

## The impact of sulfur on the transfer of platinumoids by geological fluids

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Knowledge of the mobility of platinum group elements (PGE) in magmatic-hydrothermal fluids is a key to understanding PGE deposit formation and fractionation. Yet, existing data on aqueous chloride, sulfate, and hydroxide PGE complexes predict far too small metal contents (<ppb) in fluids from most geological settings [1, 2, 3], thus calling upon an important role of the sulfide and, potentially, trisulfur ion ligands in PGE transport. In an attempt to quantify the effect of sulfur in PGE mobility, we combined solubility measurements, in-situ X-ray absorption spectroscopy (XAS), thermodynamic, and molecular dynamics modeling based on recent advances of our knowledge of S speciation in crustal fluids [4, 5]. Our solubility and spectroscopic measurements performed at 300°C and 500 bar demonstrate enhanced solubility of Pt in H<sub>2</sub>S/SO<sub>4</sub>/S<sub>3</sub><sup>-</sup> hydrothermal solutions over a wide pH range (4-7), with Pt concentrations as high as 10s ppm, which is ~5 orders of magnitude higher than the Pt average lithospheric abundance. Our solubility and XAS data suggest formation of Pt-HS-S<sub>3</sub><sup>-</sup> complexes, similar to those proposed for gold [4], and the presence of species of tetravalent Pt(IV), which have never been considered in previous experimental studies and thermodynamics models [5, 6], postulating divalent Pt(II) as the major oxidation state in geological fluids. Thus, our new data highlight the role of previously ignored sulfur complexes in PGE transport and fractionation by S-bearing ore-forming fluids in the Earth's crust.

[1] Tagirov et al. (2015) *Geochem. Internat.* **53**, 327-340 [2] Bazarkina et al. (2014) *GCA* **146**, 107-131. [3] Kokh et al. (2017) *GCA* **197**, 433-466. [4] Pokrovski et al. (2015) *PNAS* **112**, 13484-13489. [5] Gammons and Bloom (1993) *GCA* **57**, 2451-2467 (1993). [6] Pan and Wood (1994) *Min. Dep.* **29**, 373-390.