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Possible Source of Sulfur in the Porphyry Cu–Mo Ore-Magmatic System: Evidence from the Zhireken Deposit, Eastern Transbaikalia

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Large porphyry Cu-Mo deposits containing hundreds of million tons of ore with high S/(Cu + Mo) values within commercial ore stockworks are surrounded by wide (up to 0.5 km or more) pyrite halos. Thus, such deposits represent a giant sulfur reservoir in the earth's crust. Therefore, deciphering their genesis provides insight into the source of sulfur. This primarily concerns deposits related to the evolution of ore-bearing granitoid-dominated porphyry complexes. As was reported in [1–5 and others], the granitoid magmas of some porphyry Cu-Mo ore districts have sulfur contents that are too low (only up to 100 ppm) to provide a complete sulfur balance in the ore-magmatic system. In particular, the amount of sulfur in melt is estimated at 2500–5000 ppm for the ore-forming quartz-diorite magma in the Santa Rita copper deposit (United States), where anhydrite phenocrysts were found in dikes of the same composition [6]. This amount is more than an order of magnitude higher than that in the orebearing granite magmas.

If acid melts are depleted in sulfur, this element is adopted from surrounding sedimentary rocks containing sulfates and syngenetic pyrite [7]. However, this scenario is hardly possible for the majority of large porphyry Cu–Mo deposits, where the magmatic δ^{34} S value in sulfides is ~0% [4]. Recent works [3–5] suggest that the sulfur could be produced during the mixing of basic melts with acid magma in the chamber. Of certain interest in this aspect is the ore-bearing porphyry complex (Cu/Mo in the ores is 1–2) of the Zhireken Cu–Mo deposit in Eastern Transbaikalia, granites of which show mixing evidence. The δ^{34} S value in sulfides (pyrite, molybdenite, and chalcopyrite) at this deposit varies from -0.6 to $+ 4.1\%_{o}$, which corresponds to the magmatic sulfur source. No sulfur-bearing sediments were found near the deposit.

The Zhireken ore-bearing complex with a ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ age of 160–158 Ma (Fig. 1) is made up of a stocklike body of granite porphyries and subordinate granodiorites that crosscut coarse-grained biotite granites (178 ± 1.7 Ma) and leucogranites (168.1 ± 1.9 Ma) of the Amanan Complex of the large Bushulei Massif [8]. In some places, thin dikes of quartz diorite porhyrites and kersantites intruded before and after the emplacement of



Fig. 1. Geological structure of the Zhireken porphyry Cu– Mo deposit. Amanan Complex: (1) Coarse-grained biotite granites; (2) leucogranites; (3) Zhireken ore-bearing complex (granite and granodiorite porphyries); (4) outlines of the ore stockwork; (5) faults.

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Fig. 2. Globular crystalline segregation in the granite porphyry groundmass (microphotograph). (a) General view; (b) closeup of internal structure.

granite (granodiorite) porphyry stock. The $({}^{87}\text{Sr}/{}^{86}\text{Sr})_0$ ratio (0.70642) in granite porphyries suggest a mixed mantle–crust origin [9].

The granite porphyries contain 40–50 vol % phenocrysts represented by K-feldspar, plagioclase (albite–oligoclase), quartz, and scarce biotite. The finegrained (0.01–0.05 mm) groundmass consists of the same minerals. The groundmass also includes rounded and oval fine-grained segregations (up to 5–10 mm across) with a distinct hypidiomorphic texture (Fig. 2). These globular enclaves are composed of elongated plagioclase laths, interstices between which are filled with biotite, K-feldspar, and quartz. As compared to plagioclases in the groundmass and phenocrysts, plagioclases in globules have a higher content of the anorthite component (andesine). Columnar plagioclase is often rimmed by K-feldspar. Accessory minerals are represented by magnetite, apatite, and celestine.

In terms of major components, the globular segregations sharply differ from granite porphyry and some-



Fig. 3. 39 Ar/ 40 Ar age spectrum of (a) globular segregation and (b) granite porphyry groundmass. The measurements were conducted on a MI-1201 mass spectrometer in the Analytical Center of the United Institute of Geology, Geophysics, and Mineralogy, Novosibirsk.

what resemble the late kersantite dikes (table). However, they differ from the kersantite by higher SrO and SO₃ contents. Magnetite from these enclaves has high contents of Cr (Cr₂O₃ up to 3.20 wt %). This mineral also contains Cu (up to 1500 ppm), Mo (1–2 ppm), Co, and Ni (30–50 ppm). Accessory magnetite in the granite porphyry is characterized by a higher content of Mo (3–10 ppm) but lower contents of Cr₂O₃ (0.27–0.40%) and Cu (up to 100 ppm). The segregations also contain thin acicular (from 0.05×0.004 to 1.0×0.1 mm) apatite with an elevated Cl content (up to 0.4–0.5 wt %), whereas accessory apatite in the granite porphyry contains only ~0.1 wt % Cl.

The presence of globular enclaves of such morphology and composition in granitoids is commonly attributed to injections of mafic melts into partially solidified magma chambers [10, 11, and others]. In addition to petrochemical features of the segregations, elevated contents of Pd and Pt in molybdenites (684 and 299 ppb, respectively) [12] and high crystallization temperatures of the granites also support the participation of basic melts in the formation of the Zhireken granite porphyries. The melt inclusions in plagioclase and quartz phenocrysts from granite porphyry homogenize at 1020– 910°C [13]. Figure 3 shows that the groundmass and the globular enclaves have almost identical 40 Ar/ 39 Ar datings (158.5 ± 0.3 and 158.9 ± 1.3 Ma, respectively). Chemical composition (wt %) of granite porphyries and globular crystalline segregations in them

Component	Granite por- phyry (GP)	Globular segregations in GP	Kersantites
SiO ₂	70.60	54.62	59.00
TiO ₂	0.25	0.96	0.86
Al_2O_3	13.43	13.80	14.60
Fe ₂ O ₃	1.01	3.84	2.61
FeO	3.23	3.63	4.67
MnO	0.03	0.08	0.06
MgO	0.57	5.66	4.91
CaO	1.20	2.94	3.02
Na ₂ O	3.33	3.50	4.33
K ₂ O	4.50	3.48	3.67
P_2O_5	0.05	0.28	0.22
SrO	n.d.	2.80	n.d.
SO ₃	n.d.	2.20	0.30
L.O.I.	0.99	1.76	1.60
Total	99.16	100.45	100.07

Note: Analyses were performed in the Chemical Analytical Laboratory of the United Institute of Geology, Geophysics, and Mineralogy, Siberian Division, Russian Academy of Sciences (E. S. Guletskaya, analyst).; (n.d.) not determined.

The presence of quartz and K-feldspar phenocrysts (often with reaction rims) in the diorite porphyrite and kersantite dikes also indicate the mixing of basic and silicic magmas during formation of the Zhireken orebearing porphyry complex. The typically rounded or amebiform quartz grains (up to 2–3 mm) are often corroded by groundmass. Quartz aggregates are also present. The quartz contains crystallized melt inclusions, which are similar to groundmass in composition and texture. K-feldspar forms large (up to 1×1.5 cm) grains with resorbed margins and thin plagioclase rims in some places.

In the field of globular segregations, the granite porphyries contain resorbed cross-hatched plagioclase crystals with more calcic rims. According to experimental data [14], this structure arises from partial dissolution of sodic plagioclase in the mafic melt.

The sulfur content in apatite from globular enclaves is as much as 5700–7200 ppm. Taking into consideration the distribution coefficient [15], the above content is translated into 630–800 ppm S in the parental melt. At the same time, the sulfur content of 600–1000 ppm in the accessory apatite from enclave-free granite porphyry dikes corresponds only to 65–100 ppm in the parental melt. Hence, the injection of such sulfur-rich basic melt into the sialic magma could significantly affect the total sulfur balance in the porphyry Cu–Mo ore-magmatic system. The high Cu content (1500 ppm)

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in magnetite from the globular enclaves indicates its high content in the basic melt.

Thus, data on the evolution of the ore-bearing porphyry magmatism at the Zhireken deposit suggest that the mixing between sialic and basic magmas exercised a significant influence on the formation of Cu–Mo mineralization with variable proportions of Cu and Mo, which show different types of behavior in the magmatic processes. Copper is the typical chalcophile element associated with basic magmatism, while molybdenum is ascribed to lithophile–chalcophile elements accumulating in granitic magmas. The mixing of different magmas is the key to understanding the nature of the porphyry Cu–Mo formation, which comprises deposits with the Cu/Mo ratio in the ores varying from Cu-rich deposits to Mo-rich varieties.

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REFERENCES

- 1. N. G. Banks, in *Sulfur and Copper in Magma and Rocks* (Univ. Arizona, Tuscon, 1982), pp. 227–257.
- 2. P. J. Wallace and T. M. Gerlach, Science **265**, 497 (1994).
- J. D. Keith, E. N. Christiansen, D. T. Maughan, and K. A. Waite, Geol. Assoc. Can. Short Course, 26, 211 (1998).
- 4. K. H. Hattori and J. D. Keith, Miner. Deposita **36**, 799 (2001).
- 5. D. T. Maughan, J. D. Keith, E. H. Cristiansen, et al., Miner. Deposita **37**, 14 (2002).
- A. Audetat, T. Pettke, and D. Dolejs, Lithos 72, 147 (2004).
- H. Ohmoto and M. B. Goldhaber, in *Geochemistry of Hydrothermal Ore Deposits*, Ed. by H. L. Barnes (Wiley, New York, 1997), pp. 509–567.
- V. A. Ponomarchuk, V. I. Sotnikov, and A. N. Berzina, Geochem. Int. 42, 587 (2004) [Geokhimiya, No. 6, 679 (2004)].
- V. I. Sotnikov, A. V. Ponomarchuk, A. N. Berzina, et al., Geol. Geofiz. 41, 1112 (2000).
- 10. R. Goldie, Can. J. Earth Sci. 15, 132 (1978).
- W. Büsch and J. Otto, Neues Jahrb. Mineral. Monatsh. 6, 269 (1980).
- 12. V. I. Sotnikov, A. N. Berzina, M. Economou-Eliopoulos, and D. G. Eliopoulos, Ore Geol. Rev. 18, 95 (2001).
- V. I. Sotnikov, A. G. Poliveev, and A. N. Berzina, Dokl. Akad. Nauk SSSR 283, 1463 (1985).
- 14. A. Tsuchiyama, Contrib. Mineral. Petrol. 89, 1 (1985).
- 15. Trans. R. Soc. Edinburgh, Earth Sci. 87, 243 (1996).