PGEs behaviour and Os isotopes in hydrothermal-magmatic fluids

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PGEs behaviour is still little known in hydrothermal and magmatic fluids due to their low concentrations, approaching the detection limit. In this work, the PGEs behaviour and Os isotopes were studied in the high-temperature mainly magmatic fluids from the Kudrivay volcano, as well as in hydrothermal ore facies from three distinctly different Urals VHMS deposits.

The Kudryavy volcano in the Kurile Islands (Russia) is passively degassing with fumarole temperatures of up to 940° C, offering the possibility for the direct study of magmatic volatiles. The concentration of each of the PGE does not exceed 1 ppb, with the highest Os and Pt contents reaching 907 and 490 ppt, and the Pt/Pd ratio ranging from 0.3 to 2.3. The Os is the most vapor-compatible element. While Pt and Pd are the less vapor-compatible, they are still enriched by 2–3 orders of magnitude in the volatile phase relative to the volcanic rocks. Fumaroles have relatively unradiogenic ^{187}Os/^{188}Os isotope ratios in a range from 0.122 up to 0.152, similar to these of peridotite xenoliths from the underlying mantle wedge within the Kurile–Kamchatka subduction zone.

The modern hydrothermal fluids have unradiogenic Os isotopes pointing to a nearly complete domination of osmium isotopes from the host volcanics (mostly basalts). The Os concentration in fluids is typically buffered at seawater concentration. In Urals VHMS deposits, the PGEs are enriched in first-stage high-temperature portions of hydrothermal systems and correlate with Co and Au contents. ^{187}Os/^{188}Os ratio increases with depth in the hydrothermal system in the following order: seafloor altered sediments – clastic sulphides – massive sulphides – stockwork zone – sulphide chimney. The straight line correlation between initial ^{187}Os/^{188}Os and 1/Common Os shows the mixture of two components, which could be identified as hydrothermal fluid and seawater.

In conclusion, even little contribution of PGEs-rich magmatic fluid into hydrothermal system will significantly influence the Os isotope composition.

Investigating gallium speciation in hydrothermal conditions by X-ray absorption spectroscopy

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Context

The importance of gallium in high technology applications (opto- and semiconductor- electronics, thin-films, metal alloys, etc.; see [1] and references therein) calls for a comprehensive understanding of its geochemistry. An exhaustive set of speciation and thermodynamical data was already determined for the system Ga-O-H, in a broad range of aqueous conditions up to 250°C (see [2] and references therein). But speciation of gallium at higher temperatures in presence of other ligands remains unknown: what element/ligand is likely to play a major role in hydrothermal Ga transport?

In this context, we aimed at determining the speciation of gallium from ambient to 425°C, at 300 bar, in acidic conditions, in presence of nitrate, bromide and chloride ligands. Our study is based on X-ray absorption spectroscopy measurements, EXAFS (Extended X-Ray Absorption Fine Structure) analysis and *ab initio* XANES (X-ray Absorption Near Edge Spectroscopy) calculations which permit to determine both the gallium speciation and molality as a function of temperature [3].

Results

The fate of aqueous gallium as a function of temperature can be described in several temperature steps. First, precipitation of GaOOH above 100°C in agreement with previous studies ([2,4] and references therein); then redissolution of gallium driven by bromide and chloride ligands for intermediate temperatures; finally, for T> 300°C, possible existence of an aqueous nitrated complex in contact with a precipitate.

The role and relative strength of the different ligands, and the consequences for transport of gallium in hydrothermal conditions will be discuted. In light of these results, the pertinence of using bromide ligands as analogues for chloride ligands (for spectroscopic reasons) will also be considered.

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