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# Sulfidation of native gold

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**ABSTRACT -** We used microscopic and electron microprobe techniques to study samples of ores containing native gold with dark rims of Au-Ag sulfides from six deposits and ore occurrences of Russia: Khopto (Au-Cu-skarn), Ulakhan, Yunoe (Au-Ag epithermal), Dorozhnoe, Konechnoe and Yakutskoe (Au-quartz). Dark rims around native gold are uytenbogaardtite ($Ag_3AuS_2$) or petrovskaite (AgAuS), or a mixture of acanthite ($Ag_2S$) with uytenbogaardtite or uytenbogaardtite with petrovskaite. In the ore samples from the Khopto and Ulakhan deposits we have found microrims of higher fineness gold at the contact of native gold and Au-Ag sulfide. The reactions of native gold sulfidation occurring in natural processes are proposed based on the compositions of Au-Ag sulfides, their mutual textural relationships. The composition of Au-Ag sulfides rims was found to depend on the primary fineness of native Au: uytenbogaardtite after medium fineness gold (electrum) (>380‰) and petrovskaite forms after high fineness gold (>650‰). We propose that the fineness of gold and silver may be used for forecasting presence of uytenbogaardtite or petrovskaite, or a mixture of acanthite with uytenbogaardtite or uytenbogaardtite with petrovskaite in the sulfide ores at Au–Ag epithermal, Au-skarn, Au-Cu volcanic-hosted massive sulfide, Au-quartz-sulfide and other deposits.

***Keywords****:* uytenbogaardtite, petrovskaite, native gold, fineness, reactions of sulfidation

## INTRODUCTION

Gold and silver in nature occur in a native state, forming a continuous Ag-Au solid solution (White et al. 1957; Yushko-Zakharova et al 1986; Morrison et al. 1991; Pal'yanova 2008; Spiridonov and Yanakieva 2009). The fineness ($N_{Au}$) equal to 1000·Au/(Au+Ag) (by weight) is used for the characterization of the composition of Au-Ag alloys or native gold and silver. Depending on the fineness (in ‰), the following native gold and silver are distinguished: "Au-

rich electrum" or "high fineness gold" (1000÷700), "electrum" (700÷250), "Ag-rich electrum" or old term as "kustelite" (250÷100) and native silver (100÷0) (Boyle 1979; Petrovskaya 1993). Silver nuggets are commonly covered with black crusts of silver sulfide - acanthite ($Ag_2S$). The study of the chemical composition of dark rims on native gold has led to the discovery of the Au-Ag sulfides - uytenbogaardtite ($Ag_3AuS_2$) (Barton et al. 1978) and petrovskaite (AgAuS) (Nesterenko et al. 1985). Mineral assemblages with these Au-Ag sulfides were found in Au–Ag epithermal, Au-skarn, Au-Cu volcanogenic massive sulfide and Au-quartz-sulfide deposits (Zhen-jie et al. 1979; Castor and Sjoberg 1993; Marcoux et al. 1993; Sheets et al. 1995; Dill 1998; Al'shevskii 2001; Greffie et al. 2002; Warmada et al. 2003; Chauvet et al. 2006; Koneev 2006; Majzlan 2009; Pal'yanova and Savva 2008; 2009; Anisimova et al. 2008; Proskurnin et al. 2011; Savva et al. 2012; Cocker et al. 2013). Au-Ag sulfides coexisting with native gold also were stricken in the gold-placer mines of northeastern Russia (Al'shevskii 2001).

Au-Ag sulfides form veinlets, isolated microinclusions and 10-100 μm rims occurring in native gold, rarely as single crystals and their aggregates 3-4 mm in size. Reaction rims are formed when two phases or assemblages that cannot coexist stably are in contact and react to produce a new phase or an assemblage along their interface (Fisher 1973). The specific chemical mechanisms of reaction rim formation are not well understood for these systems. Numerous disembodied data can be found in literature cited above on the fineness of native gold and compositions of associated Au-Ag sulfides. The concentration of gold and silver in Au-Ag sulfides, as well as in native gold, varies in a wide range (Savva and Pal'yanova 2007; Pal'yanova 2008; Pal'yanova et al 2011). The objectives of the present study are to summarize the available data on the sulfidation of native gold, to reveal compositional variations and regularities and to explain the mechanism of Au-Ag sulfide formation. Uytenbogaardtite and petrovskaite are related to rare minerals which are not so widespread. However, the formation mechanism of Au-Ag sulfides in natural conditions is important for understanding the geochemistry, transport, and deposition of noble metals. Au-Ag sulfides were found in sulfide ores of some deposits in amounts comparable to native gold, for example, Yunoe (Pal'yanova and Savva 2009), Nazareno, Pongkor (Greffie et al 2002) and Broken Hills (Cocker et al. 2013), and, therefore, their presence should be taken into account in the development of technological schemes of Au and Ag concentration and recovery.

## MATERIALS AND METHODS

We have thoroughly studied some polished sections of ore samples or mounts containing grains of native gold with dark rims of Au-Ag sulfides from 6 deposits and ore occurrences of Russia: Khopto (Au-Cu-skarn), Ulakhan, Yunoe (Au-Ag epithermal), Dorozhnoe, Konechnoe

and Yakutskoe (Au-quartz). Few grains of native gold with dark rims were found in concentrates of ore minerals that remain after washing loose rocks (from Khopto and Dorozhnoe) with water or dissolving the silicate matrix of dense ore samples (from Yunoe and Yakutskoe) with hydrofluoric acid (Neuerburg, 1961) that allowed us to keep them from mechanical damage and explore their surface. Before analysis, the surfaces of the polished sections and mounts were thoroughly cleaned. Diagnostics of Au-Ag sulfides was performed using optical microscopy, scanning electron microscopy (SEM) with energy-dispersive and wavelength-dispersive spectrometers (WDS and EDS) and X-ray diffraction (XRD) methods.

The native gold, Au-Ag sulfides and other minerals were analyzed using JSM-6510LV SEM (JEOL Ltd) combined with microanalysis system INCA Energy 350+ X-Max EDS (Oxford Instruments) and MIRA 3 LMU SEM (TESCAN Ltd) combined with microanalysis system INCA Energy 450+ on the basis of the high sensitive silicon drift detector XMax-80, and WDS INCA Wave 500 (Oxford Instruments Ltd) (Novosibirsk, IGM SB RAS). The analyses were conducted at 20 kV accelerating voltage and 1.5 nA probe current. Pure metals (Au and Ag), Au-Ag alloys and pyrite ($FeS_2$) were used as the standards. Most analyses were performed using SEM-EDS at 15-20 seconds live acquisition time of spectrum. Acquisition of spectra was performed in the raster mode with the scanning area from 0.5x0.5 $\mu m^2$, for fine phases, and to 2x2 $\mu m^2$ for larger phases with a slightly defocused electron beam. This analysis mode reduces the destructive effects of the electron beam on unstable Au-Ag sulfides. For analysis we used the characteristic X-ray S K-series and L-series of Ag and Au. Under these conditions the random error of measurement caused by the counting statistic for Au-Ag sulfide, corresponding to uytenbogaardtite in composition, was 0.17, 0.37 and 0.98 wt % for S, Ag and Au, respectively. Choice of Au L-series X-ray was due to the fact that in Au-Ag sulfides the spectra of S K-series and Au M-series partially overlapped. The INCA Energy software permits deconvolution of spectral lines but, due to the inaccurate accounting of the real lines shape, errors are possible. To rule out this sort of mistakes, we carried out testing measurement of sulfur content on WDS and EDS. The peak counting time S $K_\alpha$ was 60 sec, the background counting time was twice 30 sec, live acquisition time of ED spectra was 85 sec. The standard deviation of counting statistic was 0.19 and 0.05 wt % for S (WDS and EDS), 0.17 and 0.51 wt % for Ag and Au (EDS). For comparison we used the analyses the total of which lies in the range of 100±2 wt %. The obtained testing data showed complete agreement of the results of WDS and EDS (n=20): $S_{WDS}$ – 12.23±0.45 wt %, $S_{EDS}$ – 12.25±0.33 wt %, Ag – 31.77±1.42 wt %, Au – 55.43±1.49 wt %.

X-ray diffraction (XRD) analyses of some Au-Ag sulfides were carried out using DRON-4 (Cu $K_\alpha$-radiation, Ni-filter) (Novosibirsk, IGM SB RAS) and Bruker D-8 Discovery equipment (Cu Ka, graphite monochromator) (Novosibirsk, NSU). For the Debye-Scherrer camera

exposure, Au-Ag sulfides in the rims of polished sections were powdered under the microscope using a diamond pyramid of microdrill, with the help of which an area of 20x20 μm$^2$ was destroyed. The powder was put into a droplet of rubber which was glued to the quartz rod. The X-ray studies showed that the Au-Ag sulfides are identical in characteristics to uytenbogaardtite or petrovskaite (sheets № 20-461 or 33-0587, 19-1146, JCPDS, 1999). Figure 1 shows the diffraction pattern of Au-Ag sulfide from Khopto exhibiting characteristics to petrovskaite (sheet № 19-1146). Some weak peaks in the diffraction pattern can be interpreted as belonging to uytenbogaardtite (sheet № 33-0587) and gold (sheet № 04-0784). X-ray study of Au-Ag-sulfides from the Yakutskoe deposit was performed in (Nekrasov et al. 1988; Samusikov et al. 2002). For the Au-Ag-sulfides from the Konechnoe deposit no XRD data were obtained because of the small size of grains.

The composition of Au-Ag sulfides and native gold cited in literature was also obtained on the basis of EDS and WDS-microprobe studies. Microprobe analysis of native gold and Au-Ag sulfides revealed the presence of impurity elements such as Fe, Cu, Se and Te, but their content was less than 1 wt %, and in most cases even less than 0.5 wt % (Castor and Sjoberg 1993; Marcoux et al. 1993; Sheets et al. 1995; Greffie et al. 2002; Warmada et al. 2003; Majzlan 2009).

## RESULTS

The grain of native gold with a dark rim of Au-Ag sulfide from the Khopto deposit is shown in Figure 2a,b. Fig. 2 c-g illustrates a representative energy-dispersive (ED) spectra of petrovskaite (c) and native gold of fineness 820-880 ‰ (d) as well as the distribution of Ag (e), Au (f) and S (g) on the scanning area in characteristic rays. The considerable variations of Ag and Au concentrations in Au-Ag sulfide were established with the S concentration varying in a narrower range (Table 1). This mineral has an intermediate composition between uytenbogaardtite and petrovskaite, as it is enriched in S and Ag and is depleted in Au compared to the ideal composition of petrovskaite. It is also enriched in S and Au and is depleted in Ag compared to ideal composition of uytenbogaardtite. Previously, the higher Ag concentrations and lower Au concentrations established for a Au-Ag sulfide from the Khopto deposit were assigned to uytenbogaardtite (Gas'kov et al. 2006).

However, a higher resolution study of the grains of native gold with dark rims from the Khopto deposit under the MIRA 3 LMU SEM at magnifications of about x70000-10000 showed that they consists of several phases (Fig. 3). One of the minerals (3-5 μm thick) (Fig. 3a, grey) is close to petrovskaite (Fig. 3d), whereas another one (Fig. 3a, dark-grey) is Ag-enriched and Au-depleted and is close to uytenbogaardtite (Fig. 3c) (Table 1). In addition, there is a microrim of

higher fineness gold (930‰) on the contact between native gold (820‰) and Au-Ag sulfides (Fig. 3a,e,f). Backscattered electron images (BSE) reveal that, when in contact with petrovskaite, native gold has a higher Au content producing a brighter zone in the BSE (Fig. 3a). Line scans of the contact zone between native gold and Au-Ag sulfides show changes in the Au, Ag, and S contents, with Au-rich areas near grain boundaries with petrovskaite (Fig. 3b).

Similar to previous observations (Savva and Pal'yanova 2007) we also found microrims of higher fineness gold (660 - 720‰) on the contact between Au-Ag sulfides and native gold of fineness 350 - 370 ‰ in the Ulakhan samples (Fig. 4). Native gold in the rim has a higher Au content producing a brighter zone in the BSE (Fig. 4b-d). Au-Ag sulfides are intimately intergrown with each other (dark-grey and grey phases) and with Au of higher fineness (Fig. 4c,d). The dark-grey phase corresponds to acanthite, and the grey phase is uytenbogaardtite (Table1). Both phases are characterized by high S contents as compared to the $Ag_2S$ and $Ag_3AuS_2$ stoichiometric composition.

Detailed analysis of samples from the Yakutskoe deposit showed the absence of high fineness gold micro rim on the contact between petrovskaite and native gold (Fig.5a-c). Native gold has a fineness of 650 - 680 ‰, and the composition of Au-Ag sulfide corresponds to petrovskaite with lower Ag contents and higher Au and S contents (Table1). Figure 5d shows the concentrations of Au, Ag and S in the points of scanning in the section across native gold and Au-Ag sulfide. The variations of Au and Ag in native gold and those of Au, Ag and S in petrovskaite are minor. The compositions of native gold and petrovskaite compositions from the Yakutskoe deposit in our study agree well with earlier data (Nekrasov et al. 1988). Study of intermediate micro rims with Au of high fineness was not found on the contact between native gold with rims of Au-Ag sulfides (Table1) from the Yunoe, Dorozhnoe and Konechnoe deposits.

We analyzed the composition of native gold and Au-Ag sulfides and identified types of intergrowths of these minerals based on previously published data and our analysis. The five types of sulfide intergrowths associated with the fineness of native gold at the contact with Au-Ag sulfides for some deposits were summarized in Table 2. We distinguish the occurrences of Au as "primary" (generation I) and "secondary" gold (generation II). "Secondary" gold is present between Au-Ag sulfide and primary gold, and corresponds to late stage Au mineralization after sulfidation. In some cases, the higher fineness native gold is also considered secondary (later gold) relative to early generation gold (Castor and Sjoberg 1993; Greffie et al. 2002; Cocker et al. 2013).

The first type of intergrowths (1) is characterized by a sharp contact of one of the Au-Ag sulfides (acanthite, uytenbogaardtite or petrovskaite) with native gold. The petrovskaite rims around native gold, shown in Fig. 5a-c, are an example of type 1 intergrowths. Dark rims in type

2 are represented by thin intergrowths of two Au-Ag sulfides - acanthite with uytenbogaardtite or uytenbogaardtite with petrovskaite around the grains of native gold. This type is very common and typical of many deposits (Table 2). Types 3 and 4 differ from types 1 and 2 with high fineness Au (II) micro rims in contact with native primary gold (I) and sole Au-Ag sulfide or two Au-Ag sulfides, respectively. The third type of intergrowth relationships is typical of Lac and Original Bullfrog, Nazareno and Broken Hills (Table 2). Sharp contacts between native gold I, II and Au-Ag sulfides (acanthite and uytenbogaardtite or uytenbogaardtite and petrovskaite) (type 4) are described for the Ulakhan (Fig. 4), Khopto (Fig. 3a), Nazareno, Pongkor and other deposits (Table 2). Barton et al. (1978) and Greffie et al. (2002) showed the 5-th type of intergrowths, when acanthite is replaced by uytenbogaardtite followed by rims of native gold II and I. It is typical of the Comstock and Pongkor deposits (Table 2).

The summary on the chemical composition of acanthite, uytenbogaardtite and petrovskaite at the contact with native gold and silver in the mutual intergrowths suggests that the composition of the Au-Ag sulfides and fineness of secondary gold depends on the fineness of the primary gold. Native silver and Ag-rich electrum (0-250 ‰) is replaced by acanthite (Comstock and others), native gold of fineness 350-520 ‰ by uytenbogaardtite (Konechnoe) and high fineness gold (above 650 ‰) by petrovskaite (Yakutskoe and others) (Table 2, type 1). The native gold of fineness 360-700 ‰ is replaced by a mixture of acanthite with uytenbogaardtite (Tambang Sawah and others). The native gold of fineness 870-880 ‰ is surrounded by a mixture of uytenbogaardtite with petrovskaite (Dorozhnoe, Krutoe) (Table 2, type 1). It is established that the fineness of native gold II in the intermediate micro rims is higher than the fineness of primary gold (Table 2, types 3 and 4). So, the native gold in the rims between uytenbogaardtite and the native gold I (560-740 ‰) has higher fineness (700-870 ‰) at the Lac Bullfrog and others. The central part of the native Au grains is enriched in silver (450 ‰) compared to the intermediate micro rim (600 ‰) located at the contact with uytenbogaardtite around native primary gold and enclosed by acanthite at the Comstock deposit (type 5) (Barton et al. 1978).

The triangular diagram of the Ag-Au-S system (Fig. 6a,b) demonstrates that the Ag/Au proportion in primary gold and Au-Ag sulfides is regularly higher then secondary gold for the Khopto and Ulakhan deposits (type 4). Fig. 6c shows that the Au/Ag proportion in Au-Ag sulfides and native Au of Yakutskoe deposit is identical (type 1). The data presented in triangular and binary diagrams, showing the compositions of Ag-Au-S-minerals for other deposits (Barton et al. 1978; Greffie et al. 2002; Cocker et al. 2013), confirm that the composition of the Au-Ag sulfides and fineness of secondary gold depends on the fineness of primary gold.

## DISCUSSION

It is well known that silver is not stable in the presence of hydrogen sulfide ($H_2S_{(g)}$) and other sulfide phases even in small abundances. Under the effect of $H_2S_{(g)}$ on metal silver in the presence of atmospheric oxygen $Ag_2S$ forms by the following reaction:

$$2Ag + H_2S_{(g)} + 0.5O_{2(g)} = Ag_2S + H_2O \quad (1).$$

The appearance of a dark rims on native gold are also attributed to $Ag_2S$ (Meretukov 2008). Here, however, we also show that tarnishing of the native gold is related not only to the occurrence of silver sulfide $Ag_2S$, but also to $Ag_3AuS_2$ and AgAuS sulfides.

Reactions involving sulfides are controlled by the chemical potentials of sulfur or S-bearing components in the environment in which they occur. In geologic environments, S exists in liquid (l), solid (s) and volatile (g) phases (Simon and Ripley 2011). Sulfur in the solid state is found as native S and as the base for all sulfide and sulfate minerals. Elemental S (l or s) is abundant near hot springs, in volcanic fumaroles, in salt domes, and in evaporates. Sulfur in the gaseous state exists dominantly as $H_2S_{(g)}$ and $SO_{2(g)}$. Common oxidation states in near-surface geologic reservoirs include $S^0$, $S^{2-}$, and $S^{6+}$, where S is bonded with oxygen as sulfate $SO_4^{2-}$. The chemical potential of sulfur in geologic systems is represented by the use of the fugacity of sulfur ($fS_2$) (Garrels and Christ 1965). Formation of sulfide mineral assemblages in the current models of ore deposits genesis are usually solid-phase reactions involving gaseous sulfur (Sillitoe and Hedenquist 2003; Einaudi et al 2003; Simon and Ripley 2011 and other). For example, Barton and Toulmin (1964) express the formation of $Ag_2S$ in laboratory experiments under the effect of $S_{2(g)}$ on metal silver in the absence of other S-bearing components by the following reaction:

$$2Ag + 0.5S_{2\,(g)} = Ag_2S \quad (2).$$

Sulfidation reactions of native gold or alloy $Au_xAg_{1-x}$ ($0<x<1$, where x - atomic fraction of gold) with $S_{2(g)}$ may take place along with the precipitation of Au-Ag sulfides (Fig.7a):

$$4Ag_{1-x}Au_x + S_{2\,(g)} = 2(1-4x)Ag_2S + 4xAg_3AuS_2,\ 0<x_{Au}<0.25 \quad (3),$$

$$4Ag_{1-x}Au_x + S_{2\,(g)} = 2(1-2x)Ag_3AuS_2 + 2(4x-1)AgAuS,\ 0.25<x_{Au}<0.5 \quad (4),$$

$$4Ag_{1-x}Au_x + S_{2\,(g)} = 4(1-x)AgAuS + 2(2x-1)Au_2S,\ 0.5<x_{Au}<1 \quad (5).$$

These reactions were also proposed by Gurevich et al. (2011), when interpreting experimental data in the system Ag-Au-S. Reactions 3 and 4 explain the formation of two Au-Ag sulfides simultaneously, but do not explain the formation of intermediate microfilm of higher fineness gold observed in some natural samples. We suggest, therefore, that metastable formation of $Ag_2S$, $Ag_3AuS_2$ or AgAuS and secondary Au of high fineness are more applicable to natural processes (Fig.7b):

$$Au_xAg_{1-x} + 0.25\,(1-x)S_{2\,(g)} = 0.5(1-x)Ag_2S + xAu,\ 0<x_{Au}<1 \quad (6),$$

$$Au_xAg_{1-x} + 0.33(1-x)S_{2\,(g)} = 0.33(1-x)Ag_3AuS_2 + 0.33(4x-1)Au,\ 0.25<x_{Au}<1 \quad (7),$$

246 $$Au_xAg_{1-x} + 0.5(1-x)S_{2\,(g)} = (1-x)AgAuS + (2x-1)Au,\ 0.5<x_{Au}<1 \quad (8).$$

247 Changes in the composition of native gold and coexisting mineral assemblages are schematically
248 shown in the ternary Ag-Au-S composition diagram (Fig.7a,b). The formation of AgAuS
249 (reaction 8) or AgAuS with $Ag_3AuS_2$ (reaction 4) can occur at $0.5<x_{Au}<1$, when the fineness of
250 primary Au-Ag alloy is 650 – 999 ‰. Precipitation of $Ag_3AuS_2$ (reaction 7) and $Ag_3AuS_2$ with
251 $Ag_2S$ (reaction 3) is possible at $0.25<x_{Au}<0.5$, when the fineness of primary Au-Ag alloy is 380 –
252 650 ‰. Reaction 5 is theoretically feasible when $x_{Au} < 1$. $Ag_2S$ forms at $x_{Au} < 0.25$ along with
253 $Ag_3AuS_2$ and AgAuS. When $x_{Au}$ equal 0.25 or 0.5 (primary Au of 380 or 650 ‰ fineness),
254 reactions 7 and 8 become identical 3 and 4, because the molar ratio Ag/Au in the initial native
255 gold (0.75/0.25 = 3/1 or 0.5/0.5=1/1) corresponds to the molar ratio of Ag/Au in
256 uytenbogaardtite (3/1) or petrovskaite (1/1). Reactions 7 and 8 proceed without formation of
257 secondary gold, and reactions 3 and 4 form only one Au-Ag sulfide ($Ag_3AuS_2$ or AgAuS):

258 $$4Au_{0.25}Ag_{0.75} + S_{2\,(g)} = Ag_3AuS_2 \quad (9),$$

259 $$Au_{0.5}Ag_{0.5} + 0.25S_{2\,(g)} = 0.5AgAuS \quad (10).$$

260 Reactions of sulfidation in the Ag-Au-S system depend on temperature and sulfur fugacity
261 (Barton et al. 1978; Barton 1980; Gurevich et al. 2011). Phase equilibrium constraints on a log
262 $fS_2$ - 1 / T diagram suggest that uytenbogaardtite and petrovskaite occur at very high sulfur
263 fugacity near the phase boundary of $S_{(l)}$-$S_{(g)}$ [Barton et al. 1978; Barton 1980]. However,
264 Gurevich et al. (2011) calculated the univariant reactions 2, 9 and 10 and concluded that
265 equilibria involving petrovskaite and uytenbogaardtite do not necessarily require such elevated
266 sulfur fugacity. As for reaction 5, it does not occur in natural processes since gold sulfide is
267 metastable at ambient conditions (Barton 1980; Renders and Seward 1989). $Au_2S$ decomposed
268 into Au and S under inert atmosphere or Au and $SO_{2(g)}$ over 217°C and atmospheric conditions
269 (Ishikawa et al. 1995). A thermodynamic model for "invisible gold" as a tri-atomic surface
270 complex $Au_2S$ or $AuS_2$ dispersed in the crystalline structure of the pyrite ($FeS_2$) and arsenopyrite
271 (FeAsS) has also been developed (Yang et al. 1998; Simon et al. 1999). Gold sulfide is not
272 formed even when the gold reacts with liquid sulfur or under conditions of elevated temperature
273 and sulfur fugacity (Barton and Toulmin 1964; Pal'yanova et al 2011).

274 The formation of rims with uytenbogaardtite (Konechnoe) or petrovskaite (Yakutskoe,
275 Maikain, Broken Hills) (Table 2, type 1) is most likely the result of reactions 9 and 10 (Fig.7a,b),
276 when the composition of native gold is close or equal to $x_{Au} \approx = 0.25$ and 0.5, corresponding to
277 the fineness 380 and 650 ‰. Type 2 intergrowths, which include mixture of Au-Ag sulfides with
278 native gold (see Table 2), are formed by reactions 3 or 4 (Fig.7a). Formation of type 3
279 intergrowths with a microrim of higher fineness gold II between uytenbogaardtite and Au I (the

Lac Bullfrog, Original Bullfrog, Nazareno, Broken Hills) (Table 2) most likely is attributed to the reaction 7 (Fig.7b).

The rims of type 4 formed during the sulfidation of native gold in the Morning Star, Nazareno, Cirotan, Ulakhan and Broken Hills deposits (Table 1), are explained by the reactions 3 and 7 (Fig.7a,b). The rims of 4 type formed during the sulfidation of native gold at the Khopto are apparently the result of reactions 4 and 8. Type 5 of intergrowths are explained by the reactions 6 and 7 (Fig.7b).

Extraction of silver from Au-Ag alloy to form acanthite or uytenbogaardtite or petrovskaite would cause an increase in gold fineness. As the result of disequilibrium processes during sulfidation, a rim with higher fineness secondary gold II is formed between primary native gold I and Au-Ag sulfides by reactions 6-8 (Fig.7b). During sulfidation of native gold the appearance of Au-Ag sulfide can be accompanied by the formation of higher fineness gold, because the enrichment with gold takes place at the expense of silver spent on the formation of $Ag_3AuS_2$ or AgAuS. The corrosion-disordering/diffusion-reordering mechanism of enrichment of the surface of low fineness Au-Ag alloys due to the removal of silver is described by Rapson (1996). The dissolution of Ag atoms and inward migration of the vacancies is the result of the action of different reagents. High fineness rims are typical placer of native gold (Craig and Vaughan 1981; Petrovskaya 1993). Silver is more mobile and is carried out from the surface layer by meteoric waters (Savva and Pal'yanova 2007; Savva et al. 2010).

Thus, Au-Ag sulfides form in a wide temperature range in the presence of S-containing compounds. Reactions 1-10 are oversimplified with respect to natural reactions and can be changed by any S-containing compounds. Which of the reactions is realized, depends on the primary fineness of native gold and the sulfur forms of occurrence. The composition of Au-rich microrims will depend on the fineness of primary gold.

We analyzed the surface of native gold grains from the oxidation zone of the Dorozhnoe deposit. The grains of native gold were partially covered with dark rims of Au-Ag sulfide. Figure 8 shows the porous structure of high fineness native gold (a) and the presence of Au-Ag sulfide microcrystals (b). These data show a more intensive removal of silver and redeposition of noble metals in the form of Au-Ag sulphide. Uytenbogaardtite and petrovskaite at the Dorozhnoe deposit have a hypergene genesis, like at the Ulakhan and the Krutoe deposits (Savva and Palyanova 2007; Pal'yanova and Savva 2008; Savva et al. 2010).

The obtained results and available published data show that conditions of metastable equilibria play a significant role in the formation of uytenbogaardtite and petrovskaite. The replacement of one mineral by another encompasses most processes of nonequilibration.

The probable genesis of uytenbogaardtite and petrovskaite was discussed in a number of studies (Barton 1980; Castor and Sjoberg 1993; Marcoux et al. 1993; Sheets et al. 1995; Dill 1998; Al'shevskii 2001; Greffie et al. 2002; Warmada et al. 2003; Chauvet et al. 2006; Majzlan 2009; Pal'yanova and Savva 2008; 2009; Savva et al. 2012; Pal'yanova et al. 2012; Cocker et al. 2013 and other). Depending on the composition of mineral associations and their formation conditions, Au-Ag sulfides can be both of hypergene and hypogene origin. At the majority of deposits (for example, Ulakhan, Krutoe, Nazareno, Pongkor) they were found in the zone of oxidation together with acanthite, high fineness gold and hypergene minerals such as ferric hydroxide, jarosite, melanterite, malachite, azurite, chrysocolla, covellite, scorodite, pyrolusite, and manganite. We suggest that the formation of Au-Ag sulfides in these deposits corresponds to sulfidation of primary native gold and during oxidation of pyrite or other sulfides (galenite, sphalerite, and acanthite) by natural surface waters. In other ore deposits (for example, Cirotan, Yunoe, and other) Au-Ag sulfides were found in mineral hypogene parageneses. These minerals can form in high-temperature hydrothermal solutions enriched in $H_2S_{aq}$. Sulfidation reactions of earlier deposited native gold driven by S-bearing volcanic gases ($H_2S_g$, $SO_{2g}$) or by $H_2SO_4$-rich hydrothermal-meteoric waters have been suggested as a plausible mechanism for the formation of Au-Ag sulfides at the Kupol deposit (Savva et al 2012).

The mechanism of native gold formation from volcanic gases has been confirmed by many researchers (Symonds et al. 1990; Korzhinskii et al. 1996; Vergasova et al. 2000). Native gold and silver were found in fumaroles' fields of Russian (Kamchatka) and Mexican volcanoes (Naboko and Glavatskikh 1996; Taran et al. 2000). The presence of modern sulfurous fumaroles on the walls of craters and thermal $H_2SO_4$-rich lakes (Giggenbach 1987; Pasternack and Varekamp 1997) in craters suggests that Au–Ag sulfides can be formed at epithermal deposits during solfatara and postsolfatara processes (Savva et al 2012). At temperatures of 113-1040ºC ($T_{melt}$ - $T_{critical}$) sulfur may not only be as gas but also as liquid phase. Liquid sulfur is characterized by high reactivity (Malyshev 2004), favoring the kinetics of these reactions. Such a mechanism can be realized in a metamorphic process, when under the influence of temperature and pressure native sulfur melts and interacts with the early native gold.

Uytenbogaardtite and petrovskaite were also stricken in magmatic rocks and ores. For example, Au-Ag sulfides of $(Au,Ag,Fe)_2S$ composition were found together with the sulfides of iron, copper and nickel in carbon-bearing chondrites (Geiger and Bischoff 1995). Uytenbogaardtite in association with electrum has been found in ijolite and nepheline syenites from the Goryachegorskii massif (Sazonov et al. 2008).

Barton (1980) introduced corrections into the evaluation of sulfur fugacity by electrum-tarnish method developed by Barton and Toulmin (1964). Only acanthite was taken into account,

because the fineness of Au-Ag alloys in association with uytenbogaardtite was higher than 890 ‰ ($x_{Au}$>0.82) and petrovskaite was higher than 940 ‰ ($x_{Au}$>0.9), according to experimental and calculated results. In all natural assemblages the native gold is Ag richer than was predicted for the three phase assemblages acanthite-electrum-uytenbogaardtite and uytenbogaardtite-electrum-petrovskaite. The results obtained in our work indicate the need for further adjustments to the method of tarnishing electrum in applying it to natural processes and taking into account of non-equilibrium and the variety of ore-forming environments.

## IMPLICATIONS

Dark rims on native gold are related to the presence of Au-Ag sulfides – acanthite ($Ag_2S$), uytenbogaardtite ($Ag_3AuS_2$), petrovskaite (AgAuS) or their mixtures - acanthite with uytenbogaardtite or uytenbogaardtite with petrovskaite. Sulfidation of native gold occurs through the chain of local equilibria involving phases $Ag_2S$, $Ag_3AuS_2$, AgAuS and a secondary high fineness gold. The composition of dark films depends on the fineness of native gold: petrovskaite forms after high fineness gold (>650‰) and uytenbogaardtite after medium fineness gold (electrum >380 ‰).

The revealed dependence of composition of Au-Ag sulfides on native gold fineness has implications for the treatment of gold-sulfide ores and for understanding the origin of some unusual assemblages in nature. From the fineness of native gold one can forecast the composition of associated Au-Ag sulfide(s). The established main regularities of sulfidation of native gold may also take place in artificial Au-Ag alloys. Our estimations show that a rim of AgAuS composition forms after 18 carat gold (750 ‰), $Ag_3AuS_2$ develops after 14 – 9 carat alloys (583-375 ‰), whereas $Ag_2S$ forms after low fineness alloys and silver.

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546

547 **Figure captions:**

548 **Figure 1.** X-ray diffraction pattern showing that the Au-Ag sulfide from Khopto (1) is
549 petrovskaite (2) (sheet № 19-1146). Some weak peaks in the diffraction pattern belong to
550 uytenbogaardtite (3) (sheet № 33-0587) and gold (4) (sheet № 04-0784).

551 **Figure 2.** A rim of petrovskaite after native gold at the Khopto deposit (Tyva, Russia): a –
552 reflected light; b – BSE image; c, d – representative ED spectra of the minerals in listed points
553 shown in b; e-g - X-ray images Ag*L*α (e), Au*L*α (f) and S*K*α (g).

554 **Figure 3.** A rim of Au-Ag sulfide after native gold (820 ‰) with an intermediate micro rim of
555 higher fineness gold (920 ‰) at the contact: a – BSE image; c-f – representative ED spectra of
556 the minerals in listed points shown in a; d - graphs of EDS results (1-13 points) across native
557 gold and Au-Ag sulfides grains showing variations in the proportions of Au, Ag and S. In photo
558 a: 1–28 are the points of measurement of mineral composition.

559 **Figure 4.** Native gold and Au-Ag sulfides (acanthite, uytenbogaardtite) filling a fracture in
560 quartz at the Ulakhan deposit: a - reflected light; b - BSE image; c, d – details of the previous
561 photo showing native gold grains with a Au-Ag sulfides rim and intermediate veinlets (c) and
562 microrim (d ) of higher fineness gold (white).

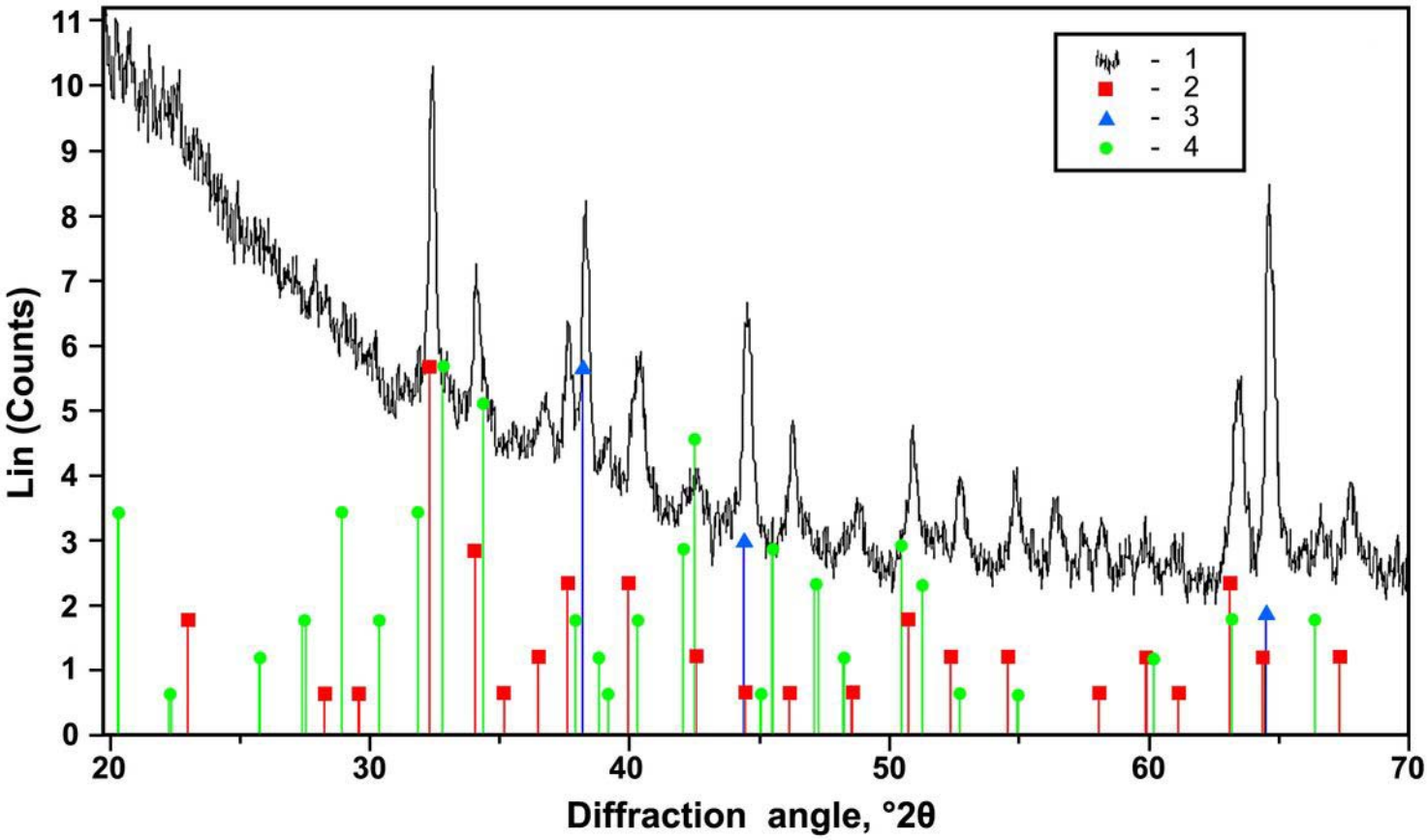
563 **Figure 5.** Rim of petrovskaite after native gold at Yakutskoe deposit (Russia): a – reflected light;
564 b – BSE image; c - BSE image fragment of grain in b (outlined by a line); d - graphs of EDS
565 results (1-10 points on c) across native gold and petrovskaite grains showing variations in the
566 proportions of Au, Ag and S.

567 **Figure 6.** The compositions (in mole fraction) of native gold and associated Au-Ag sulfide rims
568 from the Khopto (a), Ulakhan (b) and Yakutskoe (c) deposits.

569 **Figure 7.** Overview of the proposed sulfidation reactions of native gold: a - with the formation
570 of two Au-Ag sulfides, b – with formation of one of Au-Ag sulfides - $Ag_2S$, $Ag_3AuS_2$ or AgAuS
571 and higher fineness or pure gold. Numbers of reactions 2-10 correspond to numbering in the text.

572 **Figure 8.** Microcrystals of uytenbogaardtite on the dark surface of native gold (a) and porous
573 structure of native gold nearby Au-Ag sulfide (b). Dorozhnoe deposit.

574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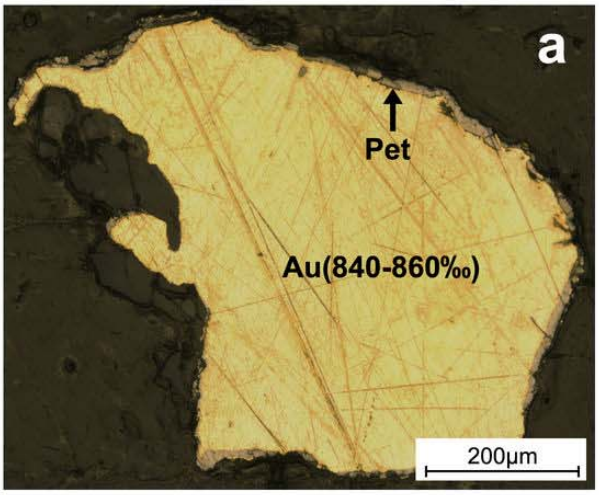
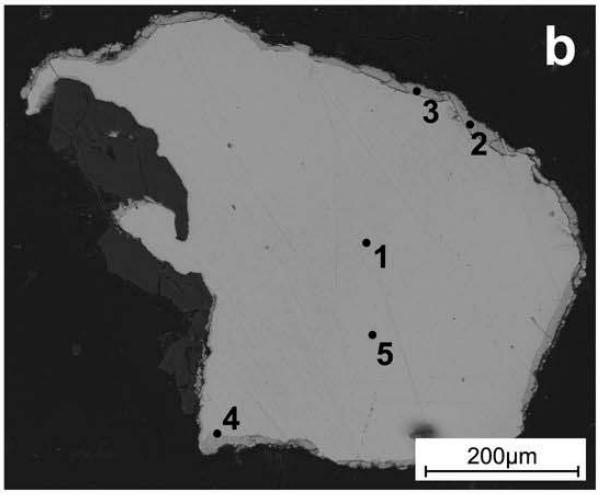
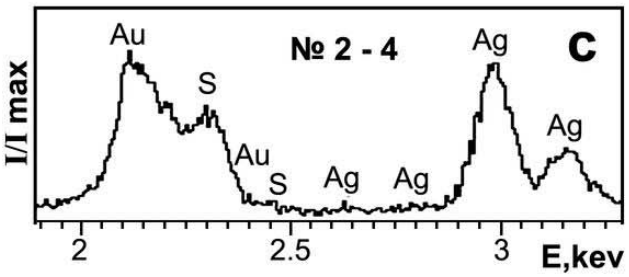
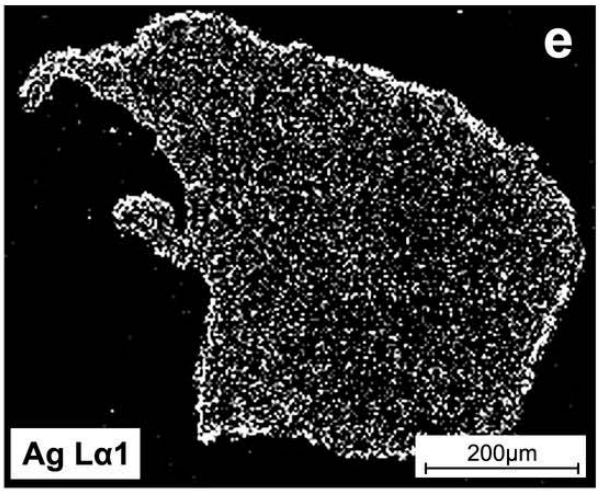
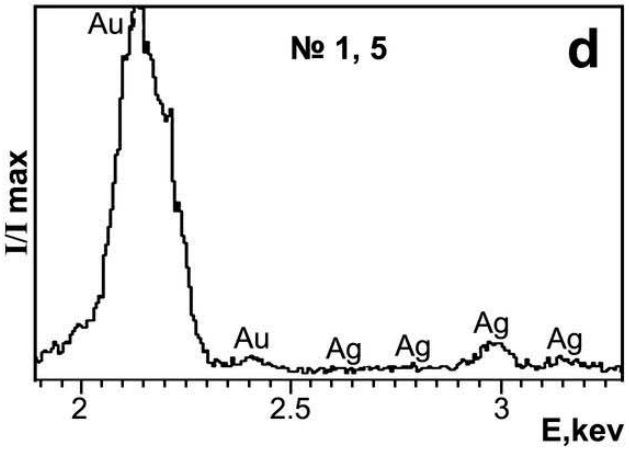
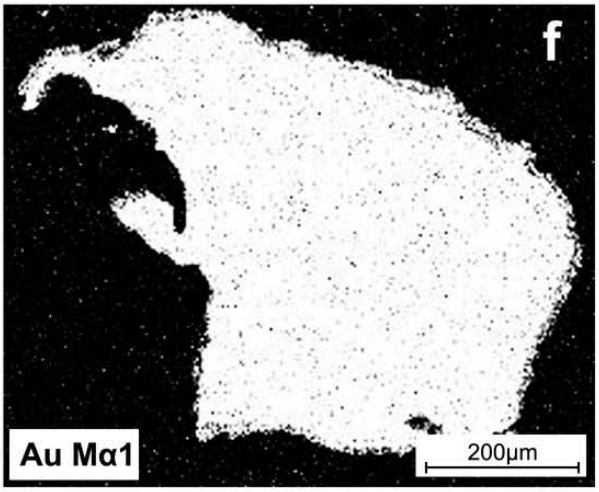


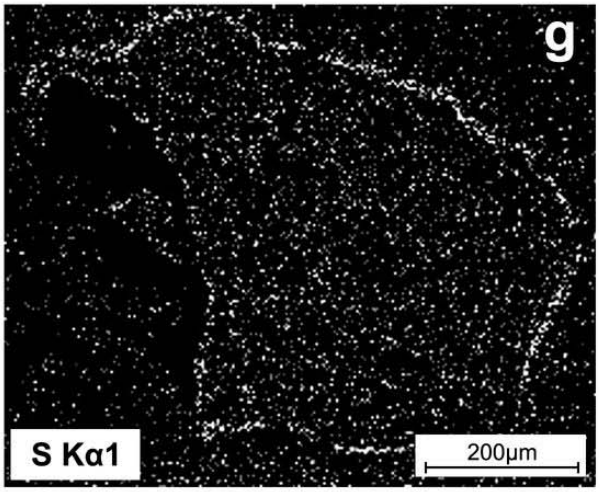



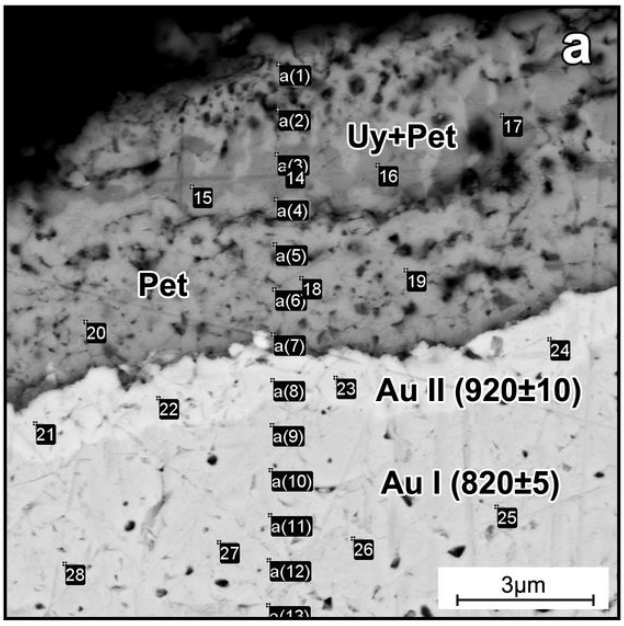



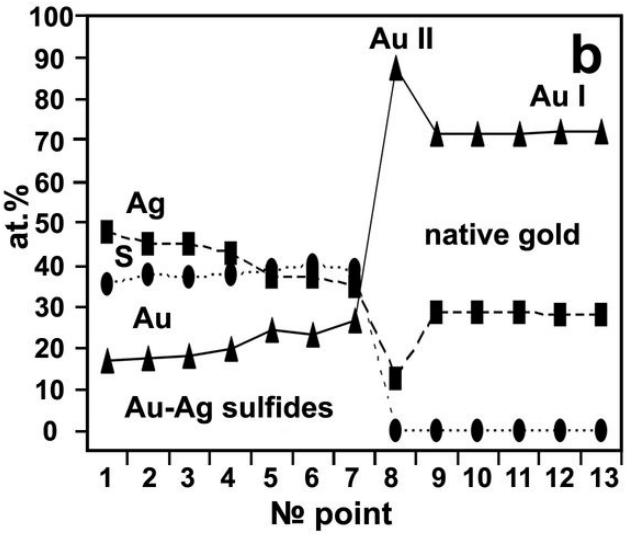



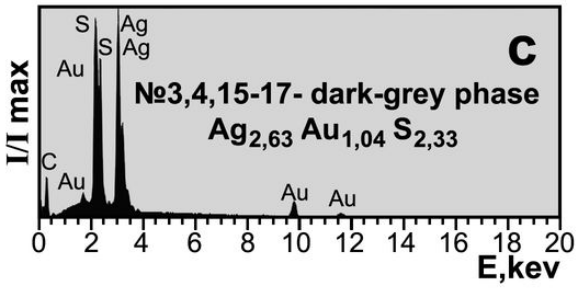



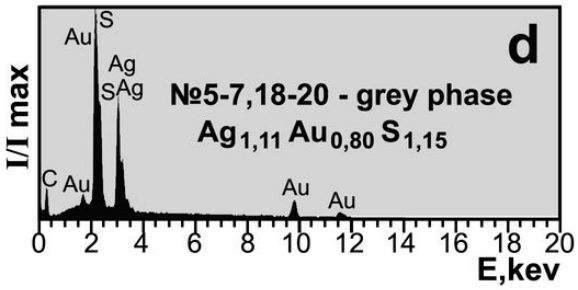



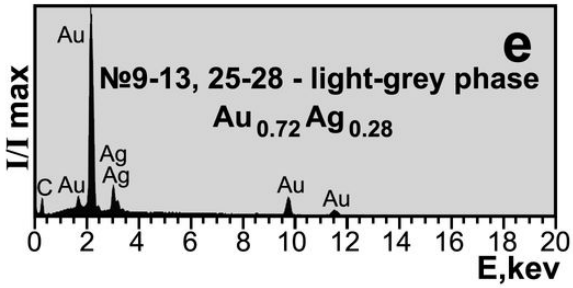



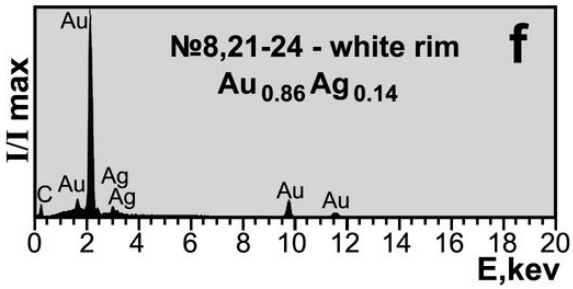

a
Uy+Pet
Pet
Au II (920±10)
Au I (820±5)
3μm


b
Au II
Au I
Ag
S
Au
native gold
Au-Ag sulfides
at.%
№ point


c
№3,4,15-17- dark-grey phase
Ag2,63 Au1,04 S2,33
I/I max
E,kev


d
№5-7,18-20 - grey phase
Ag1,11 Au0,80 S1,15
I/I max
E,kev


e
№9-13, 25-28 - light-grey phase
Au0.72 Ag0.28
I/I max
E,kev


f
№8,21-24 - white rim
Au0.86 Ag0.14
I/I max
E,kev

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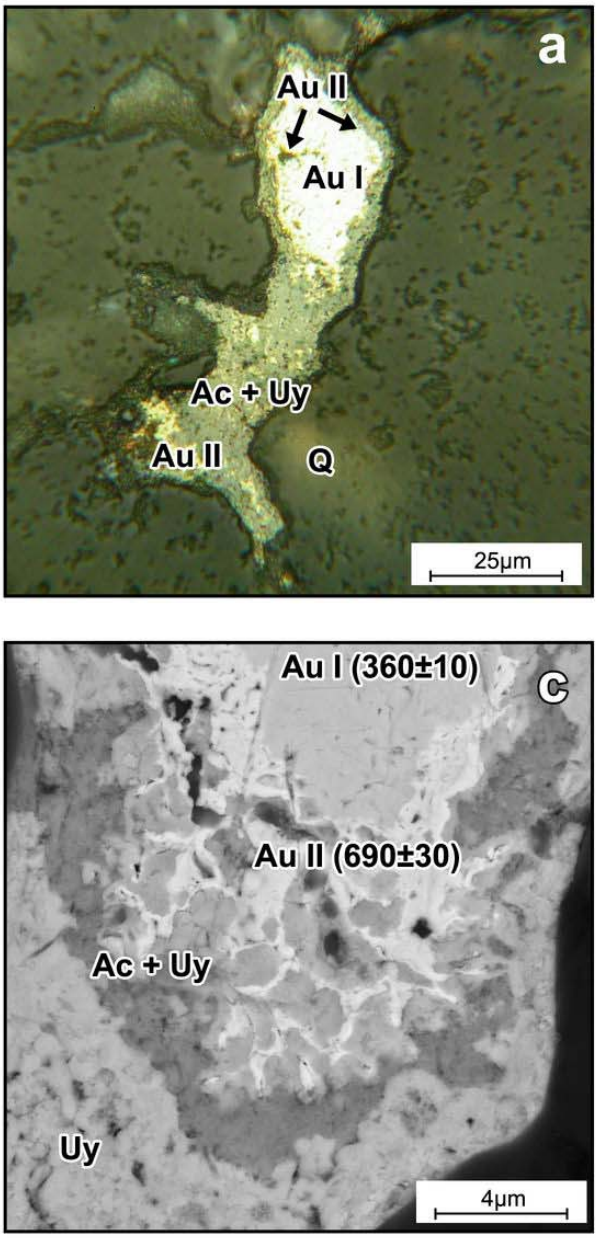
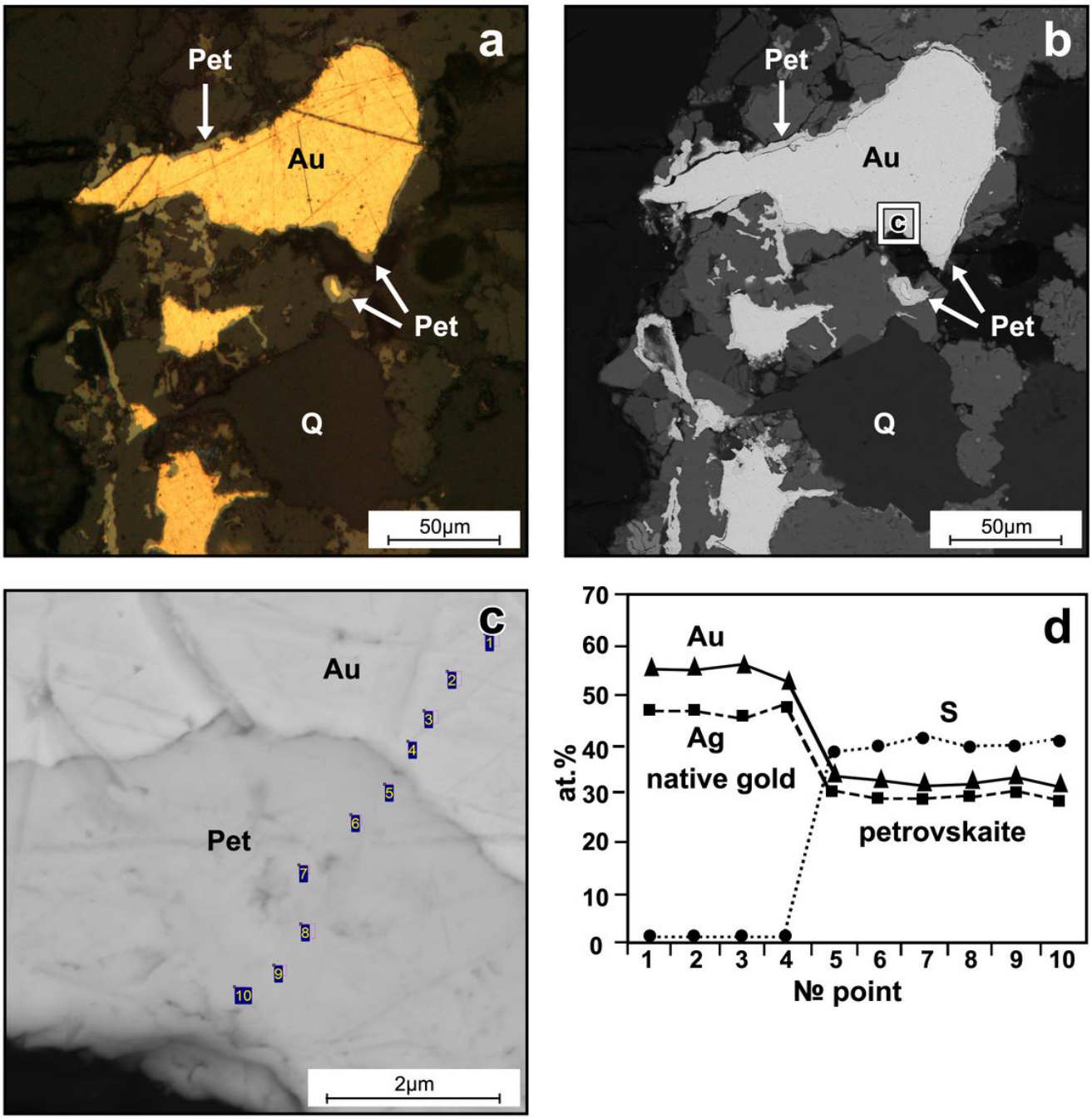
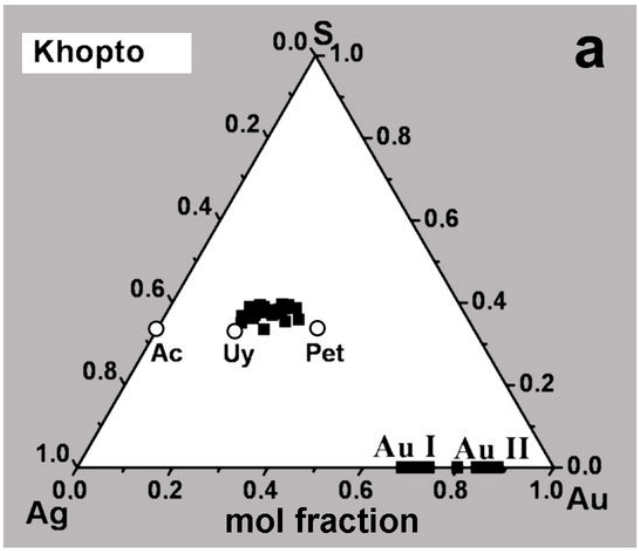
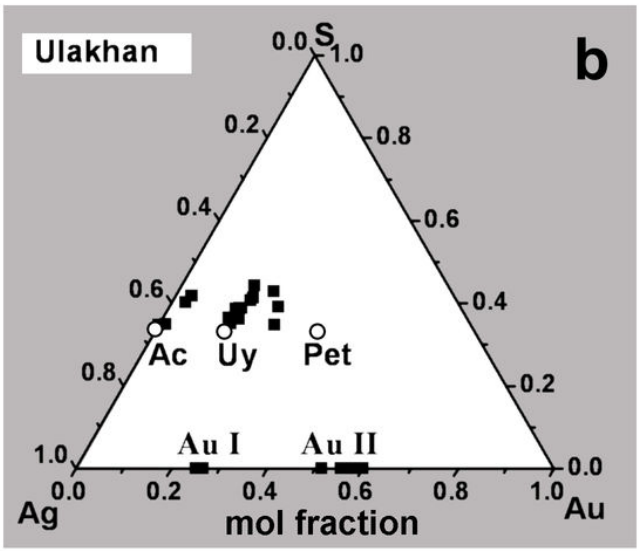
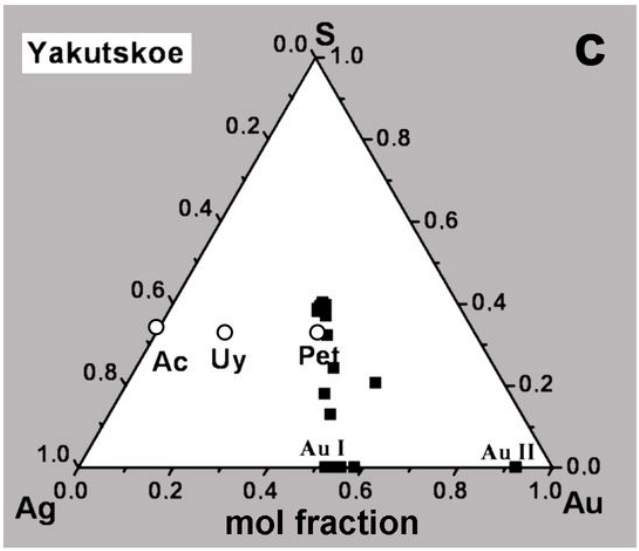



a
Pet
Au
Pet
Q
50μm
b
Pet
Au
c
Pet
Q
50μm
c
Au
Pet
1
2
3
4
5
6
7
8
9
10
2μm
d
Au
Ag
native gold
S
petrovskaite
at.%
70
60
50
40
30
20
10
0
1 2 3 4 5 6 7 8 9 10
№ point


Khopto
a
S
Ac
Uy
Pet
Au I
Au II
Ag
Au
mol fraction


Ulakhan
b
S
Ac
Uy
Pet
Au I
Au II
Ag
Au
mol fraction


Yakutskoe
c
S
Ac
Uy
Pet
Au I
Au II
Ag
Au
mol fraction

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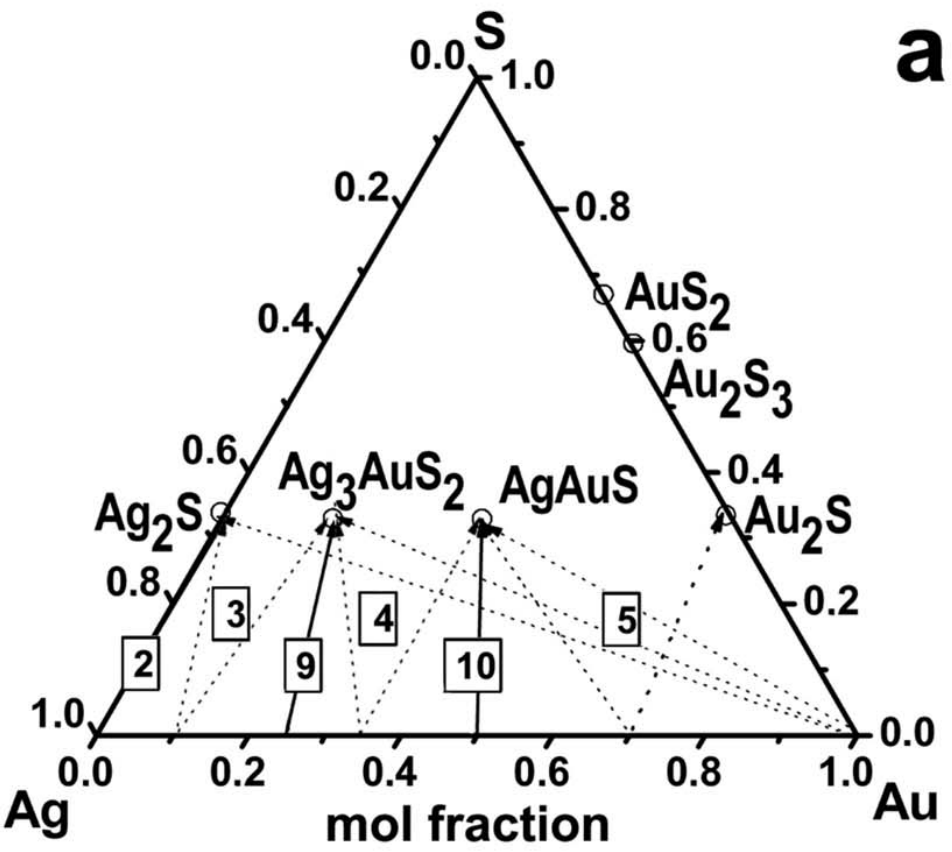


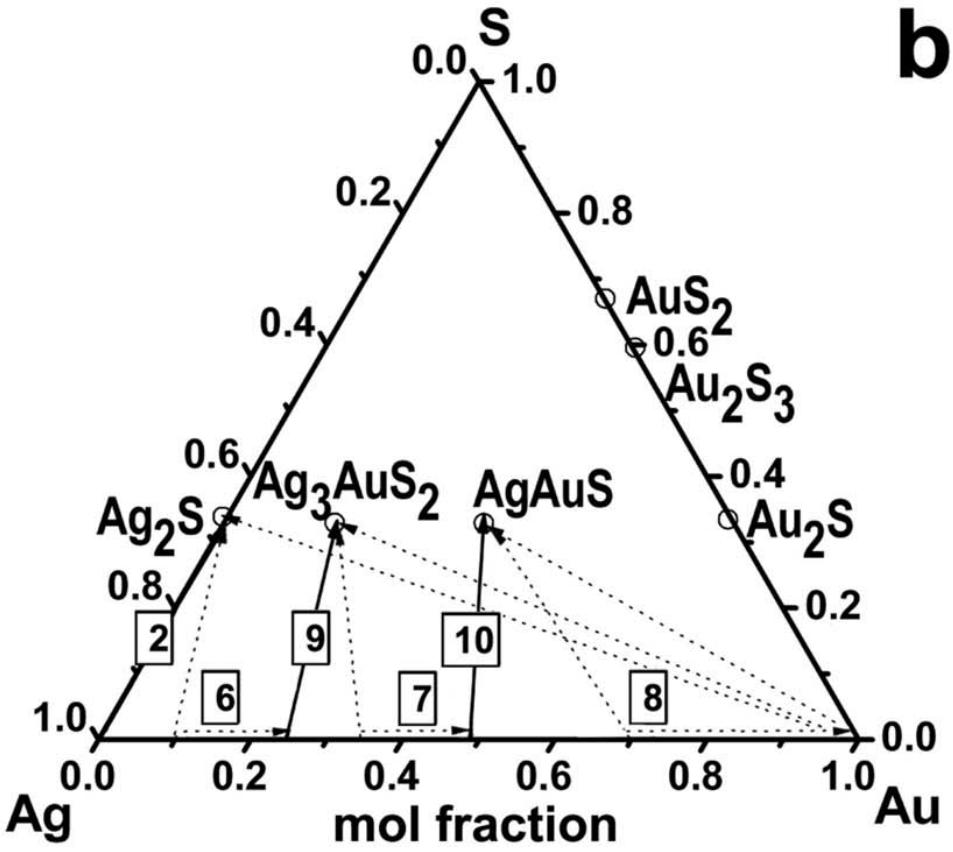

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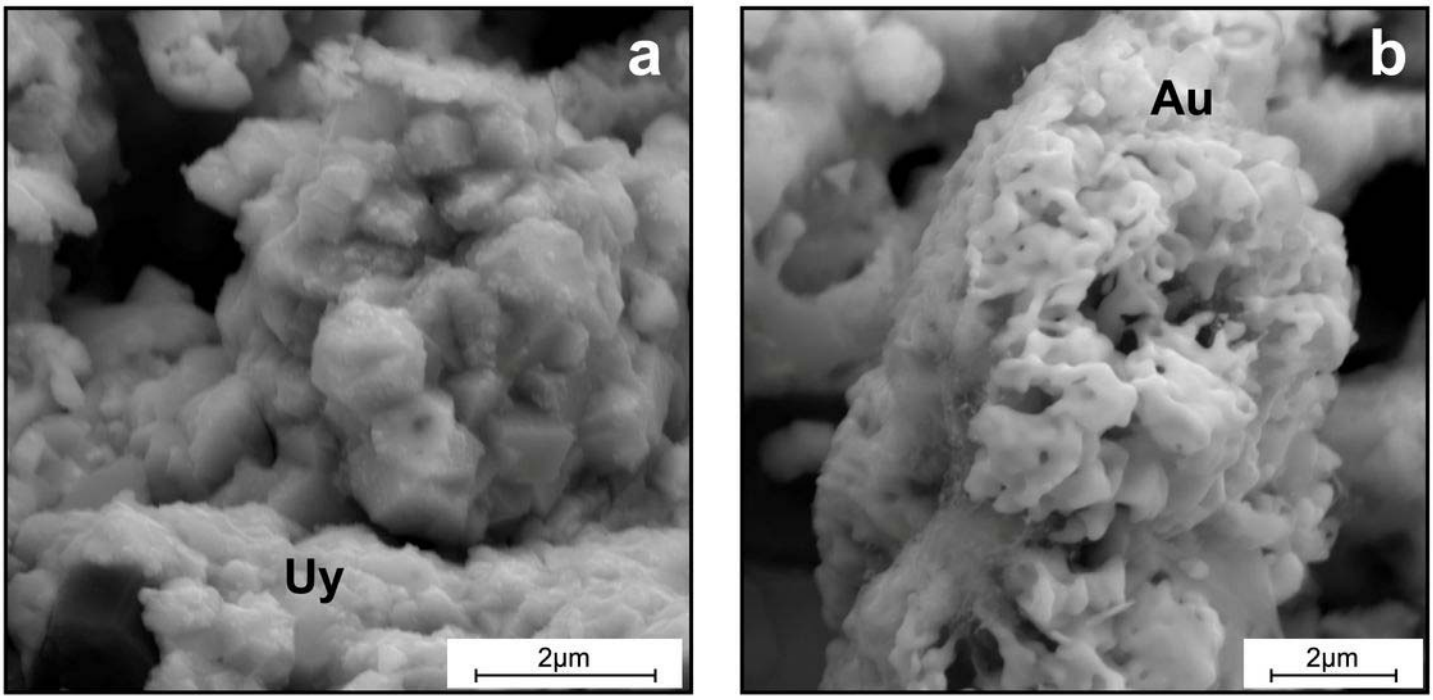

**Table 1.** Representative electron microprobe analyses of Au-Ag sulfides (in wt %)

| Deposits | n | Au | Ag | S | minerals | References |
|---|---|---|---|---|---|---|
| Khopto | 30 | 40.46÷48.56 | 40.38÷46.82 | 11.06÷12.72 | Uy+Pet | this paper |
| | 6 | 34.01÷44.00 | 43.44÷56.74 | 10.08÷11.53 | Uy | Gas'kov et al. 2006 |
| | 37 | 47.21÷51.13 | 36.22÷41.11 | 11.99÷13.04 | Pet | this paper |
| | 43 | 36.52 ÷ 39.88 | 46.55÷50.23 | 12.24÷13.22 | Uy | - " - |
| Ulakhan | 7 | 30.95÷29.72 | 57.15-58.65 | 11.90-12.75 | Uy | this paper |
| | 5 | 0 | 84.29÷85.88 | 13.49÷13.76 | Ac | - " - |
| Yakutskoe | 24 | 58.48÷59.18 | 29.19÷29.93 | 11.31÷12.29 | Pet | this paper |
| | 4 | 56.1÷60.8 | 29÷35.3 | 7.3÷7.9 | Pet | Nekrasov et al. 1988 |
| | 10 | 39.4÷51.8 | 36÷44 | 6.8÷7.4 | Pet | Samusikov et al. 2002 |
| Dorozhnoe | 7 | 30.55÷35.18 | 54.18÷57.91 | 10.46÷10.98 | Uy | this paper |
| | 11 | 49.68÷56.71 | 33.96÷42.15 | 7.78÷8.82 | Pet | - " - |
| | 3 | 48.1÷55.6 | 33.3÷40.9 | 8.3÷10.1 | Pet | Al'shevskii 2001 |
| Konechnoe | 6 | 30.53÷33.87 | 44.6÷52.74 | 12.21÷14.5 | Uy | Proskurnin et al 2010 |
| Yunoe | 15 | 23.40÷26.10 | 64.80÷66.90 | 8.50÷9.00 | Uy | Pal'yanova and Savva |
| | 8 | 0 | 84.10÷85.00 | 14.20÷14.80 | Ac | 2009; this paper |
| Ideal | | 33.69 | 55.35 | 10.97 | Uy | $Ag_3AuS_2$ |
| composition | | 58.46 | 32.02 | 9.52 | Pet | AgAuS |
| | | 0 | 87.06 | 12.94 | Ac | $Ag_2S$ |
| | | 92.47 | 0 | 7.53 | - | $Au_2S$ |

n - number of analyses, Ac – acanthite, Uy – uytenbogaardtite, Pet – petrovskaite.

**Table 2.** Types of textural relationships between native gold (silver) and acanthite, uytenbogaardtite and petrovskaite at some gold deposits, the fineness of primary and secondary native gold at the contact with Au-Ag sulfides.

| **Deposits, ore occurrences** | **Boundaries** | | **fineness, ‰** | | **References** |
|---|---|---|---|---|---|
| | | | **I** | **II** | |
| Nazareno | Ac / Ag | Type 1 | 0 | no | Greffie et al. 2002 |
| Kubaka | - « - | - « - | 0-100 | no | Savva 1995 |
| Comstock | Ac / Au | - « - | 250 | no | Barton et al. 1978 |
| Konechnoe | Uy / Au | - « - | 350-520 | no | Proskurnin et al. 2011 |
| Yakutskoe | Pet / Au | - « - | 630-670 | no | Nekrasov et al. 1988 |
| - « - | - « - | - « - | 650-680 | - « - | this paper |
| Maikain | - « - | - « - | 650-999 | no | Nesterenko et al. 1984 |
| Broken Hills | - « - | - « - | 620-670 | no | Cocker et al. 2013 |
| Tambang Sawah | Ac + Uy /Au | Type 2 | 570 | no | Barton et al. 1978 |
| Kupol | - « - | - « - | 590-690 | no | Savva et al. 2012 |
| Kubaka | - « - | - « - | 600-700 | no | Savva 1995 |
| Yunoe | - « - | - « - | 560-700 | no | this paper |
| Rabenstein | - « - | - « - | 360-610 | no | Majzlan 2009 |
| Broken Hills | - « - | - « - | 560-670 | no | Cocker et al. 2013 |
| Dorozhnoe | Uy+Pet/Au | - « - | 680-800 | no | this paper |
| Krutoe | - « - | - « - | 870-880 | no | Savva et al. 2010 |
| Lac Bullfrog | Uy/Au II/Au I | Type 3 | 650-680 | 840 | Castor and Sjoberg 1993 |
| Original Bullfrog | - « - | - « - | 570-670 | 870 | - « - |
| Nazareno | - « - | - « - | 560-740 | 700-800 | Greffie et al. 2002 |
| Broken Hills | - « - | - « - | 560-740 | 820-900 | Cocker et al. 2013 |
| Morning Star | Ac+Uy/Au II/Au I | Type 4 | 610-720 | 780-930 | Sheets et al. 1995 |
| Nazareno | - « - | - « - | 560-740 | 700-800 | Greffié et al. 2002 |
| Cirotan | - « - | - « - | 320-760 | 780-930 | Marcoux et al. 1993 |
| Ulakhan | - « - | - « - | 200-390 | 750-850 | Savva and Pal'yanova 2007 |
| - « - | - « - | - « - | 350-390 | 660-720 | this paper |
| Broken Hills | - « - | - « - | 560-570 | 620-640 | Cocker et al. 2013 |
| Khopto | Uy+Pet/Au II/Au I | - « - | 820±5 | 920±10 | this paper |
| Comstock | Ac/Uy/Au II/Au I | Type 5 | 450 | 600 | Barton et al. 1978 |
| Pongkor | Ac/Uy /Au II/Au I | - « - | 420-700 | 700-800 | Greffie et al. 2002 |

**Legend:** Au I - early generation of native gold, Au II – later generation of native gold (in microrims between Au-Ag sulfides and native gold I), Ag – native silver.