БЪЛГАРСКА АКАДЕМИЯ НА НАУКИТЕ • BULGARIAN ACADEMY OF SCIENCES
GEOCHEMISTRY, MINERALOGY AND PETROLOGY • 43 • SOFIA • 2005

Au-Ag-Te-Se deposits
IGCP Project 486, 2005 Field Workshop, Kiten, Bulgaria, 14-19 September 2005

Oscillatory zoning in goldfieldites as a possible indicator of their formation conditions

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Abstract. Goldfieldites from four epithermal gold deposits were examined: Prasolovskoe, Ozernovskoe (Russia), Kochbulak (Uzbekistan) and Elshitsa (Bulgaria). All goldfieldites were characterized by a complicated zonal structure and in some grains oscillatory zoning was revealed. The latter can be subdivided into two types: (1) heterophase, consisting of interlacing of different minerals or mineral assemblages (e.g., goldfieldite and tennantite + native Te), and (2) homophase, consisting of fluctuations of Te contents in goldfieldite. Different mechanisms were proposed to explain each type of oscillation. The heterophase zoning is supposed to be a result of fO_2 and aH_2S fluctuations due to auto-oscillating processes in a self-organizing system. The homophase zoning is believed to be caused by the difference between Te absorption rate and Te diffusion rate in the growing zone of the goldfieldite crystal. Oscillatory zoning is proposed to be an indicator of isolated, quiet and equilibrium mineral-forming conditions.

Key words: goldfieldite, epithermal, gold deposits, oscillatory zoning, self-organizing processes

Introduction

Goldfieldite, i.e., fahlore of composition $(Cu,Ag)_{10}(Cu,Fe,Zn,Cd,Hg)_2(Te,Sb,As,Bi)_4(S,Se)_{13}$, where the Te content exceeds two atoms per formula unit (apfu) is notable thanks to its occurrence – along with enargite or famatinite. It is a typical mineral of high-sulfidation epithermal mineralization, and usually marks shallow levels of epithermal deposits (Kovalenker and Rusinov, 1986; Trudu and Knittel, 1998).

Chemical and crystal structural characteristics of goldfieldite have been considered by a number of authors (for example, Trudu and Knittel, 1998; Shimizu and Stanley, 1991; Mozgova and Tsepin, 1983; Spiridonov et al., 1990, etc.). However, in spite of this, oscillatory zoning within goldfieldite (periodically alternating maxima and minima of any attribute values) has not been reported before, except for a single report by Plotinskaya et al. (2005). In the present paper, goldfieldites from four Au-Ag Te-Se-bearing epithermal deposits are described: Prasolovskoe and Ozernovskoe (Russia), Kochbulak (Uzbekistan) and Elshitsa (Bulgaria).

The chemical composition of goldfieldite and associated minerals were studied using JEOL 5900 LV SEM and LEO-1455-VP scanning electron microscopes and Cameca-SX-50 electron microprobe at NHM, London.

Brief characterization of the deposits and goldfieldite assemblages

The *Prasolovskoe* mineralization is located on Kunashir Island, Kuril island arc, and is confined to a circular intrusion of diorite, granodiorite, and tonalite in volcanic rocks (dacite and rhyolite lavas and tuffs) of Miocene to Quaternary age. The Au-Ag Te-Se-bearing mineralization was formed in the Late Pliocene (So et al., 1995). Three stages of hydrothermal activity were identified: pyritic, polymetallic, and the main gold-silver stage. Goldfieldite occurs within the main stage in an assemblage with tetrahedrite, native gold, altaite, native Te, clausthalite, Bi- and Ag tellurides, and sphalerite (Kovalenker et al., 1989).

The *Ozernovskoe* deposit occurs on the Kamchatka Peninsula within the Central-Kamchatka volcano-plutonic belt and in a volcanic edifice of Neogene age. Mineralization is hosted by basalt and andesite lavas and tuffs intruded by granodiorite porphyrites and subvolcanic andesites. Pre-ore alteration is represented by quartzites with alunite, diaspore, pyrophyllite, and kaolinite (Naumova and Alysheva, 1995). Two stages of mineralization were revealed: early (pyrite) and main (gold-polymetallic) ones. Goldfieldite usually occurs in assemblage with pyrite, chalcopyrite, Au, Ag, and Bi tellurides, clausthalite, and, rarely with molybdenite (Spiridonov et al., 1990).

The *Kochbulak* deposit is situated on the northern slope of the Kurama Ridge (Middle Tien Shan) in a volcanic caldera composed of andesite-dacite tuffs, lavas, and subvolcanic intrusions of C_{2-3} age. The volcanic rocks are intruded by diabase dikes and granodiorite porphyrites of C_3-P_1 age. Pre-ore alteration is represented by quartzites with alunite, pyrophyllite, diaspore, and kaolinite, as well as by quartz-carbonate-sericite rocks (Kovalenker et al., 1997). Goldfieldite occurs in assemblage with famatinite, tetrahedrite, clausthalite, Au and Ag tellurides, Cu- and Fe sulfostannates, and Bi sulfosalts.

The *Elshitsa* deposit occurs in the central part of the Srednogorie metallogenic zone; the mineralization is hosted by andesite-dacite volcano-plutonic complex and granite-granodiorite of Late Cretaceous age. Mineral deposition occurred during two stages of mineralization: pyrite and copper-pyrite. Goldfieldite was found within the copper-pyrite stage products at upper parts of the deposit (Bogdanov et al., 1997) in an assemblage with native Te, tennantite, pyrite and, rarely, with luzonite.

Zoning in goldfieldites

Goldfieldite from the *Prasolovskoe* deposit forms irregularly-shaped grains, 200-300 μm in size, with a complicated zonal structure: rectangular cores (mostly no more than 100 μm) with up to 2 apfu of Te and Sb:As ratio 1:2 to 3:4, surrounded by rims (50-100 μm) with up 1.8 to 2.5 apfu of Te at average Sb:As from 1:5 to 1:2.

In the rims, along growth zones, ‘chains’ of small (1 to 10 μm) grains of hessite, native Te, sometimes, covellite, tellurite, Bi and Pb tellurides, occur with a period of 10-20 μm. Ultra thin oscillation of Te contents takes place in some grains. Aggregates are overgrown by tennantite or Sb-tennantite at Sb:As from 1:6 to 3:4.

In the *Ozernovskoe* deposit, goldfieldite occurs as tetrahedra or irregular grains of 0.5 to 1 cm in size. Central parts of the grains are rectangular in shape (200-300 μm) and are characterized by Te content 2.5 apfu and Sb:As ratio 1:2. Abundant inclusions of chalcopyrite and clausthalite, up to 10 μm in size, are irregularly distributed throughout the rectangles (Fig 1a). The periphery of grains (up to 300 μm wide) is represented by goldfieldite with an Sb:As average ratio 1:1. The periphery establishes oscillatory zoning with a period of about 20 μm; there, Te contents range from 1.25 to 2.5 apfu, As – from 0.75 to 1.63, and Sb – from 0.86 to 1.33 (Fig 1b-d). These grains are surrounded by a rim (20-30 μm) of goldfieldite, with more than 2.5 apfu of Te and Sb:As = 5:4, followed by a thinner rim (10-20 μm) of goldfieldite with 2.3 apfu of Te and Sb:As = 1:20.

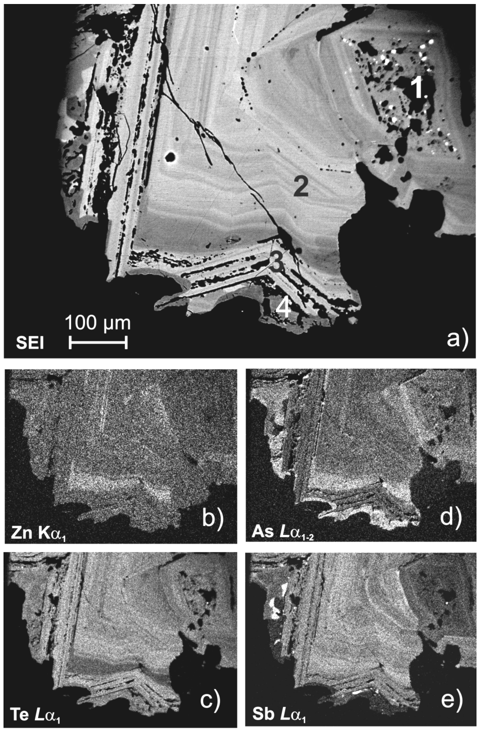

Fig. 1. Secondary electron image (a) and X-ray maps (b-e) of goldfieldite grain from the Ozernovskoe deposit. 1 – core, 2 – periphery with a monophase oscillatory zoning, 3 and 4 – rims. See text for explanations

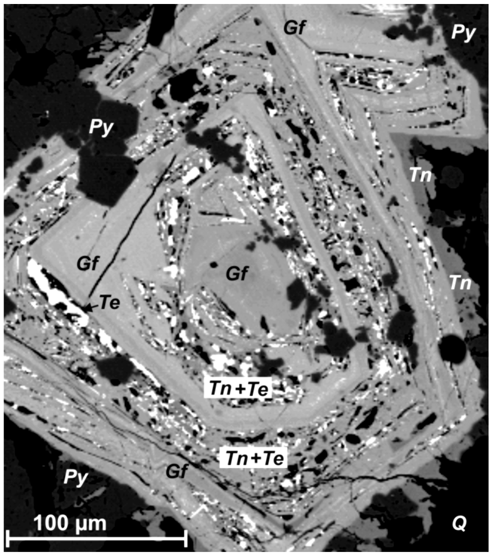

Fig. 2. Secondary electron image of a goldfieldite from the Elshitsa deposit: bands of goldfieldite (Gf) and tennantite (Tn) with native tellurium (Te); Py–pyrite, Q – quartz

Goldfieldites from the *Kochbulak* deposit are represented by irregularly shaped grains up to 1 cm or by bands up to 1 cm wide within famatinite veins. Te content ranges from 1.5 up to 2.1 apfu, whereas the Sb:As ratio varies from 3:4 to 5:1 and usually 2:1 to 3:1. Some goldfieldites are surrounded by rims of tetrahedrite with altaite and Bi tellurides, but no regular zoning was observed.

At the *Elshitsa* deposit goldfieldite forms tetrahedra 200 to 500 μm in size. They are characterized by the most complicated zoning consisting in a regular interlacing of bands of goldfieldite with bands of Te-tennantite with abundant small (usually less than 1 μm) inclusions of native Te, sometimes with bands of quartz with native Te, and, rarely, with bands of native Te or tellurite. The width of such bands ranges from 1-2 to 50-100 μm (Fig. 2).

Te-tennantite contains 1.5 to 2 apfu of Te, goldfieldite - to 3.2 apfu of Te; Sb contents do not exceed 0.05 apfu. Bands of goldfieldite, in turn, establish oscillatory zoning with a period of 2-3 to 10 μm consisting in variations of Te contents from 2.3 to 3.2 apfu and As from 1.8 to 0.7 apfu (Fig. 3). Goldfieldite grains are surrounded by tennantite which carries no mineral inclusions.

Oscillatory zoning was thus revealed in most of the goldfieldite grains examined. Two types of oscillatory zoning were observed: heterophase, consisting of interlacing of goldfieldite bands and bands of tennantite with native Te or tellurides (Prasolovskoe and Elshitsa deposits), and homophase, consisting of fluctuations of Te and As or Sb contents in goldfieldite (Prasolovskoe, Ozernovskoe, and Elshitsa deposits).

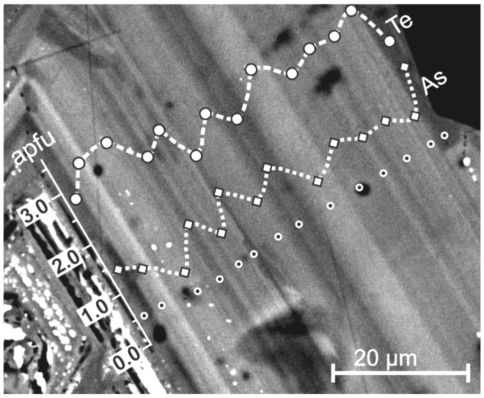

Fig. 3. Monophase oscillatory zoning (SEI) and Te and As fluctuations

Discussion

A periodic interchange of tennantite + native Te paragenesis and goldfieldite resulted in a heterophase oscillatory zoning observed at Elshitsa should result from the reaction:

$Cu_{12}As_4S_{13} + 4.8Te^0 + 2.6H_2S + 3.4H_2O + 4.3O_2 = 1.2\ Cu_{10}Te_4S_{13} + 4\ As(OH)^0_3$,

and due to the increase of H_2S and O_2 activities in the solution. Banding of goldfieldite and tetrahedrite + tellurides of Au, Ag, Pb, or Bi, observed at Prasolovskoe, can be expressed by similar equations. Periodic variations of H_2S and O_2 activities are likely to be a result of auto-oscillating processes described in the study by Petrovsky et al. (1996). In such a model, the growing goldfieldite crystal concentrates Te, thus reducing the H_2S and O_2 concentrations in the solution until a certain limit is reached. The system, maintaining equilibrium, elevates H_2S and O_2 activities resulting in deposition of tennantite with micro- and nano-dimensional native Te particles.

The most feasible explanation for the origin of the monophase oscillatory zoning, i.e., fluctuations of Te and As (or Sb) contents, is believed to be the growth rate of goldfieldite crystals, which is in turn determined by concentrations of goldfieldite-forming components in the reaction zone. Concentrations of Te in a reaction zone depend on the ratio of its diffusion rate in a solution and rates of adsorption and desorption of Te by a solid phase (Meyer, 1984; Ortoleva et al., 1987):

$$\partial[Te]_{sol}/\partial t = k_{des}[Te]_{cr} - k_{ad}[Te]_{sol} + D(\partial[Te]_{sol}/\partial x),$$

where $[Te]_{sol}$ – Te concentration in a reaction zone, $[Te]_{cr}$ – Te concentration in a growing crystal face, t - time, k_{des} – rate coefficient of Te desorption, k_{ad} – rate coefficient of Te adsorption. At every instant, the Te distribution between the goldfieldite crystal and near-surface solution can be expressed by a kinetic distribution coefficient

$$K_k = (\partial[Te]_{cr}/\partial t) : (\partial[Te]_{sol}/\partial t).$$

Thus, the Te concentration in a growing crystal face is a function of its alteration rate in a reaction zone. In this case the coefficient of Te distribution between a solution and a crystal in a reaction zone is determined by a possible degree of Te incorporation into the goldfieldite lattice on a growing surface, as well as by Te concentration in near-surface solution.

Let us consider a simplified model consisting of Te and As. If we express the Te (or As) adsorption rate as a number of atoms, bonding to a crystal during a time unit (r_{Te} and r_{As}), then the relative rate of Te adsorption $f_{Te} = r_{Te}/(r_{Te} + r_{As})$. Let X_{Te} and Y_{As} be Te and As concentration in a solution and their ratio – $q = X_{Te}:Y_{As}$. Then the relative rate of Te adsorption is:

$$f_{Te} = (qk):(1 + qk),$$

then $q = f_{Te}/[k(1 - f_{Te})]$.

Hence, if k fluctuations are insignificant, q can vary from 0, if $f_{Te} = 0$, to infinity if $f_{Te} = 1$. However, as shown in (Ortoleva et al., 1987), then X_{Te} exceeds an exact value X_{Te}^{max} (point A and trend 1 on Fig. 4a), k rises abruptly along with f (trend 2 on Fig. 4a).

Subsequently, X_{Te} decreases further while f remains relatively constant until a value B (trend 3 on Fig. 4a). After that, f falls and another loop begins. Thus, there are conditions of restriction of q increase and of $X_{Te}:Y_{As}$ maximum appearance, as shown on Fig. 4 a. The $X_{Te}:Y_{As}$ maximum causes oscillation of the variations in Te adsorption rate and that is reflected in periodical fluctuations of the kinetic coefficient of Te distribution and in an appearance of limit cycle-type contour on a phase diagram (Fig 4b). An occurrence of an oscillatory regime of goldfieldite crystal growth is possible due to the appearance of feedback between rate coefficients of fast reactions in a solution (oxidizing-reducing Te^{4+} <=> Te^0) and slow sorption and desorption on a crystal surface.

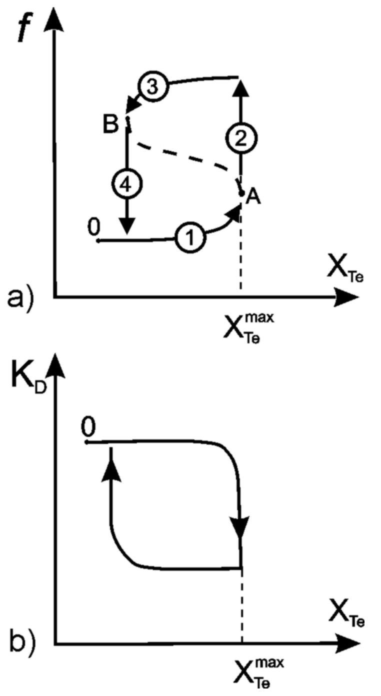

Fig. 4. Te concentration *vs*. adsorption rate diagrams in a reaction zone of a growing goldfieldite crystal; (a) – positions of X_{Te} maximums on a f-X diagram, (b) – path of parameters variations of a limit-cycle type in a goldfieldite-solution system; see text for explanations

In experimental studies describing synthesis of crystals with oscillatory zoning (for example, Reeder et al., 1990) oscillatory zoning on crystals growing from solutions appears only in cases when the solutions were not stirred. Consequently, the existence of oscillatory zoning in crystals grown in natural environments can be considered as an indicator of isolated and relatively quiet mineral-forming conditions that are quite rare in epithermal environments. Apparently, it explains the absence of oscillatory zoning in most of the goldfieldites from the Kochbulak deposit.

Conclusions

1. Heterophase oscillatory zoning is a result of auto-oscillating processes in a self-organizing system. These processes can control modes of existence of Te, Ag, and other economical elements in ores.
2. Monophase oscillatory zoning occurs thanks to auto-oscillating processes near the surface of a growing crystal. The existence of such a zoning is supposed to be an indicator of relatively quiet and equilibrium mineral-forming conditions.

Acknowledgements. Authors are thankful to C. Stanley (NHM) for his critical remarks and to T. Williams, J. Spratt, A. Kearsley, A. Ball, and B. Williamson (NHM) for their assistance in EPMA analyzing. This study is a contribution of IGCP projects 486 and 473 and has been supported by: Natural History Museum (CERCAMS program), RFBR project N 04-05-64407, RAS program “Nanoparticles in Nature”, and Russian Science Support Foundation.

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