3</sub>], calaverite [AuTe<sub>2</sub>], krennerite, rickardite [Cu7Te5], vulcanite [CuTe] and weissite in the Radka ores, most of them as rare inclusions in chalcopyrite and bornite. Kouzmanov (2001) noted the presence of emplectite and wittichenite, as well as aikinite-bismuthinite series minerals in both deposits; and the rare sulphotelluride buckhornite [Pb2AuBiTe2S3] at Elshitsa and miharaite [Cu<sub>4</sub>FePbBiS<sub>6</sub>] at Radka. Bogdanov et al. (2004) mentioned the presence of tsumoite [BiTe], hessite, petzite [Ag<sub>3</sub>AuTe<sub>2</sub>], krupkaite [PbCuBi<sub>3</sub>S<sub>6</sub>], buckhornite and tellurobismuthite as µm-scale inclusions in pyrite and chalcopyrite from Radka. The most common Bi- and Te-bearing mineral for both deposits is tetradymite, forming tabular idiomorphic crystals up to 100 µm in length (Fig. 2a-c).

Goldfieldite and tennantite associated with Bi- and Te-bearing minerals are relatively enriched in Bi (up to 10 wt.%), always contain minor amount of Se (up to 0.2 wt.%), and tennantite is always enriched in Te (up to 10 wt.%; Kouzmanov, 2001). Goldfieldite, as a rule, occurs as a replacement product of Tebearing tennantite (Fig. 2d). Chalcopyrite usually contains minor Bi (500-5500 ppm), As (500-1400 ppm) and Zn (600-2400 ppm). Galena, which is commonly present as trace mineral in the studied assemblages (Fig. 2a, c), is enriched in Se (up to 5.7 wt.%), and contains minor Bi (up to 2.6 wt.%) and Ag (up to 1 wt.%). Thus the studied mineral assemblages have a very particular Cu-As-Bi-Te-Se-Pb geochemical signature. Gold and silver are present mainly as electrum, but also form Au-, Ag-, and Au-Ag tellurides and complex sulphotellurides (buckhornite).

#### **Genetical features**

Temperature conditions of formation of the Biand Te-bearing assemblages in the epithermal deposits from the southern Panagyurishte district are typical for the epithermal environment. Fluid-inclusion data for the Radka deposit are available in Kouzmanov et al. (2004). The studied assemblage was formed from mildly acidic low-salinity (2.4-3.8 wt.% eq. NaCl) fluids showing temperatures of homogenisation in the range 218-260°C, with a mode at 250°C. Presence of CO<sub>2</sub>, H<sub>2</sub>  $\pm$  N<sub>2</sub> in the volatile phase has been also identified by micro-Raman spectrometry.

Strashimirov and Kovachev (1992) reported 220-240°C as temperatures of homogenisation for fluid inclusions, measured in quartz associated with chalcopyrite from the Elshitsa deposit. This temperature range fits well with the observation that native bismuth at Elshitsa occurs as idiomorphic crystals (Fig. 2a) and not as droplet-like inclusions, thus indicating temperature of formation <271°C, the latter corresponding to the melt temperature of bismuth.

Stable and radiogenic isotope studies (Kouzmanov, 2001; Moritz et al., 2004) indicate clearly a magmatic origin of the oreforming components in the epithermal Cu-Au deposits from the Panagyurishte corridor, showing close genetical features with the



Fig. 2. Back-scattered electron (BSE) images of Te- and Bi-minerals from Elshitsa (a-d) and Radka (e-f) deposits: a) Tetradymite and native bismuth inclusions in galena, associated with chalcopyrite. Note the idiomorphic morphology of the bismuth crystal; b) Tabular tetradymite idiomorphic inclusion in chalcopyrite; c) Tabular tetradymite and idiomorphic buckhornite adjacent to galena within chalcopyrite; d) Goldfieldite, replacing tennantite in association with stannoidite and chalcopyrite; e) Complex polyphase wittichenite-chalcopyrite-bornite inclusion in pyrite; f) Miharaite associated with chalcopyrite and bornite in the interstices of fine-grained massive pyrite. *Abbreviations*: Tdy - tetradymite; Bi – native bismuth; Cp - chalcopyrite; Gl - galena; Buc - buckhornite; Gdf - goldfieldite; Stn - stannoidite; Tn - tennantite; Wit - wittichenite; Bn - bornite; Mih - miharaite; Py - pyrite; Qtz - quartz

porphyry copper systems in the district.

Recently, Heinrich (2005) proposed a thermodynamic model exploring the physical evolution of low- to medium-salinity magmatic fluids of variable density, en route from their magmatic source through the porphyry regime to the near-surface epithermal environment, and the chemical conditions required for effective transport of gold and other components from the magmatic to the epithermal domain. In this sense, low-salinity mineralising fluids at Radka and Elshitsa could be tentatively regarded as magmatic vapour analogues and the Te-bearing assemblages - as formed by contracted magmatic vapour, tellurium being highly volatile in hydrothermal conditions and transported mainly in the vapour phase.

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