Mineralogy and Geochemistry of Metal-Bearing Formations Associated with the Sikhote-Alin Ultrabasites (Primorye)

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Abstract. A new promising type of multimetal ores and placers, spatially and genetically associated with the intrusion of the ultrabasites of the Sikhote-Alin orogenic belt has been discovered. The features of mineralogy and geochemistry of ore-placer occurrences of gold-ilmenite and gold-antimonite ores belonging to the Ariadnoye massif of ultrabasic rocks have been studied. The composition of the major industrial (economic) minerals has been revealed, the complex of associated high-technology metals being determined. The obtained data confirm the participation of these ore bodies (motherlodes) in the formation of the placers. The occurrences of titanium mineralization were the suppliers of ilmenite, platinum, copper and mercury gold, as well as of associated strategic metals. The antimonite-quartz veins were another power supply source for the placers.

1. Introduction

The national security of any developed modern country depends to a great extent on the state of the mineral resource base of strategically important metals used for high-tech industries. Thus, gold does not only provides the financial security of the state, but is also in demand in many sectors of the national economy. Recently some other metals have also become of critical importance for many industrial sectors. Having moved from the category of exotic metals into the one of strategic resources, they have proved to be extremely popular technologies of the future [1]. More than 90 per cents of titanium raw materials are used for the production of white pigment in the paint-and-coating and paper-and-pulp industry as well as in the manufacture of plastics, synthetic fibers, and rubber. Their role in the production of catalysts is increasing; the substitution of silicon semiconductors by the titanium nanodioxide in solar cells with the purpose of using of the unique properties of the last one is considered to be very promising. The remaining part of the titanium raw material is used to produce a titanium sponge, which is transformed into a compact, extremely corrosion-resistant, lightweight, high-strength, biocompatible structural material, widely used in aviation and astronautics, shipbuilding, the manufacture of offshore drilling platforms, sports equipment, and medicine. It is appropriate to mention that rare earth elements (REE) play a key role in almost all high-tech fields of industry, being usually insignificant in the terms of percentage, but very important as functional components of innovative materials and products that affect the current global market situation. Expanding areas and increasing rates of consumption of individual REE together with the compounds and alloys of the last ones, require the involvement of various sources of raw materials and industrial production of the entire range of rare earth products in the processing. Niobium can be distinguished...
among other metals, being irreplaceable in heat-proof, heat-resistant and stainless steels. Ferroniobium in low-and micro-alloyed carbon steels provides high corrosion resistance, increased plastic property, weldability, strength, increases throughput and reduces costs in the operation of oil, gas and casing pipes, extends the service life of constructions of heavy machine building, agricultural, vehicle engineering, shipbuilding, etc. Niobium alloying of molybdenum, titanium, zirconium, aluminum, and copper improves the properties of these metals and the alloys of the last ones dramatically. Niobium alloys with titanium and zirconium are most often used for the manufacture of industrial superconducting solenoids. Metallic niobium and its alloys are mainly used in aviation, space technology, radio engineering, electronics, and nuclear power. Many of these high-tech metals (titanium, zirconium, platinum group metals, niobium, tantalum, hafnium, vanadium, cobalt, antimony, etc.) occur in the ores and placers of the southern Far East, with the last ones spatially and genetically tending to the intrusions of the ultrabasite-Sichote-Alin orogenic belt [2].

An urgent need to involve these high-tech metals in the industrial turnover has arisen by now. The solution of this problem should be based, first of all, on the study of mineral forms of concentration and the features of distribution of high-tech metals which determined the direction of our research.

2. Methodology of experiment
Performing a complex of mineralogical, geochemical and technological studies was necessary for solving of these problems. The samples of stone material were selected within the studied ore-placer occurrences, the first ones served as the subjects of the research. The mineralogical studies were carried out using the Jeol Superprobe JXA 8100 electron probe microanalyzer with the INCA Energy 350 Oxford Instruments system and the EVO-500XVP electron scanning microscope with the INCA Energy 350 Oxford Instruments system. The trace element composition of the samples was analyzed using an Agilent 7500c inductively coupled plasma mass spectrometer (ICP-MS) (Agilent Technologies, Japan) equipped with a Babington sprayer, a Scott cooled spray chamber, and a grounded Fassel burner. Nickel cones of sampler and skimmer were used. The determination of petrogenic elements was carried out on an atomic emission spectrometer with inductively coupled plasma iCAP 6500 Duo (ICP-NPP) (Thermo Scientific, USA).

Technological studies were carried out according to the traditional scheme for the enrichment of ilmenite-containing sands with preliminary gravity enrichment and subsequent electromagnetic separation. At the same time serial concentration tables and wet-type electromagnetic separators were used.

3. Results of experiment and their discussion
The primary placer-forming role in the formation of titanium placers belongs to deposits of plutogenic origin with the most important place being occupied by:

- (considering shields and platforms location)-mineralization in anorthosite and gabbro-anorthosite massifs, represented by ores of apatite-ilmenite composition, sometimes with an admixture of titanomagnetite;

- (considering the orogenic belts location): a) ilmenite-magnetite and ilmenite-titanomagnetite mineralization in the gabbro-diorite-diabase formation massifs; b) ilmenite-titanomagnetite mineralization in differentiated gabbro-norite massifs.

A special place in this series is occupied by gold-ilmenite ores and placers of the Ariadne metallogenic belt associated with basite-ultrabasite plutos which intrude into the Samarkinsky terrane of Jurassic accretion prism of the Sikhote-Alin orogenic belt [3]. This type of ore-bearing intrusions new to the orogenic belts was formed in the early Cretaceous transform shift of lithospheric plates after the Jurassic subduction had been completed. The basite-ultrabasite intrusions of the Ariadne belt are characterized by the stratal form of bodies (tabular bodies) and sub-concordant beddings with the host sediments. Therefore in case of high-dip of the massifs shown in the plan the last ones are pipe veins stretched in the north-east direction (according to the strike of the layers of the host rocks) with a length equal up to hundreds of meters to 10-15 km and with a thickness ranging from 10 m to 1 km.
In case of flat (low)-dip of the intrusive massifs the last ones have a closely isometric lenticular shape. The sharply crosscutting discordant ore bodies are also quite common along with the concordant ones. Most intrusions are biphasic: the first phase is represented by pyroxenite, dunite, and peridotite; gabbro, diorite, and syenite occur in the second phase. Metal-bearing formations are mainly represented by the bedding plane deposits zones (with a thickness equal to several tens and a length in the limits of first hundreds of meters) of disseminated and massive gold-ilmenite ores (often impregnated with platinum group minerals) in gabbro and pyroxenites. Titanium-magnetite and apatite ores occur rarely.

Figure 1. The scheme of the geological structure of the Ariadnoye ore-placer cluster. Composed by the authors with the use of the materials of V.M. Losiva (1990) and I.V. Kemkin et al. [4]. (a) Location of the area studied; (b) the Quaternary alluvial deposits; (2) the Upper Jurassic turbidites and olistostromes of the accretional prism with inclusions of Late Paleozoic and Lower Mesozoic oceanic cherts, schists, limestones, and basalts; (3) dikes of (a) basic, (b) acidic composition (K2); (4) diorites, quartz diorites, granodiorites (K2), (5–8) rocks of the Ariadnoye massif (K1); (5) diorites, monzodiorites, and sienites; (6) gabbro; (7) ilmenite gabbro with schlieren of peridotites; (9) dislocations; (10) boundaries of different-age stratigraphic and intrusive formations: (a) reliable, (b) facial); (11) (a) ilmenite placers, (b) sampling points.

The basic objects of research were ores and placers associated with the Ariadne massif of ultrabasites (Fig), located in the middle reaches of the Malinovka River (the catchment area of the river Ussuri, a tributary of the Amur River). This is one of the largest massifs of ultrabasic rocks of the Sikhote-Alin. Its southern part is composed of peridotites and olivine pyroxenites, to the north it is dominated by ilmenite and hornblende gabbro grading into diorites, monzodiorites and syenites. The occurrence of the primary (igneous) noble-metal mineralization is a distinctive feature of the Ariadnoye ultrabasites. For example the gold content reaches 1.6 g/t in diorites. High-grade gold particles (Au from 90.17 to 92.43 and Ag from 7.5 to 9.83 wt. %) are detected in association with silicates, and low-grade ones (Au from 76.52 to 80.37 and Ag from 16.91 to 23.43 wt. %) are more
often found in the intergrowths with pyrite. The precious metal minerals are represented by spherelite in ultrabasites, which is a high-and low-karat gold with an admixture of copper and mercury, respectively (up to 0.5-0.8 wt.%). The high-grade grains (Au - 93.53 and Ag-6.6 wt. %) occur together with ilmenite, and low-grade (Au-50.59, Ag-49.7 and Pd-0.11 wt. %) are found in late sulfides.

The Arqiadne manifestation of ilmenite mineralization (the middle course of the Pad Todokhov River) is associated with the ilmenite gabbro. The ore bodies are the deposits with a complex morphology located on the north-eastern strike with a length of up to 2200 m and a thickness of up to 400 m, and followed along the dip up to 400 m. The average contents of TiO₂, V₂O₅, Fe₂O₃, Sc in them are 6.16 %, 0.086 %, 13.28 % and 0.0045 % respectively. The concentration of Cu and Ni in the ores grows in the direct proportion to the increase of the depth ratio reaching 0.1 and 0.3 % respectively. The predicted resources of TiO₂ (P₁ +P₂ categories), V₂O₅, Cu, Ni, Ni and platinum metals are 71 million tons, 944 thousand tons, 400 thousand tons, 450 thousand tons, 22.5 thousand tons respectively.

Ilmenite is a source of titanium dioxide which is one of the most popular titanium-containing products on the world market. [5]. It is a mineral of variable composition FeTiO₃, where Fe²⁺ can be isomorphically replaced by both Mg²⁺ and Mn²⁺ [6]. The stoichiometric composition of ilmenite is characterized by the presence of 31.6 wt. % of Ti or 52.6 % of TiO₂ if expressed in the terms of oxygen. The Ariadnoye ilmenites are characterized by (wt. %) rather close to the stoichiometry of the TiO₂ content (49.5), relatively high concentrations of V₂O₅ (1.8), and moderate magnesia (1.5 wt. %), trace limited SiO₂ impurities (1.02 wt. % ) and Sg (0.2 wt. %), as well as a specific set of trace elements (up to 800 g/t) such as Nb, Nd, Co, Si.

Two mineral associations are distinguished in ores according to the age relationships of ore minerals and the degree of productivity. Ilmenite which determines the industrial significance of the object is the most common. Its accessory companion mineral is pentlandite, which is usually found in the form of isometric or drop-shaped grains, reaching up to 1-2 mm in diameter. Late sulfides (pyrrhotite, chalcopyrite, sphalerite) are recorded much less frequently.

The network of north-eastern ruptures is widely developed to the east of the Ariadnoye deposit in the upper reaches of the river Pad Todokhovo, controlling the position of antimonite-quartz veins of the Todokhovo ore occurrence. They are mainly caused by the exocontact of ultrabasites with siltstones of the Ariadnoye suite. They are traced up to 4000 m along the stretch, and up to 400 m along the dip. The authors established the gold mineralization of antimonite-quartz veins for the first time. Besides the content of the major commercial components varies within the following limits: Au up to 12.5 g/t, Ag- up to 500-1820 g/t, Sb – up to 0.18-23.4 wt. %.

Antimonite which is a major ore mineral occupies up to 50 per cent of the vein mass in some areas. The composition of this sulfide (Sb₂1.1S₈₀.₈₉) differs from stoichiometry by a small excess amount of antimony. Native gold is usually observed in the form of fine grains (less than 0.25 mm) of cloddy outlines, which is often detected in the intergrowths with galenite. Ag concentrations in native gold range from 17.2 to 10.3 wt. % with a slight admixture of Rb (up to 0.9 wt. %) being found in it occasionally. Silver minerals are represented by small grains of native silver (sometimes with an admixture of Au equal up to 2.5 wt. %), argentite (Ag₂1.1 S₈₀.₈₉) and myargyrite (Ag₁1.₀₁Sb₁₀₉S₁.₉₉). Arsenopyrite, pyrite, and marcasite are less common.

The Ariadnoye massif produces a number of large titanium-bearing placers. The native gold and platinum were discovered for the first time in the poorly consolidated sediments of the river Pad Todokhovo and its right tributary called the Potapova sike [3]. The extension of this alluvial placer of the valley type is equal to 4.8 km, respectively, with a thickness of up to 520 m, with an average capacity of the productive formation being equal to 7.4 m and an ilmenite content being equal to up to 375.5 kg/m³. The balance reserves of TiO₂ of category C₁+ C₂ according to the data obtained by 01.01.2021 are equal to 702 thousand tons with the forecast resources reaching the point of 500 thousand tons.

Five large-volume samples (weighing up to 500 kg each) were enriched in a gravity unit in the course of the research. The resulting concentrates were separated into magnetic and non-magnetic
fractions by means of electromagnetic separation. The material composition of gravity concentrates is characterized by a high yield of the magnetic fraction (93-95 wt. %) and low-non-magnetic (5-7 wt. %). The basis of the magnetic fraction is ilmenite (up to 95%). Occasionally, titanomagnetite grains are recorded. The chemical composition of the magnetic fraction is characterized by high concentrations of TiO₂ (39.79 wt. %), Fe₂O₃ (34.47 wt. %), MgO (1.8 wt. %), MnO (0.42 wt.%). It should be noted that the increased concentrations of SiO₂, Al₂O₃, and CaO must be associated with the presence of ilmenite ingrowths with amphibole, pyroxene, and plagioclase in the fraction. A distinctive feature of the magnetic fraction material is the high level of presence of the following elements (g/t): V-800, Nb-210, Nd-100, Co-290, Si-490 and Zr-280.

Ilmenite which is mostly free, has a black in color and submetallic luster is detected in the form of crystals and the fragments of the last ones. The crystals are thick-columned, bladed (flattened) and isometric, the fragments are angular and subrounded having a size of 0.05 - 2.0 mm. The faces of the crystals and the boundaries of the fragments are often uneven and rough-pitted.

According to microprobe analysis, the composition of ilmenites is characterized by quite significant variations in the content of the major components (hereafter, the concentration of elements in wt. %): Fe - 31.30 - 35.15; Ti - 31.09 - 35.15; O - 30.02 - 32.82. In addition, they contain the stable impurities of Si (up to 1.20); Al (up to 0.05); Mg (up to 0.49); Ca (up to 0.16); V (up to 1.10); Mn (up to 1.94); Hf (up to 1.32). Leucoxenization is manifested in the pits and on individual faces of ilmenites (wt. %): Ti-30.29; Fe-6.71; Cr-0.30; Ca-1.07; Si-2.37; Al-0.61; Mg-1.33; O-57.32. Studies of the natural surfaces of ilmenites revealed the presence of the grains of apatite (P-11.98; Ca-0.88; O-45.79; Al-1.21; Si-3.27; Fe-1.85; Ni-0.13; La-8.99; Ce-19.46; Nd-6.42 wt. % ), as well as of native nickel and intermetallides of Pb-Sn.

The non-magnetic fraction consists of a mixture of anorthite, quartz, hornblende, sphene, and zircon. The monazite, rutile, and apatite are present in small amounts. The ore minerals sulfides predominate in the fraction (to be more exact they are single grains of pyrite, arsenopyrite, antimonite, and galena). Non-magnetic concentrate is characterized by the following chemical composition (wt. %): SiO₂-49.6; CaO -13.2; Al₂O₃-11.0; TiO₂-9.4; ZrO₂-4.23; P₂O₅-4.15; Fe₂O₃-3.23; MgO-1.84; Na₂O - 1.67; K₂O - 1.18; V₂O₅ - 0.096. The trace elements of the concentrate can be divided into two groups. The first one includes rare and rare earth elements (g/t): Hf-830, Ce-320, Y-220. The second group includes noble metals-Au, Ag and Pt, with the concentrations of the last ones varying within the limits from 0.5 g/t to 3.0 g/t. The native metals are represented by ferrous platinum and gold.

According to the peculiarities of chemistry, all the gold grains isolated from the non-magnetic fraction can be divided into three groups, namely: silver, mercury and copper. The first and the most widely-spread group (constituting up to 70% of all studied samples) includes low-and high-grade, in accordance with the classification [7], varieties of gold-silver compounds. Macroscopically low-grade phases are minor (less than 0.25 mm) lamellar, sometimes cloudy yellow particles. The surface of the gold grains is finely-pitted, the roundness is medium and well-formed sometimes. They are characterized by the sample variations with narrow range from 770 to 880%. The hypergenic high-grade coating with a thickness of 30-50 microns are quite often observed on the periphery of the grains, with the concentrations of Ag (1.6-1.8 wt. %) being significantly lower compared to the one in the central part. The transition from the matrix to the boundary is sharp and well-traced. The appearance of these coatings must be caused by the subtraction of impurities from the gold in the hypergenesis zone. Small ingrowths of arsenopyrite are observed in some separate metal grains. The chemical composition of this mineral (Fe-32.3, As-42.6, S -19.6 wt. %) is characterized by an excess of sulfur and a deficiency of arsenic in relation to stoichiometry. Another variety of gold-silver compounds is characterized by high values of the purity of the gold sample (up to 970-999%).

Mercury gold is represented (wt. %) by low-grade mercury-containing phases (Au, Ag and Hg, ranging from 53.72 to 55.37, from 39.1 to 41.45 and from 3.47 to 4.31 respectively). They are characterized by low hypergenic stability. The peculiarity of the secondary transformations was expressed in the formation of a highly porous diffusion zone with a width of up to 100 microns, in which Hg is almost completely absent. Hypogenic mercury gold underwent similar changes during the
formation of numerous placers in the Urals [8], being characterized by low values of purity the gold sample, a monolithic (dense) internal structure, and a direct correlation of Ag and Hg concentrations. The studied mercury phases have similar characteristics. This allows us to draw a conclusion that the synchronous crystallization of mercury and gold, there being an absence of any man-made "contamination". Thus the studied mercury gold must be attributed to the natural solid solutions of the Au-Ag-Hg system.

Copper gold is represented by thin (less than 0.1 mm) isometric grains of bright yellow color with a reddish tinge. Cu (0.1 - 3.2 at. %) can be considered to be the typomorphic impurity of these medium-sized gold grains (850-900 %). The uneven nature of the distribution of this element was established in the course of microprobe studies. The size of homogeneous areas rarely exceeds the first tens of microns.

The first findings of native platinum deserve particular scientific attention. Placer (alluvial) platina is usually found in the form of lumpy grains of irregular or oval, flattened shape, not exceeding 0.3 mm in diameter. Platinum minerals are represented by solid solutions of Fe-Pt, where the leading mineral-forming element is established to be Pt (87.1-90.8 wt. %). According to the well-known classification they can be attributed [9], to isoferroplatin with a concentration of Fe+Cu varying within the range of 25.7-27.9 at. %.

Comparison of placer and ore gold, frequent findings of antimonite grains, arsenopyrite accretions with gold indicate that the gold-antimonite mineralization caused the formation of the placer. Native gold of mercurous and copper composition has been repeatedly noted in ore-placer occurrences belonging to ultrabasites of the Urals [10] and the Amur region [11]. The proximity of the macro-compositions of copper-mercury-containing varieties of placer gold and the analogues of the last ones detected in ultrabasic rocks is another evidence that the motherlode was of the "ultrabasic" type in this case. The fact of preserving the geochemical characteristics of placer gold deposits of primary magmatic origin is of fundamental importance, since it can be used for both making the metallogenic constructions and assessing the prospects for the resource potential of territories not only in the south of the Far East, but also in other regions.

4. Conclusion

The manifestations of gold-ilmenite and gold-antimonite mineralization formed the Ariadnoye intrusion of ultrabasites were revealed In Primorye, which is one of the oldest areas of gold mining in Russia [12]. The active participation of these two processes in the formation of placers are proved by the performed mineralogical and geochemical studies. Manifestations of titanium mineralization were suppliers of ilmenite, platinum, copper and mercury gold, as well as of high-tech metals. Another source of power for the placers was quartz-antimonite veins. All of the above said indicates that the ore potential of the region is far from being exhausted, but new finding new approaches to forecasting and searching for sources of strategic mineral raw materials is required.

5. References

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