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

Te and Se mineralogy of Ozernovskoe and Prasolovskoe epithermal gold deposits, Kuril – Kamchatka volcanic belt

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Abstract. We describe two epithermal telluride-selenide bearing Au-Ag deposits: Prasolovskoe and Ozernovskoe, both located within the Kuril-Kamchatka volcano-plutonic belt. Several rare and unknown Te and Se minerals were found at both deposits. At the Prasolovskoe deposit, various Te-Se minerals, including an unnamed Te_3Se_4 phase are widespread, while at the Ozernovskoe deposit selenides and sulfoselenides are typical. Te-Se mineralization at both deposits was formed in a rather narrow temperature interval (250-200°C); the composition of mineral assemblages was determined by activities of S_2, O_2, Te, and Se in the system. At early stages of ore-forming process, fluids were characterized by high aS_2. With temperature decrease, aS_2 also decreased, resulting in aTe_2 increase, and, later aSe_2 increase. That caused at first an abundant sulfides precipitation, then the formation of tellurides, followed by the crystallization of selenotellurides, and, finally, selenides.

Key words: Prasolovskoe, Ozernovskoe, Kuril-Kamchatka, epithermal Au-Ag deposits, tellurides, selenides

Introduction

Te and Se minerals occur in numerous ore deposits of different origin (magmatic, hydrothermal, metamorphic, and sedimentary), but are most abundant in some epithermal gold deposits, which since the era of Lindgren (1933) have been named as 'telluride' and 'selenide' types. Deposits of the former (telluride) type, like Cripple Creek (USA), Emperor (Fiji), Ladolam and Porgera (PNG), are usually closely related to magmatic rocks of higher alkalinity (alkalic-type, Richards, 1995). Moreover, tellurides can also play an important role in some deposits of both high-sulfidation (HS) type, for example, El Indio (Chili), Goldfield (Nevada, USA), Kochbulak (Uzbekistan), and low-sulfidation (LS) type, for example, Acupan (Philippines) and Sacaramb (Romania). Selenide mineralization usually occurs within Au-Ag epithermal deposits of LS-type, e.g., Hishikari (Japan), Sleeper, Comstok, etc. (Nevada, USA), Balei, Kubaka, etc. (Russia) and Kyzylalmasai, Arabulak, Pirmirab (Uzbekistan).

Despite the abundance and variability of the gold epithermal deposits, only rare examples are known of spatial and temporal coincidence of the telluride and selenide mineralization types within the same gold-bearing mineral assemblages. One of the most striking examples of gold – sulfide – selenide – telluride mineralization is the Kairagach high-sulfidation deposit (Uzbekistan) of late Paleozoic age. Gold-bearing assemblages of these deposits contain selenian goldfieldite, Te-Bi-containing fahlores, Se-bearing native tellurium, tellurides of Au, Ag, Hg, Bi, Sb, Fe, and Pb, Bi selenides, sulfoselenides, sulfotellurides, and sulfoselenotellurides, as well as Bi sulfosalts with high admixtures of Se (Kovalenker et al., 2003; Plotinskaya et al., 2004).

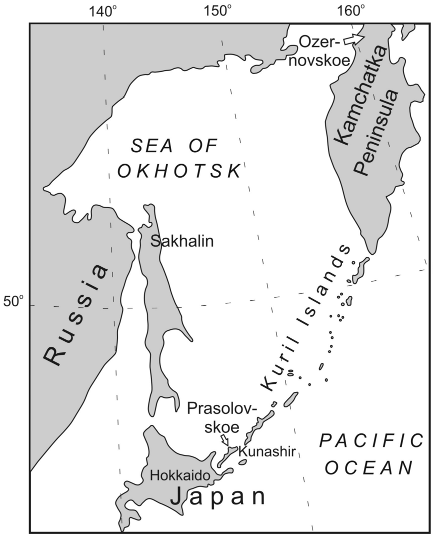

Fig. 1. Locations of Prasolovskoe and Ozernovskoe deposits

The epithermal gold deposits of Prasolovskoe (Kunashir Island, Kuril arc) and Ozernovskoe (Kamchatka Peninsula), both of Neogene age, contain similar complex sulfide-selenide-telluride ores. Besides relatively common selenides (naumannite, claustalite, etc.) and tellurides (altaite, krennerite, sylvanite, petzite, hessite, etc.), several rare and unknown phases, including selenotellurides, were found there (Kovalenker et al., 1989).

Chemical compositions were studied by Camebax microprobe (analyst, S.M. Sandomirskaya); standards used: GaAs for As, $CuSbS_2$ for Cu and S, PbTe for Pb and Te, CdSe for Se, pure Ag and Bi. Analytical lines: K_α for Cu, As, Se, S and L_α for the others.

Geological framework

The *Prasolovskoe* deposit is confined to a circular volcanic structure situated on the northwestern part of Kunashir Island, at the southern end of the Kuril volcanic belt. This belt is located in the internal zone of the Kuril Island arc and consists of calc-alkaline rocks of Miocene to Quaternary age. The host volcanic structure consists mostly of basalt and rhyolite tuffs, as well as a quartz diorite intrusion of Middle-Miocene age. These are intruded by Late Pliocene basalt to rhyolite dykes. The Au-Ag mineralization is confined to NE and NW strike faults and is represented by veins and minor breccias, usually sub-parallel to rhyolite dykes. Like the dikes, gold-bearing veins have Late Pliocene age (K-Ar dating of adularia– 1.94+/-0.10 Ma) and are believed to be genetically related to those dykes. Volcanic and intrusive rocks are subjected to an areal propylitization. The wall rock alteration zones are 0.5 to 2.5 m thick and are represented by quartz-sericite rocks with minor adularia or by hydrothermal argillizites. The most economically significant ores are confined to NE-striking steeply dipping (60-70^o) quartz veins with gold-telluride mineralization, localized mostly in the central part of the volcanic structure and confined to a quartz diorite intrusion. These veins are 1-2 m thick and have horizontal extensions of 500-600 m (in rare cases up to 3.5 km) and vertical range up to 570 m. The gold ores are characterized by variable textures: banded, colloform, brecciated, etc.

Alongside Au, Ag, Se, and Te, the ores are also enriched in Cu, Pb, Zn, Sb, As, Mo, Bi and Sn; Au/Ag ratio varies from 0.36 to 1.67 (average – 0.55). Less widespread are veins containing gold-bismuthinite-cassiterite-quartz (Au/Ag = 0.71), gold-polysulfide-quartz (Au/Ag = 0.03), and calcite-adularia quartz (Au/Ag = 0.5) mineralization (Dunchenko, 1990). As a whole, So et al. (1995), refer to the Prasolovskoe deposit to LS type, but the presence of advanced argillic alteration, as well as alunite, goldfieldite, and enargite, allows us to speak of a superimposition of two HS and LS mineralization styles.

The *Ozernovskoe* deposit occurs within the Koriaka-Central-Kamchatka volcano-plutonic belt. It is confined to a wedge-shaped segment adjoining to the central part of a local Neogene volcanic edifice 8-10 km in diameter. The volcano is localized in a large (20-25 km in diameter) Pravoukinsk volcano-tectonic struc-ture, formed at the intersection of the N-striking Main Kamchatka fault and the NW-striking Palan-Komandor transversal fault zone (Konstantinov, 1994).

The host rocks are represented by diorite porphyrites, andesite-basalts, quartz-andesites, gabbriods, and rhyolites, collectively forming a multiphase subvolcanic body which is supposed to mark the volcano's neck (Vakin and Naumova, 1994). An areal propylitization of epidote (prehnite) – chlorite, carbonate-albite-chlorite, and zeolite – chlorite facies preceeded ore deposition.

Ore mineralization is confined to linear and local areal zones of advanced argillization with mono-quartz, alunite-quartz, diaspore-quartz, diaspore-quartz-pyrophyllite, quartz-kaolinite-dickite, kaolinite-dickite-quartz, and quartz-smectite-chlorite facies typical for HS epithermal deposits (White and Hedenquist, 1995). Ore bodies occur as steep- and low dipping linear and lenticular stockworks of thin (2-5 cm) quartz veinlets, which sometimes transform to mineralized breccia zones, controlled by intersections of NW-striking steep-dipping faults and related fractures.

Most (ca. 80%) of the ore components are concentrated in lenticular-shaped bonanzas (Vakin and Naumova, 1994). The bonanzas have Au/Ag ratios of about 1 and are enriched in Te and Se with Te/Se ratio from 0.2 to 70, averaging 1.5. Ores are characterized by veinlet, breccia to cockade, colloform and structures. The portion of ore minerals (pyrite accounts for up to 90%) varies from <1 to 5-10%.

Ore mineralogy

Ores of the deposits described have a lot in common: quartz dominates among gangue minerals, the portion of ore minerals does not exceed 5-10% (usually 1-3%), among the most widespread are pyrite and fahlores, including goldfieldite. Less abundant are chalcopyrite, marcasite, arsenopyrite, bornite, chalcosite, enargite, luzonite, hematite, cassiterite, molybdenite, galena, sphalerite, acanthite, Se-containing Bi- and Ag-As-Sb- sulfosalts and sulfostannates. In addition, various Te and Se minerals, such as native Te and Se, tellurides of Au, Ag, Pb, Cu, and Bi, sulfoselenotellurides and selenotellurides of Bi, and Ag, Pb, Bi selenides are typical for the both deposits.

At the same time, however, the mineralization in each deposit has some specific features. Thus, ores of the Prasolovskoe deposit are characterized by higher Sn contents due to the abundance of cassiterite (Danchenko and Mitsuk, 1987), as well as by higher In contents because of the presence of roquesite and high In admixtures in sphalerite (Kovalenker et al., 1993).

Native As, colusite, and hemusite have been found at the Ozernovskoe deposit; enargite and famatinite-luzonite are more widespread at Ozernovskoe than at Prasolovskoe.

Specific features of Se and Te mineralization

Prasolovskoe

Four gold-bearing mineral assemblages were revealed at the Prasolovskoe deposit: (1) gold-polysulfide, (2) gold-fahlore, (3) gold-hessite, and (4) gold-selenide-telluride ones. Te- and Se- bearing minerals were identified within the last two assemblages.

Goldfieldite is one of the most important Te-bearing minerals. Some goldfieldites of the Ozernovskoe deposit contain much higher Se admixtures (up to 12 wt.%), then those at Prasolovskoe (up to 3 wt.%, usually < 1 wt.%).

Hessite is the most widespread telluride; in some cases it forms quite large (up to 0.8 mm) grains in quartz and sometimes it contains thin veinlet-like inclusions of native gold. Besides, it forms intimate subgraphical

Table 1. Chemical composition of the unnamed $(Ag,Fe)_3(As,Sb)(Se,S,Te)_3$ phase (wt%) and formulae units calculated for 7 atoms (in brackets)

	1	2	3
Ag	51.90	52.50	51.15
	(2.72)	(2.96)	(2.74)
Fe	2.90	0.99	2.30
	(0.29)	(0.11)	(0.24)
As	12.94	5.82	12.80
	(0.98)	(0.47)	(0.99)
Sb	0.17	9.10	-
	(0.01)	(0.45)	
Te	0.56	2.48	0.58
	(0.02)	(0.12)	(0.03)
Se	24.93	21.69	27.26
	(1.78)	(1.67)	(1.99)
S	6.78	6.35	5.63
	(1.19)	(1.21)	(1.02)
Total	100.18	98.93	99.72

intergrowths with petzite, or occurs as small inclusions within *fahlore*, along with *native Te, altaite,* and *tellurobismuthite* (Bi_2Te_3). Hessite has a composition closed to stoichiometric Ag_2Te and in rare cases contains insignificant (up to 0.2 wt.%) admixture of Se.

Several rare and new Se-Te minerals were identified at the Prasolovskoe deposit and are absent at Ozernovskoe.

A mineral named *'kurilite'* (Kovalenker et al., 1989) with the ideal formula $(Ag,Au)_8Te_3Se$ (calculated for 12 atoms) is relatively widespread within the gold-selenide-telluride assemblage. As a rule it occurs in quartz interstices, sometimes overgrowths fahlores or forms intergrowths with native Te, petzite, hessite, and sylvanite. EPMA data showed the following composition: Ag 65.07-65.76; Au 0.35-1.17; Te 24.64-25.06; Se 8.79-9.14; S < 0.05 to 0.10; sum 99.96-100.12.

The Te_3Se_4 phase (Te 54.11; Se 44.99; total 99.10 wt %) occurs as a thin (40-60 μm) reaction rim between clausthalite and native Te; which along with sylvanite and naumannite, form complex aggregates up to 500 μm in quartz interstices.

A mineral phase with a formula close to $(Ag,Fe)_3As(Se,S,Te)_3$, calculated to 7 atoms (Table 1) was found as small inclusions (up to 50 μm) within paratellurite TeO_2 and sometimes is surrounded by a thin rim of naumannite. In reflected light, the mineral is gray with a pink tint, isotropic with reflectance closed to fahlore.

Ozernovskoe

The Ozernovskoe deposit is characterized by more abundant and variable selenides then the Prasolovskoe deposit.

In the selenide-telluride mineralization, alongside native Te, krennerite, sylvanite, and petzite, several rare minerals occur: bohdanowiczite ($AgBiSe_2$), skippenite (Bi_2TeSe_2), rickardite, vulcanite are identified, as well as a number of unnamed phases ($AgBi_3Se_5$, Bi_2SeTe, $Bi_8Te_3Se_3$, Bi_3TeSe_3) (Kovalenker et al., 1989; Spiridonov et al., 1990).

Table 2. Chemical composition of skippenite from the Ozernovskoe deposit (wt%) and formulae units (in brackets) calculated for 5 atoms. "-" not detected

	1	2	3
Bi	59.03	59.07	57.88
	(1.88)	(2.04)	(1.99)
Pb	-	-	0.25
			(0.01)
Sb	-	-	0.15
			(0.01)
As	0.97	-	-
	(0.09)		
Te	19.48	20.01	21.58
	(1.01)	(1.13)	(1.22)
Se	19.79	19.30	19.01
	(1.67)	(1.76)	(1.73)
S	0.38	0.30	0.19
	(0.34)	(0.07)	(0.04)
Total	99.65	98.68	99.06

Skippenite (Table 2) occurs as small (80-120 μm) plate-shaped grains intergrown with *bohdanowiczite* (Fig. 3, Table 3) and native Te within selenian goldfieldite. In comparison with skippenite from Prasolovskoe, it is characterized by relatively higher Te and lower Se contents, by minor admixtures of S, and in some grains, by minor admixtures of Pb, As and Sb.

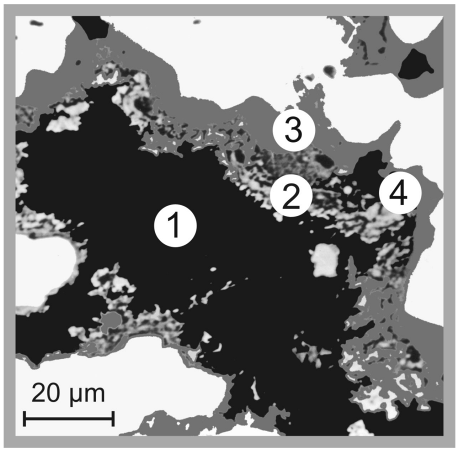

Fig. 3. Absorbed electron image: native tellurium (1) surrounded by tellurite (2), selenian goldfieldite (3), and bohdanowiczite (4); the Ozernovskoe deposit

Table 3. Chemical composition of bohdanowiczite from the Ozernovskoe deposit (wt.%) and formulae units calculated for 4 atoms (in brackets)

	1	2	3
Ag	21.35	21.40	22.28
	(0.96)	(0.97)	(0.99)
Cu	0.31	0.53	
	(0.02)	(0.04)	-
Bi	41.00	42.54	41.58
	(0.95)	(0.99)	(1.00)
Pb	3.43	0.21	1.39
	(0.08)	(0.01)	(0.03)
Se	30.28	29.74	31.08
	(1.86)	(1.84)	(1.88)
Te	2.17	2.40	2.15
	(0.08)	(0.09)	(0.08)
S	0.31	0.33	0.51
	(0.05)	(0.06)	(0.07)
Σ	98.85	97.15	98.99

The *$AgBi_3Se_5$* phase (Table 4) is sure to be a selenian analogue of pavonite ($AgBi_3S_5$) and its optical properties in a reflected light are similar to those of pavonite. Partial substitution of Ag by Cu and of Bi by Pb takes place (Table 4). The *$AgBi_3Se_5$* phase occurs as accumulations of small isolated grains in quartz in assemblage with native gold of high fineness (.960-.980) and with phase *$(Bi,As,Te,Se)_2O_3$*.

Table 4. Chemical composition of $AgBi_3Se_5$ phase from the Ozernovskoe deposit (wt.%) and formulae units calculated for 9 atoms (in brackets)

	1	2	3	4
Ag	6.10	8.56	10.15	5.85
	(0.60)	(0.86)	(1.01)	(0.57)
Cu	2.38	1.00		2.53
	(0.40)	(0.17)	-	(0.42)
Bi	59.66	56.80	55.84	56.82
	(3.01)	(2.93)	(2.86)	(2.86)
Pb		1.09	1.11	1.01
	-	(0.06)	(0.06)	(0.05)
As		0.36	0.37	0.33
	-	(0.05)	(0.05)	(0.05)
Se	27.80	26.76	27.51	26.50
	(3.73)	(3.67)	(3.73)	(3.53)
Te	0.20	0.36	0.37	0.33
	(0.02)	(0.03)	(0.03)	(0.03)
S	3.74	3.65	3.76	4.55
	(1.24)	(1.23)	(1.26)	(1.49)
Total	99.88	98.58	99.11	97.92

Formation conditions of selenide-telluride mineralization

Fluid inclusion data (Kovalenker et al., 1989, So et al., 1995) showed that the earliest quartz-cassiterite assemblage at the Prasolovskoe deposit was formed at 420 to 350°C. The next gold-quartz assemblage was formed at 320-280°C. Precipitation of sulfides (chalcopyrite, sphalerite, galena, goldfieldite) as well as sulfotellurides and Bi selenides took place at 270-220°C.

At the Ozernovskoe deposit the assemblage of selenian goldfieldite, altaite, sylvanite, native tellurium, tellurite, skippenite, bohdano-wiczite, and *$AgBi_3Se_5$* were formed at temperatures around 200°C.

Thus, tellurides and selenides at both Prasolovskoe and Ozernovskoe deposits were formed at quite a narrow temperature range (250-200°C) and composition of mineral assemblages, as well as mineral sequence were determined by activities of S_2, O_2, Te, and Se in the system.

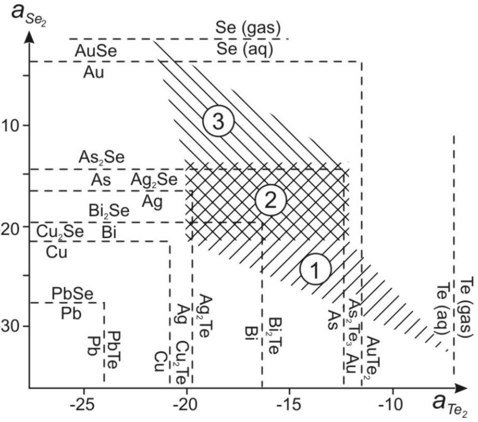

Fig. 4. Tellurium versus selenium activity diagram with selected metal-telluride-selenide equilibria at 200°C (Kovalenker et al., 1989). Areas (1) and (3) – precipitation of tellurides and selenides accordingly, area (2) – precipitation of selenotellurides and sulfoselenotellurides

In the early stages of ore-forming process within both deposits, fluids were characterized by high aS_2. With temperature decrease aS_2 also decreased; that resulted in aTe_2 increase, and, later aSe_2 increase. That caused, initially, abundant precipitation of sulfides, and then the formation of tellurides (area 1 on Fig. 4), followed by the crystallization of selenotellurides (area 2 on Fig. 4), and, finally selenides (area 3 on Fig. 4).

Acknowledgements. The authors are thankful to S. M. Sandomirskaya for EPMA analyses. The study is a contribution of the IGCP-486 project and was supported by Russian Foundation for Basic Research No 04-05-64407 and Russian Science Support Foundation.

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