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Gold Behavior during Endogenic and Supergene Alterations of Sulfides in Magnesian Skarns

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Abstract—The paper presents materials on the genesis of gold deposits of the magnesian-skarn association. It is demonstrated that sulfides are precipitated at these deposits late in the course of the mineral-forming process and often contain visible and fine gold. Post-sulfide mineral-forming processes resulted in the widespread development of hydroxisulfides: tochilinite and valleriite in high-Mg rocks and borate ores affected by serpentinization, brucitizatin, and szaibelyitization. The newly formed hydrosulfides inherit gold from the replaced sulfides. The endogenic or supergene decomposition of tochilinite and valleriite in endogenic and supergene environments stimulates the dissolution of the fine-grained gold and its remobilization, first, by hydrothermal solutions and, subsequently, by meteoric waters. The possibility is discussed of the later regeneration of gold as a consequence of electrochemical processes or at geochemical barriers. The deposition of "newly formed" gold in weathering crusts and placers is discussed, along with the significance of this process for assaying the potential of the weathering crusts and placers. It is emphasized that a significant role in this process is played by cryogenic processes, which can increase gold concentrations in naturally occurring solutions and facilitate its later regeneration. The data presented in this paper are compared with data on gold and PGE deposits of other genetic types, which are hosted in ultramafic rocks and carbonatites, i.e., rocks petrochemically similar to magnesian skarns. It is demonstrated that the occurrence of hydroxisulfides in the ores is a significant geochemical and technological problem during the exploration for sulfide ores and their mining and processing. The magnesian skarn ores of the deposits discussed in this publication were determined to be a significant source of both primary and placer gold and, perhaps, PGE also. The materials presented in the paper characterize the behavior of gold in the endogenic and supergene processes at magnesian skarn deposits.

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INTRODUCTION

Contact metasomatic mineral deposits localized in magnesian skarns are characterized by a broad spectrum of mineral resources: large deposits of iron, boron, tin, tungsten, beryllium, lithium, base and precious metals, etc., as well as economic deposits of sellaite, fluorite, phlogopite, brucite, nephrite, minerals utilized in the ceramic industry and as abrasive materials, gems, and colored stones. Marbles and calciphyres are used in cement production. This genetic group of skarn deposits still remains, however, poorly examined, as also is the potential of these deposits as sources of gold and accompanying PGE.

The main reason for this is the still inadequate scarcity of information on the chemistry and lithology of the host carbonate rocks, which are often combined in geological practice under collective names of limestones or marbles, without determining their Mg contents, their affiliation with certain types, and the character of their metasomatic alterations. Consequently, even at thoroughly examined deposits, there is often no clear classification of their carbonate rocks with limestone or dolomite, whose distinguishing is a problem of great applied significance for the exploration and revision of skarn mineral deposits.

Magnesian skarns are formed via the metasomatic transformation of dolomite in contact with magmatic melts. No calcic skarns develop after dolomites during the prograde stage, and when more mafic and ultramafic melts are emplaced, skarns at their contacts consist of abyssophobe high-temperature minerals (larnite, spurrite, and others). Calcitic rocks and even dolomites are transformed during the postmagmatic stage into calc skarns (wollastonite, salite, hedenbergite, and garnet types), and rocks with rhodochrosite compose their manganoan varieties.

Sulfide ore mineralization is precipitated late in the postmagmatic ore-forming stage and is typical of all types of skarns. This research is centered on magnesian skarn gold deposits in eastern Transbaikalia (Zheleznyi Kryazh, Bystrinskoe, and Kultuma ore fields), Aldan Shield, Norilsk, and the northwestern Baikal area in Russia, at the Hol Kol and Suan region deposits in North Korea, and the Arctic Chief in the Yukon Territory, Canada (the samples of ores and skarns were made available for us by courtesy of T.C. Mowatt of the United States Geological Survey).

We also used our original materials, as well as those of other researchers, on magnesian skarns in Central Asia and the Carpathian–Balkan region, which were determined to contain sulfides with gold also. These data were compared with materials on genetically distinct occurrences of precious metals in high-Mg rocks. A feature common for all of these deposits is the development of post-sulfide mineralization in the gold ores in the form of hydroxisulfides: tochilinite and valleriite.

GENESIS AND ZONING OF MAGNESIAN SKARNS

The types of skarns recognized according to the lithological compositions of the replaced rocks differ not only in their mineralogy but also in many other genetic aspects. Because of this, Korzhinskii [1] regarded bimetasomatic and contact–metasomatic magnesian skarns as an individual petrochemical association, which is genetically related to the replacement of dolomites and magnesites, as was proved at numerous deposits in Russia, China, and other countries [2–7].

Prograde-stage magnesian skarns replace dolomites at contacts with magmatic melts of various compositions (from granites to dunites) [5]. They are characterized by clearly pronounced metasomatic zoning, which reflects the introduction of magmatogenic Si, Al, and, partly, Fe. Intrusive rocks and their injections occur in direct contact with the outer-contact rocks, contain their xenoliths, and were not skarnified during this metasomatic stage.

The developing metasomatic aureoles have different complicated inner structures, which were controlled by the *P*–*T* parameters under which the hypabyssal skarns developed, from the periclase-free metasomatic facies to the gehlenite–merwinite and even spurrite–larnite facies. The magmatic replacement mechanisms of dolomites are also different: they can be infiltration-controlled, when the magma near the contact does not change its composition, or diffusion-controlled, associated with an increase in the basicity of the magma (from granodiorite to gabbro) and/or its alkalinity (up to nepheline syenite) as a consequence of the assimilation of the host rocks by the magma [7].

Existing data on economic copper and gold skarn deposits [8, 9] indicate that these deposits are genetically related mostly to intrusions of elevated basicity. The SiO_2 concentrations in granodiorites and diorites vary from 59.5 to 49 wt %, and these rocks contain 2.5–5 wt % MgO, 6.5–11 wt % CaO, 5.8–10.1 wt % Fe_2O_3, 4.8–2.6 wt % Na_2O, and 2.5–0.6 wt % K_2O, respectively.

The spatial restriction of gold deposits to the outer contacts of intrusions of this composition is clearly pronounced in the Altai–Sayan region, eastern Transbaikalia, Central Asia [8, 10, 11], Canadian Cordilleras [9, 12, 13], and the Rocky Mountains in the United States [14], as well as in several other areas around the world where gold-bearing magnesian skarns were found [14, 15], as, for example, in the Asian portion of the Pacific Ore Belt.

Compared to normal granites (with 72 wt % SiO_2), the rocks of the succession granodiorite ⟶ diorite ⟶ gabbro contain more mafic minerals (biotite, pyroxene, amphiboles, and magnetite), which are able to concentrate ore elements during magma crystallization and alterations by postmagmatic processes, which modify the original compositions of magmatic rocks and can produce ore mineralization.

Magmas of intermediate basicity, with SiO_2 concentrations specified above, are higher temperature than granites. The data in [16] on the melting temperatures of anhydrous magmatic rocks as a function of their silicity indicate that rocks of intermediate composition melt at 1220–1025°C, normative granites melt at approximately 800°C, their leucocratic varieties melt at even lower temperatures, and dunites melt at >1300°C.

Skarns develop in dolomites during the heating of the host rocks under the effect of transmagmatic fluids before the emplacement of the melts. Consequently, contact skarns are formed at temperatures close to those of magmatic melts, which assimilate dolomite marbles that have already been metasomatized. This is reflected in the mineral assemblages of the rocks and in the absence of chill zones in the intrusive rocks in contact with magnesian skarns at the deposits discussed in this paper.

The skarns with gold ore mineralization considered here are hypabyssal [5], and hence, their metasomatic aureoles are characterized by primitive zoning: granodiorite // fassaite and/or diopside skarn (± spinel) ⟶ forsterite calciphyre (± spinel) ⟶ (±brucitized periclase marble) ⟶ dolomite marble. This zoning can be more complicated in contacts with diorites and gabbro, with the appearance of zones made up of high-temperature abyssophobe minerals (periclase marbles and monticellite skarns) [17–19]. These magnesian skarns ubiquitously contain no quartz-bearing associations, which occasionally occur in the overprinted calcic skarns and their greisenized varieties. The skarn bodies are localized in the contact zones of the intrusions and marbles and/or form steep veins, stockworks, and chimneys up to >400 m long in the latter [5].

Sulfide ores, including those with gold, in hypabyssal skarns are very diverse and are deposited during the postmagmatic stage, selectively replacing compositionally diverse metasomatic zones of the contact aureoles. This can be illustrated by the example of the Arctic Chief Cu–Au deposit, Yukon Territory, Canada. The materials on this deposit were provided for us by courtesy of T.C. Mowatt of the United States Geological Survey. His collection of ores and rocks represents magnesian skarns from deposits in the Whitehorse copper belt in the upper reaches of the Yukon River, where gold placers are also known.

ARCTIC CHIEF SKARNS AND ORE MINERALIZATION

In contrast to magnesian skarn deposits in Russia [1–8 and others], their analogues abroad were studied relatively poorly. Literature data on the Whitehorse belt are scarce [12, 13]. It is known that primary lodes mined in 1967–1982 yielded 10 million tons of ores that contained 121 600 tons of copper, 9.7 tons of silver, and 7.7 tons of gold. The dumps of underground and opencast mines (~9 million tons) are thought to contain ~1.5 tons of Au, whose contents in the slimes can be as high as 250 ppm. These 32 deposits (including minor ore occurrences) are under exploration and considered promising as prospecting targets for Cu, Au, and Ag. The ore mineralization is hosted in Triassic rocks dominated by dolomites, whereas the quartzites, arkoses, graywackes, and younger porphyry dikes are barren [12].

The gold contents in sulfides from the Arctic Chief and related deposits vary [12, 13]. Chalcopyrite from the Arctic Chief deposit occurs in association with gold of the composition 92.29–88.02 wt % Au, 11.52–7.40 wt % Ag, and 0.21–0.40 wt % Cu and contains 0.2 wt % Au, and the bornite and chalcosine contain 0.04 wt % Au each. Valleriite, a younger hydroxisulfide, from the North Star deposit contains 0.05 wt % Au, i.e., as much as in the bornite (0.05–0.06 wt %), whereas the chalcopyrite contains no Au at all [13].

The deposits of the Whitehorse copper belt (Arctic Chief, Little Chief, North Star, and others) are restricted to the western contact of the intrusion and are hosted by metasomatically altered dolomites (Fig. 1). In the aureoles of the massif of biotite–hornblende granodiorites and diorites, these rocks are transformed into magnesian skarns, whose genesis and mineralogy are still known inadequately poorly. Geologists paid much attention to the composition of the Au- and Ag-bearing Cu ore mineralization [12, 13]. The results of the examination of skarn and ore samples from T.C. Mowatt's collection (~100 samples) allowed us to partly bridge this gap.

The dolomites of the Arctic Chief deposit are monomineralic and were progradely transformed during the magmatic stage into snow-white periclase marbles affected by brucitization. They compose the outer zone of the contact aureole of the granodiorite massif, whose contact zones consist of hornblende diorites. Closer to the intrusion, marbles give way to a zone of forsterite calciphyres with locally occurring boron mineralization, which was not found by previous researchers. The Mg–Fe borates are aggregates of ludwigite crystals.

These rocks give way to magnetite ores. At the boundary with the calciphyres, these ores contain forsterite and show a clearly pronounced rhythmically banded structure with repeatedly alternating monomineralic bands of forsterite and magnetite. Note that analogous structures, which were produced already during the prograde metasomatic stage in dolomites, also occur in the periclase marbles and calciphyres.

The magnetite ores are of postmagmatic genesis, as follows from the selective replacement of the carbonate constituent of the calciphyres by iron oxides and the preservation of the early forsterite. The rhythmically banded structures of metasomatites and ores were demonstrated [3, 5, and others] to have been produced by the thermodynamically unequilibrated process of dolomite replacement. According to I.R. Prigogine's theory, this is reflected in the spatial self-organization of the minerals. A necessary precondition of this process is the higher rates of the mineral-forming reactions than the inflow rates of endogenic fluids into the skarnified dolomites [3, 5].

Closer to the intrusion, the mineralogy of the magnetite ores that replaced the near-contact pyroxene zone of the aureole changes. The ores there contain variable (up to significant) amounts of phlogopite, which partly or completely replaced the spinel–diopside skarns. The barren varieties of the latter are in physical contact with the intrusion. The metasomatic zoning of the Arctic Chief skarns is generally characterized by the inheritance of the Mg/Ca ratio in each zone (excluding that of magnetite) from the pristine dolomites. The structures and compositions of all zones correspond to the *P–T* conditions of the periclase hypabyssal facies [5].

The magnesian skarns of the Arctic Chief deposit occur not only at contacts with the intrusion but also around injections of diorite melts into dolomites (Fig. 2). The rocks preserve their zoning and inclusions of Mg-ludwigite in the forsterite calciphyres but contain no magnetite ore mineralization.

During the postmagmatic stage, the zones of the contact aureole of magnesian skarns are replaced by magnetite ores, newly formed Mg-bearing minerals, including endogenic borates, and, later, calcic associations. The latter developed in the pyroxene zone, in intrusive rocks in contact with the skarns, and in the vein diorites. The overprinted associations of the periclase marbles consist of brucite pseudomorphs and, in the calciphyres, of clinohumite, which locally replaces forsterite, is syngenetic with the ludwigite, and contains <25 mol % of the vonsenite end member. The pyroxene zone contains phlogopite and younger salite (which bears 15–22 wt % of the hedenbergite end member [13]), vesuvianite, and tremolite. The calcic skarn minerals developing after the intrusive rocks are clinozoisite, epidote, and scapolite. Analogous transformations of the mineralogy of rocks are also typical of the contact zones of many magnesian skarn deposits [5] and are commonly identified in the American literature with postmagmatic-stage calcic skarns proper [13]. At deposits in the Whitehorse belt [12, 13], the latter are barren substratiform bodies of salite–garnet composition. They are bimetasomatic in genesis and replace silicate-bearing dolomite intercalations in the carbonate sequence.

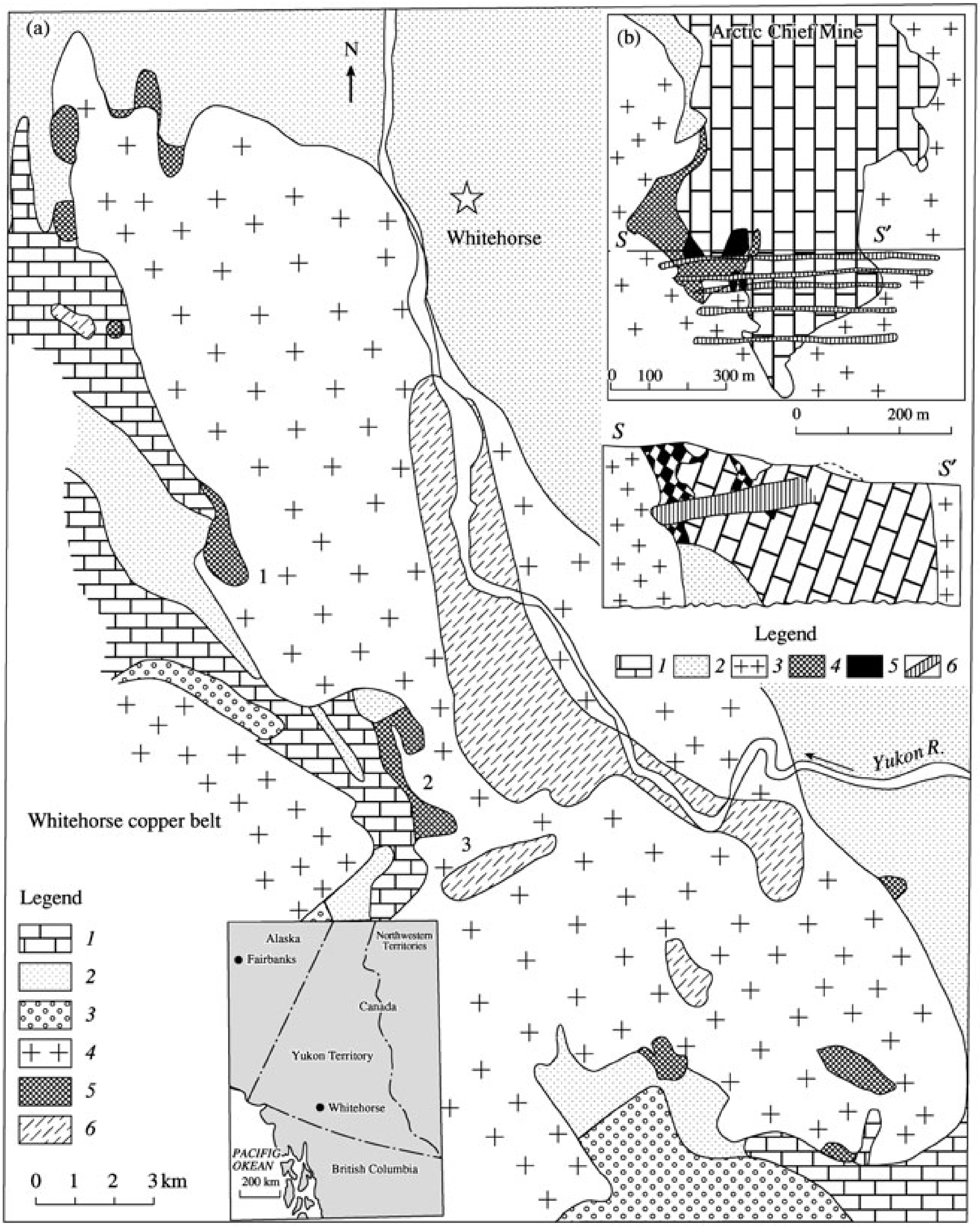

Fig. 1. Whitehorse copper belt and the Arctic Chief deposit in the Yukon Territory, Canada [17]. (a) Whitehorse copper belt. (*1*) Triassic dolomites; (*2*) Triassic terrigenous rocks; (*3*) conglomerates; (*4*) Jurassic intrusive rocks (granodiorites and contact-facies diorites); (*5*) Jurassic skarns with ore mineralization; (*6*) Quaternary basalts. (b) Map and cross section of the Arctic Chief deposit. (*1*) Dolomites; (*2*) quartzites; (*3*) diorites and granodiorites; (*4*) skarns; (*5*) orebodies; (*6*) postmineral porphyry dikes. Mineral deposits in the proximity of the town of Whitehorse: (1) Arctic Chief; (2) Little Chief; (3) North Star.

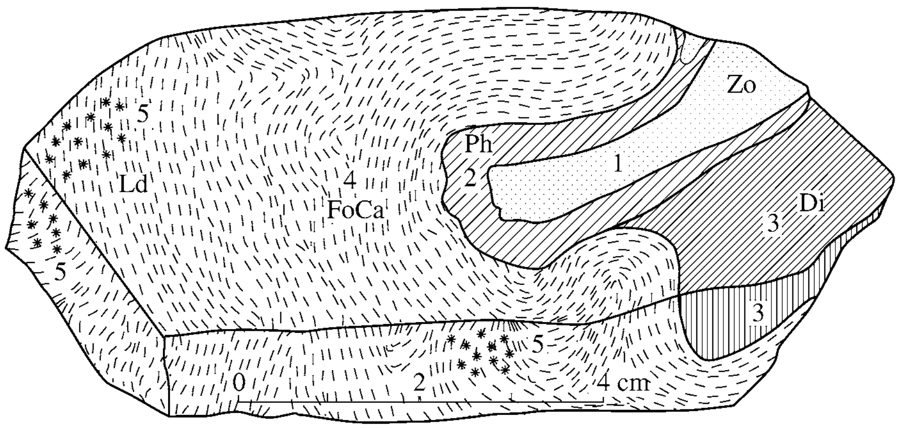

Fig. 2. Diorite injection in dolomite and zoning in magnesian skarns. Arctic Chief deposit (sample of T.C. Mowatt). (1) Diorite replaced by zoisite (Zo); (2) phlogopite–diopside skarn (Ph); (3) diopside skarn (Di); (4) rhythmlically banded forsterite calciphyre (FoCa); (5) disseminated crystals of magnesioludwigite (Ld). Magnification 2.5×.

Sulfide ore mineralization at the Arctic Chief and other deposits in the Whitehorse belt is overprinted onto the skarns and magnetite ores. It consists of lean pyrrhotite disseminations in marbles and calciphyres and of pocket-disseminated Au-bearing pyrrhotite–chalcopyrite and Ag-bearing bornite ores with chalcosine in magnetite bodies. The ores also contain electrum, native Ag, and subordinate amounts of tennantite, tetrahedrite, and Co-, Bi-, and Te-bearing minerals. The chalcosine in association with electrum contains up to 0.54 wt % Te [12, 13]. The ores sometimes contain molybdenite (T.C. Mowatt, personal communication in 2004).

The younger mineral-forming processes resulted in the replacement of the Mg-bearing minerals by brucite, serpentine, and talc. These processes at the Arctic Chief, Little Chief, and North Star deposits were related to the development of valleriite after the gold-bearing sulfide–magnetite ores [13, 20, 21].

The oxidation zone of the sulfide ores locally contains supergene cuprite, malachite, azurite, and iron hydroxides. The position of the Whitehorse belt in the permafrost zone with acutely continental climate in the Yukon Territory caused the more intense physical weathering of the rocks and ores than the chemical alterations of their minerals.

It can be concluded that the skarn deposits of this mining district in Canada show genetic and mineralogical features of their ores and rocks, including the presence of Mg–Fe borates, are similar or analogous to gold deposits in Transbaikalia, Aldan Shield, and the Russian Far East, which are localized in metasomatically altered dolomite sequences that were intruded by magmas of moderate basicity [5]. Tracing the genetic links of the gold–sulfide ore mineralization in magnesian skarns with magmas of other composition, it seems to be necessary to consider the setting of the ore mineralization at contacts of dolomites with granites or ultrabasic rocks.

SKARNS AND ORE MINERALIZATION IN CONTACTS WITH GRANITES

There are still scarce publications dealing with the gold potential of magnesian skarns genetically related to granite intrusions. Available data shed light onto the compositional features of the skarns and the *P–T* conditions under which the metasomatic zoning developed in the exoskarn aureoles and which controlled the origin of certain mineral assemblages that predated the sulfide mineralization and were coeval with it [5, 8, 17–19].

The lowest temperature types of skarns are genetically related to intrusions of leucocratic granites and alaskites into dolomites. The inner structures of their bodies correspond to the primitive type of metasomatic aureoles with the complete inheritance of the Mg/Ca ratio of each zone from the pristine carbonate rocks.

Skarns in contacts with granites are often greisenized, a feature that is weakly pronounced or is absolutely absent in contacts with more basic intrusions and is mineralogically accentuated by the occurrence of F-rich minerals (sellaite, fluorite, and fluoborite) that are associated with Sn and rare-metal (Be and Li) and with younger Au–sulfide ore mineralization [3, 5, 11, 22].

During the postmagmatic stage, the mineral composition of magnesian skarns is modified, and associated types of magnetite and borate mineralization are formed in these rocks, together with phlogopite and humites. This process is followed by the variably pronounced replacement of the metasomatites and nearby intrusive rocks by overprinted calcic skarns [2, 5, 22, 23]. This replacement can be seen most clearly in the compositional modification of the spinel–pyroxene zone in contact with intrusive rocks. The metasomatites are transformed into associations of Fe-rich pyroxenes (salite), clintonite, tremolite, vesuvianite, andradite-grossular garnet, zoisite, and even wollastonite, which are often accompanied by scheelite mineralization and high-Fe borates (vonsenite and paigeite) [2, 5, 22]. The near-contact magmatic rocks contain newly formed wollastonite, garnet, epidote, and axinite. The outer zones of the metasomatic aureole (phlogopitized skarns, forsterite- and clinohumite-bearing calciphyres, brucite–periclase marbles, and dolomites with borate mineralization) are preserved. This confirms that the earlier replaced magnesian and newly formed calcic skarns belong to the magnesian association.

It should be mentioned that magnesian skarns and their surrounding carbonate rocks are often "greisenized" in contact with leucogranites. The F-bearing mineral assemblages are associated with cassiterite and Li–Be ores, which predate the sulfide mineralization. The ores of these deposits are known to contain not only arsenides and various Cu and Fe sulfides but also Au and Ag tellurides and economic concentrations of native Au, Ag, and Bi, which are localized in both the skarns themselves and their greisenized zones, for instance, mica–fluorite rocks.

Deposits of this type in Russia are Lupikko in the Pitkjaranta ore field, Karelia, Arkinskoe, and other deposits in the Argun area, eastern Transbaikalia, magnesian skarns with ore mineralization in Khabarovsk region (Vostok II) and the Voznesenskoe ore field in Primorye in the Russian Far East. The greisens typically contain cassiterite, Li micas. and Be-bearing minerals, including helvite. Fluorite and sellaite develop (often in economic amounts) in dolomitic marbles. Many of these deposits are accompanied by genetically related gold placers.

Sulfide and gold ore mineralization of greisenized magnesian skarns in contacts with leucogranites is characterized by the following features. According to E.N. Nefedov (personal communication), he found gold grains at Lupikko in the Pitkjaranta ore field, Karelia, in mica–fluorite rocks, in which gold grains are spatially restricted to the cleavage planes of biotite and occur in association with Ni- and Co-bearing loellingite and Bi minerals. The gold inclusions were formed after the arsenide and are rimmed by younger tellurides. The magnetite ores contain graphite (?) in association with loellingite, sphalerite, and chalcopyrite and show evidence of valleriitization of Cu sulfides (Gerbets I deposit, Pitkjaranta), a process quite usual at deposits of this type.

SKARNS AND ORE MINERALIZATION IN EXOSKARNS AT ULTRABASITES

The highest temperature type of hypabyssal magnesian skarns develop in dolomites at contacts with ultramafic intrusions. The inner structures of their aureoles are largely controlled by the types of magmatic replacement of the carbonate rocks.

For example, at deposits in the Norilsk district, infiltration monomineralic forsterite skarns adjacent to monomineralic periclase rocks developed at contacts of dolomites and ultrabasites [24]. The skarns bear economic Cu–Ni postmagmatic vein–disseminated pyrrhotite and chalcopyrite ore mineralization (Table 1) with PGE, Au, and Ag. Diffusion skarn found in the area affiliate with the shallowest depth melilite- and spurrite–merwinite association [25] and are surrounded by periclase marbles (replacing dolomites) in the peripheries. These skarns are also accompanied by sulfide mineralization.

The magnesian skarns developing after dolomite xenoliths in the dunites of the Ioko-Dovyren Massif in northwestern Baikal area should also be attributed to the low-depth metasomatic facies [24, 26]. These skarns also show evidence of both infiltration and diffusion prograde metasomatism, with the former expressed in the transformation of the dolomites into monomineralic forsterite and periclase rocks in contact with dunites [24], and the latter is responsible for the development of a more complicated metasomatic zoning in dolomites: dolomite ⟶ periclase marble ⟶ forsterite calciphyre ⟶ zones of abyssophobe skarns. The abyssophobe skarns belong to the monticellite and gehlenite–merwinite associations [26, 27]. The adjacent hybrid melts were characterized by decreasing basicity and crystallized in the form of plagioclase peridotites [24, 26].

Both the skarns and the ultrabasites of the Ioko-Dovyren Massif contain sulfide ore mineralization (pyrrhotite, Co-pentlandite, chalcopyrite, valleriite, and other minerals) accompanied by gold and PGE. This is not the only example of deposits of this type in Siberia. These deposits are known in Transbaikalia (Chiniiskii and Konder massifs) and elsewhere, but their gold potential is still known relatively poorly.

PRECIOUS METALS IN THE ORES OF COPPER–NICKEL DEPOSITS AND CARBONATITES

Ultramafic rocks accompanied by Cu–Ni deposits in the Norilsk district, near the town of Monchegorsk, in eastern Siberia, and elsewhere [28, 29] and carbonatites with Au–Cu ore mineralization (Kovdor in Karelia [30], Loolekop in South Africa [31], Jacupiranga in Brazil [32], and others) are petrochemically comparable with magnesian skarns and surrounding them calciphyres [30, 31] . Similarly to skarns, they often have rhythmically banded structures [33], which reflect the thermodynamically unequilibrated crystallization processes [3, 5] of carbonatites in hypabyssal environments.

Analogously to skarn deposits, they are characterized by the development of ore mineralization in a high-Mg environment, similar or identical mineral assemblages and the succession of post-sulfide modifications of the mineral composition of the host rocks, including their serpentinization, and the occurrence of endogenic hydroxisulfides (predominantly valleririte [30, 31, 34–38] and, more rarely, tochilitine) in these rocks.

Table 1. Composition (wt %) of sulfides in outer-contact disseminated ore, Norilsk deposit

Component	1	2	3	4	5	6	7	8	9	10	11
S	37.39	37.81	34.45	34.35	34.50	34.73	34.12	34.65	34.86	36.40	33.55
As	0.04	0.04	0.04	0.09	0.00	0.00	0.11	0.06	0.08	0.00	0.01
Fe	61.98	60.43	30.89	30.67	30.59	29.92	29.80	30.21	25.23	2.45	2.16
Cu	0.20	0.06	33.11	33.63	33.22	34.13	33.88	34.23	26.83	0.10	1.42
Zn	0.06	0.08	0.06	0.07	0.00	0.00	0.02	0.02	0.00	0.01	0.01
Ni	0.87	0.92	0.09	0.00	0.03	0.03	0.01	0.05	12.21	60.77	62.62
Co	0.18	0.11	0.00	0.01	0.00	0.04	0.05	0.01	0.15	0.02	0.00
Si	0.06	0.08	0.40	0.23	0.25	0.29	0.23	0.25	0.02	0.00	0.00
Ca	0.02	0.02	0.34	0.00	0.01	0.01	0.00	0.00	0.01	0.01	0.02
Mg	0.12	0.25	0.33	0.49	0.43	0.58	0.41	0.46	0.06	0.07	0.08
Al	0.00	0.02	0.17	0.07	0.09	0.13	0.08	0.10	0.00	0.06	0.06
Total	99.92	99.82	99.88	99.62	99.12	99.86	98.71	100.06	99.45	99.89	99.93
Cation proportion											
Fe	0.935	0.992	1.03	1.02	1.00	0.99	1.00	1.00	0.83	0.04	0.04
Ni	0.015	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.38	0.91	1.00
Co	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cu	0.97	0.00	0.97	0.99	0.99	0.99	1.00	1.00	0.78	0.00	0.02
ΣM	0.95	0.93	2.00	2.01	1.99	1.98	2.00	2.00	1.99	0.95	1.08
S	1.00	1.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	1.00	1.00

Note: (1, 2) Pyrrhotite, (3–8) chalcopyrite, (9) Ni-bearing chalcopyrite, (10, 11) millerite. Microprobe analyses, analyst V.G. Senin, Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences.

In carbonatites, the former mineral replaces Cu-bearing sulfides (mackinawite, pyrrhotite, chalcopyrite, and others), while the latter replaces pyrrhotite (author's data).

Evidence of analogous processes can be observed in sulfide-bearing metasomatically altered dunites of Mount Jumbo, Washington, United States, which contain Cr-ludwigite mineralization. In these rocks, chalcopyrite is also replaced by valleriite $Cu_{0,82}Fe_{1,09}S_2 \cdot 1.6(Mg_{0,77}Al_{0.23})(OH)_{2.23}$ [39].

It was mentioned above that dolomites in contact with ultramafic intrusions also contain magnesian skarns. Their sulfide ores commonly contain Ni, Co, intermetallic compounds of PGE, and Au (including native Au).

These facts testify that the ore deposition processes in ultramafics and carbonatites and their subsequent hydrothermal alterations are geochemically comparable with analogous processes in magnesian skarns. This also pertains to the endogenic and supergene transformations of minerals containing precious metals in these rocks.

Supergene processes responsible for the migration and possible regeneration of gold and PGE during the denudation of hyperbasites, phoscorites, and carbonatites are still known relatively poorly. These metals are known to occasionally occur in placers, often in the form of large nuggets, which have never been found in the primary rocks, whose concentrations of precious metals are at the clarke levels. An example is unique placers in the Urals and the Konder deposit in Khabarovsk region.

GENESIS AND COMPOSITION OF SULFIDE ORE MINERALIZATION

The deposition of sulfide ore mineralization takes place in skarns during the latest postmagmatic stage of the mineralizing process [2, 5, 22, 28, 40]. Dolomites at some of these deposits contain anhydrite as a possible source of sulfur. This does not rule out the significant role of magmatic sulfur, as also follows from its isotopic composition in sulfides from these deposits [5].

The ore minerals are S-undersaturated pyrrhotite, arsenopyrite or loellingite, chalcopyrite, cubanite, and bornite at subordinate amounts of Fe, Cu, Zn, Ag, Bi, Sn, Te, and Se sulfides containing Au in the form of an isomorphic admixture and as a native metal. The ores contain younger As and Sb sulfosalts [4, 22, 28, 41–43] and native Ag and Bi. Pyrite is rare but is occasionally contained in the marbles and overprinted calcic skarns in the outer and inner contact zones.

Sulfides of Fe (pyrrhotite and more rare troilite and mackinawite) and Cu (chalcopyrite, bornite, cubanite, and others) are typomorphic of all zones of the magnesian skarn bodies and often replace earlier magnetite. Loellingite and arsenopyrite additionally replace Fe–Mg borates of the ludwigite and paigeite series [28] or are contained as disseminations and pockets in phlogopite and in pyroxene (salite), tremolite, vesuvianite, and garnet skarns. Other sulfides, sulfosalts, and native metals are disseminated in all of the metasomatic rocks or compose stringers in them. The highest concentrations of Bi minerals were found in overprinted calcic skarns, for example, at the Hol Kol deposit in North Korea [2, 5, 22, 40, 42, 44].

Literature on gold deposits of various genesis contain information on the occurrence of Co, Ni, and PGM in sulfide ores. Gold and PGE coexist in mineralized magnesian skarns in Siberia (Gornaya Shoriya, Norilsk mining district, northwestern Baikal area, Transbaikalia, and Khabarovsk krai) [5, 28, 43, 45] in Russia and, in Europe, at the Banat, Romania; Rhodope Mountains, Bulgaria; and elsewhere [41, 46].

GOLD IN ARSENIDES AND SULFIDES

Our data on the gold potential of sulfide ores at many magnesian skarn deposits both in Russia and elsewhere [28] make it possible to identify the occurrence modes of precious metals in them. The loellingite contains variable amounts of Au, up to 0.24 wt % at the Titovskoe borate deposit in the Cherskii Range and 0.33 wt % Au in the greisenized skarns of the Lost River Mine, Alaska, United States. At other deposits, Au concentrations are about 0.04 wt % or below the detection limit of microprobe analysis. Arsenopyrite from paigeite ores from the Moral'nyi Prospect of the Titovskoe deposit contains 0.08–0.31 wt % Au, and kotoite-bearing calciphyres of the Baita Bihor deposit in Romania, which also bear tellurides, contain up to 0.11 wt % Au. Arsenopyrite in sulfide ores from the Serdtse-Kamen' deposit in Chukotka was determined to bear up to 0.25% Au.

Iron sulfides can also contain gold. For example, troilite in sakhaite rocks from the Dokuchan deposit in the Cherskii Range contain 0.12 wt % Au. More widespread pyrrhotite from the ludwigite-bearing calciphyres of the Lebedinoe deposit in the Aldan Shield contains 0.04–0.12 wt % Au, and the analogous values are 0.06–0.20 wt % for the ludwigite ores of the Gol'tsovoe deposit, Cherskii Range, 0.06–0.10 wt % for the Krumovo deposit in Bulgaria, 0.15 wt % for the sulfide–ludwigite ores of Mount Brooks, and 0.08 wt % for the Bessie and Maple occurrence in the Lost River ore field in Alaska. Pyrrhotite in ludwigite–magnetite ores from the Dokuchan deposit contain 0.02–0.10 wt % Au. Diopside skarn in Gijhdarva, Tajikistan, contains pyrrhotite with 0.12–0.16 wt % Au, and this mineral contains 0.07–0.1 wt % Au at the nearby Taror deposit and 0.02–0.11 wt % Au in the ludwigite–kotoite marbles at Hol Kol, Suan, North Korea.

Sphalerite often is barren of gold, but marmatite contains 0.06 wt % gold when occurring in ludwigite ores at the Titovskode deposit and 0.05 wt % gold at the Baita Bihor deposit, Banat, Romania. This is likely caused by the occurrence of 2 wt % Cu in ZnS in the form of emulsion chalcopyrite dissemination.

Chalcopyrite contains variable Au concentrations, which are sometimes as high as 0.25 wt % in greisenized skarns with aikinite, bornite, and Bi-bearing minerals at the Karadjhal deposit in the Digilenskie Mountains, in Kazakhstan. Low Au concentrations (no more than 0.04 wt %) were detected in chalcopyrite from valleriitized borate ores from the Zapadnoe deposit in the Bystrinskoe ore field, eastern Transbaikalia, and 0.01 wt % in sulfide-bearing calciphyres of the Lebedinoe deposit in the Aldan Shield.

Chalcopyrite in the ores from calciphyres of the Baita Bihor deposit in Banat, Romania, contains 0.02–0.15 and 0.30 wt % Au, whereas this mineral from sulfide-bearing spinel–fassaite skarns of the Traversella deposit, Italy, contains no more than 0.05 wt %. Gold (up to 0.10–0.22 wt %) was detected in chalcopyrite from the ludwigite-bearing calciphyres of the Grizzly Gulch, Little Cottonwood Canyon, Utah, in which chalcopyrite is associated with pyrrhotite and Ag- and Bi-bearing minerals and is replaced by valleriite. Gold (0.02–0.07 wt %) is contained in chalcopyrite from the suanite–ludwigite ores of Blind Mountain, Nevada [28]. This mineral from the Bessie and Maple occurrence, Lost River, Alaska, contains variable Au concentrations, from 0.05 to 0.17 and even 0.38 wt %.

Pyrite from the Taror skarns contains 0.04–0.09 wt % Au, and this mineral from Gijhdarva, Tajikistan, bears more than 0.08–0.32 wt % Au. Analogous gold concentrations were found in iron disulfide contained in calciphyres from the Lebedinoe deposit. High Au contents (0.18–0.23 wt %) were detected in pyrite from ludwigite–magnetite ores of the Chingatai deposit in eastern Transbaikalia. Pyrite from Grizzly Gulch, Little Cottonwood Canyon, Utah, contains 0.19 wt % Au, and this mineral from the Bessie and Maple occurrence, Lost River, contains 0.42 wt % Au. Pyrite from the Hol Kol deposit in Korea bears 0.36 wt % Au.

Younger Cu-bearing sulfides also contain Au. For example, chalcosine from harkerite rocks of Camas Malag, Skye Isle, Scotland, contains 0.12 wt % Au, and the accompanying bornite contains 0.05–0.08 wt % Au.

Lead sulfide also contain gold and, often, also silver. Galena from sulfide ores of the Serdtse-Kamen' deposit in the Chukot Peninsula bears up to 0.12 wt % Au. This mineral contains 0.09 wt % Au when occurring in greisenized skarns of the Karadjhal deposit in Kazakhstan, 0.05–0.17 wt % Au in calciphyres of Baita Bihor, Romania, 0.05 wt % Au in Skye Isle, Scotland, 0.15 wt % in the Mount Brooks skarns, and 0.11 wt % at the Bessie and Maple occurrence in Alaska. Boulangerite from kotoite marbles from Baita Bihor contains up to 0.21 wt % Au, and tetrahedrite from the Hol Kol deposit, Korea, bears

0.29–0.33 wt % Au. Molybdenite from this deposit contains variable Au concentrations, from 0.03 to 0.19 and even 0.45 wt %.

The data presented above on the gold-bearing sulfides were obtained by examining hand-specimens of boron-bearing calciphyres, ludwigite and magnetite ores, and magnesian skarns from the author's collection [5, 28, 40, 47]. This study was not associated with the systematic sampling of the orebodies, and the results presented here should be considered provisional and can be taken into account when the gold potential of the sulfide ores of these and other skarn deposits is assayed.

Literature data indicate that sulfides (except their Ag-, Bi-, and Te-bearing species) contain almost no isomorphous Au. Conversely, micrometer-sized to visible inclusions of native gold occur at dislocations of their crystals and in the intergranular space [4], as was confirmed by the results of this research. Gold also forms veinlets in skarns and marbles, for example, at the Hol Kol deposit in North Korea, thus reflecting gold migration and redeposition by hydrothermal solutions.

The data presented above on gold concentrations in magnesian skarns and the contact zones of leucogranites and alaskites that were intensely greisenized with the development of fluorite and F-bearing silicates (norbergite, phlogopite, and Li-micas) and the overprinting of sulfides and tellurides indicate that this magnesian-skarn type of gold mineralization deserves more detailed examination. This also follows from the find of Au (2 ppm), Ag (5 ppm), and Pt (0.5 ppm) in rhythmically banded fluorite metasomatites of the Voznesenskoe ore field in the Russian Far East [11], which contains Be ores.

The materials presented above imply that skarns having various mineral composition and affiliating with different facies are favorable for the deposition of sulfides with gold. Their concentrations can be mined from the orebodies and related placers, as is currently done at some deposits or can be considered for future development with the application of more advanced technologies of the recovery of precious metals.

Magnesian skarns at contacts with ultramafic intrusions also contain sulfides. The hypabyssal spinel–monticellite (±perovskite, melilite, and merwinite) skarns that replaced dolomite xenoliths in dunites in the Ioko-Dovyren Massif, northwestern Baikal area, were determined to contain Co-pentlandite (38.57 wt % Co, 9.63 wt % Ni), mackinawite (9.7–10.6 wt % Co), troilite, galena, clausthalite, native gold, silver, and tin, and valleriite [26]. This is consistent with the composition of the sulfide ore mineralization in the hyperbasites, which contain troilite–pyrrhotite ores with pentlandite, chalcopyrite, and cubanite that contain unevenly distributed PGE and Au. For example, the anorthosites of this massif contain 4.1 ppm Pt, 7.8 ppm Pd, and 3.2 ppm Au, whereas the Cu–Ni ores in dunites are richer in Pd [26].

The metasomatic aureoles in marbles around hyperbasite intrusions in the Norilsk mining district are tens of meters thick. The dolomites are replaced by hypabyssal skarns, calciphyres, and overprinted calcic skarns. Their sulfide ore mineralization corresponds to the types of Cu–Ni pyrrhotite–chalcopyrite–pentlandite ores with cubanite known at the Norilsk I, Talnakh, and Oktyabr'skoe deposits. The ores ubiquitously contain valleriite (0.5–5 vol %) and precious metals: PGE (Pt, Pd, and others), Au, and Ag [33].

The ore mineralization in the outer contact zones is hosted in brucite rocks (pyrrhotite, pyrite, and magnetite), serpentinized magnesian skarns (Table 1), calciphyres, and calcic skarns (pyrrhotite, pentlandite, chalcopyrite, and millerite). These stringer–disseminated outer-contact ores pervasively contain PGE (0.5–7 ppm Pt, 1–35 ppm Pd, and 0.01–0.21 ppm Rh), Au (0.01–10 ppm), and Ag (0.77–17.6 ppm) [37].

The highest valleriite concentrations were found at the Talnakh (up to 15 vol %) and Oktyabr'skoe (up to 9.5 vol %) deposits (data of V.M. Isoitko, 1978 [37]). This provided grounds to distinguish millerite–pyrrhotite–valleriite ores as an individual type, which contains 5–7 vol % hydroxisulfide. This mineral was also found in the mineralized serpentinites and brucitites. Valleriite and tochilinite are formed during the post-sulfide stage (see below) of the hydrothermal process, simultaneously with significant transformations of the mineralogy of the gold-bearing ores.

POST-SULFIDE MINERAL-FORMING PROCESSES

Sulfide ores in magnesian skarns and other rocks of similar petrochemical composition (ultrabasites and carbonatites) typically contain mixed-layer hydroxisulfides, such as tochilinite, valleriite, and more rare haapalaite ($(Fe_{1.26}Ni_{0.74})S_2 \cdot 1.61(Mg_{0.84}Fe_{0.16})(OH)_2$ and yushkinite $V_{1-x}S \cdot (Mg,Al)(OH)_2$) [28, 40, 41, 44]. They replace sulfides and/or magnesioludwigite [2, 28, 40] and are syngenetic with the serpentinization of Mg silicates and, what is important, are coupled with the brucitization of skarn minerals, including Mg oxides and carbonates, and the szaibelyitization of Mg and Mg–Fe borates [28, 40]. Many magnesian-skarn gold deposits at contacts with granitoids, as well as copper–nickel deposits related to ultrabasites and carbonatites, ubiquitously contain tochilinite $2FeS \cdot 1.67(Mg, Fe^{2+}, Al)(OH)_2$ and, more often, valleriite $CuFeS_2 \cdot n(Mg, Fe, Al)(OH)_2$ (Table 2). Their composition reflects both the position of these minerals in the mineralogical systematics and the occurrence of $Mg(OH)_2$, $Fe(OH)_2$, $Mn(OH)_2$, $Al(OH)_3$, and other components in the oxide group of these minerals [28, 34–36, 38, 40].

Valleriite and, later, also tocilinite were first found in Cu–Ni ores genetically related to ultrabasites, in which hydroxisulfides are often rock-forming minerals. Laputina [34] and other researchers [29, 35, 36] have demonstrated that these minerals actively replace various types of sulfide ores, predominantly pyrrhotite,

Table 2. Composition of tochilinite and valleriite: $n(Fe,Cu)_{2-x}S_2 \cdot m[(Mg, Fe)(OH)_2 + Al(OH)_3]$

Deposit	Fe	Cu	ΣM *n*	S	$Mg(OH)_2$	$Fe(OH)_2$	$Al(OH)_3$	Σ *m*
Tochilinite								
Zheleznyi Kryazh, Transbaikalia*	1.95	0.05	2.00	2	0.85	0.00	0.15	1.51
	1.93	0.01	1.94	2	0.86	0.05	0.09	1.49
Titovskoe NE Russia*	1.80	0.14	1.94	2	0.54	0.23	0.23	1.53
Same* (replacing troilite)	2.00	0.00	2.00	2	0.88	0.01	0.11	1.38
Same* (replacing pyrrhotite)	1.98	0.00	1.98	2	0.84	0.11	0.05	1.40
Gavasai, Kyrgyzstan*	1.86	0.00	1.86	2	0.00	1.00	?	1.47
Kamaisi, Japan [34]	1.34	0.34	1.68	2	0.78	0.00	0.22	1.67
	1.26	0.48	1.74	2	0.79	0.00	0.21	1.65
Pensilvania, United States [38]	1.62	0.00	1.62	2	0.79	0.00	0.21	1.79
Jacupiranga, Brazil (C) [32]	1.78	0.00	1.78	2	0.39	0.31	0.30	1.67
Valleriite								
Zapadnoe, Transbaikalia*	1.12	0.88	2.00	2	0.77	0.23	0.00	1.33
	1.37	0.63	2.00	2	0.96	0.00	0.04	1.08
	1.34	0.66	2.00	2	0.94	0.00	0.06	1.16
	1.56	0.38	1.94	2	0.91	0.00	0.09	1.47
Kultuma, Transbaikalia*	0.96	1.04	2.00	2	0.90	0.10	0.00	1.64
	0.90	1.01	2.00	2	0.88	0.12	0.00	1.63
Baita Bihor, Romania*	0.93	1.07	2.00	2	0.86	0.14	?	1.67
Hol Kol, North Korea*	0.98	1.02	2.00	2	0.85	0.06	0.09	1.24
	0.92	1.08	2.00	2	0.87	0.02	0.11	1.35
Grizzly Gulch, Utah, United States*	0.99	1.01	2.00	2	0.80	0.00	0.20	1.80
Little Chief, Yukon, Canada [21]	0.81	1.19	2.00	2	0.71	0.06	0.23	1.64
	0.80	1.20	2.00	2	0.73	0.21	0.06	1.67
	1.07	0.93	2.00	2	0.68	0.00	0.32	1.53
North Star, Yukon, Canada [13]	0.80	1.20	2.00	2	?	0.12	?	–
Kaveltorp, Sweden [38]	1.16	0.84	2.00	2	0.73	0.00	0.27	1.30
Norilsk, Siberia [34]	0.95	1.05	2.00	2	0.86	0.14	–	1.51
Same**	1.61	0.39	2.00	2.2	0.05	–	0.34	1.65
Kovdor, Karelia (C) [30]	1.18	0.82	2.00	2	0.79	–	0.21	1.61
Same (C)	1.47	0.53	2.00	2	0.78	–	0.22	1.63
Loolekop, South Africa (C) [38]	1.03	0.95	1.98	2	0.73	0.00	0.27	1.57
Same (F) [38]	1.02	0.98	2.00	2	0.65	0.34	–	1.70
	1.05	0.95	2.00	2	0.76	0.22	0.02	1.66
	0.96	1.04	2.00	2	0.75	0.16	0.09	1.67
Jumbo, Washington, United States *(D)	1.09	0.82	1.91	2.1	0.77	0.00	0.23	1.60

Note: From sulfide-bearing magnesian skarns and calciphyres according to * our [28, 39, 40, 44, and others] and literature data, including hydrozisulfides from sulfide-bearing carbonatites (C), phoscorites (F), and dunites (D). **Valleriite with 61 mol % $Ca(OH)_2$ in its oxide constituent.

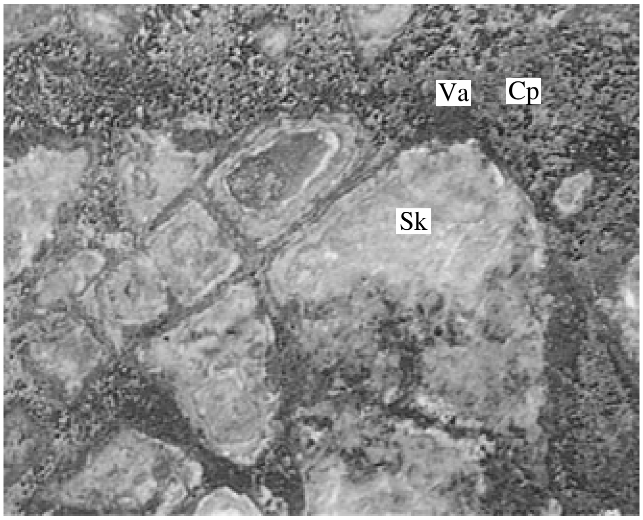

Fig. 3. Outer-contact stringer–disseminated copper–nickel ores, Norilsk. Valleriite (Va) surrounds chalcopyrite (Cp) in skarns (Sk). Magnification 2×.

Cu–Ni, and containing magnesian minerals ones, at the Norilsk group of deposits. The hydroxisulfides have variable compositions (Table 2) of their sulfide and hydroxide constituents at significant structural differences between them [35].

It was established [34] that valleriite of the Norilsk deposits contains 7–16 wt % Cu in pentlandite–chalcopyrite–pyrrhotite ores and 17–22% Cu in the millerite–bornite–chalcopyrite and pentlandite–chalcopyrite ores. The pentlandite–pyrrhotite ores with subordinate amounts (3–5 vol %) of chalcopyrite contain mostly tochilinite.

The composition of the hydroxyl constituent of hydroxisulfides is controlled by the composition of the silicates, first of all, serpentinized forsterite and iron oxides, including magnomagnetite. They are contained in both the magmatic rocks and the adjacent metasomatites that replace dolomite and often contain anhydrite. The valleriite of these associations commonly contains Mg (11–12 wt %), whereas the tochilinite bears up to 14 wt % Mg.

Hydroxisulfides of other composition (Table 2) occur less frequently at the Norilsk deposits. The massive chalcopyrite, cubanite, and talnakhite ores contain newly formed Mg-free valleriite of the composition $CuFeS_2 \cdot nFe(OH)_2$, and tochilinite of the composition $2Fe_{1-x}S \cdot nFe(OH)_2$ replaces troilite and hexagonal pyrrhotite in the monticellite skarn. The melilite–merwinite skarns were determined to contain high-Ca valleriite $CuFeS_2 \cdot n[(Ca,Al)(OH)_2]$, which replaces cubanite and pyrrhotite. The sulfides have variable Cu concentrations, from 11 to 3–4.5 wt % [35].

Valleriite (whose composition was not determined) was also found in gehlenite–spurrite skarns of shallow-depth facies at the Fuka deposit, Okayama Prefecture, Japan. I. Kusachi found this mineral in association with loellingite, arsenopyrite, chalcopyrite, cubanite, pyrrhotite, witticherite, and other sulfides (I. Kusachi, personal communication on August 27, 1998).

We established [28, 40, 43, 44] that valleriite and tochilinite are also typomorphic post-sulfide minerals at gold deposits of the magnesian skarn ore association. This significantly expands our knowledge of the occurrence of hydroxisulfides in various genetic types of sulfide ores (Table 2).

The genetic role of the replacement of Fe and Cu sulfides by hydroxisulfides in the endogenic and supergene geochemistry of Au and PGE is still poorly understood [28, 39, 40, 43, 44]. The significance of the problem of the tochilinization and valleriitizatin of sulfides in serpentinized ultramafic rocks related to the genesis of Cu–Ni ores with PGE and Au was first highlighted by the data obtained by Ramdohr [37] and other researchers of these minerals [34–36, 38].

Tochilinite and valleriite have a low hardness and are ductile and layered, i.e., possess characteristics hampering the identification of these minerals. In association with pyrrhotite, chalcopyrite, and other sulfides, these minerals are commonly misidentified as graphite based on their optical characteristics. In the ores of Cu–Ni skarn deposits, valleriite and tochilinite develop along the grain boundaries of sulfides and rim sulfide grains (Fig. 3). When these ores are technologically processed (crushed and floated), it is practically impossible to get rid of hydroxisulfides, and thus, the technological concentrating process of these ores is associated with significant losses not only of Cu but also of precious metals [31, 48].

As was recently demonstrated in [2, 28, 40, 44], when replacing Au-bearing sulfides, Fe and Cu hydroxisulfides inherit their Au in the form of fine-grained native metal. For example, tochilinite from Zheleznyi Kryazh, Transbaikalia, contains 0.01–0.4 wt % Au, and valleriite from the Zapadnoe deposit contains 0.05–0.15 wt % Au (the chalcopyrite contains 0.04 wt % Au). These concentrations are comparable with those published for deposits in the Whitehorse belt in Canada.

In the process of endogenic and supergene alterations, minute gold particles contained in hydroxisulfides are dissolved more easily than large gold grains (because of the greater specific surface of smaller grains). This process is additionally facilitated by the general chemical instability of tochilinite and valleriite in surface environments. These minerals are replaced by magnetite with the release of dissolvable Mg, Fe, and Cu sulfates. The latter, in turn, create favorable conditions for gold migration in acid hydrothermal solutions and its redeposition when conditions change, for example, at geochemical barriers (as at reactions with carbonates). Evidence of this process is the development of thin veinlets of native gold along cleavage planes of calcite in marbles, for example, at the Hol Kol borate magnesian-skarn deposit, the largest in North Korea (author's data). At this deposit, gold-bearing marbles occur near chalcopyrite–magnesioludwigite ores, which are replaced by valleriite [28, 40, 44].

Eastern Transbaikalia (at the Bystrinskoe, Koltuminskoe, Zheleznyi Kryazh, Arkinskoe, and many other deposits in the Argun–Gazimur divide), Aldan Shield (Lebedinoe and other deposits), and the Yukon Territory in Canada (Whitehorse copper belt) contain economic gold-bearing alluvial placer deposits. Their genesis was predetermined by the denudation of primary magnesian skarn deposits with gold-bearing sulfides and provide evidence of their significant role as a source of placer gold. The gold potential of these deposits is still not depleted.

For example, it is thought that mineralized skarns in the Bystrinskoe field contain 0.6 ppm Au and 1.5% Cu at predicted reserves as large as 130 tons of Au, 4 million tons of Cu, and 93000 tons of Ag [11]. Placers at the Bystrinskii group of deposits ubiquitously contain scheelite, which was mined in the Bystraya and Il'dikan river valleys in the 1940s. The sources of the valuable minerals of these placers were the Zapadnoe (Fig. 4), Vostochnoe, Malyi Mednyi Chainik, and other deposits of magnesioludwigite ores with pocket and disseminated pyrrhotite–chalcopyrite ore mineralization that is extensively replaced by valleriite during the serpentinization of the forsterite skarns and calciphyres and the replacement of the borate ores by szaibelyite [2, 5, 28, 40]. Although the black-sand panning samples contain no preserved minerals of magnesian skarns other than magnomagnetite, these samples contain garnet and, near primary deposits, also pyroxenes, scheelite, and gold (905–976 fineness) [28]. When these placers were washed for gold by small diggers, the first priority targets were sands with magnetite and scheelite as those richest in gold.

The Zheleznyi Kryazh sulfide-bearing ores and, particularly, the pyrrhotite-bearing borate ores of the Rudnichnaya body are also significantly replaced by tochilinite and valleriite (Fig. 5) [2, 28, 40]. The ludwigite and magnetite ores are localized in magnesian skarns that developed in dolomites of the Bystrinskaya Formation of Paleozoic age. They contain up to 29% fine (no larger than 0.07 mm) and coarser grained (up to 1 mm) gold, as well as lumpy and amoeba-shaped unrounded gold grains in aggregates with chalcopyrite. The denudation of the orebodies of the deposit gave rise to related alluvial gold placers in the valley.

In the oxidation zone, sulfides and hydroxisulfides are supergeneously replaced by Fe and Cu hydroxides, which can adsorb Au and release it under the effect of sulfate- and thiosulfate-bearing groundwaters. This can be exemplified by deposits in eastern Transbaikalia, whose tochilinite- and valleriite-bearing ores are transformed into magnetite sands loosely cemented with calcite. We identified such newly formed rocks at the Zheleznyi Kryazh and at the Zapadnoe deposit in the Bystrinskoe ore field. At the latter, they occur in the most deeply eroded orebodies in the southern flank of the deposit.

At many other skarn deposits, hydroxisulfides are completely oxidized but still can be identified in supergeously unaltered ores [28, 40, 43]. For example, the supergene alteration products of chalcopyrite that has been replaced by valleriite (Table 2) in the ludwigite-bearing calciphyres at Grizzly Gulch in Utah are iron hydroxides and malachite with 0.19–0.52% fine gold.

A similar situation occurs at the Kultuma ore field on the Gazimur River, but the predominant primary sulfide of the boron-bearing skarns and calciphyres is chalcopyrite, which is partly replaced by valleriite [43]. Gold-bearing placers in the valley were mined for more than one century (until 1958) and were thereby repeatedly rewashed.

Genetically analogous placers promising for gold and cassiterite are widespread along some tributaries of the Argun in the Bogdatsk–Arkia mining district in Transbaikalia. These placers are genetically related to sulfide-bearing magnesian skarns with magnetite, cassiterite, beryllium, and bismuth ore mineralization at contacts with leucogranites [11].

In the Aldan district in Siberia, gold is produced by the long-term development of the Lebedinoe deposit, which is hosted in skarnified dolomites intruded by Mesozoic syenites [49]. In addition of sulfide ore mineralization of chalcopyrite, pyrrhotite, and pyrite with subordinate amounts of galena, Bi-bearing minerals, sulfosalts, and tellurides, including calaverite, the marbles contain native gold and disseminated magnesioludwigite and szaibelyite. Our data indicate that the latter minerals sometimes contain valleriite. Along with primary deposits, gold was extracted in this area for more than 50 yr from alluvial placers. The reserves of the ore mineralization are comparable with that at the Hol Kol deposit in North Korea. Recently other gold-bearing skarn deposits (Samolazovskoe and others) were found in this area, and this confirms that the area is promising for exploration for gold.

"NEW" GOLD IN PLACERS AND WEATHERING CRUSTS

The data presented above on the spatial relation of gold placers to its primary deposits call for the analysis of gold geochemistry in supergene environments.

In spite of inconsistencies in literature data on the possible scale of supergene gold migration with groundwaters, the possibility of this process is taken for granted and is generally not questioned any more. This is directly related to the applied aspect of this problem, namely, the possibility of the origin of supergene "new" gold as a consequence of its remobilization and, what is

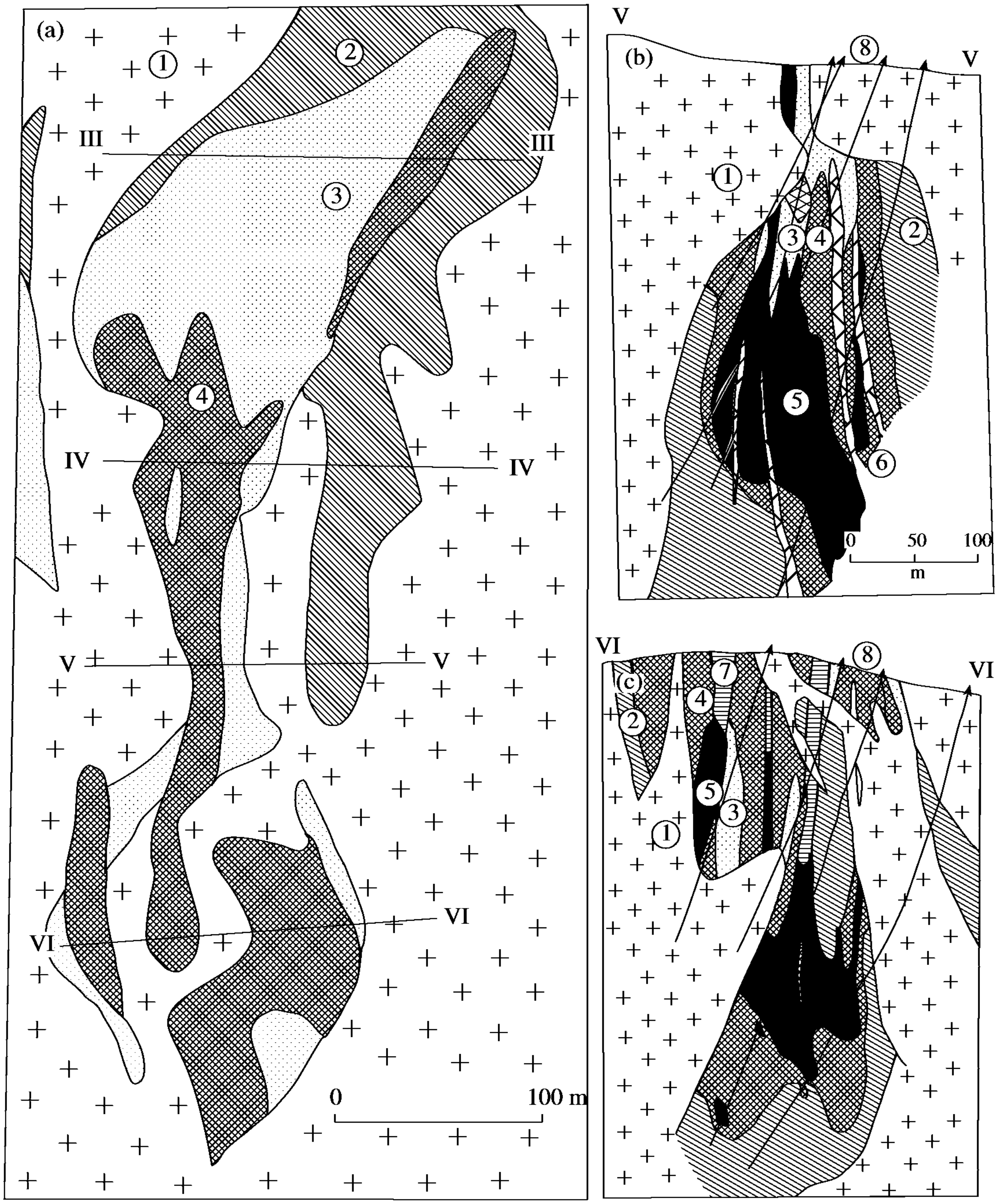

Fig. 4. Map of the Zapadnoe deposit, eastern Transbaikalia and profiles across this deposit. (a) Schematic map of the Zapadnoe deposit, eastern Transbaikalia. (1) Hercynian granodiorites; (2) pyroxene skarns; (3) forsterite skarns; (4) ludwigite–magnetite ores. (III–VI) Exploration profile. (b) and (c) Geological profiles across the deposit. (1–3) same as in Fig. 4a; (4) boron-bearing magnetite ores; (5) monomineralic ludwigite ores; (6) postmineral dikes of Mesozoic porphyries; (7) supergeneously altered ludwigite ores; (8) exploration boreholes.

particularly important, regeneration when gold-bearing weathering crusts and placers are formed.

Facts confirming the occurrence of newly formed gold in placers and weathering crusts are numerous, but the role of this phenomenon in the precipitation of economic gold concentrations was not quantified and sometimes provokes doubt. This is related, first of all, to the still poorly understood geochemistry of supergene gold regeneration.

The data of Petrovskaya [49], Nikolaeva [50], Yablokova [51], Novgorodova et al. [52], and many other researchers indicate that gold migration and redeposition in supergene environments does take place. It was definitely demonstrated that newly formed supergene gold occurs as thin films, flakes, dendrites, globules, and small crystals. It is believed that gold is transported in both solutions and colloids.

The morphology and texture of supergene gold were analyzed by Petrovskaya [49]. It was established that newly formed gold occurs at several placers in the area along the Lena River in Siberia in the form of spongy crusts and humps at the surface of gold grains or cement these grains. Other researchers confirmed and specified these observations.

According to Nikolaeva [50], newly formed gold was deposited (as humps and crystals) on pale yellow to tin-white silver-bearing rounded gold grains of low fineness. It was found in placers that were produced by the destruction of rocks that had contained sulfides (pyrrhotite and pyrite with inclusions of low-fineness gold 0.01–4 mm across). At the same time, gold was never found in placers produced by the erosion of gold-bearing quartz veins.

Newly formed gold was found in placers in the Aldan Shield by Yablokova [51], who determined that rounded coarse-grained gold in these placers is 900 to 923 fine, whereas the newly formed gold is 794–880 fine and clearly differs from the primary gold in texture. Overgrowths of newly formed gold on the primary one are fine-grained, polyhedral, and twinned.

According to Novgorodova et al. [52], newly formed gold occurs in weathering crusts in Orenburg oblast as ungeometrical lumps, angular fragments, and spongy masses of dull brownish and red-brownish color; the gold grains are never larger than 0.3 mm. In addition to high-fineness (898–982) gold, these researchers documented its new mineralogical mode of occurrence of violet–purple and purple color, which consisted of a mixture of gold hydroxide and fine-grained polymineralic aggregates of iron hydroxides and iron and bismuth tellurates.

These data and other extensive information provides evidence that supergene gold can be formed in placers and weathering crusts and can migrate with groundwaters. It was hypothesized [51, 53] that this process can be productive and can even regenerate the gold potential of previously worked out placer deposits.

For example, Voronin and Goldberg [54] believe that this process can be facilitated by electrochemical reactions related to a weak electric field around liquid flows filtrating through porous rocks. These researchers demonstrated that the separation of electric charges during the flow of solutions brings about a voltage difference and generates volumetric electric fields, which, in turn, induce the concurrent reactions of cathode reduction (precipitation) and anode oxidation. Electrons can thereby be conducted by particles of gold, sulfides, and other minerals. It was established that higher concentrations of electrically positive metals (such as Au and PGE) in the solutions are favorable for the more active precipitation of these metals on primary mineral

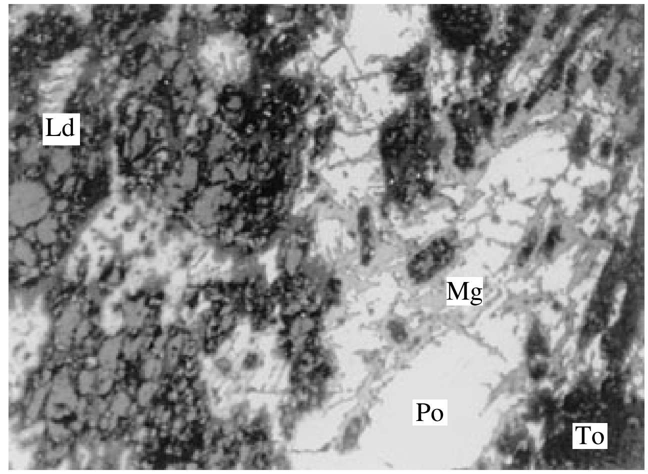

Fig. 5. Pseudomorphic replacement of magnesioludwigite crystals (Ld, dark gray) by tochilinite (To, black) and of pyrrhotite (Po, white) by stringers of magnetite (Mg, pale gray). Zheleznyi Kryazh deposit. Polished section, magnification 30^{x}.

particles. Ag and Cu, which are more electrically negative metals, occur much more rarely in placers. It is thus commonly believed that the margins of gold particles should not become enriched in silver and copper when newly formed gold is precipitated on these particles.

It is known that the margins of gold particles sometimes have a higher fineness of the gold. The higher fineness of gold particles in the margins is sometimes believed [49 and others] to be caused by the partial depletion of these particles in silver as a more mobile element in supergene environments. This does not rule out the possibility of the galvanic overgrowths of gold particles with newly formed high-fineness gold in placers. This issue deserves, however, its further studying.

In spite of the fact that newly formed gold occurs much less widely than "old" gold in placers, modern technologies make it possible to extract all gold, including its nanometer-sized particles regardless of their genesis. This approach to the problem discussed in this paper highlights the economic significance of newly formed supergene gold.

GOLD MIGRATION IN SUPERGENESIS ZONES

Vernadsky [55] evaluated the average gold concentration in riverine waters at 3×10^{-10}%. Other researchers [51] assayed this concentration in mine waters at 1×10^{-7} to 9×10^{-7}% [51]. Roslyakov et al. [56] determined that the Au solubility in waters with Ca sulfate is higher than in waters with Mg sulfate: 4.27 and 2.65 μg/l, respectively. The pH of these waters varies from 6.5 to 8.0. The supergene concentration of gold was demonstrated to be controlled by the occurrence of geochemical barriers, such as oxygen, reducing (hydrogen sulfide, sulfate, and carbonate), alkaline, and acid, as well as the evaporation of mineralized waters in arid environments or in the presence of mineral adsorbents.

Data on the role of heterotrophic microorganisms (bacteria) in the dissolution of gold particles and the later reduction of gold in the form of its newly formed masses are scarce [57]. Nevertheless, available information suggests that gold can be involved in the biological cycles of the bacteria, and this is associated with changes in the surface topography of native gold grains with the development of humps and pores whose sizes are commensurable with those of the microorganisms. The gold particles (0.1–0.2 mm across) used in the experiments lost half of their masses during experiments that lasted for one year, and the dissolved gold was reduced and occurred in the solutions in the form of very fine colloid particles. Their concentrations in the sols were 166 mg/l. The authors argue that gold oxidation and reduction proceeded concurrently, as follows, for example, from the development of newly formed crystals, botryoidal aggregates, spongy masses, and lumps of newly formed gold on the surface of primary gold particles. The fineness of this gold varies from 954 to 746, whereas the primary gold is 843 fine.

Furthermore, gold migration (and reduction) is facilitated by the presence of organic fulvic acids in the waters and the biological activity of microorganisms (fungi and others). This phenomenon is reflected in gold precipitation from groundwaters by plants, for example, reindeer lichen and other species, as was repeatedly documented during the biogeochemical studies of gold ore fields, including their magnesian skarn types.

ROLE OF CRYOGENESIS IN GOLD MIGRATION

In the context of our research and with regard for the location of the deposits described in this publication in permafrost and seasonal freezing areas, we attach particular significance to the cryogenic migration and regeneration of gold.

Studying the hydrochemical effects of cryogenic processes on the origin of aqueous solution flows disseminating gold, Plyusnin et al. [58] have demonstrated that gold concentrations in waters are usually equal to 6.6×10^{-7} g/l and increase to 11.2×10^{-7} g/l in thawed waters and to 15.0×10^{-7} g/l in waters that were preliminarily frozen at a temperature of –6°C. The authors explain these differences by the unusual properties of thawed waters, which can dissolve more gold, but do not consider the possibility of gold regeneration.

Fedoseeva [59] published data on gold migration in frozen soils and snow, a process controlled by the physicochemical characteristics of ice surface and the properties of intercrystalline liquidlike films. The presence of these films was identified within the temperature range of 0 to –10°C. It was demonstrated that Au and Cu are contained in the pore solutions in the form of ions that can form complex compounds. Gold can occur as dithousuilfate-aurate, which is stable within a broad pH range and can be readily reduced to the elementary form.

The processes of permanent (seasonal) freezing of groundwaters in certain areas in Siberia, North America, and other regions where the gold deposits discussed in this paper are situated should notably affect the concentrations of dissolved gold. The freezing of water in the active soil stratum produces ice that contains practically no dissolved salts, which are thus concentrated in the residual liquid contained between ice crystals. The gold concentrations in this liquid can increase by almost two orders of magnitude. This creates favorable conditions for gold precipitation from these solutions on the surface of gold particles in placers or at the surface of ice crystals.

The occurrence of this process in nature is confirmed by the finds of thin gold films between ice crystals at the Yellow Knife deposit in Canada [60]. The possible growth of gold dendrites from gold-oversaturated residual solutions during the seasonal freezing of the thawing stratum in placers in the Kolyma area was reported by Kolyasnikov [61], who believed that the morphology of these dendrites inherited the shapes of dendritic snow crystals and admitted that these dendrites could be overgrown by equant gold crystals and thus thickened to the sizes of normal flat gold particles. Kolyasnikov also believed that the gold potential of depleted placers in the Arctic can be naturally restored by the permanent regeneration of gold from periodically freezing groundwaters of the active stratum.

The role of cryogenesis in the migration and redeposition of native gold, including the mechanical transport and concentration of gold particles in soil polygons at the bottom of the active stratum during its seasonal freezing and thawing [62, 63] deserves more detailed study.

The materials presented above generally characterize the geochemistry of the evolutionary behavior of gold in the endogenic and supergene processes forming magnesian-skarn ore deposits. It was demonstrated that Fe and Cu hydroxisulfides (tochilinite and valleriite) are a previously unknown important link of the genetic mineralogy of gold. Our results can be used during the mining operations not only at contact–metasomatic (skarn) deposits but also at precious-metal deposits hosted in dolomites, carbonatites, and ultrabasites. The results of our research confirm the importance of and the necessity of studying the processes of gold regeneration in supergenesis zones at ore deposits, placers, and the dumps of gold deposits.

CONCLUSIONS

1. Magnesian skarn deposits of gold-bearing sulfide ores are a promising source of this metal in the form of its primary lodes and spatially related alluvial and other types of placers. A common feature of these deposits is

their spatial restriction to contacts of dolomites with intrusions of predominantly mafic composition or those of syenites, although this does not rule out the necessity of assaying the ore potential of skarns in contacts with granites and ultrabasites and in carbonatites.

2. Gold-bearing sulfides are contained at these deposits in pyroxene and forsterite skarns and calciphyres, periclase marbles, dolomites, and magnetite–ludwigite ores, including overprinted calcic–skarn associations.

3. Iron and copper sulfides contained in magnesian skarns are ubiquitously replaced by hydroxisulfides (tochilinite and valleriite) under the effect of hydrothermal solutions. These hydroxisulfides inherit fine gold from the replaced sulfide. The hydroxisulfides are unstable and are endogenically replaced by magnetite and Cu, Fe, and Mg sulfates, and this facilitates the migration of readily dissolved fine Au and its regeneration on the surface of larger Au particles or in nearby rocks. In the zone of supergenesis, tochilinite and valleriite are easily oxidized, and their gold is inherited by masses of magnetite dust and is partly adsorbed by iron and copper hydroxides and/or is dissolved in meteoric waters.

4. The problem of the tochilinization and valleriitization of sulfide ores is significant for genetically diverse deposits of copper and precious metals and is of great scientific and applied importance. This problem can be solved both by the improvement and modernization of technologies of gold recovery and, perhaps, also PGE from ores and dumps and by the deciphering of the geochemistry of the supergene migration and regeneration of native metals in placers.

5. In permafrost areas, where several gold deposits occur in Russia and Canada, dissolved gold is concentrated in the residual unfreezing liquid of the active stratum during its seasonal freezing and thawing. The gold concentration in the liquid can thereby increase by almost two orders of magnitude. The cryogenic concentrating of gold-bearing solutions in intercrystalline liquid films in ice can facilitate gold regeneration in placers on the surface of gold grains and particles or at adsorbents. The permanent freezing of soils activates this process and can result in the restoration of the gold potential of depleted placers and mine dumps.

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