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GEOCHEMISTRY

Rhenium in Ores of Porphyry Copper Deposits in the Urals

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The geochemistry of rhenium in ores of porphyry copper deposits, which serve as the major industrial source of this element, has been discussed in numerous publications [1–5 and others]. However, data on the Re distribution in ores are lacking for deposits in the Urals. It is known that the majority of porphyry copper deposits in the Urals formed in an island-arc setting associated with minor plagiogranitoid intrusions (hereafter, plutons) of elevated basicity. Such conditions are considered very favorable for the accumulation of Re in ores [1, 2]. The present paper is devoted to the concentration of Re in deposits of various geotectonic settings in the central and southern Urals. The Re–Mo relationship is discussed with consideration of the close geochemical correlations between these elements.

Porphyry copper deposits and occurrences have been discovered in all regional structures on the eastern slope of the Urals [6–8]. In the major (Tagil–Magnitogorsk–western Mugodzhary) volcanic zone, porphyry copper deposits are paragenetically associated with the Lower–Middle Devonian plagiogranitoid plutons mainly composed of diorite–quartz diorite rocks. Orebodies at these deposits and occurrences are characterized by high Cu/Mo values (400–600) and low contents of Mo (5–27 ppm) and Re (table). At the Yubileinoe porphyry Cu–Mo deposit (the Mugodzhary sector of the structure) associated with low-K (K_2O up to 2 wt %) granodiorite porphyries, the Re content in ores does not exceed 0.01–0.04 ppm. At the Salavat porphyry copper deposit (the Magnitogorsk sector of the structure) and the Karaksak ore occurrence (the Mugodzhary sector of the structure), which are associated with diorite–quartz diorite plutons (K_2O 0.3–0.6 wt %), the Re content in ores varies from 0.08 to 0.17 ppm (up to 0.47 ppm in some places). However, the Re content is generally not higher than 0.01–0.03 ppm. In the massive chalcopyrite–pyrrhotite and chalcopyrite–pyrite ores of the Gumeshev skarn porphyry copper deposit (central Urals) and skarn copper deposits of the Tur'ya group (northern Urals) associated with diorite–quartz diorite plutons (K_2O up to 1.0–1.5 wt %), the Re content is 2–29 ppm.

The largest porphyry Mo–Au–Cu ore nodes in the Urals with the maximal Re concentration in ores are located in the southern Urals. The age of ore deposits in this area ranges from Late Devonian to Early–Middle Carboniferous. They are confined to the boundary between the East Ural volcanic zone and the East Ural (Bereznyakov–Tomin) or the Transural (Mikheevo and Taruta) sialic zone. The ore deposits are associated with quartz diorite–plagiogranodiorite plutons (K_2O up to 1.5–2.0 wt %) that are transitional between the island-arc and continental-margin formations. The Cu/Mo ratio in ores of these deposits varies from 71 to 250, while the Mo content varies from 30 to 200 ppm. Molybdenite is a common mineral, because it is deposited at all stages of mineralization. In copper orebodies, molybdenite occurs in chalcopyrite–quartz or molybdenite–quartz veinlets. However, this mineral is usually developed in dry fibrolitic cracks developed after the chalcopyrite ore stage. The molybdenite content commonly does not exceed 40–70 ppm (0.01–0.03 ppm or more in some zones). In general, the aureoles of Cu and Mo coincide or are slightly displaced relative to each other. The majority of orebodies lack any correlation between Cu and Mo. Ores of the Late Devonian–Middle Carboniferous Mikheevo deposit are represented by stringer–disseminated mineralization in volcanosedimentary rocks and diorite porphyry dikes [6]. These ores are characterized by the maximal Re concentration. In pyrite–bornite–chalcopyrite orebodies (Cu 0.3–1.5 wt %), the Re content varies from 0.01 to 2.7 ppm. In general, the Re content varies from 0.2 to 0.5 ppm (Fig. 1c). The Re content is as much as 289 ppm in molybdenite from the early chalcopyrite–molybdenite–quartz veinlet. In molybdenite stringer and dissemina-

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Contents of Re, Mo, and Cu in ores of some porphyry copper deposits and occurrences in the Urals

Deposit, occurrence	Re, ppm	Mo, ppm	Cu, wt %
Salavat	0.03, 0.03, 0.47*	2–10*	0.50–1.30*
	<0.01(4), 0.12	1–15	0.5–0.7
Karaksak	0.02, 0.04, 0.13, 0.17	2–10	0.2–0.3
Yubileinoe	0.01–0.02 (5)*	2–30*	1.0–1.2*
	<0.01, 0.02, 0.04	5–27	0.2–0.5
Mikheevo	0.01–0.03 (13)	20–60	0.53–0.60
	0.03–0.09 (16)	20–40	0.32–0.65
	0.09–0.27 (12)	15–130	0.30–0.85
	0.27–0.40 (10)	70–130	0.52–0.63
	1.4, 2.7	280, 1397	1.13, 1.16
Taruta	0.02–0.20 (8), 1.4*	15–100*	0.03–5.2*
	0.01–0.59 (38)	10–200	0.5–1.4
Zelenodol'sk	0.03, 0.08, 0.09*	2–20*	0.15–0.50*
	0.01–0.06 (3)	20–50	0.2–0.5
Benkala	0.02, 0.03, 0.04, 0.06*	7–50*	0.07–0.55*
	<0.01(3), 0.12	10–40	0.4–0.7
Zhaltyrkol	0.01, 0.02, 0.03*	2–30*	0.3–0.5*
	<0.01(4)	5–50	0.3–0.8
Verkhneural'sk	<0.01(3), 0.03	30–200	0.1–0.2

Note: The Re content was determined by the kinetic method. Analyses marked with an asterisk were carried out at the IMGRE laboratory. The remaining analyses were performed in laboratories of the Uralian Geological Survey. The number of samples is shown in parentheses.

tion from the diorite, the Re content is 3025 and 2505 ppm, respectively.

The Mo–Re pair shows a strong correlation (r = 0.87–0.98). Calculations based on the regression line (Fig. 1c) show that the Re content in molybdenite varies from 2129 ppm (boreholes 3006 and 3007) to 1198 ppm (borehole 3058). In the insufficiently studied Tomin deposit, the Re content in molybdenite is estimated at 440, 469, 1177, and 3140 ppm in four ore samples with doping of this mineral. In early pyrite–chalcopyrite–orebodies of the small Taruta skarn porphyry copper deposit, the weighted average Cu content varies from 0.5 to 2.4 wt % and the Mo content usually does not exceed 10 ppm [8]. The Mo content is appreciably higher (20–45 ppm, up to 93–178 ppm or more in some places) in the case of superimposition of molybdenum stringers related to the molybdenum mineralization of the second stage associated with propylitization zones. The Cu content in such zones is low (0.01–0.2 wt %). In samples with a high Mo content (>50 ppm), the Re content is 0.05–0.3 ppm and as much as 0.2–1.4 ppm in some samples (Fig. 1). In the propylitized diorite porphyries with abundant molybdenite stringers, Re and Mo show a distinct positive correlation (r = 0.90–0.99) in ore samples from some boreholes (Fig. 1). Both measured and calculated Re and Mo contents vary from 230 to 430 ppm.

In the easternmost part of the Urals, porphyry copper deposits are located between the Transural sialic and the Transural (Turgai) volcanic zones of the southern Urals. Small deposits (Benkalin and Zhaltyrkol) are confined to the Middle–Late Carboniferous granodiorite porphyry plutons (K_2O 2.0–3.5 wt %). The Cu/Mo ratio in ores of these deposits varies from 167 to 200, and the Mo content typically does not exceed 50 ppm. The Re content in molybdenite from the Benkalin deposit varies from 40 to 210 ppm [4].

The volcanic structures incorporate porphyry Cu–Mo deposits, such as the Late Devonian–Early Carboniferous Verkhneural'sk ore occurrence (Magnitogorsk zone), the Middle Carboniferous Talitsa deposit (near the eastern boundary of the Tagil zone), and the Middle–Late Carboniferous Batalin ore occurrence (Turgai zone). These deposits are younger than the porphyry Mo–Au–Cu deposits and are located in monzogranodiorite massifs. In ore zones, the Cu content is low (0.05–0.2 wt %); the Cu/Mo ratio varies from 2 to 10; the Mo content is as much as 100–500 ppm; and the Re content is up to 0.01 ppm (0.03 ppm in one sample). As expected, the Cu content is low (40–187 ppm) in molybdenite from the Talitsa porphyry Cu–Mo deposit.

The data presented above indicate that the maximal Re concentration in ores (up to 0.3–2.7 ppm) and molybdenite therein (up to 0.1–0.3 wt %) is recorded in the Mikheevo porphyry copper deposit with the largest

Cu reserves in the study region. The Re content can also be similarly high in the Tomin deposit. These deposits are located in the East Ural bimodal (sialic–femic) volcanic structure of the island-arc type. The ore-bearing phaneritic and porphyric plutons are composed of low-K quartz–diorite granitoids of the island-arc (or island-arc/continental-margin transitional) type. Ore-bearing magmatism at these ore deposits continued from the Late Devonian to the Early–Middle Carboniferous. The ore deposits are also characterized by multistage ore formation and intense metasomatism. Many researchers believe that the long-term formation of ore fields and nodes is very favorable for the concentration of ore elements [9 and others]. The deposits are confined to large tectonic blocks of ore nodes. Therefore, they represent meso- and hypabyssal sections of porphyry copper columns. The subvolcanic level of such columns incorporates epi- and telethermal porphyry Cu–Au and base metal ore zones. At the same time, hydrothermally altered rocks associated with postvolcanic fluids are known for anomalously high Re concentrations (up to 0.8 wt % or more) in some places [1, 10, and others]. Very high femic composition of the crust and augmentation of the role of gabbrodiorites in the ore-bearing plutons is unfavorable for the concentration of Mo and Re. This is evident from the minimal Re content in ore deposits confined to the major femic island-arc structure of the Urals (Tagil–Magnitogorsk–western Mugodzhary).

High Re contents (0.1–0.3 wt %, up to 0.6 wt % in some places) have been recorded in molybdenite from the porphyry Au–Cu deposits associated with plagiogranitoid or monzonitoid intrusions in island-arc zones of several other regions [1–5, 11, and others]. As in the Urals, some of these deposits are associated with the diorite–quartz diorite plutons (Maidanpek, Yugoslavia; Sipalei, Philippines; Boshchekul, Kazakhstan; and others). Deposits associated with monzonitoid intrusions are also widespread (Ok Tedi deposit, Papua New Guinea). Re-rich ore deposits can also be located beyond structures of the island-arc type and in other geodynamic settings in association with monzonitoid massifs (Almalyk, Uzbekistan; Elazite, Bulgaria; and Kajaran, Armenia) or the granodiorite massifs (Borly, Aktogai, and other deposits in Kazakhstan). In the majority of large porphyry Cu–Mo deposits confined to the continental margin, the Re content in ores and molybdenite is relatively low (500–700 ppm, up to 0.3 wt % in the molybdenite from some deposits). The Re content in chalcopyrite and pyrite is as high as 5–80 ppm in some porphyry copper deposits commonly associated with monzonitoid plutons.

Thus, the maximal Re concentration is only typical of ores from the largest deposits of the East Ural bimodal volcanic structure. The Re concentration in ores and molybdenite from such deposits is governed by several parameters, such as the composition of ore-bearing granitoids, the level of their generation, the composition of the Earth's crust, and so on. The moderate SiO_2 content (56–65 wt %) in granitoids and their depletion in alkali metals is among the essential conditions required for the concentration of Re in the fluid.

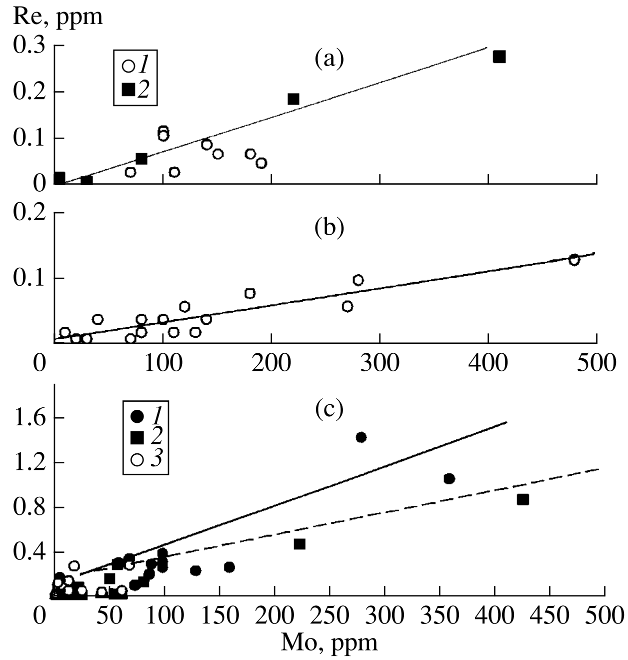

Fig. 1. Rhenium vs. molybdenum relationships in ores of the (a, b) Taruta and (c) Mikheevo deposits. (a) Chalcopyrite–pyrite ores in (*1*) propylitized diorite porphyries and (2) skarns from borehole 250. Analysis of core sample with 0.21 wt % Mo and 0.59 ppm Re is not shown in the plot. The regression line ($r = 0.99$, $n = 8$) is given for skarns; (b) propylitized diorite porphyries (Cu 0.02–0.04 wt %) from borehole 252 ($r = 0.90$, $n = 18$); (c) pyrite–chalcopyrite ores in (*1*) volcanosedimentary rocks from boreholes 3006 and 3007, (*2*) diorite porphyries from borehole 3058, and (*3*) diorite porphyries from other boreholes. The bold line shows the regression ($r = 0.87$, $n = 14$) for samples from boreholes 3006 and 3007; the dashed line shows the regression ($r = 0.99$, $n = 18$) for samples from borehole 3058 (analysis of core sample with 0.14 wt % Mo and 2.72 ppm Re is not shown in the plot). Data of E.A. Belgorodskii and B.M. Shargorodskii are taken into consideration in the plots.

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