Porphyry Cu(Mo) deposits of the Urals: insights from molybdenite trace element geochemistry

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Abstract. The first data on EMPA and LA-ICPMS study of molybdenite from four porphyry deposits of the South and Middle Urals (Tomino, Mikheevskoe and Benkala porphyry Cu and Talitsa porphyry Mo deposits) are presented. It is shown that most trace elements form mineral inclusions within molybdenite in all the deposits studied; only Re and W are most likely to be incorporated into the molybdenite lattice. Porphyry Cu deposits (Tomino and Mikheevskoe) formed within oceanic arc settings are featured by high contents of Re (mostly over 400 ppm) and low contents of W (<10 ppm) in molybdenite; porphyry Cu deposits from Andean-type geotectonic environment (Benkala) are featured by lower Re content (hundreds ppm) and high contents of W (tens ppm) in molybdenite. Molybdenite from porphyry deposits from collisional setting (Talitsa) has low content of Re and elevated W contents (tens ppm). It is demonstrated that trace element geochemistry of molybdenite is a useful tool to define the source of metal components and the geotectonic environment for porphyry Cu(Mo) deposits.

1 Introduction

Porphyry Cu (±Mo,Au) deposits of the Urals (Fig. 1) can be subdivided into the following groups according to their link to subduction zones of different ages (Plotinskaya et al. 2017):

(1) Deposits of the East-Uralian volcanic terrane related to Silurian intra-oceanic arc: porphyry Cu deposits of the Birgilda-Tomino ore cluster and several subeconomic occurrences.

(2) Deposits within the Magnitogorsk volcanic megaterrane linked to the Magnitogorsk intra-oceanic arc which was active from Early Devonian (Emsian) and collided with the East European plate in the Late Devonian (Famennian). These are Middle Devonian Salavat and Voznesenskoe porphyry Cu deposits, and Late Devonian Yubileinoe porphyry Au deposit and Verkhneuralskoe porphyry Mo occurrence

(3) Deposits located in the Trans-Uralian megaterrane and linked to the Late-Devonian to Carboniferous subduction events. This is the Late Devonian to Early Carboniferous Mikheevskoe porphyry Cu deposit linked to an intra-oceanic arc. Tevelev et al. (2006) however supposed a subduction under the accretion prism on the eastern margin of the East-Uralian continent. This group includes also Early Carboniferous deposits formed due to eastward Andean-type subduction under the Kazakh continent (Benkala porphyry Cu deposit and several occurrences).

(4) Continent-continent collision of the East European plate and the Kazakh continent in the Late Carboniferous produced the Talitsa porphyry Mo deposit located in the East Uralian megaterrane.

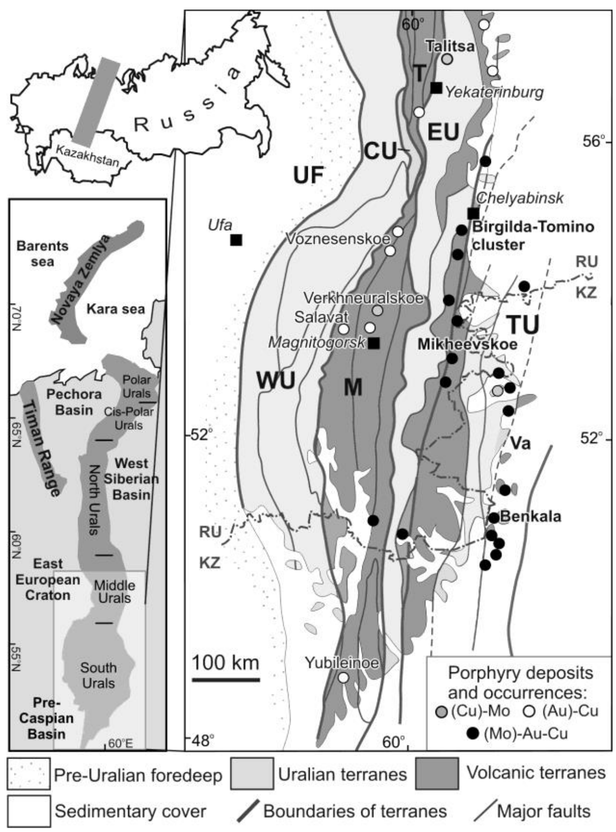

Figure 1. Simplified tectonic scheme of the Middle and South Urals, and locations of porphyry deposits and occurrences, modified after (Petrov et al. 2007; Plotinskaya et al. 2017). Terranes: WU – West Uralian; CU – Central Uralian; T – Tagyl; M – Magnitogorsk; EU – East Uralian, TU – Trans Uralian (Va – Valerianovka volcanic terrane).

This paper presents first data on EMPA and LA-ICPMS study of molybdenite from selected Cu(Mo) deposits and attempts to discuss the obtained regularities in terms of trace element geochemistry of molybdenite and geotectonic settings of the deposits.

2 Analytical methods

The chemical compositions of ore and gangue minerals were determined using a Zeiss EVO 15LS scanning electron microscope with an Oxford Instruments X-Max EDX detector (Natural History Museum, London). X-ray mapping and point analyses of molybdenite were performed using a Cameca SX-100 electron microprobe with five WDX spectrometers (Natural History Museum, London, UK). Farther details are described in Plotinskaya et al. (2018).

The trace element data of molybdenite were acquired using the New Wave 213UP laser coupled with the Thermo X Series2 quadrupole ICP-MS (IGEM RAS, Moscow). The following isotopes were measured S^{33}, V^{51}, Fe^{57}, Co^{59}, Ni^{60}, Cu^{65}, Zn^{66}, As^{75}, Se^{77}, Mo^{95}, Ag^{107}, Sn^{118}, Cd^{111}, Sb^{121},Te^{125}, W^{182}, Re^{185}, Re^{187}, Au^{197}, Hg^{202}, Tl^{205}, Pb^{208}, Bi^{209}. In addition Si^{29}, Ti^{47}, and Ca^{43} were measured in order to reveal mineral inclusions but were not calculated. External standards were in-house pyrrhotite for Re and MASS-1 for the remaining elements; S was used as internal standard based on molybdenite stoichiometry. The analyses were obtained from line profiles with laser diameter 30 and 40 μm, laser frequency of 15 Hz, 5-7mJ input power and 5 μm/s ablation speed.

3 Results

3.1 The Tomino ore field

The Tomino porphyry Cu deposit with 660 Mt @ 0.4% Cu (Russian Copper Company, 2019) consists of two diorite stocks, each ca. 2 km in diameter, dated as 427±6 Ma (U-Pb in zircons) (Grabezhev and Ronkin 2011), intruded into Ordovician basalts. The northern stock hosts the Tomino site, while the southern one – Kalinovskoe site. Molybdenite from the Kalinovskoe deposit was dated by Re-Os as 430.4 ± 2.0 Ma (Tessalina and Plotinskaya 2017; Plotinskaya et al. 2018).

Molybdenite from the Kalinovskoe site (2 samples) was described in Plotinskaya et al. (2018). EMPA study revealed uneven distribution of Re within single grains of molybdenite with micron-scale zones where Re contents reach 0.95 wt.%. LA-ICPMS data show contents of Re as much as 8.7 to 4540 ppm, geom. mean 621 ppm), W (to 4.3 ppm, geom. mean 0.46 ppm), Se (32 to 350 ppm, geom. mean 146 ppm), Cu, Fe (tens to thousands ppm), Zn, Pb, Bi (several ppm to hundreds ppm), Co, Ni, As, Ag, Te, Au (up to tens ppm), Sb (up to several ppm).

EMPA study of molybdenite from the Tomino site (1 sample) revealed Re-enriched growth zones (up to 0.68 wt.% of Re) within molybdenite flakes (Fig. 2). LA-ICP-MS data also show high contents of Re (2670 to 5800 ppm, geom. mean 3645 ppm), Se (194 to 410 ppm, geom. mean 271 ppm), low contents of W (1.5 to 5.8 ppm), as well as remarkable admixtures of Cu, Fe, Zn (tens to hundreds ppm), Ni, Te (tens ppm), As, Cd, Hg, Pb, (several ppm to tens ppm), Co, Ag, Sb, Au, Bi (up to several ppm).

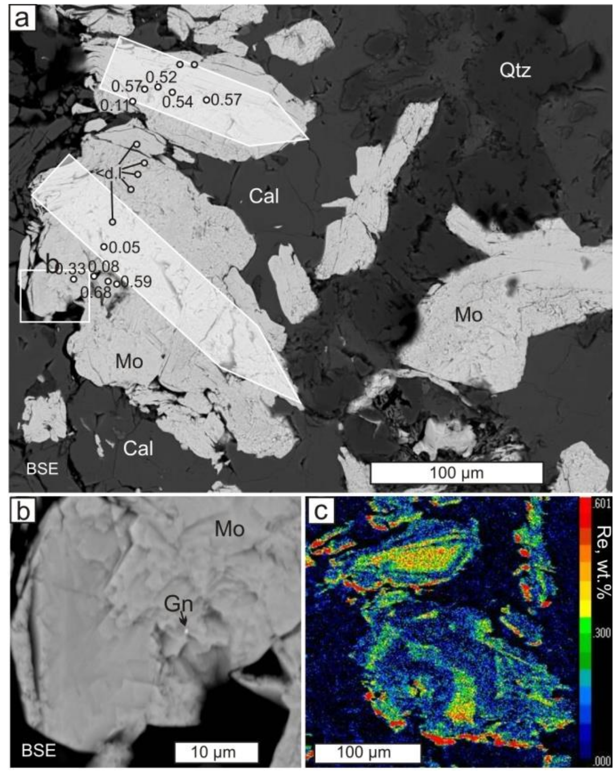

Figure 2. (a) BSE image of molybdenite (Mo) from the Tomino porphyry Cu deposit associating with quartz (Qtz) and calcite (Cal); numbers indicate Re contents in wt. %; (b) detail of (a), inclusion of galena (Gn) in molybdenite; (c) calibrated X-ray map of the Re content in wt. %.

3.2 The Mikheevskoe deposit

The Mikheevskoe porphyry Cu deposit (Shargorodsky et al. 2005), with 629 Mt @ 0.41% Cu (Russian Copper Company, 2019), is the economically most significant porphyry Cu deposit in the Urals. Mineralization is hosted by Late Devonian sandstones, tuffstones, basaltic andesites, overlain by Late Devonian to Early Carboniferous basaltic lavas, tuffs, sandstones. Intrusions are represented by quartz diorite stocks and numerous diorite and granodiorite porphyry dykes dated as 356±6 Ma (U-Pb in zircons) (Grabezhev and Ronkin 2011). Molybdenite from the Mikheevskoe deposit was dated by Re-Os as 357.8±1.8 Ma and 356.1±1.4 (Tessalina and Plotinskaya 2017).

Previous EMPA study (Plotinskaya et al. 2015) revealed micron-scale zones with up 1.34 wt.% of Re. LA-ICPMS study revealed contents of Re (83 to 3440 ppm, geom. mean 967 ppm), W (1.0 to 4.9 ppm), Se (124 to 848 ppm, geom. mean 307 ppm), Cu, Fe (tens to thousands ppm), Zn, Se (tens to hundreds ppm), as well as V, Co, Ni, As, Ag, Cd, Sb, Au, Hg, Pb, and Bi (several ppm to tens ppm).

3.3 The Benkala deposit

The Benkala porphyry Cu deposit (1.56 Mt Cu @ 0.42% Cu according to Frontier Mining (2012)) is associated with Early to Middle Carboniferous intrusions and dykes of the Sokolov-Sarbai diorite–granite complex (porphyritic quartz diorite and granodiorite, and plagiogranite porphyries) hosted by Lower Carboniferous volcano-sedimentary sequence (Gachkevich et al.1986). Intrusions were dated as 334.7±2.9 Ma (U-Pb in zircons) (Grabezhev et al. 2017).

Molybdenite of the Benkala deposit (1 sample) contains Re (364 to 744 ppm, geom. mean 574 ppm), W (29.2 to 76.8 ppm, geom. mean 46.9 ppm), Se (72 to 120 ppm, geom. mean 96 ppm), Fe (thousands ppm), Cu (hundreds ppm), V, Zn, Pb (tens to hundreds ppm), As, (tens ppm), Co, Ag, Cd, (several ppm to tens ppm), Ni, Sb, Te, Au, Hg, Bi (up to several ppm).

3.3 The Talitsa deposit

The Talitsa Mo porphyry deposit is located in the western margin of the East Uralian terrane in the Middle Urals within a sub-alkaline intrusion of about 4 km^2 hosted by Devonian ultrabasic rocks and rhyolite-basalt volcanics. The Talitsa intrusion consists of granodiorite to quartz monzonites and minor monzodiorites cross-cut by granodiorite to quartz monzonite and granite porphyry stocks and dykes. (Azovskova and Grabezhev 2008). The deposit was dated as 297.4±2.3 Ma (U-Pb in zircon) (Smirnov et al. 2017) and 298.3±1.3 Ma (Re-Os in molybdenite) (Tessalina and Plotinskaya 2017).

Molybdenite of the Talitsa deposit (5 samples, fig. 3) contains Re (40.8 to 388 ppm, geom. mean 109 ppm), W (6.0 to 232 ppm, geom. mean 17.4), Se (10 to 520 ppm, geom. mean 166 ppm), Fe, Cu, Zn, Sb, Pb, Bi (tens to thousands ppm), V, (tens to hundreds ppm), Ni, As, Cd, Ag,Te, Hg (up to hundreds ppm), Co (up to tens ppm), (several ppm to tens ppm), Au (up to several ppm).

4 Discussion

4.1 Trace elements incorporation in molybdenite

Most trace elements have positive correlations with each other (Fe, Co, Cu, Zn, Ni, As, Se, Ag, Cd, Sb, Te, Tl, Pb, and Bi) because they occur mainly as micro- to nano-scale mineral inclusions within molybdenite (Figs. 2, 3). Re and W usually have neither positive nor negative correlation with all other trace elements but show a weak negative correlation with each other (–0.26 for the whole dataset, –0.43 for the Mikheevskoe deposit). This means both Re and W substitute for Mo in the molybdenite structure. However in some LA-ICPMS profiles in molybdenite from the Talitsa deposit synchronous peaks of W^{182} and Ti^{47} indicate inclusions of rutile with W impurities (Fig. 3). Thus, the highest W contents observed in this study (over 60 ppm), are likely linked to mineral inclusions.

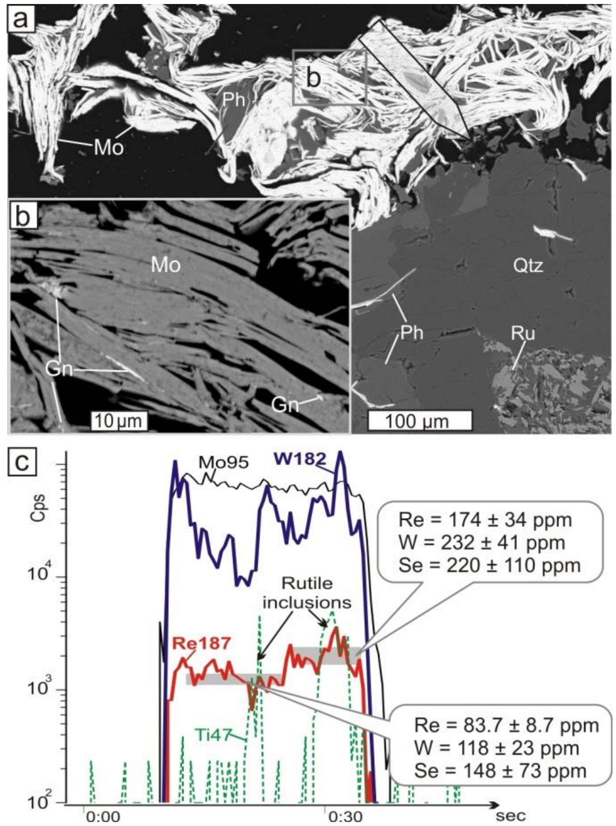

Figure 3. (a) BSE image of molybdenite (Mo) from the Talitsa porphyry Mo deposit associating with quartz (Qtz), phengite (Ph) and rutile (Ru); (b) detail of (a), inclusions of galena (Gn) in molybdenite; (c) time resolved LA-ICPMS line spectrum showing variations of selected isotopes; note synchronous peaks of W^{182} and Ti^{47} indicating inclusions of rutile.

4.2 Sources of rhenium and other metals

It is noteworthy that both Re and W are inhomogeneously distributed even within single grains of molybdenite (Figs. 2, 3) and vary in an order of magnitude within a deposit. Despite this, molybdenite from the deposits studied shows a significant difference in both Re and W contents. Molybdenite from Tomino and Mikheevskoe is featured by the highest contents of Re (mostly over 400 ppm) and lowest contents of W (<10 ppm), while molybdenite from the Talitsa deposit has lowest contents of Re (mainly below 200 ppm) and significant admixtures of W (6 to 50 ppm).

Mao et al. (2013) proposed that <10 ppm Re in molybdenite indicates crustal sources, 10 to 100 ppm indicates a mixed mantle/crustal source and >100 ppm Re in molybdenite indicates molybdenite derived from mantle sources. Therefore, the high Re contents of most molybdenites from Tomino, Mikheevskoe and Benkala deposits may indicate a predominantly mantle source for the metals, while molybdenite from the Talitsa deposit indicates a mixed mantle/crustal source (Fig. 4). Remarkable input of mantle material is in good agreement with a subduction setting of porphyry Cu deposits. Controls of W contents in molybdenite are not well understood. However continental crust is known to be enriched in W relative to mantle (Holland and Turekian 2003) and it can be supposed that significant input of crustal material may reflect elevated contents of W in molybdenite. It explains low contents of W in molybdenite from porphyry copper deposits from oceanic arc settings (e.g. in Tomino) and higher W admixtures in molybdenite from deposits formed on continental crust, i.e. Benkala deposit formed within a continental margin and Talitsa deposit formed due to continent-continent collision.

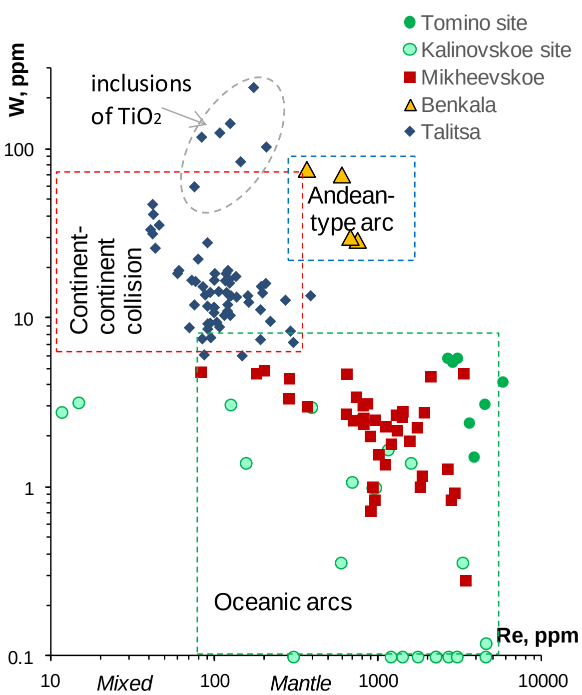

Figure 4. Re vs. W contents in molybdenite from the porphyry Cu(Mo) deposits studied. Fields for mixed mantle/crustal and mantle Re sources are from Mao et al. (2013) and references therein.

5 Conclusions

(1) Most trace elements form mineral inclusions within molybdenite in all deposits studied here; only Re and W are most likely to be incorporated into the molybdenite lattice.

(2) Porphyry Cu deposits formed within oceanic arc settings are featured by high contents of Re (mostly over 400 ppm) and low contents of W (<10 ppm) in molybdenite.

(3) Porphyry Cu deposits from Andean-type geotectonic environment (Benkala) are featured by lower Re content (hundreds ppm) and high contents of W (tens ppm) in molybdenite.

(4) Molybdenite from porphyry deposits from collisional setting (Talitsa) has low content of Re and elevated W contents (tens ppm).

(5) These results demonstrate that the study of trace element geochemistry molybdenite is a useful tool to define source of metal components in porphyry Cu(Mo) deposits.

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