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GEOCHEMISTRY

New Data on the Gold–Antigorite Association of the Urals

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Many placers of the Urals spatially associated with massifs of serpentinized ultramafic rocks contain gold–magnetite associations [7]. The bedrock analogs of this association are rare, small, and interpreted as derivatives of granitoid magmatism. Gold–magnetite occurrences in the Kagan alpinotype ultramafic massif in the South Urals, for example, served as a basis for distinguishing the Au-productive serpentinite (antigorite) metasomatic association [9]. In addition to the spatial association of gold mineralization with antigorite serpentinites, the existence of this association is substantiated by the fact of significant redistribution and mobilization of Au during the development of antigorite, which allowed us to suggest that gold mineralization in the antigorite serpentinites was formed during crustal regional or local metamorphism of the ultramafic massifs under crustal conditions [6]. The present study of gold–magnetite ores and altered rocks of the Kagan massif revealed mineralogical and isotopic–geochemical evidence for the metamorphic origin of mineralization. In this model, fluid and ore components (Fe, Cu, and Au) were mobilized from ultrabasic rocks.

The Kagan Massif is located in the Vishnevogorsk–Il'menogorsk metamorphic complex in the South Urals. Lenslike ultrabasic bodies of the complex are controlled by deep-seated faults and traditionally ascribed to the Riphean riftogenic ophiolites, which underwent Late Cambrian regional zoned metamorphism and Early Paleozoic siliceous metasomatism [2]. According to these concepts, the ultramafic rocks together with host volcanosedimentary rocks were transformed with decreasing temperature into olivine–enstatite, talc–olivine, olivine–antigorite, and antigorite serpentinites during high-grade metamorphism, while later metasomatism was responsible for the formation of enstatite, anthophyllite, and talc–carbonate rocks.

According to Varlakov, rocks of the Kagan Massif underwent zoned metamorphism. Its southern part is composed of talc–olivine and olivine–antigorite rocks, while the northern part consists of antigorite serpentinites with relicts of olivine–antigorite rocks (Fig. 1). The silicic metasomatism is weak and manifested in the development of anthophyllite in talc–olivine rocks and the development of talc in olivine–antigorite rocks and antigorite serpentinites. The occurrences of massive and vein–schlieren magnetite ores containing up to 2–3% sulfides are confined to the tectonic zone extending over 2 km along the eastern contact of the northern part of the massif. Magnetite lenses up to 5–6 m long and 0.2 m thick form chains rapidly pinching out along the tectonic zone. The ores are contained in reticulate serpentinite with abundant fine magnetite, which emphasizes the affiliation of serpentine to chrysotile. In the immediate contact with ore, the reticulate serpentinite contains spots and veinlets of antigorite with large magnetite, talc, chlorite, and amphibole.

The gold–magnetite ores were developed by two small mines in the mid 20th century. Gold assay accounts for 0.2–1.2 g/t, sharply increasing in the areas with visible gold particles. The chemical–spectral analysis of individual samples showed that the magnetite ores contain Au (up to 160 mg/t), Pd (up to 770 mg/t), and Pt (up to 20 mg/t) [5]. The contents of Rh, Ir, Os, and Ru are less than 10–20 mg/t.

Magnetite of massive and disseminated ores is characterized by a ubiquitous admixture of Mg (1.0–2.4 wt % MgO). Magnetite from the wall rocks, in addition, contains 0.4–2.0 wt % Cr_2O_3, which indicates its formation after Cr-spinel. Rare relict grains of Cr-spinels are replaced by Cr-magnetite, Cr-bearing chlorite, and magnetite. The fine dissemination of native gold and copper sulfide is sometimes observed in the rims of minerals replacing Cr-spinels [5].

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The chemical composition of relict parts of Cr-spinels is characterized by simultaneous high contents of Mn (0.8–2.4 wt %MnO) and Zn (0.4–3.5 wt % ZnO). In the Cr/(Cr + Al) versus $Fe^{2+}/(Fe^{2+} + Mg)$ diagram, its chemical composition corresponds to accessory Cr-spinel of harzburgites. The high Zn content in the accessory Cr-spinels is typically related to the replacement products of primary Cr-spinels during metamorphism or to the appearance of newly formed phases of this mineral in the metamorphic and metasomatic assemblages. Cr-spinels with simultaneous high contents of Mn (up to 6.9 wt % MnO) and Zn (up to 6.1 wt % ZnO) were found in some alpinotype ultrabasic massifs of the Urals, e.g., in the Karabash, Shabrov, and Bazhenov massifs. In these massifs, such Cr-spinels are associated with magnetite–awaruite–lizardite serpentinites formed after harzburgites and are considered metamorphic products, while Mn and Zn were mobilized from mafic rocks metamorphosed together with ultramafic rocks [10].

Sulfides form two assemblages. The early assemblage formed simultaneously with magnetite precipitation. Minerals of the early assemblage occur in magnetite as fine (less than 50 μm) rounded or oval inclusions of chalcopyrite, pyrrhotite, talnakhite, cubanite, and Cu–Co–Ni-bearing mackinawite. Sulfides of the late assemblage (chalcopyrite, bornite, pyrrhotite, Co-pentlandite, and Fe-sphalerite) fill interstices between magnetite aggregates and make up large aggregates up to 2–3 mm in size. Both assemblages contain particles of Cu-bearing native gold [5].

Magnetite accumulations are cemented by a nonore matrix, which contains relict blocks of early reticulate serpentine enclosed in the coarse-platy antigorite aggregate with subordinate talc, chlorite, and tremolite. The ores and host rocks are crosscut by a network of veinlets of late serpentine, chlorite, and dolomite.

The aggregates of early reticulate serpentinite have a mosaic or crenulated structure with laminas of different chemical compositions. In places, relict olivine was found among reticulate serpentine, which has a heterogeneous chemical composition with unusually wide variations of Fe (3.11–11.1 wt % FeO) and Cu (0.3–6.9 wt % CuO). The maximal Cu content was found in serpentine with the highest Fe content, reflecting the positive correlation between their contents (Fig. 2). An elevated Cu content (up to 0.4 wt % CuO) was also found in the relict olivine among reticulate serpentine, which corresponds to typical olivines of dunites and harzburgites in terms of the iron mole fraction (X_{Fe} = 0.008) [3]. The olivine also contains subordinate amounts of typomorphic trace elements (up to 0.3 wt % NiO and MnO).

Magnetite is cemented by aggregated plates of antigorite, talc, and chlorite. Antigorite has a more persistent composition than reticulate serpentine and a low Fe content (2.7–6.9 wt % FeO). The mineral is also characterized by a higher content of Cu (up to 4.4 wt % CuO), which has a positive correlation with Fe. One can often see alternation of antigorite plates with different Cu contents. Chlorite from this assemblage marked by low contents of Al (9.7–14.0 wt % Al_2O_3) and Fe (3.3–4.6 wt % FeO) is classified as clinochlore. The Cu content in it is typically below the measurement error of microprobe analysis, only rarely reaching up to 0.35 wt % CuO. Talc laths have a homogeneous composition, with Fe as the main admixture (1.3–1.4 wt % FeO). Other admixtures, including Ni and Cu, are below the detection limit.

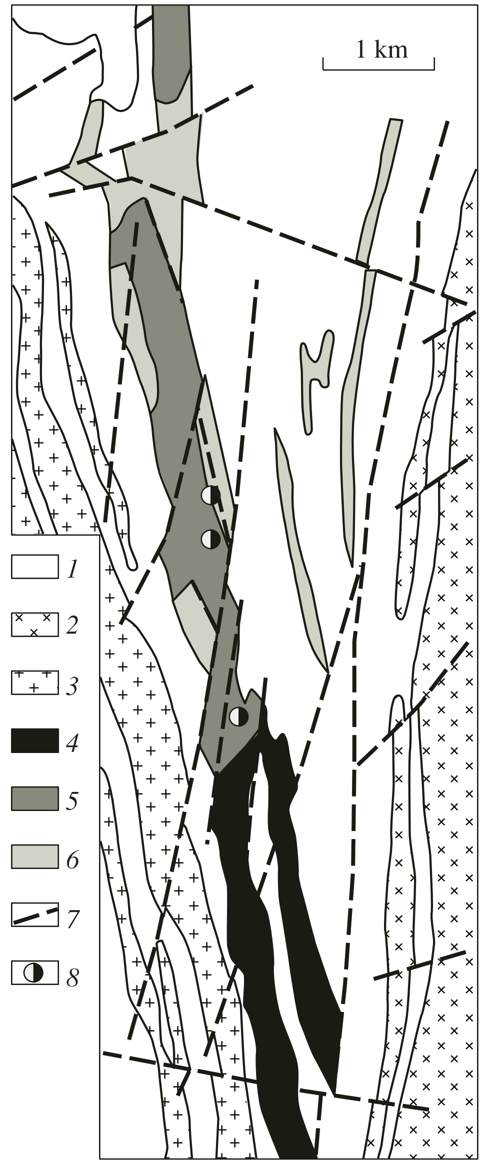

Fig. 1. Geological structure of the Kagan ultrabasic massif (modified after Varlakov [2]): (*1*) surrounding metamorphic rocks (Igish, Saitov, Arakul, and Vishnevogorsk sequences) represented by quartzites, plagioschists, amphibolites, and gneisses; (*2*) syenites and miaskites; (*3*) granites; (*4*) talc–olivine and olivine–antigorite rocks; (*5*) antigorite rocks with occasional relicts of olivine–antigorite rocks; (*6*) talc–carbonate rocks; (*7*) faults; (*8*) gold–magnetite occurrences.

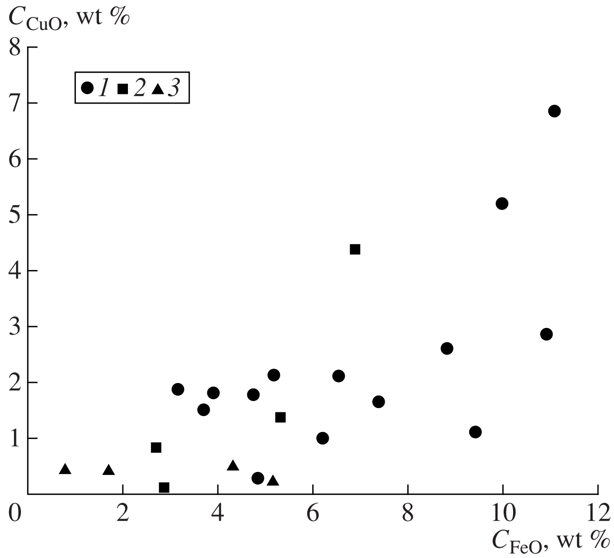

Fig. 2. Relations of Cu and Fe concentrations in serpentines of various generations: (*1*) early reticulate serpentine, (*2*) antigorite, and (*3*) late chrysotile.

Late serpentine (chrysotile) forms a parallel-columnar vein aggregate with stringer or chain aggregates of magnetite in their central part. Chrysotile has the lowest contents of Fe (0.8–5.2 wt % FeO) and Cu (0.3–0.5 wt % CuO). Chlorite associated with chrysotile has relatively low contents of Al (11.6–13.0 wt % Al_2O_3) and Fe (3.1–3.8 wt % FeO) and is ascribed to clinochlore-pennine. The Cu content is low (less than 0.15 wt % CuO). Carbonate in the magnetite ore is represented by Cu-bearing dolomite with a low ankerite component (0.9–2.2 wt % CuO and 0.15–0.20 wt % FeO). In addition, dolomite contains 0.8–0.22 wt % MnO.

According to our concepts, the gold–magnetite ores were formed by the concentration of ore matter in tectonically weakened zones during the regressive stage of regional metamorphism. The magnetite groundmass precipitated simultaneously with the development of antigorite, chlorite, and talc after olivine and the development of amphibole after clinopyroxene. In addition to Fe, Cu and Au were also introduced into the system as finely disseminated native gold and copper sulfides in magnetite and as an isomorphic admixture in serpentines (chrysotile and antigorite). During the late serpentinization and chloritization most expressed in the wall rocks, the ore components were redistributed from the silicate component into the sulfide component with formation of large sulfide grains and native gold.

The thermal decrepitation (within a temperature range of 300–600°C) of primary inclusions in minerals showed that the antigorite- and magnetite-generating fluids are identical in terms of composition, proportions of gas components, and their oxidation state. The fluids have a hydrous composition with a subordinate amount of CO_2 (X_{H_2O} = 0.975–0.978, X_{CO_2} = 0.019–0.020) (table). In terms of these characteristics, they are similar to fluids accompanying the formation of Au-bearing rodingites [8], but distinguished by the virtual absence of reduced gases (H_2 and CH_4). The oxidation state of volatiles (0.84 and 0.86 during the development of antigorite and magnetite, respectively) attests to ore formation in highly oxidizing conditions, under which Cu can enter magnesium silicates as a bivalent admixture instead of Mg.

The isotopic characteristics of oxygen and hydrogen ($\delta^{18}O$ = 5.2‰, δD = –127.7‰) show an extremely light hydrogen isotopic composition, which strongly differs from that of oceanic serpentinites or continental antigorites. However, this composition corresponds to that of continental ophiolite serpentinites of the lizardite–chrysotile type [11, 12]. Evidently, the studied antigorite serpentinites inherited their isotopic composition from earlier reticulate serpentinites, as was established for olivine–antigorite rocks (voikarites) [1]. Moreover, the light hydrogen isotopic composition was also determined for talc from the ore zone ($\delta^{18}O$ = 7.4‰ and δD = –132.7‰) and amphibole from amphibole–pyroxene ($\delta^{18}O$ = 9.3‰, δD = –124.6‰ and pyroxene–amphibole (^{18}O = 7.1‰, and δD = –126.2‰) rocks of the Kagan Massif. All these facts attest to the metamorphic origin of the fluid participating in the formation of magnetite ore and all the aforementioned rocks. Such a fluid could be formed by the release of water (deserpentinization) during prograde metamorphism of early continental serpentinites and their replacement by olivine, enstatite, and talc. These rocks are abundant in the studied massif, especially in its southern part. The mechanism

Gas composition of fluid during the formation of Au-bearing magnetite ores, rodingites, and host serpentinites of the Kagan and Karabash massifs (mol %) according to gas-chromatographic analysis

Sample no.	Rock	H_2O	CO_2	CO	N_2	H_2	CH_4	ΣC_nH_m	OSV
1315	Antigorite serpentinite	0.975	0.020	0.002	0.000	0.001	0.000	0.000	0.84
1307	Magnetite ore	0.978	0.019	0.002	0.000	0.000	0.000	0.000	0.86
1303*	Lizardite–chrysotile serpentinite	0.972	0.011	0.006	0.000	0.007	0.003	0.001	0.41
1380*	Antigorite serpentinite	0.854	0.067	0.016	0.000	0.056	0.004	0.002	0.47
1285*	Rodingite	0.981	0.003	0.002	0.000	0.012	0.001	0.001	0.16

Note: (OSV) Oxidation state of volatiles $CO_2/(CO_2 + CO + H_2 + CH_4)$.

of deserpentinization was described to explain the nature of fluid during the formation of Au-bearing rodingites of the Karabash Massif in the South Urals [4]. However, their primary rocks were oceanic serpentinites, whereas the rodingite- and serpentinite-generating fluids had a more reduced composition (table).

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