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Editorial

# Editorial for Special Issue: "Mineralogy of Noble Metals and "Invisible" Speciations of These Elements in Natural Systems"

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This Special Issue of *Minerals* covers a broad range of topics related to the mineralogy of noble metals (Au, Ag, Pt, Pd, Rh, Ru) and the forms of occurrence, formation and distribution of these elements in natural ore-forming systems. It contains eleven research articles on various problems and topics, which can be divided into four parts.

The first part of the issue includes three articles dedicated to the study of the specific features and genesis of mustard gold [1–3]. The typical features of mustard gold include low reflectivity, porous or colloform texture, and rusty, reddish, orange-red and brown-yellow colors in reflected light. The characteristics of mustard gold have been studied by many researchers [4–9], but its genesis is not fully understood and the mechanism of its formation is not completely clear. Tolstykh, Kalinin, Anisimova and coauthors [1–3] studied mustard gold from three deposits located in different regions of Russia: Kamchatka Peninsula (Maletoyvayam Ore Field) [1], Central Aldan district of Yakutia (Khokhoy ore field) [2], and Kola Peninsula (Oleninskoe Deposit) [3].

The main ore components of gold mineralization of the Gaching high-sulfidation (HS) epithermal Au–Ag deposit (part of the Maletoyvayam ore field) are native gold, tellurides, selenides, and sulphoselenotellurides of Au and oxidation products of Au-tellurides [1]. Two types of mustard gold were identified by Tolstykh et al. [1]: (a) mixtures of Fe-Sb(Te,Se,S) oxides and fine gold particles and (b) spotted and colloform gold consisting of aggregates of gold particles in a goethite/hydrogoethite matrix. This study examined different types of native gold in this ore deposit and the mechanisms and sequential transformation of calaverite ($AuTe_2$) into mustard gold.

Kalinin and coauthors [2] reported the results of the study of mustard gold from the Oleninskoe intrusion-related gold–silver Precambrian deposit of the Fennoscandian Shield. These authors showed that micropores in the mustard gold are filled with iron, antimony or thallium oxides, silver chlorides, bromides, and sulfides. They concluded that halogens (Cl, Br) played an important role in the remobilization of noble metals in the Oleninskoe deposit.

Anisimova and coauthors [3] investigated the features of native gold in karst cavities at the newly discovered Au-Te-Sb-Tl occurrence within the Khokhoy gold field of the Aldan-Stanovoy auriferous province (Aldan shield, East Russia). This was the first time the relationships between residual monolithic gold and unnamed tellurates, thallium carbonates and avicennite ($Te_2O_3$) had been described. Along with this native gold, secondary (sponge and "mustard") gold was investigated. The occurrence of monolithic, spongy and mustard gold was discussed.

The second part of the issue includes four articles on thermodynamic [10] and experimental modeling [11–13] of systems containing noble metals. Some of these articles were a continuation of the research [14,15] on the topics covered by the Special Issue "Experimental and Thermodynamic Modeling of Ore-Forming Processes in Magmatic and Hydrothermal Systems" [16].

Murzin and coauthors [10] constructed physicochemical models for the formation of magnetite–chlorite–carbonate rocks with copper–gold in the Karabash ultramafic massif (Southern Urals, Russia). These authors showed that the metasomatic interaction of metamorphic fluid with serpentinites is responsible for the gold-poor mineralization (1st type), and that the gold-rich mineralization (2nd type) was formed during the mixing of metamorphic fluid and meteoric water in the open space of cracks in serpentinites.

Sinyakova and coauthors [11] carried out the crystallization of a Fe-Cu-S melt with the impurities of Ni, Sn, As, Pt, Pd, Rh, Ru, Ag, Au, Se, Te, Bi, and Sb. The cylindrical crystallized sample consisted of monosulfide solid solution (mss), nonstoichometric isocubanite (icb), and three modifications of intermediate solid solution (iss1, iss2, iss3). The simultaneous formation of two types of liquid separated during the cooling of the parent sulfide melt was observed. Noble metals associated with Bi, Sb, and Te were concentrated in inclusions in the form of $RuS_2$, $PdTe_2$, $(Pt,Pd)Te_2$, PtRhAsS, and $Ag_2Se$, doped with Ag, Cu, and Pd, in a monosulfide solid solution. Nobel metals form $PtAs_2$, gold alloys doped with Ag, Cu, and Pd, $Ag_2Te$ and $Pd(Bi,Sb)_xTe_{1-x}$ in nonstoichometric isocubanite and intermediate solid solutions. Rhodium is present in intermediate base metal solid solutions.

The surface species formed upon the contact of the pyrite, pyrrhotite, galena, chalcopyrite and valleriite with the solutions of $H_2PtCl_6$ (pH 1.5, 20 °C) were studied using X-ray photoelectron spectroscopy by Romanchenko et al. [12]. The highest rate of Pt deposition was observed on galena and valleriite and the lowest, on pyrite and pyrrhotite. Pt(IV) chloride complexes adsorb onto the mineral surface, and then the reduction of Pt(IV) to Pt(II) and the substitution of chloride ions with sulfide groups occur, forming sulfides of Pt(II) and then Pt(IV).

Vorobyev and coauthors [13] studied the reactions and species formed at different proportions of $HAuCl_4$, $H_2Se$ and $H_2S$ at room temperature. Metal gold colloids arose at the molar ratios $H_2Se(H_2S)/HAuCl_4$ less than 2. At higher ratios, pre-nucleation "dense liquid" species followed by fractional nucleation in the interior and coagulation of disordered gold chalcogenide occurred. The reactions proceed via the non-classical mechanism involving "dense droplets" of supersaturated solution which produce $AuSe1-xS_x/Au$ nanocomposites.

The third part of the issue contains two articles on Au-bearing arsenopyrite and pyrite [17,18]. A significant number of studies are devoted to Au and other noble metals in these minerals.

Sazonov and coauthors [17] used the Mössbauer spectroscopy method to study the ligand microstructure of natural arsenopyrites from the ores of major gold deposits of the Yenisei Ridge (Eastern Siberia, Russia). The elevated gold concentrations typical of arsenopyrites occur with an elevated content of sulfur or arsenic and correlate with the increase in the occupation degree of configurations {5S1As}, {4S2As}, {1S5As}, the reduction in the share of {3S3As}, and the amount of iron in tetrahedral cavities.

Tauson and coauthors [18] studied the forms of occurrence and distribution of "invisible" noble metals (Au, Ag, Pt, Pd, Ru) in the coexisting pyrite and arsenopyrite from the Natalkinskoe, Degdekan and Zolotaya Rechka deposits (Magadan region, Russia). They used a combination of methods of local analysis and statistics of the compositions of individual single crystals of different sizes to analyze the distribution coefficients of the structural (str) and surficial (sur) forms of noble metals. The data on Ag mostly indicate its fractionation into pyrite ($D_{str}$ Py/Asp = 17). Surface enrichment was considered a universal factor in the distribution of "invisible" noble metals. A number of elements (i.e., Pt, Ru, Ag) in pyrite and arsenopyrite tended to increase in abundance with a decrease in the crystallite size. This may be due to both the phase size effect and the intracrystalline adsorption of these elements at the interblock boundaries of a dislocation. Arsenopyrite with excess As over S has a tendency to have greater abundance of Pt, Ru and Pd. Sulfur deficiency was a favorable factor for the incorporation of Ag and platinoids into the structures of the studied minerals.

The last part of the issue includes two articles [19,20] devoted to the study of ages of gold deposits in China: Nibao and Chaoyangzhai (Southeast Guizhou). These deposits are an important part of the Yunnan–Guizhou–Guangxi "Golden Triangle" region. Zheng, Tsang and coauthors [19,20] also discussed possible sources of gold mineralization.

The Nibao gold deposit includes both fault-controlled and strata-bound gold orebodies. Zheng and coauthors [19] determined the mineralization age of these gold orebodies and provided additional evidence for constraining the formation ages of low-temperature orebodies and their metallogenic distribution in South China. The results confirm the Middle-Late Yanshanian mineralizing events of the Carlin-type gold deposits in Yunnan, Guizhou, and Guangxi Provinces of Southwest China.

Tsang and coauthors [20] determined the possible source of the newly discovered medium- to large-scale turbidite-hosted Chaoyangzhai gold deposit, Southeast Guizhou, South China, using LA-ICP-MS zircon U–Pb dating, whole-rock geochemistry and in situ sulfur isotopes. Together with the evidence of similar geochemical patterns between the tuffaceous- and sandy-slates and gold- bearing quartz, these authors proposed that gold might be sourced from the sandy slates.

Overall, I hope this Special Issue will contribute to a better understanding of the genesis of gold, silver and other noble metal deposits, the behavior of these elements in endogenic and supergene environments and suggest ways forward to solve the problem of their full extraction from ores.

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