

MINERALOGICAL FEATURES OF CERTAIN MULTIMETAL DEPOSITS OF RUSSIA, CENTRAL ASIA, KAZAKHSTAN AND ROLE OF MINERAL SORBENTS IN THE CONCENTRATION OF METALS IN THE ZONE OF HYPERGENESIS

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There is evidence of genetic proximity by the similarity in distribution of the mineral assemblages in the Onega deposits, Karelia and exogenous infiltration uranium deposits of Central Asia and Kazakhstan. There are many common features of mineralization at the Onega deposits and mineralization of the North Urals and Kodaro-Udokan trough, NW Transbaikalia, where prospects of discovering large precious metal deposits are rather great. The data support the contention (Chernikov, 1977, 2001; Chernikov *et al.*, 2000, 2005, 2007) about the possibility of increasing precious metal reserves associated with uranium-vanadium Onega-type deposits. The role of the mineral sorbents in the concentration of precious and other metals in the supergene zone of deposits in the investigated districts is reviewed.

1 table, 6 figures, 56 references .

Keywords: multimetal deposits, uranium minerals, minerals of precious metals, V and Mo minerals, mineral sorbents, X-ray amorphous matter, supergene zone.

The Onega deposits in Karelia (Middle Padma, Tsarevo, Kosmozero) being large for reserves of complex vanadium ores with a great number of chemical elements: V, U, Pd, Pt, Au, Ag, Mo, Cu, and other (Bilibina *et al.*, 1991; Mel'nikov and Shumilin, 1995) are characterized by certain geological features similar to those of the discordance type deposits (Laverov *et al.*, 1992). At the same time, by association with carbonaceous matter, by number of metals in the ores, and by their restriction to schistose siltstone, they are typical deposits of black schist sequence. The Onega deposits comprise various mineral assemblages that are zoned located in geologic section (Mel'nikov and Shumilin, 1995; Chernikov, 1997, 2001). Copper and molybdenum minerals occur in margins uranium-vanadium mineral assemblages forming ore deposits, and change away from them by albitization and dispersed pyritization of the rocks. Sulfoselenides and selenides are distributed in the frontal part of U-V deposits changed by the zone of hematitized rocks (deep oxidized zone). The modern near-surface oxidized zone displayed as bleached rocks, limonite and Mn oxides follows below surface down to 60–150 m depth, less frequent 250 m limiting U-V deposits from above. The lower part of near-surface oxi-

dized zone, upper levels of cementation zone and deep oxidizing zone of the uranium-vanadium ores are significantly enriched in precious metals.

Such distribution of mineral assemblages in the Onega deposits and their character are similar to those at the exogenous infiltration uranium deposits of Central Asia and Kazakhstan. The differences are mainly in physicochemical features of mineral deposition under deep and near-surface hypergenesis. Albitized and hematitized rocks characteristic of the Onega-type deposits are absent at stratiform near-surface infiltration uranium deposits of Central Asia and Kazakhstan. However, at these deposits, there is limonitization of permeable rocks forming stratiform near-surface oxidized zone, which as like deep-seated oxidized zone at the Onega-type deposits changes along dip by uranium mineralization, occasionally with vanadium and selenium minerals. Like Onega-type deposits, uranium-vanadium, uranium-selenium or uranium ores frequently grade towards margins into zone of molybdenum minerals (jordesite and molybdenite) occasionally with copper (chalcopyrite). Similar to the Onega-type deposits, molybdenum mineralization alternates along dip by the zone of disseminated pyrite. Such consistence of geo-

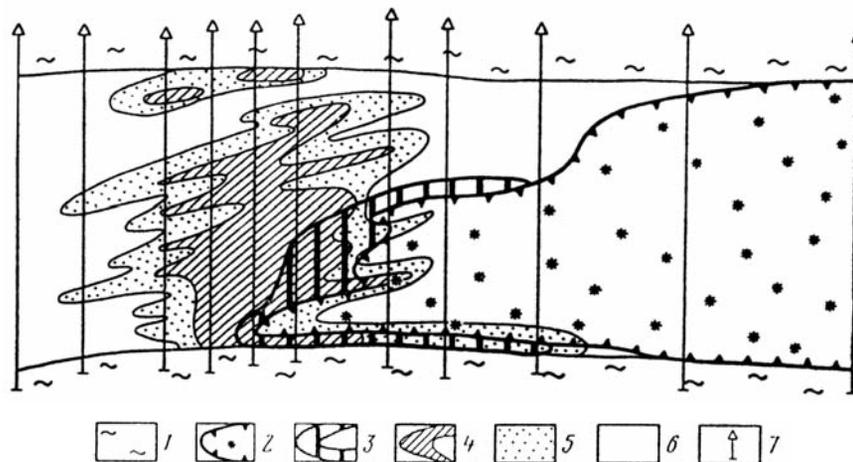


Fig. 1. Distribution of gold in sections of ore-controlling zonation in the Coniacian-Santonian estuary sediments of the Uchkuduk stratiform infiltration uranium deposit. 1 – waterproof aleurolite-clayey rocks (water-permeable sandy rocks between them); 2 – zone of stratiform oxidation and front boundary of its distribution; 3 – uranium ores; 4–6 – gold concentration, mg/t: 4 – from 30 to 60, 5 – from 10 to 30, 6 – <10; 7 – drill holes.

chemical and mineralogical zoning of ores of two types of deposits indicates their genetic similarity.

The highest grades of precious metals in the lower part of near-surface oxidized zone of the Onega-type deposits are as follows: few hundred g/t Pd, few ten g/t Au (less frequent Pt), and few thousand g/t Ag. In deep-seated oxidized zone (in hematitized dolomites) out of limits of the uranium-vanadium ores, the highest grade of precious metals is as follows, g/t: 22 Pd, 2.5 Au, 1.1 Pt, and 330 Ag. At the infiltration deposits, the highest grades of the precious metals are characteristic of uranium-coal ores (Kal'djat, Kazakhstan), where the highest Ag is identified at the boundary with oxidized rocks and is in average 12 g/t. Gold grade is lower, but in coals enriched in uranium (with Mo, Re, Ge, V, Sc, Y) it reaches 900 mg/t, less frequent, 1 g/t. In ordinary and low-grade uranium ores, gold content decreases down to 60 mg/t, and that of PGE is further lower. Precious metals are permanently observed in other deposits of stratiformoxidation. It is especially characteristic of gold, whose supergene formation has clearly demonstrated by Chukhrov (1950).

Gold is clear associated with uranium during supergene ore-forming process, although maximum accumulations of these metals do not always agree (Shmariovich *et al.*, 1992). The elevated concentration of Au ranging from 10 to 30 mg/t, occasionally to 60 mg/t is

found in the zone of stratiformoxidation (Fig. 1). However, the highest gold grade up to 60 mg/t is more frequently observed in uranium ores. Variation of gold content from 10 to 30 mg/t follows in subsequent zones of molybdenum mineralization and scattered pyritization and in the zone of near-surface oxidation.

Concentration of PGE in these deposits is still lower. Hence, content of precious metals in stratiform infiltration deposits is several orders lower than that in the Onega ores. Nevertheless, gold is recovered for decades with underground leaching of uranium at the Uchkuduk-type deposits (Uzbekistan). Grains of native gold from the oxidized zone of the Uchkuduk deposit, near-surface oxidized zone of the Onega-type deposits, and deposits of Southern Kazakhstan (Fig. 2) are similar in X-ray microdiffraction patterns, size of nanoparticles, and shape.

The role of supergene processes to concentrate precious metals at other deposits hosted in metamorphic sequences is not yet estimated and this line of investigation in this direction is rather promising. For example, Tikhomirova (2006, 2008) reported findings of native gold, silver and copper in the ores of cupriferous sandstone of the Northern Urals. In this case, native gold is observed only in one deposit and one occurrence, whereas native copper and silver are found at all studied objects. Native copper is most common in

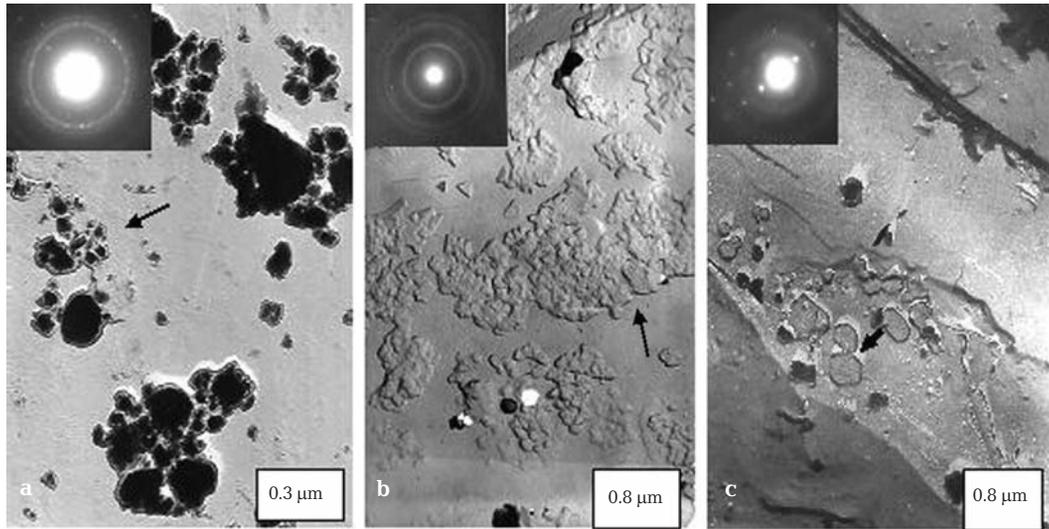


Fig. 2. Replicas with extraction. Segregations of native gold on quartz grains in oxidized zone: a – Omega type; b – Uchkuduk deposit; c – the deposits at Chu-Sorusu depression, Southern Kazakhstan. Arrows show particles, from which were microdiffraction patterns were obtained.

strong leached ores in association with cuprite. Submicron native silver and other Ag minerals are enclosed in chalcocite, bornite and chalcopyrite. And only in malachite and chrysocolla native, native silver occurs as clusters up to ten microns in size.

More data are available for cupriferous sandstone of the Udokan deposit, Kodaro-Udokan trough, NW Transbaikalia, where near-surface and deep-seated oxidized zones are intense. Therein, variegated deposits with elevated precious metals are widespread. In chalcocite-bornite ore and host sandstone of the Udokan deposit, gold grade ranges from 0.01 to 0.3 g/t, platinum, from below detection limit (bdl) to 0.06 g/t, palladium, from below detection limit to 0.009 g/t (Gongal'skiy *et al.*, 2006). The content of precious metals in oxidized malachite-brochantite ores is slightly higher (according to analytical results of three samples), g/t: 0.01–0.5 Au, bdl – 0.01, and 0.01–0.05 Pt (analyst G.E. Belousov, IGEM RAN, chemical-spectral method). Albitite-type metasomatic rocks with uranium oxides, titanates and molybdates is the characteristic feature of the Kodaro-Udokanskiy trough. Assay analysis has revealed in albitite elevated content of Pd (1.3 g/t) with gold grade 0.2 g/t and higher (Knauf *et al.*, 2000; Tatarinov *et al.*, 2000).

The aforementioned data show, that cupriferous sandstone of the Northern Urals and especially rocks of the Kodaro-Udokan trough, being promising in significant reserves of precious metals, is very similar in mineralization to those of the Onega trough. Unfortunately, in the Onega trough, detailed studies have concerned only an estimation of uranium-vanadium ores. Distribution precious metals of uranium-vanadium ores has no been studied out of the uranium-vanadium ores at the Onega-type deposits. At the same time, the applied complex of the modern high resolution analytical techniques revealed important mineralogical features of various formations at these deposits.

(1) In hydrothermal roscoelite-Cr-bearing-celadonite-dolomite veinlets, precious metals occur as selenides, selenide-sulfides, and compounds with bismuth and tellurium.

(2) Sprinklings of Powder of native metals (copper, gold, platinum with palladium) and novel natural phase, palladium analogue of auricupride occur in the near-surface and deep-seated oxidized zones.

(3) Native gold in hydrothermal veinlets of the Onega deposits is not found. Therefore, three analyses (№№ 11–13; Kuleshevich, 2008) of such native gold from the Pedrolampe deposit located at the northwestern boundary of the Onega trough are given

Table 1. Chemical composition of native gold of the Pedrolampi deposit and from deep-seated and near-surface supergene zones of the Onega deposits (wt.%)

El/№	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Au	85.7	84.5	84.9	86.6	83.0	70.2	70.8	86.4	93.5	77.6	93.27	93.64	86.69	86.5	84.4
Ag	13.8	14.9	14.3	13.1	13.1	28.2	24.9	13.0	6.3	22.0	4.33	5.66	4.45	11.5	10.6
Fe	—	0.1	0.3	0.1	—	0.3	0.1	—	0.2	—	0.6	0.7	2.89	—	0.2
Hg	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.19	—	4.98	n.d.	n.d.
Pd	0.3	0.3	0.2	0.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	—	—	—	—	—
Cu	—	—	—	—	—	—	—	—	—	—	—	—	—	1.9	2.4
Σ	99.8	99.8	99.7	100.1	96.1	98.7	95.8	99.4	100.0	99.6	99.99	99.00	99.01	99.9	97.6

Note. (1–10) Deep supergene zone the Onega deposits (Middle Padma and Tsarevo, (11–13) hydrothermal gold-sulfide deposit Pedrolampi, (14, 15) near-surface oxidized zone of the Onega deposits. Analyses 1–10 and 14–15 were performed with a electron microprobe Superprobe-8100, All-Russia Institute of Mineral Resources; analyses 11–13 were performed with a Tescan electron microprobe, Institute of Geology, Karelian Scientific Center, Russian Academy of Sciences

in Table 1, Comparison of these analyses with those from deep-seated (№№ 1–10) and near-surface (№ 14, 15) oxidized zones of the Onega deposits show that hydrothermal gold appreciably differs from supergene gold in composition. It is characterized by high fineness (Au content 86.69–93.64 wt%), whereas supergene gold is of lower fineness (Au content 70.2–86.6 wt%). Hydrothermal gold contains Fe (0.6–2.89 wt%) and Hg (1.19–4.98 wt%), whereas maximum Fe content in supergene gold is 0.3 wt% Fe. At the same time, Ag concentration ranges from 4.33 to 5.66 wt% in hydrothermal gold and from 6.3 to 28.2 wt%, in supergene gold. In addition, Cu was occasionally detected in supergene gold (1.9 and 2.45 wt%) and Pd (0.2–0.3 wt%).

(4) Gold in near-surface oxidized zone containing less than 10 g/t of precious metals occurs as irregular-shaped cloddy particles up to 0.1 microns in size.

(5) In the upper deep-seated oxidized zone, gold occurs as broken spindle-shaped particles of 2–3 microns in size. Closer to the middle deep-seated oxidized zone, gold is disseminated in polycrystalline blades of native copper of tens microns in size. Therein, segregations of native Pd-bearing platinum were identified.

Thus, the results obtained testify substantial supergene processes at the Onega deposits. In this case, leaching and redistribution of precious metals in the oxidized zone decrease downward, whereas grain size of native metals increases in this direction, that suggest a great concentration of precious metals in the lower part of the deep-seated

oxidized zone. In addition to the previous data, this conclusion is an additional criterion, favor possible large or unique reserves of precious metals, at the first place, near explored U-V deposits (Chernikov, 1997, 2001 *et al.*; Chernikov *et al.*, 2000, 2005, 2007) about.

Role of mineral sorbents and X-ray amorphous matter in concentration of precious and other metals in supergene zone

All rocks of supergene zone as reported by Ginzburg and Rukovishnikova (1951), Chukhrov (1955), Nikitina (1968), Chernikov (1981, 1982), Vitovskaya and Bugel'skiy (1982), Chernikov *et al.* (2006), Savko *et al.* (2007) contain clay minerals, oxides and hydroxides of Fe, Al, Mn, Si, poor crystallized and X-ray amorphous products, which absorb various ore elements. Previously, Chernikov (1992) distinguished five main groups of strong natural sorbents of chemical elements and compounds, which are characteristic of supergene assemblages of the Onega and other deposits. Natural sorbents of these five groups involve numerous mineral and organic matters. Most of them are of crystal structure and minors are X-ray amorphous, opal, allophone, non-crystallized or nanoscaled oxides and hydroxides of Al, Si, Fe and Mn, and abundant in weathering profile of various crystalline rocks and in supergene zone of the aforementioned deposits.

Among crystalline mineral sorbents, which are complex and variable in composi-

tion, the majority has a great sorption capacity. First of all these are montmorillonite-saponite, where interstack cations are easily exchanged and can be varied from simple monovalent – Li^+ , Na^+ , K^+ , NH_4^+ or bivalent Ca^{2+} , Mg^{2+} to complex $[\text{Al}(\text{OH})_2]^+$ or RNH_3^+ .

Mineral sorbents and poor crystallized, non-crystallized mineral or organic matter of five above mentioned groups are the major components of such prevalent supergene rocks and minerals, as bentonite, bauxite, laterite, zeolite, perlite, sapropel, coal, turf, and bitumen. They were described in numerous Russian and foreign publications.

It must be emphasized that natural sorbents are composed of several, frequently significantly different mineral sorbents, non-crystallized mineral and organic matter, and in many assemblages of weathering profile, soil, and turf, living matter occurs in great number. (Vernadsky, 1926; Study..., 1970; Turf and sapropel deposits, 1982; Shkol'nik *et al.*, 2004; Savko *et al.*, 2007). Biomorphic matter occurs in bauxite, phosphorite, certain manganese, iron, and gold ores. These ores possess a complex of properties characterizing their sorptive features. In particular, most natural sorbents, especially limonite, laterite, and opoka have polymodal character of distribution of pore volume, fissures and channels by sizes and are attributed to mixed-porous. Micropores, mesopores and macropores are distinguished in them. Macropores are the largest arteries, along which material is transported to mesopores and micropores. Matter is predominantly absorbed in micropores (Tarasevich and Ovcharenko, 1975; Kel'tsev, 1984) in production units, whereas mesopores and macropores under natural conditions, in addition to transport functions, play substantial role during chemisorption,

desorption, and transformation, because they are unique channels, along which natural solutions circulate; subsurface water percolate incomparably slower than liquid circulation in experimental unit. Therefore, macropores, channels, and fissures under natural conditions contain the bulk of products of such processes (Fig. 3). Veinlets and ore minerals are formed along them, in this case, uranophane-beta and according to radiography, sorbents, zeolite and clay, are also enriched in uranium.

Mineral sorbents, colloidal particles, organic matter and microbes are enriched in chemical elements due to: (1) coprecipitating sorbent and adsorbed matter, (2) exchange reactions from solutions, percolated through sorbent, and (3) adsorption, absorption, chemisorption, biosorption, and capillary condensation from solutions and gases, with which sorbents are in contact.

During coprecipitation, sorption of chemical elements by colloidal particles and microbes begins in solution. This phenomenon is the most common during sedimentation in oceans, lakes and rivers. In sediments (including iron-manganese nodules), accumulation of Pb, Bi, Th, U, Au, Ag, Ta, Se, Ge, Tl and many other chemical elements are accumulated as a result of coprecipitation. This contention is supported by both experimental data and observation (Perel'man, 1979; Bowen, 1979; Eisler, 1981; Baturin *et al.*, 1989; Gordeev and Oreshkin, 1990; Pertsev *et al.*, 1990).

Exchange reactions and other sorption processes (the second and third methods of extraction of chemical elements and compounds from subsurface waters by natural sorbents) have complex relations. Considering just ion exchange makes no sense in such

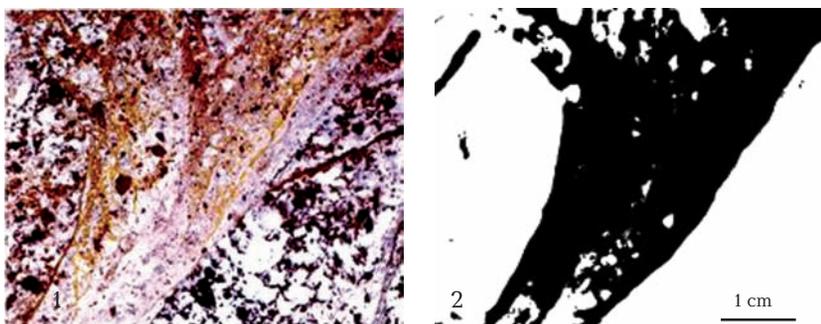


Fig. 3. Segregation of β -uranophane in zeolite-clayey breccia and in zeolitized granite. Yellow spots and veinlets – β -uranophane. Dark-brown spots – gematitized granite. 1 – polished section, 2 – radiography of thin section.

mineral as zeolite and smectite, which combine different modes of extraction of ions from solutions. It has been just as a result of ionic exchange and other sorption processes, pH, Eh, mineralization, and chemical composition of fissure waters of folded areas and formation water of artesian basin change downward and phyllosilicates through disordered and ordered mixed-layered minerals to chlorites and micas are transformed. Supergene carbonates, sulfates, water-soluble silicates, phosphates and other minerals are formed by the same procedure (Chernikov, 1992, 2001; Chernikov *et al.*, 1994). It should be stressed that poor stable nepheline, major rock-forming mineral of the alkaline massifs, under supergene conditions, suggests its easy transition into supergene silicates as a result of leaching K and Na from tetrahedral aluminosilicates framework transformed into octahedral-tetrahedral aluminosilicates sheet due to water percolated from surface to deep levels of the massifs. Partial leaching of Na and

K from nepheline and incorporation H_3O^+ in crystalline lattice lead to the formation of illite or mixed-layered minerals; complete leaching of alkalis from nepheline and saturation by OH^- of the lattice of newly formed mineral result in the precipitation of kaolinite, pyrophyllite, and other clay minerals, which contain only OH^- in their structures. In this connection, percolated weak-acidic surface water at the depth of few meters become weak-alkaline and the depth of few hundred meters, occasionally fluorsilicate strong alkaline with pH = 12 (Krainov *et al.*, 1969). Sorption and transformation processes cause the formation of easy soluble gangue minerals as a result of interaction of host rocks and subsurface water, during interaction of the alkaline underground waters with host rocks takes place formation of. Formation processes of such minerals were described repeatedly (Dorfman, 1962; Dorfman *et al.*, 1981; Chesnokov *et al.*, 1982; Chernikov *et al.*, 1994; Chernikov, 2001). These are typomorphic minerals formed as a result of deep-seated hypergenesis of alkaline rocks.

An accumulation of gold and other metals in the oxidized zone and weathering profile at the Ural, Altai, Kazakhstan, and Uzbekistan deposits (Shadlun, 1948; Chukhrov, 1950; Golovanov, 1961; Petrovskaya, 1973; Murzin, Malyugin, 1987; Chernikov, 1992) is caused by these processes. Figure 4 shows segregation of native gold on jacobsonite, iron-manganese oxide, as result of such process.

At the Olympiada deposit (Enisei Ridge), where large gold and PGE reserves were revealed in weathering profile, native gold as globular segregations of 0.3 to 4.0 microns in size is identified on the surface metacolloidal nodules of W-bearing tripuhyte (Sergeev & Samotin, 1990). The Native gold most frequently precipitates as fine powder on metacolloidal iron hydroxides (Petrovskaya, 1973). In the gold-bearing weathering crusts, gold is usually hosted in zoned limonite nodules in zones clay minerals. This was observed at the deposits Golden Grove and Coolgardie, Australia, Fazenda Nova, Brazil, Nulambur, India and the weathering profile after quartz-muscovite schist at the Svetlinskiy and Katablinskiy deposits,

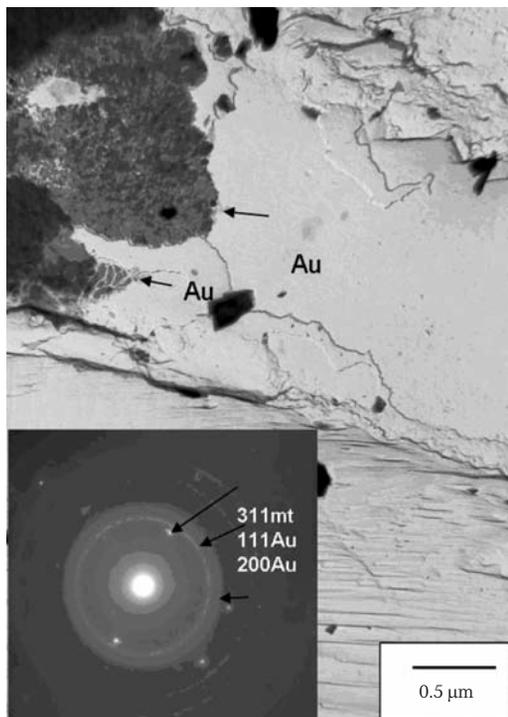


Fig. 4. Film segregations of native gold (shown by arrows) on the surface of jacobsonite (Usinsk deposit, Kuznetsky Alatau). Microdiffraction image with reflection circles of native gold and jacobsonite (311 mt) is nearby.

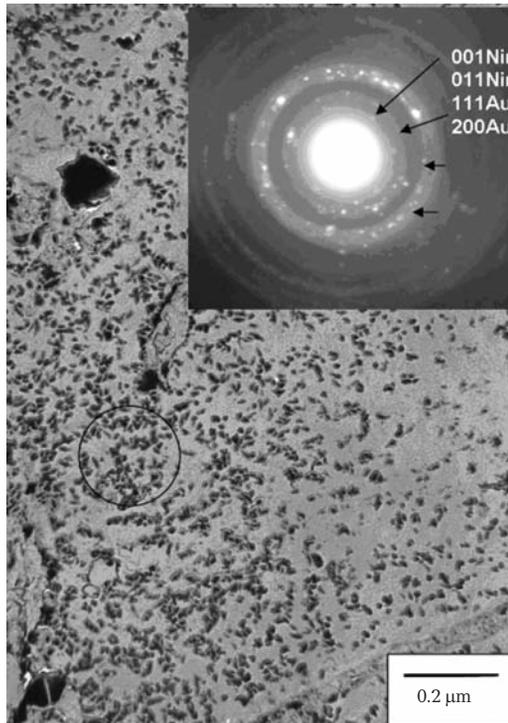


Fig. 5. Fine segregations of native gold and ningyoite (field of image) on the surface of quartz grain, Khiagda deposit, Vitim Plateau. Microdiffraction image (right upper angle) was obtained from the area marked by circle. It document reflections of native gold (111) and (200) and ningyoite (011).

Urals (Wilson, 1984; Bhaskara *et al.*, 1983; Nair *et al.*, 1987; Kuznetsova, 2000).

Sorption and ion-exchange processes may result in accumulation of other chemical elements and compounds. Chemosorption as well as subsequent transformation and desorption transformation lead to the formation of pitchblende-zeolite, β -uranophane-zeolite (Fig. 3), uranyl phosphate-clayey, schroëckingerite-clayey (Boitsov, Legierski, 1977; Chernikov *et al.*, 1983; Chernikov, 1981, 1992, 2001), silver-clayey, silver-zeolite, silver-goethite, and gold-goethite (Artemenko, 1981; Sakharova *et al.*, 1983; Shilo *et al.*, 1992; Chernikov, 1992; Dvurechenskaya, 2001) ores. At the Khiagda deposit, Vitim plateau, similar processes formed ningyoite segregations with gold and fine-grained associations of native gold and ningyoite on quartz grains (Fig 5).

In addition to known cases of sorption (Ni and Co by goethite and nontronite, uranium and REE by apatite), high concentrations of

Au, Pd, Pt, and Ag in iron, manganese, and aluminum oxides were established in weathering crusts in the Urals, Altai, Transbaikalia and other regions of Russia and foreign countries (Chernikov *et al.*, 2006; Savko *et al.*, 2007). At the Nikopol' manganese deposit, Ukraine such segregations of native gold occur on manganese oxides (Fig. 6).

These sorption processes played a major role in the formation of rare metals (Nb, Ta, Be, Zr, TR, Li, Ti) in the weathering crust in several regions of Russia.. There s a good possibility that detailed geological and mineralogical work in these regions will discover economic deposits of uranium, precious, and other metals.

Conclusions

Similar features in the distribution of mineral assemblages and geochemical zoning in the Omega multimetal deposits and the exogenetic infiltration deposits of Central Asia and Kazakhstan testify to their genetic similarity.

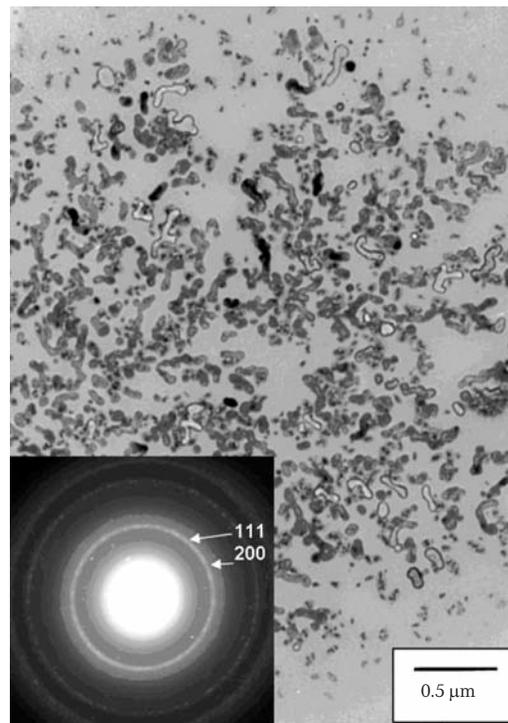


Fig. 6. Segregations of native gold (dark-grey, grey and light-grey) on the surface of manganese oxide (field of image), Nikopol' deposit, Ukraine. Microdiffraction image is at the left lower angle.

Some differences in their mineralogy correspond to physicochemical features of formation at deep and near-surface hypergenesis of these two types. These differences are also in the content of precious metal. In the Onega deposits, which show deep hypergenesis and mineralogical features of different origin, there are higher concentrations of precious metals. The size and character of their distribution in these zones support the contention that it is possible to discover large (and unique) reserves of precious near known uranium-vanadium deposits.

There are close similarities in mineral assemblages in the rocks of the Onega trough, the Southern Urals and the Kodaro-Udokanskiy trough, where prospects of discovering significant reserves of precious metals are good.

Complex of sorption, ion-exchange, and chemisorption processes explain the causes of zoned distribution of typomorphic mineral assemblages and formation of subsurface fluor-silicate waters with high pH in alkaline massifs. Sorption and subsequent transformation and desorption transformation led to important geochemical and mineral assemblages and ores in the zone of hypergenesis of the Ural, Altai, and Transbaikalia deposits in our country and abroad. Consequent geochemical, mineralogical and geological study of the supergene zone of these deposits, occurrences, and anomalies of these regions should result in substantial increase of the reserves of uranium, precious and other metals in our country and abroad. The presence of easily soluble minerals of uranium at the deposits suggests recovery of uranium by underground or heap leaching. Such methods would be economically profitable to work borderline ores (up to 0.01% U) and rocks with low uranium content (possibly, up to 0.005%). Reserves of these ores would increase significantly, even producing large and superlarge deposits. First, this concerns schroëckingerite deposits in Mongolia, Kazakhstan, and possibly, in the USA and other countries with arid climate, as well as β -uranophane-zeolite ores and ores with uranyl minerals associated with clay at the Transbaikalia deposits and other regions of Russia and foreign countries.

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