

Origin and significance of highly siderophile elements in the upper mantle of the Earth

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The metals Os, Re, Ir, Ru, Pt, Rh, Pd and Au are called highly siderophile elements (HSE) because of their strong siderophilicity as reflected in the very high metal/silicate partition coefficients. Advances in analytical techniques, new experimental results on the solubility of HSE in silicate melts and the precise determination of the Os-isotopic composition of geological samples have stimulated new research on HSE-abundances in the Earth's mantle.

Abundances of HSE in the Earth's mantle

Abundances of HSE in the Earth mantle are obtained from analyses of upper mantle rocks: xenoliths from alkali basalts, massive peridotites, abyssal peridotites and ophiolites. From a large number of studies the following conclusions can be drawn: (1) Absolute HSE-abundances in upper mantle rocks are at around 0.7% of those in CI-chondrites. (2) Ratios among HSE in upper mantle rocks are approximately chondritic, including chondritic Re/Os-ratios. Both statements require some modification: (1a) There are variations in Ir contents of up to a factor of two to three within rocks with the same major element composition, including Ni and Co. Thus Ir and probably other HSE are decoupled from moderately siderophile elements such as Ni and Co (Spettel *et al.*, 1991). (2a) Ratios are less constant than previously thought. In particular Pd/Ir ratios are variable within a factor of two. Variations are also found for Rh/Ir and Ru/Ir ratios (Pattou *et al.*, 1996; Schmidt *et al.* 1998). Data on abyssal peridotites suggest even stronger fractionation of HSE than in samples from the continental mantle (Snow and Schmidt, 1998).

Solubilities and metal/silicate partition coefficients of HSE in silicate melts

Solubilities of HSE in silicate melts have been determined recently. From these data metal-silicate partition coefficients were calculated. HSE-solubilities increase with increasing oxygen fugacity reflecting the ionic nature of HSE in silicate melts. The solubilities of Ir and Pt are two to three orders of magnitude lower than those of Pd and Au, leading to large differences in metal-silicate partition coefficients between these two groups of elements (e.g. Borisov and Palme, 1997). Results of high pressure experiments have shown that metal/silicate partition coefficients for Pd and Pt show no pressure dependence for pressures up to 20 GPa, corresponding to a depth of about 600 km within the Earth (Holzheid *et al.*, 1998).

Geochemical significance

There is little doubt that the HSE in the upper mantle of the Earth cannot be the result of equilibration of core-forming metal with silicate melts. The greatly variable partition coefficients and their weak dependence on temperature and their independence of pressure (so far for Pd and Pt) would not allow metal-silicate equilibration to produce the rather uniform pattern of chondrite normalized HSE observed in upper mantle rocks. The HSE inventory of the present upper mantle is best explained by the addition of a late veneer after the core had formed (e. g., Kimura *et al.*, 1974). This is consistent with the chondritic Os/Re ratio inferred for the primitive upper mantle (Meisel *et al.*, 1996).

Separation of core-forming metal from silicate must occur at low oxygen fugacity to produce the low FeO content in the upper mantle. Under these conditions present upper mantle abundances of Pt and Ir (but not Pd and Au) would by far exceed their solubilities in a hypothetical magma ocean, leading to precipitation and separation of PtIrFe-alloys. However, fractionations of Pt and Ir from Pd and Au are not observed in rocks from the upper mantle indicating that the HSE were never dissolved in a terrestrial magma ocean under the conditions that would enable metal/silicate separation. At oxidizing conditions solubilities of Pt and Ir are much higher, at QFM+2 they are significantly above upper mantle abundances. If homogenization of HSE occurred via a magma ocean then it must have occurred at oxidizing conditions where metallic iron would not be stable, consistent with the late veneer hypothesis (Borisov and Palme, 1998).

The variations in HSE-ratios observed in upper mantle rocks have been ascribed to addition of core metal that is thought to be fractionated in HSE because of preferred partitioning of the more refractory metals (Ir, Pt) by the solid inner core, in analogy with fractionation models of iron meteorites (Snow and Schmidt, 1998). Contamination of plume material with core metal has also been suggested to explain elevated Os isotope ratios in plume derived magmas (Walker *et al.*, 1995). Such processes are hypothetical as little is known about compositional differences between inner and outer core. It is, however, worthwhile to explore 'normal' geochemical processes for producing HSE variations before invoking core-mantle interaction.

A general idea about fractionation of HSE in the silicate Earth is obtained from HSE-crustal abundances. The crust/mantle ratios for Ir and Os are around 0.0,1 significantly below those of Pt, Rh and Pd with crust/mantle ratios of about 0.2 (Schmidt and Palme, 1998). The similarity of the crust/mantle ratios for Ir and Os with Ni may indicate the involvement of olivine in fractionating Ir and Os

from Pd and Pt. Variations of Pd/Ir, Rh/Ir and Ru/Ir ratios in upper mantle rocks may reflect addition of crustal components high in Pd, Rh and also Ru, although some concentration of crustal siderophiles would be required before mixing to the mantle. The host phases and the behaviour of HSE during mantle melting are still insufficiently known.

Cosmochemical implications

A late chondritic veneer as source of the HSE fits well into current accretion models for the Earth which assume impacts of large bodies in the late stages of the accretion of the Earth which may be as late as 100 million years after formation of the solar system. The last material to contribute to the growing Earth is likely to have been derived from a very different heliocentric distance than the Earth (Wetherill, 1994). The hierarchical growth of the Earth is compatible with the inhomogeneous accretion model, where increasingly oxidized material is added to the growing Earth (see discussion in O'Neill and Palme, 1998), with the latest clearance of the mantle of radiogenic ^{182}W by separation of core forming metal as late as 60 million years after the beginning of accretion (Lee and Halliday, 1995).

References

- Borisov, A., Palme, H. and Spettel, B. (1994) *Geochim. Cosmochim. Acta*, **58**, 705–16.
- Borisov, A. and Palme, H. (1997) *Geochim. Cosmochim. Acta*, **61**, 4349–57.
- Borisov, A. and Palme, H. (1998) (in prep.).
- Holzheid, A., Sylvester, P., Palme, H., Borisov, A. and Rubie, D.C. (1998) *Lunar Planet. Sci.*, **XIX**, Lunar Planet. Inst., Houston, 1296 (CD-ROM).
- Kimura, K., Lewis, R.S. and Anders, E. (1974) *Geochim. Cosmochim. Acta*, **38**, 683–701.
- Lee, D.C. and Halliday, A.N. (1995) *Nature* **378**, 771–4.