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Typomorphic minerals oxidation zone of gold-copper porphyry ore of the Malmyzh deposit (Svoboda)

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Abstract. The Malmyzh gold-copper porphyry deposit located in the central part of the Khabarovsk region has a rather developed oxidation zone. The object was identified during the exploration and evaluation work in the 70s, but received a negative assessment in terms of prospects for ore gold. LLC "Amur-Minerals" began to geological study of Malmyzh zone in 2005. Exploration work continues at the present time. The mineral composition of primary ore deposits is well studied. While the common minerals like a limonite and goethite are marked for the oxidation zone the most of minerals that may have a typomorphic meaning in solving genetic and other issues are beyond the purview of researchers. The study relevance of the mineral composition of the oxidation zone are due to the fact that its share and intensively oxidized ores account for up to 7 % of gold and copper.

The authors carried out a mineralogical and technological composition research of the oxidation zone of one of the sites of the Malmyzh deposit using small technological samples. The main part of samples is kaolinized and limonitized diorite porphyrites. In the oxidized ores, there are: limonite, goethite, magnetite, pyrite, less often – arsenopyrite, galena, sphalerite, chalcopyrite, and developed on copper and iron sulfides, covelline, bornite, azurite and malachite. Visible grains (0.2-0.7 mm) were established using mineralogical analysis including instrumental. They are: native gold, platinum, platinum zirconium intermetallic, copper, aluminum, zinc; diamonds are typomorphic minerals of both practical and theoretical importance. Blast tube consisting magmatic-hydrothermal breccias was opened in the northwestern part of site.

Thus, the association of the listed minerals is unique and allows to restore the conditions of formation of the oxidation zone and the genesis of primary ores.

Keywords: Malmyzh deposit, Svoboda site, porphyry ore, oxidation zone, mineralogical analysis, gold, platinum, diamonds

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Introduction

The object of the study is Svoboda site oxidation zone (to a depth of 42 m) of the Malmyzh gold-porphyry copper field. The field is located in the central part of the Khabarovsk Territory, 12-15 km from the federal highway. It belongs to the category of unique reserves with relatively moderate copper contents (Cu – 0.27-0.39 % and Au – 0.12-0.24 g/t) (Chitalin et al., 2013; www.emxroyalty.com) dispersed in a very large volume. Large-volume deposits of non-ferrous metals, including porphyry objects, are the most attractive for the mining industry (Krivtsov et al., 1986; Evstrakhin, 1988; Vlasov, 1990; Puchkov, 2010; Chitalin, 2013). At the moment, the Central site is the most studied at the Malmyzh field. The presence of other noble metals was also established in the ores of the field – platinum (up to 0.18 g/t) and palladium (up to 0.20 g/t), silver up to 1 g/t (Ivanov et al., 2013).

The group of gold-platinum-bearing complex porphyry deposits includes copper-porphyry and copper-molybdenum-porphyry, as well as the actual gold-porphyry ore objects. They are detected in various geodynamic settings, but most of all they are characteristic of island-arc and marginal-continental formations. Such ore objects were formed during the formation of bodies of basalt-andesite volcanic and gabbro-diorite-plagiogranite plutonic formation of sodium series in areas of active riftogenesis and tectono-magmatic activation of individual blocks of the earth's crust (Korobeinikov, Grabezhev, 2003).

In the Amur region, porphyry-type occurrences are known with a fairly wide range of leading useful components: gold ore, gold sulfide, gold-tungsten, gold-tungsten-tin, gold-copper-molybdenum,

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copper-molybdenum, copper-molybdenum-tin (Kryukov, 2013).

The purpose of the research is to determine the mineral composition of the oxidation zone of the Svoboda site of the Malmyzh field to solve technological and genetic tasks.

The mineral composition of the primary ores of the field in the Central site has been fairly well studied (Bukhanova, 2012; Chitalin et al., 2013; Ivanov et al.,2013; Bukhanova, 2016). Common minerals are noted in the oxidation zone – limonite, goethite. A significant number of minerals that can play a typomorphic role in solving genetic and other issues have remained outside the scope of researchers. Therefore, the authors focus on the composition of the oxidation zone. In this regard, it is of interest to analyze the sequence of exploration and thematic work, the results of which are data on the mineral composition of the Malmyzh field of gold-copper porphyry ores.

Studies of the mineral composition of the Malmyzh field

The object was identified during prospecting and exploration in the 70s. Vast fields of secondary quartzites and quartz-sericite metasomatites developed over terrigenous and Late Cretaceous intrusive rocks of moderate acid and medium composition were mapped on the area. 7 extended linear quartz stockworks are allocated. Ore mineralization in veins is represented by pyrite, chalcopyrite, arsenopyrite, magnetite; gold content in veins reached 4.2-5.0 g/t. According to the results of prospecting work carried out without drilling, Malmyzh area received a negative assessment for ore gold; at the same time, it was assumed that secondary sulfide enrichment associated with gold copper mineralization could be detected at a depth of the zone.

A modern study of the mineralization of the Malmyzh gold-copper porphyry system is associated with the work of the Russian-American-Canadian company (Chitalin et al., 2013). From 2006 to 2013, the following areas were outlined: Central, Western, Ploskiy, Northern, Stockwork, Sharga, Eastern, Dolina, ABV, Zet, Svoboda, Sudba, Ravnina. With the industrial parameters of the estimated copper and gold reserves in the Malmyzh ore field, 4 large areas (Central, Ploskiy, Valley, Freedom) have been identified, the exploration of which so far corresponds to the prospecting and partially estimated stages (Shashorin et al., 2018). Researchers of the Far Eastern institutes of the Russian Academy of Sciences (Ivanov et al., 2013; Bukhanova, 2016) were engaged in studies of the mineral composition of primary ores, mainly of the Central site. According to the results of these works, the composition of the ores is established. Primary ore mineralization is represented by nests, impregnations and veins of magnetite, pyrite, chalcopyrite. Bornite, sphalerite, pyrrhotite, galena, and very rarely molybdenite are observed in a subordinate amount. Native gold is present in the form of very fine precipitates in chalcopyrite, magnetite, and pyrite. The size of gold inclusions is usually not more than 3-5 microns. Under surface conditions, primary sulfides are almost completely oxidized and leached with the formation of cellular structures. The Institute of Volcanology and Seismology of the FEB RAS, Petropavlovsk-Kamchatsky, conducted a detailed study of the ores and the host metasomatites of the Central field site. There are 4 stages of the formation of ore-metasomatic formations (Bukhanova, 2016). The first, alkaline stage is characterized by silicification, biotitization and potassium feldsparization of rocks. It is characterized by mineral associations: biotite-magnetite ± apatite, quartz-chlorite-pyrite, quartz-potassium feldspar-chalcopyrite ± epidote, quartz-chalcopyrite-bornite. The acid stage is characterized by chloritization, sericitization and silicification of rocks with the formation of quartz-chlorite-chalcopyrite (+ sphalerite, galena, maybe molybdenite), quartz-chlorite (magnetite or hematite may be present), sericite-quartz-pyrite communities. In the ultra-acid stage, secondary quartzites with pyrite and argillizites were formed, in which sericite ± chalcosine-kaolinite association with sulfosalts, chalcopyrite, tellurides and selenides was observed. In the late alkaline stage, carbonation and zeolitization of rocks containing relict or redeposited sulfides that do not have industrial interest occurs.

Pyrite, chalcopyrite, bornite, chalcosine, galena, molybdenite, faded ores, sulfides and sulfosalts of tellurium, selenium and silver, gold and electrum are described in detail. Mostly finely dispersed forms of gold are noted in pyrites and chalcopyrites of the Central section of the deposit. It should be emphasized the presence in the ores of rare-earth minerals represented by monazite, xenotime, apatite, allanite (orthite), hattonite, inchisite, davidite. Studies of the Far Eastern Geological Institute are highly technological in all processes. As a result of the study of ore mineralization and metasomatites of the Malmyzh gold-copper ore field (Ivanov et al., 2013), researchers distinguished biotitized quartz diorite porphyrites, epipods of the composition actinolite-chlorite-plagioclase-quartz – calcite and fully manifested metasomatites with carbonate-chlorite-epidote associations, chlorite-sericite-carbonate-quartz, carbonate-sericite-quartz-potassium feldspar. Ore mineralization is localized in “propylites” and sericite-potassium feldspar metasomatites. Ores are of medium and sour type, poor arsenic and tellurium-selenium subtypes. Pyrite and chalcopyrite are dominant, in some areas the role of bornite and arsenopyrite becomes noticeable, sulfides of lead, zinc and silver play a secondary role. Magnetite, pyrite, chalcopyrite, bornite, galena, arsenopyrite, sphalerite are described in detail. The association of greenokite with palladium minerals, finely divided gold in the magnetite-chalcopyrite-bornite association is fixed. The "typomorphic" value of tennantite, pyrargyrite, and also the minerals of selenium and tellurium is noted. It is necessary to further study phases containing chromium, molybdenum, tin, bismuth, as well as phases with phosphorus, rare earths, zircon, uranium, and thorium. The presence of gold in the ultrafine and finely disseminated native, telluride mineral forms in the composition of various associations of minerals, thin silver-containing and cuprous gold in the form of phases Au-Ag-(Cu) and Au-Cu. Researchers note that, in addition to submicron particles of natural gold holding alloys detected under a microscope, gold should be expected in a sulfide and silicate matrix and "invisible" as nanoscale particles and clusters. Native gold is present in the form of very fine precipitates in chalcopyrite, magnetite, and pyrite. The size of gold inclusions is usually not more than 3-5 microns.

Copper-porphyry and gold-copper porphyry deposits, in addition to the main noble metals – gold and silver – may contain platinum mineral groups, mainly platinum and palladium, and very rarely other platinoids. Although their contents in known porphyry deposits are usually small (Tarkian et al., 1991; Korobeinikov, Grabezhev, 2003; He Xiaohu et al., 2014; John, Taylor, 2016). At the end of 2017, the Institute of Mining of the Far Eastern Branch of the Russian Academy of Sciences (FEB RAS) together with the Far East Geological Institute of the FEB RAS and LLC "Amur-Minerals" began work on a draft Program of the Presidium of the Russian Academy of Sciences related to the study of porphyry copper ores of the Malmyzh field.

Research Methods of the Institute of Mining of the FEB RAS

Laboratory studies of the mineralogical and technological properties were performed on core material of oxidized ore from the AMM-052 well of the Liberty section of the Malmyzh field. The sample is composed of a core taken in the range of 30.0-42.0 m (sample weight 13.6 kg). The core material was crushed to 1 mm, weighed samples for analytical studies, and the sample was further subjected to gravitational enrichment without the use of magnetic separation.

After enrichment, concentrates were obtained with a total weight of 16.16 g. The concentrates were separated by Sochnev's laboratory magnet into magnetic, electromagnetic and non-magnetic fractions. Next, a shortened mineralogical analysis for precious metals was carried out with the determination of the weight content of visually determined grains of a valuable component. A detailed study of grains isolated by mineralogical analysis was performed using a scanning electron microscope.

Sample preparation was carried out using modern Fritsch equipment (Pulverisette jaw crusher 1, Pulverisette 13 disc mill, ultrasonic bath for cleaning screens Laborette 17, vibrating screen Analyte 3). Visual determination of the composition of the concentrate was carried out using a Stemi 2000C stereo microscope (Germany, Carl Zeiss). Electron microscope their composition was studied using a JEOL scanning electron microscope (Japan) equipped with a JCM-6000 PLUS energy dispersive analyzer. The accelerating voltage is 15 kV, the probing current is 7.475 nA, and the increase is from 20 to 2000.

Research results

According to Amur Minerals, the characterized ore body of the Svoboda site is intensely limonized and clayed diorite porphyrites. Ores are oxidized, disintegrated to sandy loam and loam, fired diorite porphyrites. The most characteristic ore minerals are limonite (jarosite, goethite, hematite), tenorite (?), magnetite. The estimated copper content in the sample (weighted average by weight) –0.09 %, gold – 0.52 g/t. A study of the prepared schlich samples by the authors revealed their basic composition:

- The magnetic fraction of the test material is represented mainly by magnetite with a touch of ocher limonite.
- The limonite (including ocherous), goethite, jarosite, hematite, amphiboles predominates in the electromagnetic fraction, pyrolusite is present. The earthy differences of limonite and jarosite is difficult to distinguish by eye, only in one of the grains of limonite on the cleaved surface is a sheaf drusen of jarosite marked.
- The non-magnetic fraction is most diverse in mineral composition. Pyrite predominates in the form of cubic crystals and bubble formations, as well as in intergrowths with chalcopyrite, with inclusions of covellite and bornite developed along it. Covellite is in earthy differences of blue-black and indigo. Digenite, chalcosine, cuprite and tenorite, molybdenite are noted. In some cases, crusts and single grains of an alloy (?) Fe-Mo-W are allocated. Often, these minerals represent a complex finely accreted bubbly or kidney-like aggregate with the development of earthy crusts, less often – polymineral microdruzes (up to 250 microns). In some cases, an impurity of silver of up to 6-7 % was noted in the composition of chalcopyrite and covellin, and in pyrite an admixture of Co was up to 2 %. In small amounts, sphalerite, galena, arsenopyrite are identified. Short-celled arsenopyrite crystals are characterized by the presence of a constant magnesium impurity; rutile ingrowths (up to 5 μm) are also noted.

Barite in intergrowth with quartz is noted slightly in the sample. Azurite and malachite form blooms on copper minerals. Four grains of native copper were found (from 0.1 to 0.5 mm in size), three of which were of an unusual golden yellow color and one pale yellow with a matte kidney surface. Accessory zircon occurs in the form of transparent, almost colorless, short-prismatic (2 : 1) crystals up to 0.2 mm in size. Seven gold marks were distinguished: one grain – 0.7 × 0.2 mm, the rest within 0.2 × 0.1 mm, weighing about 0.2 mg.

Lamellar grains, with an uneven rough surface, hooked edges, light yellow. During electron microscopic examination, all selected gold grains show a slightly smoothed bizarre elongated shape, often openwork (Fig. 1). The size of the studied grains is from 170 to 700 micrometers. Gold has a complex structure: it consists of individual crystals of cubic and prismatic appearance, plate packets and irregular grains, the value of which varies from 2-5 microns to 20-70 microns (Fig. 1). The composition of gold is quite stable – with a silver content of up to 17-26 % by weight – electrum.

In the cases in the total mass of the electrum, the presence of elongated crystals of argentite Ag_2S (20-50 microns) was noted; lead up to 6 % and galena was present in some cases. Depths between grains were made by ferruginous aluminosilicates (similar in composition to garnet almandine) and sodium (in composition close to albite), clay minerals, in some cases pyroxenes, amphiboles, and mica. The inclusions of distorted pentagonal or hexagonal graphite plates (25 μm) with a large fraction of nitrogen impurity, with outgrowths of sylvin and halite cubes (0.5 μm) were singly detected in gold grains. Two grains (0.06 mg) of platinum are with a slightly elongated flattened shape, similar to smoothed crystals (Fig. 2 a), 0.2 × 0.15 mm in size, light gray in color, with a dull fossil surface. However,

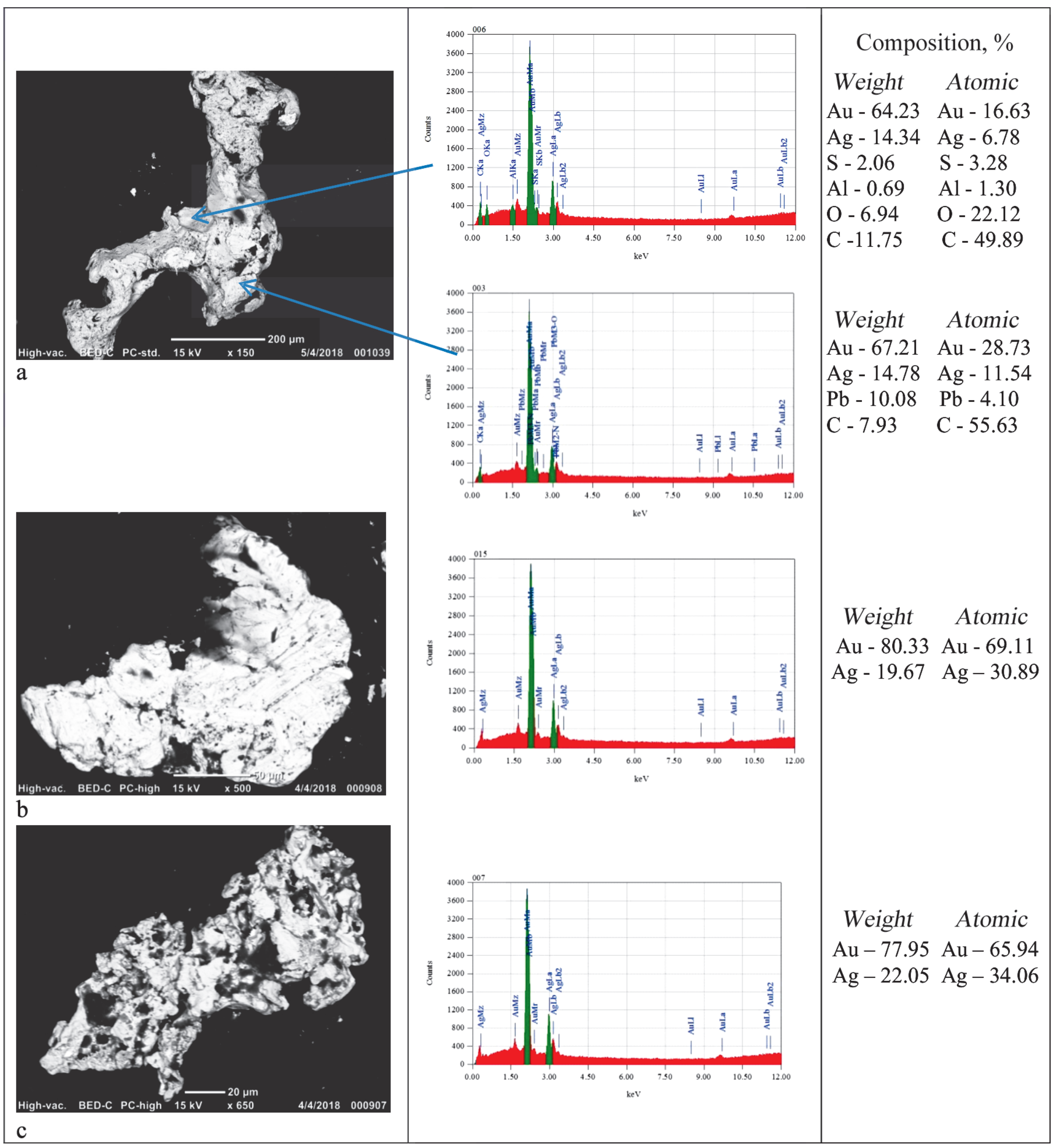

Fig. 1. Gold grains (electrum) with dimensions up to 200 microns of complex shape and structure from oxidized ores of the Liberty section of the Malmyzh gold-copper-porphyry field: a) Pb-containing electrum; b) lamellar grain; c) openwork grain.

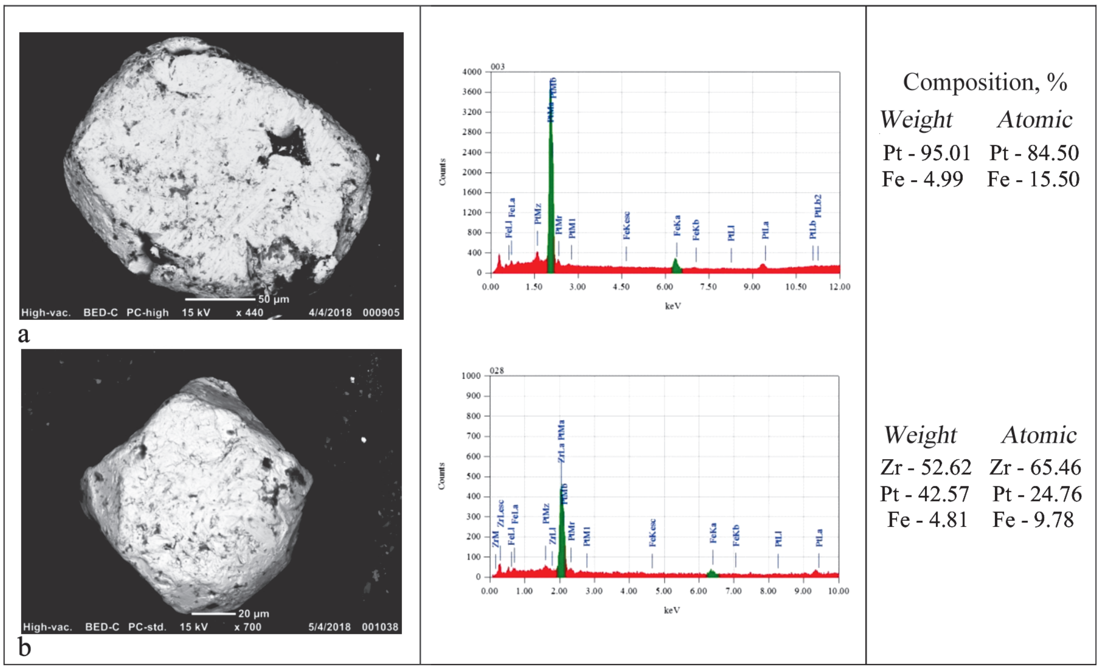

Fig. 2. Platinum minerals from the oxidized ores of the Svoboda site (Malmyzh field): a) a flattened platinum crystal with an admixture of iron; b) a crystal of iron-platinum zirconium intermetallic compound.

their structure is complex – formed by the intergrowth of small grains, crystals and plates. The surface is uneven: in notches and indentations containing non-metallic minerals. An admixture of iron in the composition of platinum is up to 5 %. In one case, in a nest up to 10 μm in size, pyrrhotite grains (up to 1 μm) and a splicing (5 μm) of prismatic (2 : 1) grains with pointed tips of ZrO_2 baddeleyite crystals of 2-3 μm in size were noted. Ingrown graphite plates up to 20 microns in size are singly noted. One grain (0.1 mm) is similar to platinum, but light, white with a metallic sheen. An electron-microscopic analysis of it showed a platinum zirconium composition, which varies somewhat in the grain of iron-platinum zirconium intermetallide, but in general it can be defined as $FePt_{2.5}Zr_{6.5}$ (Fig. 2 b). Cubic habit crystal shape is distorted flattened cuboctahedron. All faces are smoothed. The crystal structure is mosaic, formed by intergrown grains or crystals up to 10 microns in size. The surface is uneven pitted, grooved. In the initial study of the schlich fraction, 10 transparent crystals with a greenish-yellowish color, as in the epidote, were found to be 0.2-0.4 mm in size. Crystals are without visible inclusions, with a diamond sheen – 6 cubic octahedra, 2 elongated broken crystals and 2 fragments (the energy dispersive spectrum showed carbon, i.e. diamonds). The total crystal weight is 0.67 mg. The surface of diamond crystals can be fairly even and smooth in isometric crystals or uneven, containing recesses from the intergrowths of other minerals (Fig. 3 a, b), chipped conchoidal. Crystal faces are clear, clean or slightly knocked down. Some crystals contain vague nest-shaped inclusions (or disturbances). On the energy dispersive spectrum, it is noticeable that there are some other inclusions, but their contents are too small. Only one flattened cuboctahedral crystal, up to 200 microns in size, is covered with a crust of complex composition with Ba, Mo, Fe, K, Cl, Si, Al, Na, Zr. One diamond grain, close to the octahedral form, up to 25 μm in size, was found in a thin aggregate (600 μm) of sulfides using an electron microscope. Among the aggregate components of minerals, Cu_9S_5 digenite, pyrrhotite, bornite, covellite, pyrite, and molybdenite in the form of crusts on copper minerals were identified. Clay minerals are present. The surface of the diamond crystalline is uneven – it has the finest deposit of tenardite Na_2SO_4 (?) and one oval gold grain up to 2 microns in size. An admixture of N, Al is also noted in diamond (Fig. 3 c). The metal-like grain (0.15 × 0.25 mm) is grayish-blue in color, soft, malleable, identified on a scanning electron microscope as native aluminum. Individual fragments of grain are tablets (15-20 microns) of a tetragonal shape with truncated tips. The grain of aluminum is heterogeneous in composition: in some areas there is an admixture of silicon forming an Al_6Si type silicide; diffuse impregnation (1-2 microns) of native tungsten, singly with an admixture of Se. The recesses are filled with clay minerals.

Native Zinc is an irregularly shaped lamellar grain. The grain size is 300 × 250 microns. The grain surface is uneven pitted. On the surface of zinc, an earthy coating of zincite ZnO is noted, in the recesses – albite. Native copper – isometric and elongated kidney-shaped grains up to 400 microns in size, consisting of individual cubic, densely fused crystals. In some cases, copper is covered with an earthy crust of cuprite Cu_2O and tenorite CuO. Quartz, clay minerals with impurities of Mg, Ca, Na, and K are noted in the depressions.

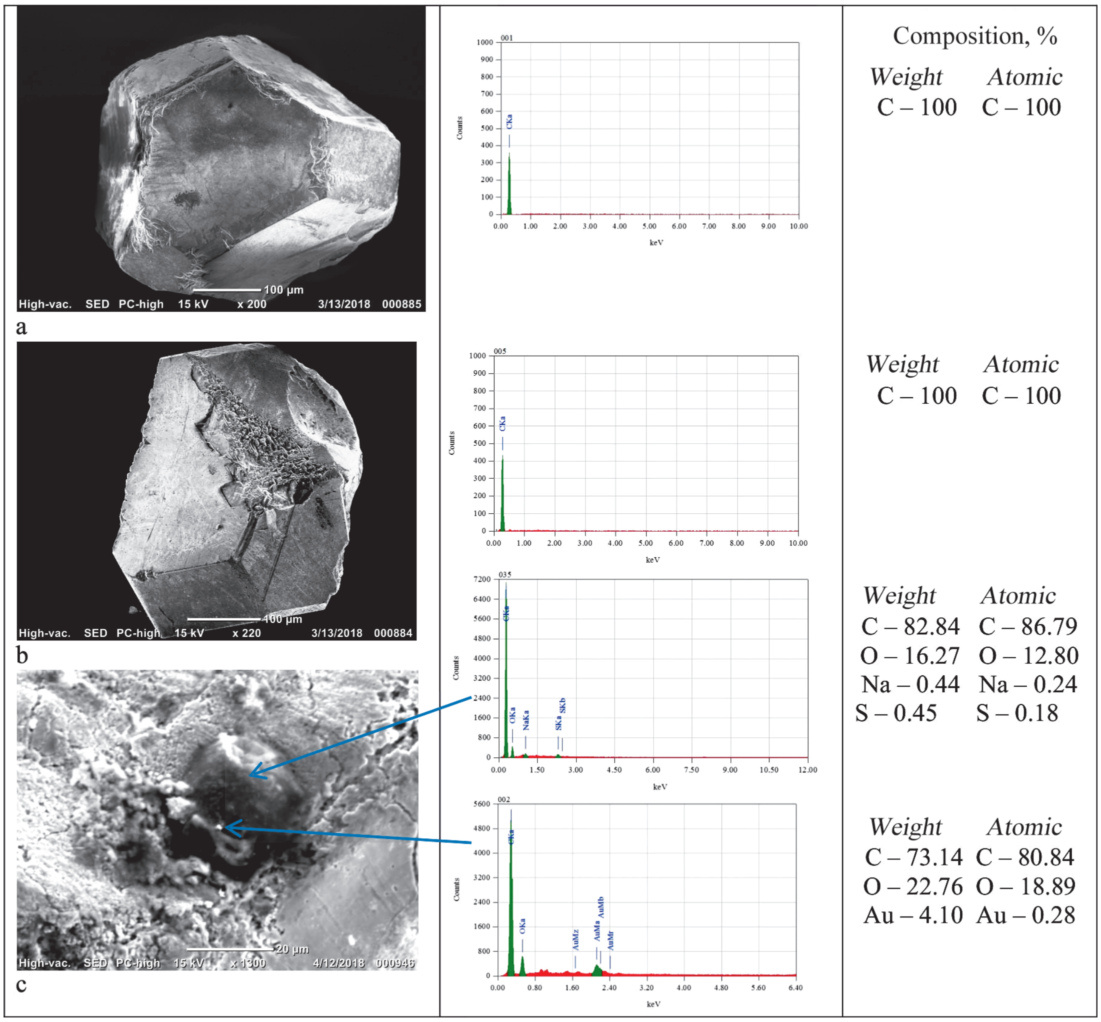

Fig. 3. Diamond crystals from oxidized ores of the Malmyzh field, the Svoboda site: a) an isometric crystal up to 0.4 mm; b) an elongated flattened crystal with imprints from the growths of other minerals; c) octahedral crystal (20 μm) with a crust of tenarditis.

The discussion of the results

The results of previous work on the mineral composition of ores of the Malmyzh gold-copper porphyry field indicate a very uneven distribution of space distribution of various associations. This explains some discrepancy in the results of studies of primary ores of the Far Eastern Geological Institute and the Institute of Volcanology and Seismology, especially regarding the composition of ore-bearing metasomatites. The oxidation zone of the field, in contrast to primary mineralization, is characterized by a fairly laterally mineralized composition of mineralization with vertical variations in the mineral communities. Therefore, private samples in the oxidation zone are more likely to reflect the average situation with a set of secondary minerals.

Mineralogical studies at the Institute of Mining of the Far Eastern Branch of the Russian Academy of Sciences of the oxidation zone small samples of the Malmyzh gold-copper porphyry field revealed, first of all, free gold grains with an admixture of silver, platinum (palladium was not detected), platinum-zirconium intermetallic compound and diamonds. The association is quite specific, despite the possible "infection" with synthetic diamonds crumbling from drill bits, as it seems for various complexes in the south of the Far East (Pakhomova et al. 2015). It should be emphasized that the association of gold-platinum-diamonds with zircon is known in placers in the Urals (Godovikov, 1983). According to the latest geological data from EMX Royalty Corporation (www.emxroyalty.com), an explosion tube with a diameter of about 800 m was discovered in the northwestern part of the Svoboda site of the Malmyzh gold-copper porphyry field, which coincides with a circular magnetic anomaly identified by the results of recent Earth magnetic studies. The pipe is predominantly composed of magmatogen-hydrothermal breccias and can be traced to a depth of 650-850 m. The company has developed a special deep drilling program for the study of breccias explosion and determine their ore potential. The authors tried to note all the features of the discovered diamonds. In particular, the fact of the presence of small crystals of diamonds (up to 20 μm) and diamond with a dimension of 200 μm, covered with a crust of complex composition, may be of interest. Our goal is to provide specialists with additional information for their own research. The problem with diamonds at the Malmyzh field requires further study. The dimension and composition of noble metals (gold, platinum, silver) of the oxidation zone differ from the similar characteristics of primary ores. Their grains have larger sizes – up to 0.4-0.7 mm, and a simpler composition of impurity elements. The refinement and enlargement of crystals is a characteristic feature of hypergenic processes. Accordingly, these properties must be taken into account when studying the technology of ores from the oxidation zone. The mineral composition of the oxidation zone of the Svoboda site in the field depends on the composition of the initial ore and to some extent inherits individual minerals from primary ores. Garnet, albite, zircon, baddeleyite, graphite are not among these minerals, as well as relicts of primary sulfides and sulfosalts with high contents of magnesium, nickel and other metals and metalloids. The complex, including native elements, owes its origin to deep sources in connection with the functioning of large faults.

Conclusion

The Malmyzh gold-porphyry copper field belongs to the category of unique reserves. It is characterized by a rather powerful oxidation zone, which can be traced to a depth of several tens of meters. Its significant volume determines the need to study the mineral composition to solve technological and genetic issues. The results of studies conducted at the Institute of Mining of the FEB RAS show that free ores of gold are present in the ores of the oxidation zone of the Malmyzh gold-copper porphyry field (Svoboda site) and platinum fineness up to 0.2-0.7 mm. Native forms of some other elements are also noted (platinum-zirconium intermetallic compound, aluminum, zinc, copper). In addition, 10 crystals and diamond fragments (sizes from 20 μm to 0.4 mm) were revealed, the origin of which is ambiguous and requires further investigation of minerals in both oxidized and primary ores of this object. The "accompaniment" of native metals is of particular interest. Garnet, albite, baddeleyite, graphite, pyroxenes and amphiboles are found in gold crystals and platinum. More complete composition of associated silicates, phosphates and other minerals in the primary ores of the Malmyzh field was noted in the works of previous researchers. Such an association represents part of the mineral complex of carbon metasomatites, characteristic of both the noble metal proper and the complex, with gold and platinum, fields of the Far East. The specifics of the mineral composition of the oxidation zone, which consists in the association of native metals, semimetals and non-metals, sulfides, sulfosalts, halides, oxides and hydroxides, silicates, phosphates, carbonates, reflects the complex conditions of hypergenesis on the area, their duration and evolutionary completeness. There is no classical zonation of the oxidation zone inherent in arid environments. Nevertheless, elements of the complete leaching and sulfide enrichment sub-zones are recorded.

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