RIVER TRANSPORT – INDUCED CHANGES IN CHEMICAL COMPOSITION OF ALLUVIAL GOLD (DOCUMENTED ON LOCALITIES THE WESTERN CARPATHIANS)

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Abstract: Alluvial gold is influenced by various physical, chemical and biological factors. As type–localities for study of changes in chemical composition of alluvial gold we chose Pukanec (Central Slovakia Neovolcanic Field) and Magurka and Nižná Boca (Nízke Tatry Mts). The most distinctive are morphological and chemical changes (dissolution and precipitation), the latter is most commonly represented by the formation of gold–rich rims.

Key words: alluvial sediments, gold–rich rim, morphology

During transport in a river environment, alluvial gold is influenced by various physical, chemical and biological factors. These include: the character of primary gold, river energetics, river bed morphology, residence time, transport length, and chemical composition of river water. The significance of these factors varies with climate, weathering intensity, vegetation cover and human activities (e.g., pollution, urbanization). As a result of these processes, the characteristics of primary gold are changed. The most distinctive include morphological and chemical changes (dissolution and precipitation), the latter is most commonly represented by the formation of gold–rich rims.

Intermetallic Au–Ag alloy is unstable in oxidizing river environments and dissolution processes take place. Because Au^{+} and Au^{3+} ions are unstable in this environment, dissolved Au complexes with a variety of organic and inorganic ions (Webster 1986, Vlassopoulos & Wood 1990). The most common inorganic complexes are formed with halogenides (F^{-}, Cl^{-}, I^{-}, Br^{-}), sulfur (HS^{-}, $S_2O_3^{2-}$) and hydroxides (OH^{-}). Natural waters contain these ions in variable concentrations. Vlassopoulos & Wood (1990) state $Au(OH)(H_2O)$ to be the dominant Au–complex in the Au–S–Cl–H_2O system ($[Au] = 10^{-11}$; 2 ng/l) in a pe–pH range typical for most natural waters, whereas in waters draining weathering sulfide deposits, $Au(S_2O_3)_2^{3-}$, $AuHS^0$ and $Au(HS)_2^{-}$ are the dominant Au–species. In industrially polluted rivers, very stable complexes with CN^{-} might be of importance (Groen et al. 1990). Abundance of various functional groups in humic (HA) and fulvic (FA) acids enables them to bind Au along with other heavy metals (Wood 1996).

Gold precipitates by reduction of Au^{I} and Au^{III} to metallic gold (Au^{0}) when the solution enters an environment with lower Eh or with sufficient concentrations of reducing substances (e.g., organic matter, Fe^{2+}) (Macheski et al. 1991, Wood 1996).

Groen et al. (1990*)* stipulates three models of gold–rich rim formation:

Preferential silver dissolution – based on different solubilities of Au and Ag. The model is chemically feasible, but fails to explain how Ag atoms in the structure deeper than a few angstroms from the surface get into contact with the solution and how ions move through the labyrinth of vacancies in the structure.

Precipitation (cementation) – dissolved gold in the solution precipitates on the surface of the Au–Ag alloy, thus forming gold–rich rim.

Self–electrorefining – is a hydrometallurgical process in which an Au–Ag alloy is electrochemically dissolved with subsequent precipitation of gold on the surface of the alloy. The driving force for this process is electromotoric force (EMF) between two different metals in solution with Eh higher than that in which the alloy is stable.

As type–localities for our study we chose Pukanec (Central Slovakia Neovolcanic Field) and Magurka and Nižná Boca (Nízke Tatry Mts). All localities have sufficiently mineralogically and geochemically defined primary ore mineralizations and are drained by rivers with suitable conditions for gold deposition in their alluvial sediments.

Pukanec

The Pukanec deposit is located in the S–W part of the Štiavnica stratovolcano. Two stages of mineralization were distinguished: 1) Older Cu–porphyry with stockwork base metal mineralization (high–sulfidation type) and 2) Younger Au–Ag vein mineralization (low–sulfidation type). Primary Au–Ag mineralization is represented by electrum, which forms flake–shaped grains and wires in quartz cavities. Supergenic gold prevails at the deposit, usually located in sub–surface horizons in Au–enriched zones of tectonic breccias (Bahna & Chovan 2001).

Alluvial gold (Bahna & Chovan 1999) is typical of a diverse morphology. In the vicinity of primary occurrences, wires and dendrites prevail and aggregates of octahedral crystal are common. With increasing travel distance, flake–shaped gold becomes more abundant. The

Ag–content of alluvial gold varies between 32 to 50 wt.% (average fineness 630) and other analyzed elements do not exceed 1 wt.%.

During transport in supergene conditions, Ag is dissolved from the surface of the Au–Ag alloy thus creating a high–fineness, Au–rich rim, 10–20 μm thick (Fig.1). In case of rim disintegration, an ”uncorroded” alloy is exposed and Ag–dissolution continues towards the center of the gold particle.

Nižná Boca

The Nižná Boca deposit is located on the northern slopes of the Nízke Tatry Mts. (~ 5 km from the Čertovica saddle). The sources of alluvial gold in the Boca brook are veins of Sb–Au hydrothermal mineralization in the area of Vyšná and Nižná Boca (Smirnov 2000). The alluvial gold has a diverse morphology with dominating flakes and small nuggets of various thickness and roundness (Fig.2). The surfaces of gold particles are often porous (pores 1–5 μm in size) with scratches and dents indicating mechanical damage during transport. Ag–content of alluvial gold varies from 7 to 30.5 wt.% with no other elements exceeding 1 wt.%.

Gold–rich rim thickness varies from 1 to 20 μm and Ag–content in rims doesn't exceed 3 wt.%. Because of intense abrasion during transport, the rims are rarely preserved around the entire particle. The percentage of particles with a gold–rich rim generally increases with the transport distance.

Gold–rich rims with anomalously high Hg content (~ 22 wt.%) were rarely observed, while the core was also significantly depleted in Ag (2–6 wt.%). This phenomenon was assigned to the amalgamation process, which was used in past centuries for gold extraction.

Magurka

The Magurka Sb–Au deposit is located on the northern slopes of the Nízke Tatry Mts. Hydrothermal ore veins contain gold of two generations: 1) Older, high–fineness (950) gold associated with arsenopyrite and pyrite in quartz veins; 2) Younger, low–fineness (880) gold associated with Sb, Pb and Cu sulfides (Fig. 3).

Bakos & Chovan (1999*)* studied alluvial gold in the Lupčianka river, which drains the deposit. Alluvial gold is generally very small in size (0.X to 0.0X mm). In the vicinity of the primary source, 92 % of gold is in the < 0.2 mm fraction and the size of gold particles decreases with travel distance. Flake–shaped gold particles are prevailing, which is the result of high stream velocity and also primary gold morphology. Gold overgrown with quartz and nuggets (dendrites) are less abundant and usually found farther from the primary source, where the morphology of the valley and low stream velocity allow deposition of alluvial sediments (Fig. 4). No optical or chemical inhomogenities were observed. Ag–

content in alluvial gold is 2–3 wt.% lower compared to primary gold of both generations. The absence of gold–rich rims and lower Ag–content compared to primary gold suggests, that dissolution of Ag from gold particles is even, owing to their small size and very thin flake shape.

Conclusions

During river transport and deposition, alluvial gold undergoes morphological and chemical changes. Based on our observations: 1) Alluvial gold size generally decreases with increasing travel distance; 2) Percentage of rounded flake–shaped gold particles and gold–rich rims increases with travel distance; 3) Very fine–grained alluvial gold (Magurka) shows that Ag is depleted evenly the entire particle.

References

Bahna B. & Chovan M. 1999: Morfology and chemical composition of gold from Pukanec. *Mineralia Slov., 31, 259–262. [in Slovak]*

Bahna B. & Chovan M. 2001: Low–Sulfidation Type of Epitermal Au–Ag Mineralization near Pukanec (Central Slovakia Neogene Volcanic Fields). *GeoLines, 13, 11–17.*

Bakos & Chovan M. 1999: Genetic types of gold in the Magurka area. *Mineralia Slov., 31, 217–224. [in Slovak]*

Groen J.C., Craig J.R.. & Rimstid D. 1990: Gold–Rich Rim Formation on Electrum Grains in Placers. *Canadian Mineralogist,28, 207–228.*

Macheski L.M., Andrade O.V. & Rose A.V. 1991: Adsorption of Gold(III) Chloride and Gold(I) Thiosulphate Anions by Goethite. *Geochim. Cosmochim. Acta, 55, 769–776.*

Smirnov A. 2000: Sb–Au mineralization in the Nižna Boca area(Nízke Tatry). *Manuscript–MSc Thesis, Dpt. of Mineralogy and Petrology, Comenius University, Bratislava, 1-130. [in Slovak*]

Vlassopoulos D. & Wood A.S. 1990: Gold Speciation in Natural Waters: I. Solubility and hydrolysis reactions of gold in aqueous solution. *Geochim. Cosmochim. Acta, 54, 3–12.*

Webster J.G. 1986: The solubility of gold and silver in the system Au–Ag–S–O_2–H_2O at 25 °C and 1 atm, *Geochim. Cosmochim. Acta, 50, 1837–1845*.

Wood 1996: The role of humic substances in the transport and fixation of metals of economic interest (Au, Pt, Pd, U, V). *J. Geochem. Explor., 11, 1–31.*

Fig.1. High–fineness gold–rich rim (Pukanec)

Fig. 2. Rounded flake–shaped gold particle (Boca)

Fig. 3. Two generations of gold both in primary mineralization and alluvial sediments: A) high–fineness and B) low–fineness gold (Magurka)**at8**

Fig. 4. Changes in morphology during transport in river sediments (Magurka)

Fig. 1.

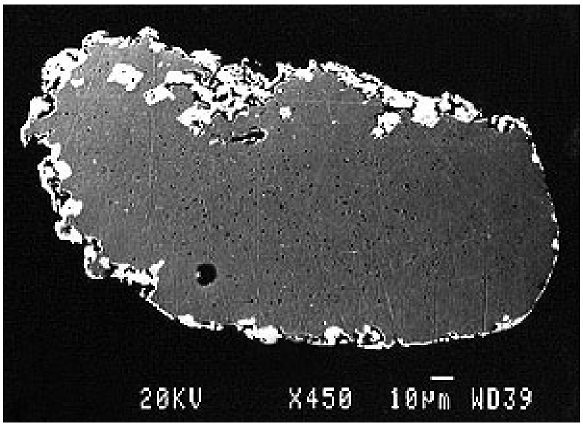

Fig. 2.

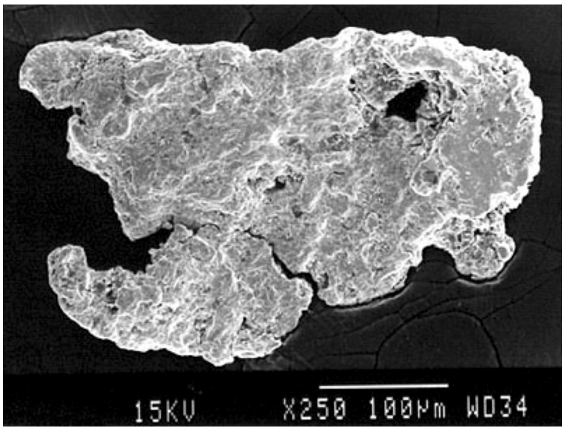

Fig. 3.

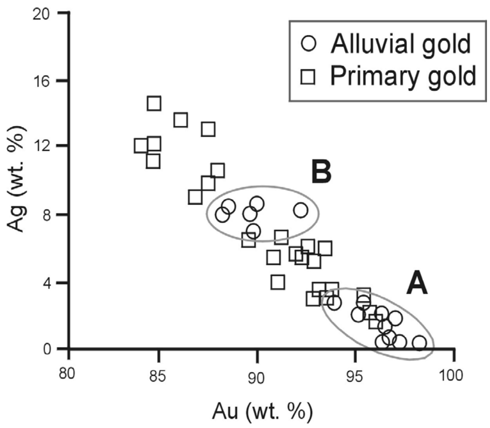

Fig. 4.