First finding of merenskyite (Pd,Pt)Te₂ in porphyry Cu-Mo ores in Russia

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Abstract

Contents of Pt and Pd were determined in weakly mineralized rocks, ores, and flotation concentrates of the Aksug porphyry Cu-Mo deposit, northeastern Tuva. In all studied samples they are above the detection limits: Pt = 17–96 ppb and Pd = 9–924 ppb. These elements are unevenly distributed throughout the rocks and ores, with Pd/Pt varying from 0.5 to 37. Study of Pd-rich ores (up to 924 ppb, Pd/Pt = 37) on a JEOL JSM 5600 scanning electron microscope revealed finest (2–5 µm) merenskyite inclusions (25.20% Pd, 1.21% Pt, 72.31% Te) in chalcopyrite. The calculated crystallochemical formula of merenskyite from ores of the Aksug deposit is (Pd₀.₈₆₂Pt₀.₀₂₃Cu₀.₀₂₆Fe₀.₀₂₅)Te₂.₀₆₄. The merenskyite is associated with electrum (79.92% Au, 18.96% Ag), monazite, cobaltite, tennantite, and Sr-containing barite (4.6–18.0% Sr). Palladium mineralization occurs in massive chalcopyrite veinlets in zones of intensely propylitized rocks. The Devonian Aksug ore-bearing porphyry complex developed in the field of Early-Middle Cambrian intrusions of gabbro-diorite-plagiogranites associated with basalt-andesite effusions of island-arc complex. This might have led to high PGE contents in the Aksug rocks. The deposit formation proceeded with the participation of ore-bearing CI-enriched fluids favoring the concentration and transport of PGE in porphyry copper systems.

Keywords: Merenskyite; PGE; Aksug porphyry Cu-Mo deposit; Tuva; Russia

Porphyry Cu-Mo deposits are one of the sources of platinum group elements (PGE) (Economou-Eliopoulos, 2005; Mutschler et al., 1985; Sotnikov et al., 2001; Tarkian and Koopmann, 1995; Tarkian and Stribny, 1999), first of all, Pt and, particularly, Pd. In flotation sulfide concentrates, the Pd + Pt content reaches 2–4 ppm (and even up to 20 ppm at the Copper King Mine deposit, US (Mutschler et al., 1985)). Higher Pd + Pt contents are typical of deposits formed in island-arc settings (Tarkian and Stribny, 1999).

Platinum group minerals (PGM) in porphyry Cu-Mo ores are reported for a few deposits. These minerals (mainly Bi-free merenskyite (Pd,Pt)Te₂ and, less often, solid solutions of merenskyite–moncheite PdTe₂–PtTe₂) were identified as fine inclusions in chalcopyrite, bornite, and, seldom, pyrite at the Boshchekul’ (Kazakhstan), Skouries (Greece), Elacite (Bulgaria), Majdanpek (Serbia), Santo Tomas and Biga (Philippines), and Kal’makyr (Uzbekistan) deposits (Filimonova, 1984; Kozlov et al., 2000; Petrunov et al., 1992; Tarkian et al., 1991; Tarkian and Koopmann, 1995; Tarkian and Stribny, 1999). At some deposits, occasional grains of moncheite (Pt,Pd)Te₂, kotsuliske PdTe, sperrylite PtAs, and pallad-arsenide Pd₃As (Petrunov et al., 1992; Tarkian and Koopmann, 1995; Tarkian and Stribny, 1999) were discovered. At the specific Ryabinovoe porphyry Cu-Mo deposit, Central Aldan (Russia), related to alkali-basic magmatism, moncheite and Os-containing mineral — Ir-Ru erlichmanite OsS₂ (8.18% Ir, 2.87% Ru) — were found in ores (Kovalenker et al., 1996).

We studied the distribution of Pt and Pd in ores of the Aksug porphyry Cu-Mo deposit (Fig. 1), northeastern Tuva, localized within the Aksug pluton composed mainly of pyroxene-amphibole and amphibole quartz diorites (⁴⁰Ar/⁴⁰Ar age is 489 and 462 Ma, respectively) and tonalites with gabbro relics (497 Ma) (Sotnikov et al., 2003). The pluton is cut by stocks of porphyry tonalites and quartz-plagioclase porphyry I and II bearing stockwork Cu-Mo mineralization. The ⁴⁰Ar/³⁹Ar age of early porphyry is 401–404 Ma (Sotnikov et al., 2003). All intrusions, including an Early Cambrian tonalite-plagiogranite association (522–532 Ma), commonly juxtaposed with rocks of the Mainsk complex, are characterized by (⁸⁷Sr/⁸⁶Sr)₀ = 0.70427–0.70496 (Sotnikov et al., 2003). The latter, along with the similar petrochemical composition of the intrusions, implies a common deep-seated magma source during the evolution of the Aksug magmatic
The Aksug rocks contain 9–31 ppb Pd and 17–34 ppb Pt. Analysis of flotation sulfide concentrates yielded the following contents of these elements: 62 ppb Pd and 96 ppb Pt in copper concentrate (19.7% Cu, <0.1% Mo); 83 ppb Pd and 76 ppb Pt in copper-molybdenum concentrate (10.2%, 1.45% Mo). Extremely high contents of PGE were found in an ore sample (BH-8, depth 195 m) from the Severnaya (Northern) occurrence near the Aksug fault (Fig. 1). The sample is propylitized tonalite with massive chalcopyrite veinlets and nests. It contains 924 ppb Pd, 25 ppb Pt, and 5.4% Cu (Sotnikov et al., 2001). The high content of Pd suggests the presence of separate platinum-group minerals.

Scanning electron microscop (SEM) studies revealed copper mineralization of two stages. Stage 1 consists of pyrite, chalcopyrite, rutile, monazite, F-apatite, and zircon. Chalcopyrite of stage 2 (Fig. 2) contains finest (2–5 µm) rounded and oval inclusions of mineral identified as merenskyite (Fig. 3). The calculated crystallochemical formula of merenskyite, (Pd<sub>0.862</sub>Pt<sub>0.023</sub>Cu<sub>0.026</sub>Fe<sub>0.025</sub>)Te<sub>2.064</sub>, fits the stoichiometric element ratios of this mineral (Table 1). The other minerals of the second stage are electrum (18.96% Ag, 79.92% Au), monazite, coberline, and tennantite. Sulfate-bearing barite (4.6–18.0% Sr) occurs as small grains along cracks in metallic minerals and as disseminations in silicate minerals.

The high PGE contents in ores of the Aksug deposit are obviously due to its specific formation. The Devonian ore-bearing porphyry complex of the deposit developed in the field of Early-Middle Cambrian intrusions of gabbro-tonalite-plagiogranites associated with island-arc basalt-andesite effusions (Sotnikov et al., 2003). The rocks of the complex inherited many petrochemical features of island-arc magmatism. This might explain the high PGE contents of ores.

According to experimental studies, significant amounts of Pd and Pt can be transported as chloride complexes by hydrothermal fluids in highly oxidized (log f<sub>O2</sub> > −25) or acidic (pH < 2–4) conditions at 300–500 °C (Gammons et al., 1992; Hanley, 2005; Wood, 2002). Platinum group elements dissolved as chloride complexes may be deposited in response to reduction, pH increase, dilution, or temperature decrease (Gammons et al., 1992). Ore-forming fluids of the Aksug deposit were enriched in chlorides (Sotnikov et al., 2003). The presence of sulfates (anhydrite and, less often, barite and celestine) in metasomatites of the deep deposit horizons and results of gas chromatography of porphyritic-rock leucosome ((CO + CH<sub>4</sub>)/CO<sub>2</sub> = 0.05–0.02) indicate that the oxygen fugacity was relatively high at the early stages of the porphyry system evolution (Berzina et al., 2005). Such conditions favored the transport of Pt and Pd as chloride complexes. At

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![Fig. 1. Schematic geologic structure of the Aksug porphyry Cu-Mo deposit.](image)

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Table 1

<table>
<thead>
<tr>
<th>Content, wt.%</th>
<th>Pd</th>
<th>Pt</th>
<th>Cu</th>
<th>Fe</th>
<th>Te</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25.2</td>
<td>1.21</td>
<td>0.46</td>
<td>0.38</td>
<td>72.31</td>
<td>99.56</td>
</tr>
</tbody>
</table>

* Crystallochemical formula (Pd<sub>0.862</sub>Pt<sub>0.023</sub>Cu<sub>0.026</sub>Fe<sub>0.025</sub>)Te<sub>2.064</sub>.
the later stages of ore formation, propylitization took place, which evidenced a change of the solutions from acid to nearly neutral and weakly alkaline, which might have led to the deposition of Pd minerals from Pd-containing solutions in these zones. The uneven distribution of Pd and Pt in ores of the Aksug deposit (Pd/Pt = 0.5–37) (Sotnikov et al., 2001) might be determined by the local depositional conditions (Cl activity in the fluid, temperature, \( f_{O_2} \), pH). The difference in the final contents of Pd and Pt reflects the deposition effectiveness under variable conditions.

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References


