

Highly siderophile elements and mantle heterogeneities: The interplay between accessory sulfides and trace minerals.

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Highly siderophile elements (HSE = Platinum-group elements, Au, Re, Se, Te) occur at ppb concentration levels in the Earth's upper mantle. The HSE are now currently used as geochemical tracers, owing to their wide range of compatibility. Accessory (<0.1 vol.%) Fe-Ni-Cu sulfides (BMS) are the main HSE carriers in the fertile upper mantle. In contrast to lithophile elements, the HSE are versatile elements which easily change their host minerals as a function of sulfur-saturation, redox conditions, pressure, fugacity of sulfur, melt compositions. Recent studies put strong effort to unravel which phases control the HSE budget of mantle rocks after partial melting, metasomatism and magmatic refertilization. Each stage generates specific interplay between BMS and a wide range of micron-sized trace platinum-group minerals (PGMs).

By progressively eliminating sulfur, adiabatic partial melting processes and porous flow percolation systems at high melt/rock ratios transfer the HSE systematic of mantle residues from the BMS to refractory monosulfides, and then to PGMs. The HSE may form their own minerals (refractory PGMs, i.e. Os-Ir-Ru alloys/sulfides; Pt-Ir-(Os) alloys) which carry the whole-rock HSE budget at the micron scale. The inhomogeneous distribution of these micron-sized PGMs may cause extreme nugget effects in the whole-rock budgets. They may also decouple elements that are usually considered to be proxies in sulphur-saturated conditions (e.g. Se and Te, Pt and Pd).

Magmatic erosion at the lithosphere-asthenosphere boundary and magmas fluxing through the lithospheric mantle may completely rejuvenate the PGE budgets inherited from melting events. Melt/mantle reactions redistribute the HSE systematics into newly formed, metal-rich BMS, while generating a wide variety of Pt-Pd-Te-Bi microphases. Arsenic may also play an important role in the sub-arc mantle or in volatile-rich metasomatic processes, generating immiscible Ni-As-S liquids in the most As-rich environments. Refractory PGMs may survive these rejuvenation, dispersing the Os isotopic compositions of ancient melt depletion events on a regional scale through refertilized peridotites and melt vein-conduits (e.g. chromitites, pyroxenites). Thus, understanding mantle heterogeneities from whole-rock HSE systematics requires appropriate tools for evaluating the different HSE carriers and their origin.

Basalt weathering on Mars: insights from Li-isotope fractionation models

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Lithium is incorporated as trace element in most of basalt bearing minerals, namely olivines, clinopyroxenes and plagioclase feldspars, where Li abundance lies in the order of 1-200 ppm depending on their source area. For modeling purposes, we assume an initial value of ⁷Li = 5 ‰ that corresponds to the average isotopic signature of unweathered MORB basalts [1,2]. It is also assumed that dissolution of basalt leads to release of both isotopes, without significant isotope fractionation. Secondary minerals incorporate a significant fraction of the dissolved Li, with selective uptake of ⁶Li by clays through cation exchange reactions [3].

Modelling clay-water Li isotope fractionation

Geochemical Models dealing with the selective uptake of each Li isotope by clays were achieved by implementing in the *Phreeqc* code a specific algorithm that splits the total amount of sorbed Li between ⁶Li and ⁷Li isotopes under the assumption that fractionation occurs following a Rayleigh distillation process. Li-isotopic signature in H₂O resulting from weathering of basalt was analyzed in two scenarios: (1) at near equilibrium conditions and constant temperature, (2) along simultaneous freezing and evaporation buffered by a CO₂ atmosphere. Resulting models were used to describe possible paths of Li isotopic fractionation and the extent of basalt weathering on early Mars conditions, as a function of supersaturation, temperature and evaporation rates. We suggest, using MSL capabilities for Li detection, to complete an initial screening for targets relevant for an eventual analysis of Li isotopes.

[1] Tomascak, P.B., 2004. Reviews in Mineralogy and Geochemistry. Vol. 55, 153-195. [2] Tang *et al.*, 2007 *Int. Geol. Rev.*, 49, 374-388. [3] James, R.H., Palmer, M., 2000. *Geochim. Cosmochim. Acta* 64, 3111-3122.