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Te and Se mineralogy of the high-sulfidation Kochbulak and Kairagach epithermal gold telluride deposits (Kurama Ridge, Middle Tien Shan, Uzbekistan)

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Summary

The Late Paleozoic Kochbulak and Kairagach deposits are located on the northern slope of the Kurama Ridge, Middle Tien Shan, in the same volcanic structure and the same ore-forming system. Au-Ag-Cu-Bi-Te-Se mineralization is confined to veins and dissemination zones accompanied by quartz-sericite wall-rock alteration. The tellurides, calaverite, altaite, hessite, and tetradymite are widespread at both deposits; at Kairagach selenides and sulfoselenides of Bi and Pb are common, while at Kochbulak Bi and Pb telluroselenides and sulfotelluroselenides are typical. The paragenetic sequence of telluride assemblages are similar for both deposits and change from calaverite + altaite + native Au to sylvanite + Bi tellurides + native Te, Bi tellurides + native Au, and, finally, to Au + Ag tellurides with time. These mineralogical changes are accompanied by an increase in the Ag content of native gold that correlates with a decrease in temperature, fTe₂ and fO_2 and an increase in pH.

Introduction

Most volcanic-hosted epithermal gold deposits (*White* and *Hedenquist*, 1990; *Bonham*, 1986; *Heald* et al., 1987; *Henley*, 1991) are of Neogene or Paleogene age. However, some of the largest deposits, including Kochbulak, Uzbekistan, are Paleozoic in age. The Kochbulak and smaller Kairagach deposits are located 3.5 km apart near the town of Angren on the northern slope of the Kurama Ridge

in the Middle Tien Shan. The Kurama Ridge forms the eastern part of the extensive Bel'tau-Kurama volcano-plutonic belt. Some modern geotectonic reconstructions of this belt (Dalimov and Ganiev, 1994; Zonenshain et al., 1990) consider it to have been an Andean-type continental margin volcanic belt that formed in the Late Paleozoic on a Precambrian and Early Hercynian continental basement. This belt is unusual in that it contains Paleozoic porphyry Au-Cu-Mo, Ag-Pb-Zn skarn and epithermal Au-Ag-Te-Se deposits (Fig. 1). The total gold resources of this region exceed 2000 tonnes (Islamov et al., 1999), which makes this region a worldclass gold province. The estimated reserves of the Kochbulak deposit are 120t of Au and 400 t of Ag. Major ore components are Au (13.4 ppm) and Ag (120 ppm), also Cu (0.2%), Se (4 ppm), Te (101.6 ppm) and Bi (0.01%). Reserves of the Kairagach deposit are relatively small and are estimated to be 50t of Au and 150t of Ag. Gold is present mostly in native form but approximately 20–25% of the total gold reserves of these two deposits occur as various precious metal tellurides. Some researchers suggest that the Kochbulak and Kairagach deposits are part of a single Kochbulak-Kairagach ore field (Islamov et al., 1999).



Fig. 1. Schematic geological map of the central part of the Kurama Ridge (after *Kovalenker* et al., 2003)

Te and Se mineralogy

The geological, geochemical, and mineralogical features of the Kairagach and Kochbulak deposits have been described by a number of workers (*Genkin* et al., 1980; *Badalov* and *Spiridonov*, 1983; *Badalov* et al., 1984; *Spiridonov* and *Badalov*, 1983; *Kovalenker* and *Heinke*, 1984; *Kovalenker* et al., 1979, 1980, 1997, 2003; *Plotinskaya* and *Kovalenker*, 1998; *Koneev* and *Gertman*, 1997; *Plotinskaya* et al., 2001). However, no comparative mineralogical description of these deposits has been undertaken.

The objective of the present communication its to describe and to compare the telluride and selenide mineralogy of the Kochbulak and Kairagach deposits using both published and recently obtained mineral chemistry to refine the conditions of tellurides deposition at the both deposits.

Geological setting

The Kochbulak and Kairagach deposits occur in the Karatash (or Kochbulak– Kairagach) caldera in the northern part of the Lashkerek volcano-tectonic depression (Figs. 1 and 2) at the intersection of the South Angren and Lashkerek-Dukent fault zones (*Islamov* et al., 1999). The caldera is filled with volcano-sedimentary and subvolcanic rocks (>1.5 km thick) of andesite–dacite and rhyolite composition. The andesite–dacite unit (C_{2-3}) consists of andesitic and dacitic lavas, tuffs, and sandstones that were intruded by subvolcanic dacite–porphyry and diorite–porphyry stocks. The rhyolite unit (C_3 -P₁) consists of rhyolitic lavas and pyroclastic rocks. Numerous north–east trending diabase porphyry and granodiorite porphyry dikes (C_3 -P₁) occur throughout the Karatash caldera. In the central part of the caldera a stock-shaped subvolcanic intrusion of porphyritic trachyandesite (C_3 -P₁), which is considered to be a volcanic neck, separates the Kochbulak and Kairagach ore fields (*Islamov* et al., 1999; *Kovalenker* et al., 1997, 2003). Volcanic rocks were affected by synvolcanic albite-chlorite and sericite-chlorite alteration.

Precious metal mineralization Kochbulak and Kairagach is confined to silicification and breccia zones accompanied by quartz-sericite wall-rock alteration. At Kochbulak, three types of ore bodies have been recognized: (1) pipe-like ore bodies,





(2) flat (20–40°) lenticular lodes, and (3) steeply dipping veins. At Kairagach, steeply dipping (75–80°) vein-like lodes and disseminated ore zones (sometimes flattening up to 10° at shallow levels) are typical. K–Ar and Rb–Sr dating of sericite yielded ages of 280 ± 8 Ma and 270 ± 8 Ma for pipe-like ore bodies and flat lodes plus veins at Kochbulak, respectively, while an age of 280 ± 5 Ma was obtained for the lodes at Kairagach (*Kovalenker* et al., 2004).

Ore mineralogy

The ore-forming processes at Kochbulak and Kairagach can be subdivided into preore, ore, and post-ore stages. Mineralization of the pre-ore stage consists of vuggy silica with pyrophyllite, diaspore, kaolinite, and alunite, as well as quartz-carbonate-sericite-pyrite rocks. The vuggy silica is present mostly at shallow levels of the Kairagach deposit, whereas quartz-carbonate-sericite-pyrite rocks are widespread throughout the Kochbulak and Kairagach ore fields.

Three ore stages were recognized in the Kochbulak deposit by *Kovalenker* et al. (1980, 1997). Mineralization of the first stage consists of fine-grained to cryptocrystalline gray silica with variable amounts of pyrite, followed by quartz and minor dolomite and barite with native gold, tellurides, and sulfosalts (Figs. 3a, 4a). The second stage consists of banded silica, which in places occurs as a matrix cementing clasts of quartz-pyrite aggregates of the first ore stage or altered porphyries (Fig. 3a), and contains native gold, bismuthinite, and tellurides. Hydrothermal mineralization of the third stage includes white quartz with pyrite, goldfieldite, famatinite-luzonite, and minor Au and Ag tellurides (Fig. 4b), followed by fine-grained quartz with tetrahedrite, chalcopyrite, Sb- and Bi sulfosalts, Cu–Fe sulfostannates, tellurides, and sulfosalts of the lillianite series (Fig. 4c).

Fluid inclusion data (*Kovalenker* et al., 1997) showed homogenization temperatures from ~100 to 400 °C for the first ore stage, ~100 to 300 °C for the second ore stage, and ~100 to 320 °C for the third ore stage. Fluid inclusions in quartz at the beginning of each ore stage exhibited low to moderate salinity (0.5–6.5 wt.% equiv NaCl) with NaCl and KCl being the dominant salts. Fluids responsible for the formation of quartz and barite spatially associated with tellurides and sulfosalts had temperatures ~250 to 130 °C. The salinities of these fluids were 8–25 wt.% equiv NaCl, with Fe²⁺, Mg²⁺ and Ca²⁺, or Na⁺ and Ca²⁺ being the dominant cations in solution.

At the Kairagach deposit there are two ore stages. The first (early) ore stage consists of gray metasomatic quartz with disseminated pyrite and minor chalcopyrite, and rare sphalerite, galena, and fahlores. Native gold is interspersed as inclusions in quartz and pyrite (Fig. 3b).

The second (main) ore stage includes several assemblages that are closely related in time and are often telescoped spatially. The earliest assemblage consists of segregations of native gold in quartz-barite aggregates while the next assemblage is composed of goldfieldite and famatinite-luzonite. Later mineral assemblages include: native gold with early tellurides, native tellurium with Au, Ag, Sb, and Bi tellurides, and Cu and Fe sulfostannates (mawsonite, stannoidite, kesterite, nekrasovite, volfsonite, hemusite). A bismuth-sulfoselenide assemblage contains native bismuth, Bi-selenides, sulfoselenides, sulfotellurides, and sulfoselenotellurides, and



Fig. 3. Specimens showing mineral successions of the Kochbulak (a) and Kairagach (b) deposits. (a): 1. altered andesite porphyry cluster, 2. quartz of the pre ore stage, 3. quartz of the first ore stage, 4. matrix-banded quartz of the second ore stage. (b): 1. pre ore alteration – quartz-sericite-pyrite-carbonate rocks, 2. the first ore stage – vuggy silica with pyrite and disseminated native gold, 3. the second ore stage – chalcedonic silica with native gold (3a), and barite with gold-telluride-sulphosalts mineralization (3b)



Fig. 4. Reflected light photomicrographs of mineral assemblages of Kochbulak (a–d) and Kairagach (e–f) deposits. (a) first ore stage – native Au and pyrite (Py) in quartz (Q); (b) native Au, altaite (Alt), hessite (Hs), galena (Gn), and tetrahedrite (Td) in quartz (Q) in the third ore stage; (c) native Au with hessite and altaite in tennantite–tetrahedrite (Tn–Td) in the third ore stage; (d) petzite (Pt), volynskite (Vol) and tetradymite (Td) in quartz; (e) native Au, calaverite (Cal), petzite (Pt) and chalcopyrite (Cp) in barite (Bar); (f) native Te, sylvanite (Syl), and chalcopyrite (Cp) in barite (Bar)

chalcopyrite. The Bi-sulfosalts assemblage consists of minerals of the bismuthiniteaikinite series. Near the end of the main ore stage, hessite, electrum, and chalcopyrite are common. Fahlores are intergrown with chalcopyrite to form aggregates up to several millimeters in length and contain numerous inclusions of native gold, Bi-sulfosalts, sulfostannates, tellurides, and selenides and minerals of the junoite and pavonite homologue series (*Plotinskaya* and *Kovalenker*, 1998; *Kovalenker* et al., 2003).

The main ore stage was formed at 120 to $309 \,^{\circ}$ C whereas telluride-bearing barite and quartz formed at 150 to 240 $^{\circ}$ C from low to moderately saline (0.9–13.4 wt.% equiv NaCl) fluids dominated by Na⁺ and K⁺ (*Plotinskaya* et al., 2001; *Kovalenker* et al., 2003).

Post-ore stage mineralization for both deposits consists of quartz-carbonatebarite veinlets that crosscut minerals of the preceding stages. These veinlets also contain galena and sphalerite with rare chalcopyrite, pyrite, and tetrahedrite.

Electron microprobe analyses

Chemical compositions of ore minerals were obtained with JEOL 5900 LV SEM and LEO-1455-VP scanning electron microscopes equipped with EDXdetectors (both NHM) and with Cameca MS-46 (IGEM RAS), Camebax-Micro (TsNIGRI), Camebax SX-50 (IGEM RAS), and Cameca-SX50 (NHM) WDX electron microprobes with the following operating conditions and standards. Each instrument used an accelerating voltage of 20 kV and possessed a beam diameter of $1-2\,\mu m$. The Cameca MS-46 electron microprobe used a sample current of 15–25 nA (depending on minerals analyzed) and the analytical lines: K_{α} (for S, Fe, Cu, and Zn), K_{β} (for As); L_{α} (for Ag, Sb, Te, Bi, and Se). Standards used were stoichiometric FeS₂, CuFeS₂, NiAs, Ag₈SnS₆, and PbSe, as well as pure metallic V, Zn, Sb, Ag, Te, and Bi. The Camebax-Micro electron microprobe used a sample current of 15 nA and analytical lines: K_{α} (for Cu, As, S, and Se) and L_{α} (for other elements). Standards used were synthetic PbTe, CdSe, CuSbS₂, and GaAs and chemically pure Au, Ag, and Bi. The Camebax SX-50 electron microprobe used a sample current of 20 nA and analytical lines: K_{α} (for Cu, As, S, and Se) and L_{α} (for other elements). Standards used were synthetic PbTe, HgTe, FeS₂, ZnS, and GaAs and chemically pure metals.

The Cameca-SX-50 electron microprobe used a sample current 20 nA and beam diameter of $1-2 \mu m$ and up to $10-20 \mu m$ for petzite and empressite. The analytical lines measured were K_{α} (for Cu, S, Fe and Zn), L_{α} (for Te, Ag, Sb, As, and Se), M_{α} (for Bi, Pb, and Au). Standards used were HgTe for Te and Hg, BiTe for Bi, PbS for Pb, ZnS for S and Zn, GaAs for As, PbSe for Se, chemically pure metals for Ag, Au, Sb, Cu, and Fe.

Gold, telluride and selenide mineralogy

Telluride and selenide mineralization at Kochbulak and Kairagach consists of >30 minerals including several unknown and possible new minerals. Tellurides usually

occur as small inclusions in gangue minerals (quartz at Kochbulak and in barite and rarely calcite at Kairagach) or in fahlore group minerals. They also form intergrowths with native gold and sulfides (chalcopyrite, pyrite, and galena). Native gold and tellurides are most abundant in pipe-like ore bodies at Kochbulak where gold grades reach several thousands ppm and where tellurides locally form segregations up to 10-15 cm in length.

Native gold

Native gold from both deposits has a variety of morphologies: xenomorphic, elongate, lumpy, stringer-shaped, rounded, and oval. Grains vary in size from $<2 \,\mu\text{m}$ in the assemblage quartz + sericite in the Kairagach deposit, to 2–3 mm in telluride assemblages in the Kochbulak deposit. Native gold occurs in almost all mineral assemblages and shows marked compositional variations (Tables 1 and 2, Fig. 5a and b).

The main metal with which native gold forms an alloy is Ag (up to 46.0 wt.% in Kochbulak and up to 46.6 wt.% in Kairagach), but it also contains Hg (up to 0.9 wt.% in Kochbulak and up to 11.3 wt.% in Kairagach), and Cu (up to 2.9 wt.% in Kochbulak and 2.4 wt.% in Kairagach). Most of the gold was deposited in the assemblage quartz + sericite or in chalcedonic silica prior to the deposition of tellurides. As shown in Fig. 5a, each ore stage at Kochbulak commences with native gold of very high fineness with a subsequent increase in Ag content from early to late assemblages. A similar trend was observed for the second ore stage of native gold in the Kairagach deposit (Fig. 5b). In places, relatively high Hg contents (up to 11.4 wt.%) were identified in veinlet-like electrum within fahlore grains at Kairagach (assemblage 10 in Table 2 and Fig. 5b).

Gold and silver tellurides

Calaverite (AuTe₂) is one of the most common tellurides in both deposits. At Kairagach, it occurs within early assemblages of the second ore stage together with native gold of high fineness, petzite, altaite (Fig. 4d), and, in places, with tetrahedrite and tellurantimony. At Kochbulak, it is typically present in early assemblages of all three ore stages, and forms aggregates with native gold, petzite, altaite, krennerite, and galena (Fig. 4b). Calaverite contains up to 1.8 wt.% Ag, up to 0.9 wt.% Cu, and up to 3.0 wt.% Sb (Table 3).

Hessite (Ag_2Te) is also a common telluride. At Kairagach, it occurs in contact with native gold and chalcopyrite, whereas at Kochbulak it also coexists with petzite, lillianite, and tetradymite (Figs. 4b and c). As a rule, it is confined to mineral assemblages formed late in the paragenetic sequence. Stützite ($Ag_{5-x}Te_3$) occurs in the same assemblages as hessite but is much less common. Petzite (Ag_3AuTe_2) forms intergrowths with calaverite, hessite and native gold (Fig. 4e) whereas sylvanite ($AuAgTe_4$) is less common than the other precious metal tellurides but it occurs with native tellurium, empressite (AgTe), and Bi and Sb tellurides (Fig. 4f), and rarely, with other Au–Ag tellurides. At Kairagach, sylvanite contains 1.9–4.7 wt.% Cu, which occupies an intermediate position in the

Table 1. Chemical	comp	osition of native gold and electrum fi	om as	semblag	es in the Kochbu	ılak deposit (mc	odified after K	covalenker et	al., 1997)
		Assemblage	u		Au wt.%	Ag wt.%	Cu wt.%	Hg wt.%	Ag at.%
First ore stage	-	Quartz \pm Pyrite \pm Sericite	15	range mean	93.40–98.25 95.98	0.46-6.40 3.21	0.04-0.49	<0.52	6.4
	0	Calaverite \pm Krennerite \pm Sylvanite \pm Altaite	4	range mean	91.77–93.61 92.45	5.52–7.62 6.51	0.04–0.10 0.07	n.d.	11.3
	ξ	Altaite \pm Petzite \pm Coloradoite \pm Tellurobismutite \pm Melonite \pm Tellurantimony	11	range mean	85.56–92.52 89.19	7.61–12.49 9.96	n.d.	n.d.	16.9
	4	Petzite + Hessite \pm Chalcopyrite	×	range mean	80.12-85.35 81.93	14.77–19.06 17.41	0.00-1.41 0.26	0.00-0.87	27.8
	S	Hessite \pm Petzite \pm Lillianite	1		50.31	45.98	0.86	0.17	61.2
Second ore stage	9	Quartz + Sericite	6	range mean	94.38–99.70 97.90	0.00-5.68 1.84	0.02-0.06 0.04	0.10–0.52 0.32	3.3
	Г	Calaverite + Altaite	5	range mean	90.24–95.02 92.31	2.69–10.62 6.74	0.02–0.75 0.16	0.09–0.29 0.20	11.7
	8	Altaite + Tellurobismutite \pm Coloradoite \pm Chalcopyrite	7	range mean	86.06–88.25 87.15	$\frac{11.50-11.93}{11.71}$	0.00-0.10 0.05	0.06–0.40 0.23	19.7
	6	Bismuthinite + Tetradymite	٢	range mean	79.88–87.63 84.88	11.40–18.87 14.71	0.06–0.64 0.26	0.05-0.15 0.11	23.9
	10	Petzite + Hessite \pm Sylvanite \pm Tetradymite \pm Chalcopyrite	\mathfrak{S}	range mean	81.07–82.61 81.74	16.45–18.25 17.64	0.19–0.36 0.18	0.11–0.33 0.19	28.1
	11	Hessite + Chalcopyrite	\mathfrak{c}	range mean	75.51–77.89 75.61	20.91–25.03 22.88	0.06-0.54 0.34	0.15-0.16 0.15	35.3

Te and Se mineralogy

195

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Tab

		Assemblage	u		Au wt.%	Ag wt.%	Cu wt.%	Hg wt.%	Ag at.%
Third ore stage	12	Calaverite + Sylvanite \pm Altaite	2	range mean	85.12–91.09 88.58	6.76-14.90 10.57	$0.04{-}1.10$ 0.35	n.d.	17.5
	13	Petzite \pm Sylvanite \pm Tetradymite	\mathfrak{S}	range mean	85.83–88.22 87.16	10.29–13.38 12.03	0.12 - 1.50 0.69	0.02–0.07 0.05	19.7
	14	Petzite + Hessite \pm Tetradymite	×	range mean	79.46–89.14 82.00	$\frac{11.51-22.05}{18.54}$	$\begin{array}{c} 0.01 - 0.39 \\ 0.11 \end{array}$	0.00-0.32 0.13	28.9
	15	Hessite + Lillianite \pm Petzite \pm Tetradymite \pm Chalcopyrite	12	range mean	67.50–76.82 72.26	23.43–32.28 27.29	0.05–0.27 0.12	0.00–0.21 0.12	40.6
	16	Lillianite \pm Hessite \pm Chalcopyrite	12	range mean	55.94–64.82 60.04	35.28–43.18 39.32	0.01-2.92 1.42	0.12–0.61 0.35	53.7
<i>n</i> number of anal	yses,	n.d. not detected. Analyzed with Cam	ebax-	Micro (1	[sNIGRI) and C	ameca SX50 (N	(MHI)		

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	Assemblage	u		Au wt.%	Ag wt.%	Cu wt.%	Pb wt.%	Bi wt.%	Te wt.%	Hg wt.%	Ag,at.%
1	Quartz \pm Pyrite \pm Sericite	28	range mean	87.79–99.41 97.40	0.12 - 10.90 1.55	$\begin{array}{c} 0.00-0.10 \\ 0.03 \end{array}$	0.00-0.23 0.05	0.00–0.51 0.09	0.00-0.10 0.02	$\begin{array}{c} 0.00-0.30 \\ 0.04 \end{array}$	2.8
7	Quartz + Barite	∞	range mean	87.21–97.25 93.03	0.46–9.45 4.97	0.00-0.1 0.05	0.00–0.16 0.04	0.00–1.46 0.29	0.00-0.62 0.10	$\begin{array}{c} 0.00-0.05 \\ 0.01 \end{array}$	8.7
\mathfrak{C}	Altaite + Calaverite \pm Petzite \pm Chalcopyrite	14	range mean	84.04–97.01 92.24	0.39–15.35 5.17	0.00–1.15 0.23	0.00–2.18 0.30	0.00–1.55 0.21	0.00–2.70 0.23	0.00-0.30 0.05	8.9
4	Tetradymite \pm Volyn-skite \pm Chalcopyrite	٢	range mean	86.38–98.81 93.35	0.45 - 11.73 4.95	0.00-0.07 0.02	0.00-0.36 0.10	0.00–1.66 0.63	0.00-0.24 0.05	0.00-0.20 0.03	8.4
S	Bismuthite-Aikinite \pm Chalcopyrite	25	range mean	71.78–95.48 86.89	2.18–27.14 11.39	$\begin{array}{c} 0.00{-}1.87 \\ 0.18 \end{array}$	0.00-0.51 0.16	0.00–0.82 0.22	0.00-0.07 0.02	0.00-0.17 0.02	18.7
9	Fahlore \pm Chalcopyrite \pm Cu-Fe-Sulfostannates	26	range mean	82.53–95.56 90.20	1.08–16.01 7.68	0.26-2.52 0.79	0.00–0.50 0.12	0.00–1.11 0.30	0.00–0.19 0.04	$\begin{array}{c} 0.00 - 1.28 \\ 0.36 \end{array}$	12.9
٢	Hessite \pm Chalcopyrite	13	range mean	77.94–95.22 85.80	4.32–20.26 12.58	0.00-0.47 0.11	0.00–0.76 0.19	0.00–0.87 0.16	0.00-0.36 0.05	0.00–0.11 0.02	20.7
∞	$Emplectite \pm Chalcopyrite$	4	range mean	72.00–93.13 86.92	6.41–24.32 11.96	0.04 - 0.34 0.22	0.00-0.15 0.07	0.00–2.02 0.78	n.d.	n.d.	19.3
6	Chalcopyrite	12	range mean	67.11–82.69 78.64	16.15-29.26 19.69	$\begin{array}{c} 0.02{-}1.78 \\ 0.53 \end{array}$	0.00-0.56 0.19	0.00-0.90 0.26	0.00 - 1.11 0.14	0.00-0.81 0.09	30.7
10	Fahlore	15	range mean	40.02–86.16 74.50	12.33–46.58 22.13	0.13-2.35 1.20	0.00-0.14 0.06	n.d	n.d.	0.00–11.26 2.08	32.7
u n	number of analyses, n.d. not d	letect	ed. Aní	alyzed with C	ameca MS-46	and Cameba	ix SX-50 (IC	JEM RAS)			

Table 2. Chemical composition of native gold from different assemblages of the second ore stage of the Kairagach deposit

Te and Se mineralogy



Fig. 5. Ag contents of native gold from different mineral assemblages of Kochbulak (a) and Kairagach (b) deposits. Q quartz; *Ser* sericite; *Alt* altaite; *Bsm* bismuthinite; *Cld* coloradoite; *Cp* chalcopyrite; *Cu–Fe–Sn* sulfostannates of Fe and Cu; *Cv* calaverite; *Empl* emplectite; *Fhl* fahlores; *Hs* hessite; *Kr* krennerite; *LHS* sulphosalts of lillianite series; *Ml* melonite; *Ptz* petzite; *Py* pyrite; *Sv* sylvanite, *Tat* tellurantimony; *Tbs* tellurbismuthite; *Te* native tellurium; *Trd* tetradymite; *Vol* volynskite

sylvanite–kostovite (AuCuTe₄) isomorphous series. Volynskite (AgBiTe₂) occurs in assemblages with Bi tellurides and petzite (Fig. 4d). Krennerite $[(Au,Ag)_2Te_4]$, empressite, and kostovite are extremely rare and have been found only in the Kochbulak deposit.

Bismuth tellurides and selenides

Bismuth tellurides are intergrown with each other as well as with petzite (Fig. 4d) and native gold in early ore assemblages or they occur as decomposition products of Te- and Se- containing Bi-sulfosalts in relatively late assemblages.

Tetradymite (Bi_2Te_2S) is the most common Bi telluride and occurs with bismuth sulfosalts (bismuthinite–aikinite, junoite, and minerals of the lillianite series),

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	Ag	Au	Cu	Pb	Fe	Hg	Bi	Sb	Te	Se	S	Total	√ u	Ag A) N	Cu I	b I	و ا	Цg	Bi	Sb	le	Se	S
1	0.64	41.46	0.01	0.04	0.05	0.33	0.00	0.49	56.98	0.07	0.01	100.07	3 0	0.03 0	94 (00.0	00.0	00.	0.01	0.00	0.02) 66.1	00.0	0.00
0	61.96	0.17	0.08	0.15	0.01	0.00	0.09	0.30	36.52	0.04	0.05	99.35	3 1	.98 0	00.	00.0	00.0	00.	0.00	0.00	D.01 () 66.0	0.00	0.00
б	41.29	24.06	0.00	0.01	0.00	0.00	0.00	0.15	32.44	0.00	0.00	97.94	6 3	.02 0	.96	00.0	00.0	00.	0.00	0.00	0.01	2.00	00.0	0.00
4	44.51	0.01	0.02	0.04	0.02	0.22	0.04	0.42	53.19	0.05	0.00	98.52	2	0 66.0	00.	00.0	00.0	00.	0.00	0.00	0.01	00.1	0.00	0.00
s,	12.96	24.74	0.00		I		0.00	0.30	63.40		0.00	101.40	6 0	.97 1	.01	00.0			-	0.00	0.02	4.00	-	0.00
9	7.72	25.62	2.91	0.14	0.00		0.00	0.45	63.64	0.06	0.00	100.54	6 0	.57 1	2.	0.37 (0.01 0	00.	-	0.00	0.03	3.98 (0.01	0.00
7*	10.64	28.41	0.02		0.21		I		61.15	0.05	0.06	100.54	6 0	.81 1	.19	00.0	J	.03		•	00.0	3.95 (0.01	0.02
8	19.14	0.01	0.05	0.00	0.00	0.06	35.29	0.23	43.84	0.16	0.04	98.81	4	.02 0	00.	00.0	00.0	00.	0.00	0.97	0.01	1.97	0.01	0.01
6	0.48	0.13	0.04	0.17	0.04	0.26	57.39	0.28	35.56	0.95	4.09	99.40	5 0	0.03 0	00.	00.0	0.01 (.01	0.01	1.95	0.02	98 (60.0	0.91
10	0.27	0.01	0.04	0.30	0.01	0.26	56.90	0.33	34.93	1.89	3.79	98.72	5 0	0.02 0	00.	00.0	0.01 (00.	0.01	1.95	0.02) 96.1	0.17	0.85
11^*	0.86		0.19	13.47	0.00		38.14	0.35	45.07	0.19	0.01	98.28	7 0	60.0	-	0.03 (0.73 (00.		2.06	0.03	3.98 (0.03	0.00
12^{*}	0.46		0.08		0.01		50.70	0.82	48.67	0.16	0.04	100.94	5 0	0.03	-	0.01 (00.0	00.		1.90	0.05	2.98 (0.02	0.01
13	0.65	0.04	0.09	0.18	0.01		49.87	1.40	47.98	0.21	0.02	100.44	5 0	0.05 0	00.	0.01 (0.01 (00.		1.87	0.00	2.94 (0.02	0.01
14	0.50	0.06	0.00	0.87	0.01	0.15	0.12	38.38	59.13	0.07	0.00	99.27	5 0	0.03 0	00.	00.0	0.03 (00.	0.00	0.00	1.99	2.93 (0.01	0.00
15	0.71	0.15	0.02	0.13	0.04		34.47	12.45	50.64	0.13	0.02	98.76	5 0	0.05 0	.01	00.0	00.0	.01		1.22	0.76	2.93 (0.01	0.00
16	0.00	0.00	0.02	1.00	0.04		49.61	4.05	36.00	9.51	0.06	100.28	5 0	0 00.0	00.	00.0	0.04 0	00.		1.74	0.24	2.07 (0.88	0.01
17^{*}	0.29	0.37	1.39			0.71	55.92	0.44	30.58	9.12	1.75	100.57	5 0	0.02 0	.01	0.15 (00.0	00.	0.02	1.88	0.03) <u>69</u> .1	0.81	0.38
18^*	0.15		0.34	0.26	0.10		80.19	0.10		17.00	2.44	100.58	7 0	0.01 0	00.	0.05 (0.01 (.02		3.83	0.01 (00.0	2.15	0.76
19	0.29	0.00	1.44	1.17	0.18	0.00	85.68	0.03	0.05	7.06	7.13	103.04	2	0.01 0	00.).06 (0.01 (.01	00.0	1.08	D.00 (00.0	0.24	0.59
20	0.22	0.06	0.00	61.80	0.00	0.00	0.18	0.25	36.88	0.49	0.07	99.94	2	0.01 0	00.	00.0) 66.(00.	0.00	0.00	0.01 ().96 (0.02	0.01
21^{*}			2.31	69.63	1.45		0.26			23.39	3.63	100.67	0		0) 60.0	0.83 (.06	-	0.00	U	00.0	0.73	0.28
22	0.00	0.06	0.71	0.00	16.89	0.39	0.07	0.54	81.22	0.00	0.02	99.90	3 0	0 00.0	00.	0.04 (00.0	.95 (0.01	0.00	0.01) 66.1	0.00	0.00
23	0.14	0.06	0.00	0.04	0.05	59.45	0.00	0.36	38.12	0.01	0.00	98.22	2	0 00.0	00.	00.0	00.0	00.	.99	0.00	D.01 () 66.(0.00	0.00
24	0.09	0.03	0.07	0.01	0.01		0.00	0.70	98.62	0.15	0.01	99.66												
25*	0.05		0.01	0.08	0.01			0.39	90.31	10.25	0.09	101.19												
Note	* Can	neca N	1S 46.	other 8	inalvse	ss – Car	neca S)	X 50: n	numbe	r of atc	ms: 7	calaver	ite:	2 hessi	te: 3	netzit	a: 4 er	nnres	site:	5 svlva	nite: (6 Cu-6	svlvar	nite.
7 kre	nnerite	s 8 vol	vnskit	e: 9 tei	tradvm	ite: 10	Se-tetra	dvmite	11 / .e	cklidge	ite: /	2 nhase	Bi,	Ге., /	felli	Irohisi	muthi	e. 14	tellin	rantim	.vno	15 (Bi	Sh),	Ţ,
<i>16</i> (E	3i,Sb) ₂	,Te ₂ Se	; <i>17</i> k	awazu	lite; $I_{\rm c}$	8 laitak	ariite;	<i>19</i> Bi (S,Se);	20 alta	ite; 2	l claust	halit	e; 22	froht	bergite	, 23 (olora	idoite	; 24,	25 nat	ive Te	1000	(<u>)</u>

Au–Ag tellurides, and native gold. Tetradymite contains up to 4 wt.% Se. Rare rucklidgeite (PbBi₂Te₄) and tellurobismuthite (Bi₂Te₃) occur with tetradymite in both the Kochbulak and Kairagach deposits. Joseite [Bi₃Te(Se,S)] and tsumoite (Bi₃Te₂Se) occur at Kochbulak whereas sulfotsumoite [Bi₃Te₂(S,Se)] occurs at Kairagach. Kawazulite (Bi₂Te₂Se) and Sb-kawazulite [(Bi,Sb)₂Te₂Se] were observed at Kairagach in intergrowths with native tellurium. An unnamed mineral with the formula [(Bi,Sb)₂Te₃], occurs within empressite, sylvanite and tetradymite at the Kochbulak deposit. It is presumably transitional within the tellurobismuthite (Bi₂Te₃)-telluroantimony (Sb₂Te₃) isomorphic series. Other unnamed phases with the following formulas: AgBi₃Te₅, Ag₃Bi₅Te₉, and Pb₂Bi₆Te₁₁ were reported at Kochbulak by *Kovalenker* et al. (1980, 1997).

Bismuth selenides and sulfoselenides were observed only in ores from Kairagach. These minerals are guanajuatite (Bi_2Se_3), laitakarite [$Bi_4(S,Se)_3$], nevskite [Bi(Se,S)] and unnamed phases with formulae Cu $Bi_3(S,Se)_5$ and Cu₂ $Bi_{15}(S,Se)_{11}$. The following unnamed phases Bi_2SeS , Bi_3TeSe and Bi_3Te_2SeS were also reported by *Spiridonov* and *Badalov* (1983).

Lead tellurides and selenides

Altaite (PbTe) is as abundant as calaverite and hessite and occurs in both deposits in an assemblage with calaverite and native gold. Clausthalite (PbSe), as well as Se-rich galena [Pb(S,Se)] with S contents from 2.4 to 11.6 wt.% occurs at the Kairagach deposit in assemblages with famatinite-luzonite, Te-tetrahedrite, chalcopyrite, and Cu–Fe-sulfostannates. At Kochbulak, small ($<5 \mu$ m) single grains of Se-rich galena from the first ore stage were identified by EDX in an assemblage with chalcopyrite, tetrahedrite, famatinite, and goldfieldite.

Other tellurides and selenides

Coloradoite (HgTe) and frohbergite (FeTe₂) occur at both deposits but are relatively rare and spatially associated with the same minerals as altaite. Telluroantimony (Sb₂Te₃) occurs in both deposits in assemblages with calaverite, native tellurium, and Sb-kawazulite. Melonite (NiTe₂) occurs with altaite, petzite, and coloradoite only within the first ore stage at the Kochbulak deposit.

Cu tellurides vulcanite, (CuTe), rickardite (Cu₇Te₅) and weissite (Cu₅Te₃) were found in the Kochbulak deposit as intergrowths with covellite, chalcocite, and tellurite (TeO₂) and are presumably of supergene origin.

Native tellurium

Native tellurium was found at both deposits. At Kairagach, it occurs as intergrowths with tellurantimony, calaverite, Cu-sylvanite, clausthalite, and Sb-kawazulite where, in places, it is overgrown by chalcopyrite. At shallow levels, native Te contains up to 10.3 wt.% Se and up to 0.5 wt.% Sb whereas at deep levels it contains up to 0.2 wt.% Se and up to 0.7 wt.% Sb. At the Kochbulak deposit native Te occurs mostly within the first ore stage in pipe-like ore bodies where it forms

Te and Se mineralogy

crystals up to 2 cm in size and as intergrowths with empressite, sylvanite, altaite, and an unnamed phase [(Bi,Sb)₂Te₃] within the third ore stage.

Discussion

Tellurides within three ore stages at the Kochbulak deposit and the main ore stage at Kairagach precipitated in similar paragenetic sequences that can be generalized as follows: calaverite + native Te, altaite + calaverite + native gold, petzite + Bitellurides + native gold, and hessite + native gold. The observed trend of assemblages in the system Au-Ag-Te is native Au + calaverite, followed by native Au + petzite \pm hessite and, finally, native Au + hessite \pm petzite. The Ag content of native gold increases from early to late in the paragenetic sequence corresponding with the Ag content in tellurides.

As shown by *Zhang* and *Spry* (1994), the change in dominance of calaverite to hessite in the precious metal assemblage (trend 1-2-3 on Fig. 6) can be caused by an increase in the activity of Ag in solution, by an increase in pH (trend 1 on Fig. 7),



Fig. 6. Phase relationships in the system Au–Ag–Te (atomic %) observed at Kochbulak and Kairagach deposits. Mineral assemblages: (1) native tellurium \pm empressite \pm sylvanite; (2) native tellurium + krennerite; (3) calaverite + native gold; (4) hessite + petzite + native gold, (5) hessite + native gold. Arrow shows the general temporal trend for both deposits



Fig. 7. Log fO_2 versus pH diagram for the stabilities of calaverite and hessite (hatched areas), barite (dotted lines), calcite (dashed lines), and for minerals of the Fe–S–O system (dashed-dotted lines) for the following conditions: $\Sigma Au = 1$ ppb, $\Sigma Ag = 1$ ppb, $\Sigma Te = 1$ ppb, and $\Sigma S = 0.01$ m. Arrows show general temporal trends for Kochbulak (1) and for Kairagach (2). Sources of data are listed in text

or by a decrease in fO_2 (trend 2 on Fig. 7). All three processes may have taken place as tellurides formed at Kochbulak and Kairagach. At the same time, an abundance of barite and the presence of calcite within the main ore stage of Kairagach suggests that fO_2 was maintained at a relatively high level (>-35 log fO_2 units for 250 °C). Thus the evolution of telluride assemblages at Kairagach was caused by an increase in pH (trend 2 on Fig. 7 was dominant). Barite and calcite are rare in ore assemblages at Kochbulak, whereas sulfides (pyrite and chalcopyrite) are more abundant than at Kairagach and suggests that a decline in log fO_2 to -40 could have been the main factor in the changing the dominance of calaverite to hessite as the main precious metal telluride (i.e. trend 1 on Fig. 7 was dominant within each ore stage).

According to the experimental studies of *Cabri* (1965), the assemblage native Te + sylvanite at both deposits and the assemblage native Te + krennerite at Kochbulak, suggest that they formed below $335 \,^{\circ}$ C. Temperature estimates using the assemblage native Te + sylvanite + empressite cannot be made since it was not reported in the experimental studies of *Pellini* (1915), *Markham* (1960), *Cabri* (1965), and *Legendre* et al. (1980). However, *Cabri* (1965) reported that the assemblage native Te + sylvanite + stützite is stable at 290 °C, which is in good agreement with the fluid inclusion data.

Thermodynamic data for sulfides and tellurides by *Barton* and *Skinner* (1979) and *Afifi* et al. (1988) were used to calculate phase boundaries in Fig. 8. At the beginning of telluride deposition at approximately $250 \,^{\circ}$ C, $\log f S_2$ (-14.6 to -8.6) was controlled by the stability of pyrite and chalcopyrite. $\log f \text{Te}_2$ for the formation of native Te, calaverite and tellurantimony was >-7.8 (area 1 in Fig. 8a) and decreased to a minimum of approximately -11.5 log units during the deposition

Te and Se mineralogy



Fig. 8. Log fTe₂ versus log fS₂ diagrams calculated for 250 °C (a) and 150 °C (b). 1. native Te + calaverite + tellurantimony, 2. native gold + altaite and native gold + calaverite, 3. native gold + Bi tellurides, 4. native gold + Bi sulfosalts, 5–7. hessite + native gold with: 5. 10 to 32 at.% of Ag (Kairagach), 6. 28 to 35 at.% of Ag and 7. 40 to 60 at.% of Ag (Kochbulak). Arrows show general trends for Kochbulak (1) and Kairagach (2). Sources of data are listed in text

of native gold + altaite + calaverite (area 2 on Fig. 8a) and further to a minimum of -13 where the assemblage native gold + tellurobismuthite was stable.

As the temperature decreased to $150 \,^{\circ}$ C, coexisting pyrite and chalcopyrite are stable between log $fS_2 = -22.0$ and -13.6 (Fig. 8b). Since they coexist with native gold, galena and tellurobismuthite this suggests that log fTe_2 was constrained to between -18.0 and -13.6 (area 4 on Fig. 8b).

Later-formed assemblages contain native gold coexisting with hessite. Using the thermodynamic data of *Afifi* et al. (1988) and assuming that the Ag content was buffered only by fTe_2 allows fTe_2 to be determined. For native gold associated with hessite from the Kairagach deposit, Ag contents range from 10 to 28 at.% (mean 20.7 at.%), which corresponds to values of log fTe_2 that range from -18.9 to -11.6 (area 5 on Fig. 7a). At Kochbulak, the Ag content of native gold ranges from 28 to 35 at.% in the assemblage native gold + hessite + chalcopyrite and from 40.6 to 61.2 at.% for the assemblage native gold + hessite + lillianite. Values of logTe₂ range from -19.3 to 18.2, and from -22.5 to -20.1 for these assemblages, respectively. Thus, at Kochbulak the deposition of native gold and Ag tellurides was accompanied by a drop in fTe_2 of five orders of magnitude whereas fS_2 likely remained constant (trend 1 on Fig. 7a). At the Kairagach deposit, fTe_2 could have been constant or decreased slightly as fS_2 increased (trend 2 on Fig. 8a). In general, paragenetic sequence of telluride assemblages during each ore stage at both. Kochbulak and Kairagach was the result of a decrease in temperature and log fTe_2 .

At Kairagach, selenides and sulfoselenides of Bi and Pb are common, in contrast to the Kochbulak deposit, where only Bi and Pb telluroselenides and sulfotelluriselenides were formed. Despite the absence of thermodynamic data for some

O. Yu. Plotinskaya et al.



Fig. 9. Log fSe_2 versus log fTe_2 (a) and versus log fS_2 (b) diagrams calculated for 300 °C. Shaded areas show the stability fields of selenides, tellurides, and sulfides at Kochbulak (1) and Kairagach (2) deposits. Sources of data are listed in text

minerals in the systems Bi–Te–Se and Bi–S–Te, the ore forming conditions can be estimated from the stability fields of guanajuatite (Bi₂Se₃) and clausthalite (PbSe) and data from *Barton* and *Skinner* (1979) and *Simon* and *Essene* (1996) (Fig. 9a and b). Values of log $fSe_2 = -14.0$ to -6.5 and log $fTe_2 = -11.0$ to -6.2 are obtained for the Kairagach deposit at 300 °C based on the presence of guanajuatite, clausthalite and hessite (rather than naumannite). At Kochbulak, the value of log fSe_2 was <-8.5.

The values of fS_2 , fTe_2 , and fSe_2 may be reflecting multiple inputs of magmatic components into the Kochbulak ore-forming system while a magmatic contribution to the Kairagach ore-forming system is less apparent. The precipitation of sulfides, tellurides, and selenides were associated with decreasing fS_2 and fTe_2 and increasing fSe_2 conditions.

The deposition of abundant native gold of high fineness preceded telluride deposition in both deposits. Native gold has higher Ag contents where spatially associated with tellurides, as well as with lillianite at Kochbulak or fahlores and chalcopyrite at Kairagach. As noted by *Afifi* et al. (1988), in most epithermal deposits native gold usually precipitates either with or follows the deposition of tellurides. This has been observed at, for example, Golden Sunlight, Montana (*Porter* and *Ripley*, 1985), and Emperor, Fiji (*Pals* and *Spry*, 2003). However, in some high sulfidation deposits (e.g., Elshitsa and Radka deposits, Bulgaria, *Bogdanov* et al., 1997), native gold precipitated in the early quartz-pyrite stage, which is similar to that observed in the Kochbulak and Kairagach deposits. The most plausible explanation for this observation is that at the beginning of each stage of hydrothermal activity the initial fS_2/fTe_2 ratio was too high and allowed only sulfides and native gold to be deposited with the residual fluid being enriched in Te.

Conclusions

- 1. Tellurides at Kochbulak are more abundant and variable than at Kairagach but they occur in similar assemblages and three ore stages. The generalized telluridebearing sequence is: 1. altaite + Au tellurides + native Te, 2. calaverite + native gold, 3. Bi tellurides + Au-Ag tellurides + native gold, followed by 4. Ag tellurides + native gold.
- 2. The Ag content of tellurides and native gold increases from early to late in the paragenetic sequence, which corresponds to a decrease in temperature and fO_2 , and a concomitant increase in pH.
- 3. Values of log fTe_2 ranged from -13.0 to -7.8 at the beginning of telluride deposition (around 250 °C) and decreased to <-20 as the temperature declined.
- 4. The main difference in telluride and selenide assemblages between the two deposits is the presence of selenides and sulfoselenides of Bi and Pb at the Kairagach deposit which was, in part, caused by higher fSe_2 conditions compared to those observed at Kochbulak.

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