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Goldschmidt 2023 Abstract
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Platinum group elements and sulfur in hydrothermal fluids: a love story told by in situ spectroscopy, molecular dynamics, and thermodynamics

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Knowledge of Platinum Group Elements (PGE) speciation in hydrothermal fluids is essential to better understanding the transport of these metals in the Earth's crust and to identifying potential hydrothermal deposits where PGE may be present in economic grades. Existing data on aqueous chloride, sulfate, and hydroxide complexes of PGEs indicate extremely low metal contents (< ppt to ppb) in fluids from most geological settings [1-3] that cannot explain multiple instances of PGE concentration and mobilization in hydrothermal systems, thus appealing to an important role of sulfide (HS^-) and, potentially, trisulfur (S_3^-) ligands [4] in PGE transport. To quantify the effect of sulfur on the solubility of platinum and palladium in hydrothermal fluids, we combined in situ solubility (Fig. 1A) and X-ray absorption spectroscopy (XAS; Fig. 1B) measurements with molecular dynamics (MD; Fig. 1C) and thermodynamic (TD) simulations [5]. Our results show that two main complexes transport these metals in hydrothermal fluids across a wide pH range (4–8), temperature and pressure (up to at least 350 °C and 1000 bar): $Pt(HS)_4^{2-}$ and $Pd(HS)_4^{2-}$ in H_2S/HS^- solutions, $Pt(HS)_2(S_3)_2^{2-}$ and $Pd(HS)_2(S_3)_2^{2-}$ in $H_2S/SO_4^{2-}/S_3^-$ solutions. The role of the trisulfur ion in PGE hydrothermal transport thus appears to be particularly crucial [5,6], with solubilities (10s ppm Pt, Pd) up to 10,000 times higher than those of the 'traditional' complexes with H_2S/HS^-. Our results offer perspectives for the exploration of new PGE resources, their extraction and recycling, and hydrothermal synthesis of PGE-based nanomaterials. Future research on other metals in fluid-mineral systems will benefit from the combined approach implemented in this study, as well as an open-access database of XAS spectra of Pt reference compounds acquired in our work [7].

[1] Bazarkina et al. (2014), *GCA* 146, 107–131; [2] Kokh et al. (2017), *GCA* 197, 433–466; [3] Tagirov et al. (2019), *GCA* 254, 86–101; [4] Pokrovski and Dubessy (2015), *EPSL* 411, 298–309; [5] Laskar et al. (2022), *GCA* 336, 407–422; [6] Pokrovski et al. (2021), *PNAS* 118, e2109768118; [7] Laskar et al. (2022), *Minerals* 12, 1602.

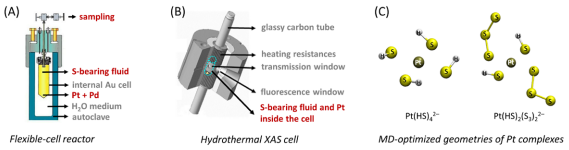

Figure 1: Solubility and molecular structure were measured using a flexible-cell reactor (A) and a hydrothermal XAS cell (B). MD-optimized geometries of the $Pt(HS)_4^{2-}$ and $Pt(HS)_2(S_3)_2^{2-}$ complexes (C).