=== MINERALOGY ====

Features of the Chemical Composition of Gold Minerals from Gabbro Massifs in the Uralian Platinum Belt, Russia

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Abstract—Comparative characteristics of gold minerals from gabbro of the Uralian Platinum Belt based on the author's (Kumba massif, Serebryanskii Kamen massif, and Volkovskoe deposit) and literature (Volkovskoe deposit and Baronskoe ore occurrence) data are presented. The studied assemblages are dominated by native gold characterized by the following types: native gold without any impurities, copper gold, and copper—palladium gold. An unnamed phase with a composition similar to the Cu_2PdAu stoichiometry has been found in gabbro of the Kumba massif for the first time in the Uralian Platinum Belt and Russia. The formation conditions of all types of gold minerals identified have been evaluated.

Keywords: Uralian Platinum Belt, gabbro, copper, noble metals, native gold, gold minerals

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INTRODUCTION

The Uralian Platinum Belt (UPB) is well-known due to the mining of large and unique Pt placers, as well as numerous studies on the primary Pt mineralization in dunites ([1, 2], etc.). However, the predominant rock of the UPB is gabbro with various compositions which makes up large intrusions often spatially contiguous with ultramafic clinopyroxenite—dunite massifs [3].

Recent years have been marked by a greater interest in gabbro associated with Ural-Alaskan type massifs as a major source of copper and precious metals. Most of these studies are focused on the province of British Columbia where the Cu-precious metal mineralization in gabbro and pyroxenites was described ([4], etc.). Meanwhile, knowledge of the regularities in the precious metal mineralization in UPB gabbro remains extremely insufficient. Although many UPB gabbro massifs were revealed to be enriched in precious metals ([5], etc.), to date, minerals of gold and other precious metals have been found only in the ores at the

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Volkovskoe deposit [6] and in the Baronskoe ore occurrence [7] related to the Volkovskii massif.

As a result of systematic research, precious metal minerals were first discovered in sulfide Cu ores and mineralized zones of two more large gabbro massifs making up the UPB structure such as the Serebryanskii Kamen [8] and Kumba massifs. Commercial concentrations of Cu and precious metals were identified in the Kumba massif for the first time.

Our research is focused on native gold from gabbro of the Kumba and Serebryanskii Kamen massifs, as well as the Volkovskoe deposit (author's data) and Baronskoe ore occurrence (literature data). The research objective is to conduct a comparative description of the native gold composition in UPB gabbro massifs based on results obtained for the first time. These data will complement the earlier reviews of gold minerals ([9], etc.).

SAMPLING AND METHODOLOGY

The studied gabbro massifs making up the UPB (Fig. 1) are located in the Northern (Serebryanskii Kamen and Kumba massifs) and Middle (Volkovskii gabbro-diorite massif) Urals. The Serebryanskii Kamen massif forming the Kytlym pluton is composed mainly of amphibole gabbro, where the precious metal mineralization is associated with the bornite-chalcopyrite dissemination [8]. The Kumba massif is an intrusive body with a complex polyphase structure that resulted from various intrusions [9]. In

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Fig. 1. Position of the gabbro massifs studied in the UPB structure [10].

this massif, samples were taken from olivine gabbro of Mount Bolshaya Bruskovaya and amphibole gabbro of Mount Zolotoi Kamen. The local precious metal mineralization is related to the bornite-chalcopyrite and bornite-digenite dissemination. The superimposed pyrite-chalcopyrite mineralization also developed within Mount Zolotoi Kamen.

The copper-titanomagnetite samples from taxite olivine-bearing gabbro were the main object of investigation at the Volkovskoe deposit. We used the results obtained by the precursors in the course of study of copper-titanomagnetite and apatite-titanomagnetite ores from olivine gabbro [11]. The material characteristics obtained earlier of the Baronskoe ore [1] occurrence were used to provide the widest coverage of copper-precious metal mineralization in the UPB massifs for comparative purposes.

The precious metal mineralization in sulfide copper ores in gabbro was described using chip samples of 20-50 kg in weight taken from the zones with a visible sulfide dissemination. The ore mineral concentrates were obtained from the samples, including the concentrates with native gold, by crushing them to a particle size of 1.0 mm and subsequent gravitational enrichment.

The morphological features and chemical composition of native gold were determined using a JSM-6390LV scanning electron microscope (JEOL) with an energy dispersive spectrometer (Geoanalitik Central Center for Collective Use, Zavaritsky Institute of Geology and Geochemistry, Ural Branch, Russian Academy Sciences, Yekaterinburg, analysts L.V. Leonova and N.S. Chebykin); the mineral composition was determined using a Cameca SX100 electron probe microanalyzer (Geoanalitik Central Collective Use Center, Zavaritsky Institute of Geology and Geochemistry, Ural Branch, Russian Academy Sciences, Yekaterinburg, analyst I.A. Gottman). The samples studied are mainly native gold with Ag, Cu, and Pd impurities in different proportions. The accurate diagnosis of mineral species in the Au–Pd–Cu system requires systematic crystallographic instrumental studies, which will definitely be carried out in the future. To avoid uncertainty in the diagnosis of individual mineral species, as well as intermetallic compounds and alloys under the study of the Au(Ag)– Pd–Cu system, the following nomenclature is used in the paper: native gold (Au–Ag alloy), Cu gold (gold containing Cu impurities), and Cu–Pd gold (gold with Cu and Pd impurities).

STUDY RESULTS

Native gold from the Kumba gabbro forms individual grains of up to 150 µm in size (Fig. 2a) and is also intergrown with rock-forming silicates, chalcopyrite, bornite, and Pd and Pt sulfides and tellurides. The gold grains are mostly homogeneous, sometimes with large zones enriched in impurity components (Fig. 2d). The gold composition varies over a very wide range (Fig. 3a), differing in the contents of both Ag (from 0.6 to 61 wt %) and Cu (up to 5.8 wt %). Meanwhile, about half of the analyzed gold grains do not contain Cu impurities. In addition to native gold with a Cu impurity, the studied mineral assemblage contains Au–Cu–Pd alloys with various compositions (Table 1). Among them, Pd gold with up to 5 wt % Pd and 2– 3 wt % Cu is widespread. Unnamed phases $Cu_{0.54}Au_{0.29}Pd_{0.17}$ and $Cu_{0.45}Pd_{0.42}Au_{0.07}$ and other composition variations were found. Such alloys are



Fig. 2. SEM BSE photo images of native gold from gabbro of (a-d) Kumba and (e-f) Serebryanskii Kamen massifs. (Au I) Native gold without Pd impurity, (Kt) kotulskite, (Au II) Cu–Pd gold, (Pl) plagioclase, (Cpr) cuprite, and (Bn) bornite.

similar to Cu(Pd,Au) or Cu₂PdAu stoichiometry with variable Pd from 1.3 to 49.3 wt %, while forming an almost continuous range with relatively constant Cu (Fig. 3b) and occurring within the tetraauricupride (AuCu)–skaergaardite (PdCu) solid solution range.

Another distinguishing feature of these alloys is the complete absence of Ag impurities, while the Ag content in Cu–Pd gold varies within a fairly wide range.

Native gold in the Serebryanskii Kamen gabbro occurs as inclusions in Pd minerals or in intergrowths

No.	Cu	Ag	Pd	Au	Total	Formula
1	_	12.37	_	87.46	99.83	Au _{79.47} Ag _{20.53}
2	0.95	11.01	_	87.29	99.25	Au _{79.11} Ag _{18.22} Cu _{2.67}
3	—	0.69	—	99.18	99.87	Au _{98.75} Ag _{1.25}
4	0.46	61.71	—	37.64	99.81	Ag _{74.26} Au _{24.80} Cu _{0.94}
5*	33.1	—	45.32	19.33	99.96	$Cu_{48.03}Pd_{39.27}Au_{9.05}Fe_{3.65}$
6	29.21	—	10.11	60.4	99.72	Cu _{53.37} Au _{35.60} Pd _{11.03}
7	25.23	—	1.38	72.1	98.71	Cu _{51.16} Au _{47.17} Pd _{1.67}
8	0.86	13.94	—	85.31	100.11	Au _{75.21} Ag _{22.44} Cu _{2.35}
9	2.47	28.32	—	69.15	99.94	Au _{53.81} Ag _{40.24} Cu _{5.96}
10	1.82	6.07	—	92.10	99.99	Au _{84.63} Ag _{10.18} Cu _{5.18}
11	9.45	8.29	—	80.68	98.42	$Au_{64.49}Cu_{23.41}Ag_{12.10}$
12		27.89		72.03	99.92	Au _{58.58} Ag _{41.42}
13	7.19	1.85	11.62	78.58	99.24	Au _{62.49} Cu _{17.72} Pd _{17.11} Ag _{2.69}

Table 1. Composition of different types of gold from gabbro of (1-7) Kumba massif, (8-9) Volkovskoe deposit, and (10-13) Serebryanskii Kamen massif, wt %

(*) Fe content 2.21, wt %. The formulas are 100% calculated.

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Fig. 3. Compositions of (a, b) native gold and Au–Ag–Cu–Pd alloys in atomic percent and in mass percent against the background of the liquidus surfaces of (c) Au–Ag–Cu and (d) Au–Pd–Cu alloy systems [11]. Asterisks mark the positions of intermetallic compounds, tetraauricupride (AuCu), and skaergaardite (PdCu). Grains taken from gabbro: (1) Kumba massif, (2) Serebryanskii Kamen massif, (3) Volkovskoe deposit (author's data), (4) Volkovskoe deposit [6], (5) Baronskoe ore occurrence [7].

with them. More rarely, this mineral is observed as individual, mostly homogeneous grains [8]. The chemical composition of native gold is highly variable (Fig. 3). Among all varieties of this mineral, three types were identified according to the chemical composition: native gold without Cu impurities, Cu gold with 9.4 wt % Cu, and Cu–Pd gold. Cu–Pd gold is very rare in Serebryanskii Kamen gabbro (only two grains were found). Pd can reach 12.6 wt %, and Cu is 4.7 wt % in it. Native gold is associated with rockforming silicates and Cu sulfides, while Cu–Pd gold is intergrown with Pd sulfides and tellurides.

Native gold in the copper ores at the Volkovskoe deposit occurs as inclusions of up to 15 μ m in size in

chalcopyrite and bornite or as small veinlets in sulfides [11]. The chemical composition of this mineral from the Volkovskoe ores is characterized by low Pd (up to 0.3 wt %), despite its paragenetic coexistence with merenskyite, the most common Pd mineral in copper sulfide ores at the deposit [10]. In titanomagnetite ores, gold prevails over other precious metal minerals and forms two generations: inclusions of pure native gold with a fineness of 1000‰ (up to 10 µm) in magnetite and fine native gold grains (850–860‰) in association with keithconnite (Pd_{3-x}Te) and chlorite.

The Baronskoe ore occurrence is characterized by two stable assemblages of precious metal minerals such as sulfide and arsenoantimonide assemblages [7]. Gold minerals are dominated by Cu–Pd gold which occurs in both assemblages. In most cases, it forms small homogeneous inclusions in Pd minerals and is intergrown with them [12]. There are also individual gold grains with a lower Pd content usually in the silicate matrix. Native gold without impurities is associated with low-temperature silicates such as chlorite and garnet [12]. There are also individual grains of high-grade Pd–Cu gold.

DISCUSSION

The concentration and distribution of precious metals in the Ural-Alaskan type gabbro massifs ([4], etc.) make it possible to conclude that gold minerals should be major in the assemblage of precious metal minerals. The distribution of precious metals in the UPB gabbro [5, 13, 14] is also indicative of the important role of gold minerals among the assemblages of precious metal minerals. This regularity was confirmed earlier by the mineralogical studies of the ores at the Volkovskoe deposit and the Baronskoe ore occurrence. Based on the new results, a wide distribution of native gold in the assemblage of precious metal minerals was found for gabbro of Kumba and Serebryanskii Kamen massifs. These facts confirm the assumption of a wide distribution of native gold in bornite-chalcopyrite ores in gabbro of the dunite-clinopyroxenite-gabbro system. Hence, it becomes possible to re-estimate the metallogenic load of these island-arc plutonic structures which are widespread both within the Ural region and in many other fold systems [15].

Based on the chemical composition variations, several types of native gold can be distinguished: gold without Cu impurity, Cu gold, and Cu–Pd gold. Other elements, such as Fe, Te, and Hg, are impurities with a content of no more than 1-2 wt %, which are extremely limited in distribution. The identified native gold types are dominated by Cu gold. The highest Cu is typical for gold from the Serebryanskii Kamen gabbro (Fig. 3). Cu-free native gold is most characteristic of the Kumba massif. Gold inclusions in magnetite found in the Volkovskoe ores are characterized by the highest fineness [6].

In addition to Cu, native gold often contains Pd as an isomorphic impurity forming Cu–Pd gold. Such minerals are widespread in most assemblages we study. The only exception is the Volkovskoe ore where Pd does not exceed 0.3 wt % [6]. Earlier, Pd gold with up to 20 wt % Pd was described in the literature [16]. However, the Cu–Au–Pd alloys with 49 wt % Pd were found among the precious metal minerals from the Kumba gabbro in the course of our studies. Such compounds have not been described earlier. These phases occurred as independent grains or in association with platinoid chalcogenides. These compounds are the most similar to an unnamed phase with the Cu₂PdAu stoichiometry found in river sediments overlying the Bushveld complex in South Africa [17]. On the other hand, V.D. Beghizov identified Pd tetraauricupride with 18.9 wt % Pd in dunites of the Nizhnii Tagil massif [18]. This fact makes it possible to assign the grains we identified to the tetraauricupride—palladic tetraauricupride solid solution with this range continued almost to skaergaardite.

The chemical composition of native gold in the UPB gabbro makes it possible to assume three main varieties of this mineral likely formed under different conditions. The Te activity and concentration in mineral-forming systems became a controlling factor in the formation of Pd varieties of native gold. According to Murzin et al. [6], the earliest Cu sulfides in the Volkovskoe gabbro were crystallized under high Te fugacity conditions. This suggestion explains the predominance of merenskyite (PdTe₂) in the mineral assemblage among the PGEs. Thus, at high Te fugacity and sufficient Te concentrations in the ores of the Volkovskii massif, all of the Pd was bound in the telluride form, while native gold was devoid of Pd impurities.

In addition to merenskyite, other Pd minerals are also widespread under a wide range of conditions in sulfide copper ores from Kumba and Serebryanskii Kamen gabbro [8]. This fact demonstrates a wider range of crystallization conditions for precious metal minerals in this gabbro in comparison with the Volkovskoe deposit. It can be assumed that the Te fugacity and/or concentration in the Kumba and Serebryanskii Kamen ore-forming systems were insufficient for the formation of a precious metal assemblage dominated by merenskyite. For this reason, Pd was included in the Cu-Pd-Au alloy at the early development stage of the ore-forming system. With a further drop in temperature, the chalcogenide fugacity increased. It led to the crystallization of vysotskite, melonite, kotulskite, etc., and the following depletion of the sulfide melt in Pd, formation of Cu–Pd gold, and then native gold devoid of Pd impurities, but characterized by higher Cu. In general, the evolution of the ore-forming system, according to the study of the Serebryanskii Kamen gabbro, is reduced to the supersaturation of sulfide copper melts with Cu as the temperature decreases and to the transition from bornitechalcopyrite sulfide to the later digenite-bornite assemblage [8]. A similar Cu trend was revealed for the ore-forming systems of the Polaris and Tulamin massifs located in British Columbia [19].

The latest native gold devoid of Pd and Cu impurities is noted for the Baronskoe ore occurrence, where its grains are associated with rock-forming silicates without any apparent connection with platinoid chalcogenides [7]. Similar native gold containing only an Ag impurity is noted in the Kumba pyrite—chalcopyrite mineralized zones. The joint occurrence of this native gold type in association with late low-temperature silicate minerals, as well as with pyrite, can be indicative of the fact that it was formed in the course of the late hydrothermal-metasomatic or metamorphic processes not directly related to the evolution of the gabbroid melt.

The wide range of structural and material patterns found, such as the intergrowth of native gold and its chemical varieties with rock-forming gabbro minerals hosting mineralization, structural and textural features of the ores, homogeneous Cu gold grains, etc., is indicative of the fact that the Cu-precious metal mineralization was formed in the course of the magmatic process. This suggestion is confirmed by the latest studies of the Ural-Alaskan type massifs in British Columbia [18]. Taking this model into account and based on the chemical composition of gold varieties, we can approximately estimate the liquidus temperatures in the Au(Ag)–Cu–Pd system. Judging from the liquidus surface diagrams of Au-Cu-Ag and Au-Cu-Pd alloys (Figs. 3c-3d) [11], the liquidus temperatures of all studied samples of native gold are in the range of 1250–1000°C. In this case, the liquidus temperature for the total native gold, Cu gold, and Cu–Pd gold is within the range from 1050 to 1000°C. The liquidus temperature range of greater than 1050°C includes Au–Pd–Cu samples enriched in Pd (Fig. 3d) in the Kumba gabbro and a few samples from Serebryanskii Kamen and Baronskoe gabbro also enriched in Pd. We are aware of the fact that the liquidus temperature calculations obtained experimentally for a system of pure metals are loosely based on the natural mineral-forming systems. However, the general trend of decreasing minerogenic temperature from high-Pd varieties of native gold to Au–Ag alloys can be used in genetic interpretations, given the igneous origin of most Cu-precious metal mineralization in the UPB gabbro. The location of composition points on the diagram (Fig. 3d) confirms a regular decrease in the Pd concentration in native gold due to a decrease in temperature in the mineral-forming system up to the formation of native gold without Pd impurities.

CONCLUSION

In gabbro of the Uralian Platinum Belt, gold minerals are absolutely dominated by Au(Ag)–Cu–Pd alloys. In the course of this study, we found native gold without any impurities, Cu gold, and Cu–Pd gold, as well as unnamed phases with a composition similar to the Cu₂PdAu stoichiometry earlier not described for UPB and Russia and likely referred to intermediate phases of the tetraauricupride–skaergaardirite solid solution. Given the orthomagmatic origin of a substantial part of the copper–precious metal mineralization in the UPB gabbro, the liquidus temperatures for gold are estimated at $1250-1000^{\circ}$ C, although this interval is narrower ($1050-1000^{\circ}$ C) for most native gold, Cu gold, and Cu–Pd gold.

An important result of this study is the discovery of native gold not only in the ores at the Volkovskoe deposit, but also in virtually all large gabbro massifs making up a substantial part of the Uralian Platinum Belt. The precious metal accumulation trend revealed in these rocks makes it possible to assess the commercial ore potential of gabbro intrusions as promising Cu, Au, and Pd sources at a new level. Hence, it is possible that the near future will be marked by the discovery of large ore objects with Cu-precious metal mineralization in the UPB structure and by considerable changes in the Ural mineral resource base.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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