Platinum-group minerals in upper mantle peridotites : Implications for our understanding of whole-rock signatures of HSE.

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Platinum-group elements (PGEs) have now been recognized to be highly sensitive geochemical tracers of Earth's mantle. However, compared to lithophile trace elements, PGEs occur as ultra-trace elements which may occasionally be present as major elements in discrete platinum-group minerals (PGMs) in addition to the base-metal sulfides (BMS). PGMs are not expected to be stable in the upper mantle because PGEs are highly soluble (at wt. % levels) in base metal sulfides (BMS), which control the largest part of the PGE budget in the uppermost mantle. However, micrometric PGMs (0.1 µm-3µm) have now been identified in a large panel of mantle-derived rocks (abyssal peridotites, orogenic peridotites, basalt-borne spinel peridotite xenoliths, cratonic peridotites) within both lherzolitic and harzburgitic compositions. These minerals may impact analytical precision (e.g. Os-Ir) and reproducibility of whole-rock analyses by generating nugget effects on some elements (e.g. Pt) and incomplete dissolution of some acid-resistant minerals (Os-Ir).

The PGMs so far recovered from the study of peridotites are invariably associated with BMS phases or derived from a BMS precursor indicating the key role of the BMS in the PGMs genesis. Decreasing temperature, decreasing activity of S or increasing semi-metal concentrations (Te, Bi, As, Sb…) are major factors triggering crystallization of PGMs. Adiabatic partial melting processes generate refractory PGMs (Pt-Ir-(Os) alloys Os-Ir-Ru alloys/ sulfides) by consuming all of the available BMS in the mantle residues. Refractory PGMs are long-lived minerals that may survive recycling and rejuvenation of residual peridotites while preserving Os isotopic signatures of Archean partial melting events. Reactions at decreasing melt–rock ratios (« mantle metasomatism ») as well as magmatic « refertilization » concentrate volatile semi-metals (Te, As, Bi…) which precipitate as high-temperature Pt-Pd-Te-Bi or Pt-As-S microphases intimately associated with Cu-Ni-rich sulfides. Transient fluid - rock interactions, subsolidus cooling, crustal contamination and serpentinization are also PGM-maker (PdSb, PdCuNi, Pt-Bi-Sb phases ; Pt-Fe-Ru alloys; Pd sulfides, native gold….). These non cogenetic HSE-rich minerals have thus important implications for our interpretation of the mantle HSE signatures and their use to constrain planetary processes.

Experimental insights into fluid-rock interactions in granite-hosted and CO_2-saturated geothermal systems

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Hydrothermal experiments and geochemical modeling were conducted at 250°C and 25 to 45 MPa to evaluate geochemical and mineralogical relationships in a granite-hosted geothermal system. Experiments and geochemical models emulate geothermal conditions of typical granitic reservoirs and are based on the Roosevelt Hot Springs thermal area, Utah, USA. Additional experiments and modeling were also conducted to determine how these geothermal systems may respond to CO_2.

Hydrothermal experiments were conducted in rocker bombs and Au-Ti reaction cells (Dickson cells) using established methods. The granite consists of 75% ground (<45 um) and 25% chipped (0.1-0.7 cm) mineral separates, including sub-equal portions of quartz, perthitic K-feldspar (~25% wt% albite and 75% wt% K-feldspar), oligoclase (An_{23}), and 4 wt% Fe-rich biotite. The use of mineral chips allows post-experimental examination of textures, while use of powder enhances reactivity and kinetic rates. The synthetic brine ($I \cong 0.1$) contains ~ 0.1 molal Na and Cl and millimolal quantities of SiO_2, Al, Ca, Mg, K, SO_4, and HCO_3.

Five water+granite+/-epidote experiments reacted for ~28 days (water:rock ≅ 20:1). Two water+granite experiments and one water+granite+epidote experiment were subsequently injected with supercritical CO_2 and reacted for an additional 42 days. Excess CO_2 is injected to produce a separate supercritical fluid phase, ensuring aqueous CO_2 saturation for the duration of each experiment.

Prior to injection of CO_2 into water-granite experiments, relatively constant concentrations of aqueous Cl, Na, SO_4, and ΣCO_2, increasing aqueous SiO_2, K, and Al, and decreasing aqueous Mg are observed. Aqueous Ca concentrations initially increase and then decrease over time. Relatively constant concentrations of aqueous Cl, Na, and K are observed post-injection. Concentrations of aqueous Ca, SO_4, and Al decrease during the first 5 days after injection while concentrations of aqueous Mg and ΣCO_2 increase over the same period of time. Post-injection concentrations of aqueous SiO_2 gradually decrease over time.

Mg-Fe-rich illite and kaolinite precipitated in water+granite experiments whereas illite, kaolinite, and Fe-rich smectite precipitated in water+granite+CO_2 experiments. Decreasing aqueous Mg concentrations during the first 5 days of each experiment are consistent with illite formation. Increasing aqueous Mg concentrations during the first 2 days after injecting CO_2 may signal a shift in stability from illite to smectite. No carbonate minerals were observed as reaction products. These results are relevant to understanding processes in natural and enhanced geothermal systems.