

**Experimentally determined solubilities of the HSE Re, Os, Pt, and Rh applying the mechanically assisted equilibration technology.** W. Ertel<sup>1</sup>, and Don B. Dingwell<sup>1</sup>, <sup>1</sup>Ludwig Maximilian University Munich, Theresienstr. 41, D-80333 Munich, Germany ([ertel-ingrisc@lmu.de](mailto:ertel-ingrisc@lmu.de));

**Introduction:** The platinum group elements (Ru, Os, Rh, Ir, Pd, and Pt) together with Re and Au are defining a group of elements known as the Highly Siderophile elements (HSE): the geo-chemically characteristic feature are their extremely high metal/silicate partition coefficients ( $D^{\text{met/sil}} > 10^4$ ) determined in 1 atm experiments. In consequence, their concentrations in Earth's upper mantle material are very low ranging from 0.3 ppb for Re as the least abundant to 8 ppb for Pt, the most abundant HSE. In fact, their crustal rock concentrations are even much lower due to their high sulfide/silicate distribution coefficients, which make them stay in residual sulfide portions during partial melting processes.

However, two observations about the HSE lead to the "enigma of the over-abundance of HSE" in the Earth's upper mantle (comp. [1]): First, according to their extremely high metal/silicate partition coefficients all HSE should be stripped completely out of the mantle by the Fe-rich liquid forming the core early in Earth's history. Second, their mantle abundances relative towards each other show the same element pattern as observed in C1-chondrites, which are believed to represent the most primitive material from which the Earth formed during accretion.

The development of new analytical techniques in the last 10 years made accurate determinations of HSE concentrations in basaltic and ultramafic rocks possible, stimulating in consequence experimental investigations of their geochemical properties starting with their partition behavior between metal, silicate and sulfide melt phases.

#### **Experimental:**

1 atm experiments regarding the solubility behavior of Re, Os, Pt, and Rh were performed applying the mechanically assisted equilibration technology of Dingwell et al. [2] between 1300°C and 1500°C over a wide range of oxygen fugacities possible. Starting melt composition corresponds to the 1 atm eutectic composition of Anorthite<sub>42</sub>-Diopside<sub>58</sub> (AnDi).

Attainment of equilibrium was demonstrated using time series sampling. Recovered glassy samples were prepared for electron microprobe analyses of the major elements. The identical mounts were used in laser-ablation inductively-coupled-plasma mass spectrometry (LA-ICP-MS) analyses, determining the HSE concentrations as described in [3]. This method run in time resolved modus operandi is a spot analytical technique capable to determine absolute Pt concentrations in the low ppb-level while supplying information on the spatial homogeneity of the sample on the laser beam size (=70 microns). This is essential

for analysis of HSE since these elements tend to form Nanonuggets ([4], [5], [6], [7]) which stay kinetically - and potentially thermodynamically - stable dissolved inside the melt. They lead in consequence to an "overprinting" of the homogeneous HSE equilibrium solubility especially at low  $fO_2$  conditions, and though to an apparent solubility several orders of magnitude higher than the real equilibrium solubility according to experimental conditions. In this respect LA-ICP-MS technique has proved to be a sufficiently sensitive, and only method capable to determine real equilibrium solubilities of HSE in experimental charges, otherwise obscured and/or entirely dominated by the Nanonugget presence.

**Results:** Applying the mechanically assisted equilibration technique in combination with LA-ICP-MS analyses performed in time resolved working mode results in minimum metal solubilities for all HSEs investigated. The Nanonugget effect well known for all experimental studies concerning HSEs can in this way be at least minimized if not avoided largely [7]. This is based on two reasons: 1.) applying forced convection, Nanonuggets present can be stirred out over extended periods of time, reducing the influence of Nanonuggets on the total trace element concentrations measured. This is unique to this experimental technique and explains differences with generally higher solubility levels observed in loop technique experiments for the same elements under identical conditions. 2.) using LA-ICP-MS for trace element analyses in a time resolved working mode allows explicitly the detection of Nanonugget contaminated sample areas which can be then excluded from the concentration determination process, and is, therefore, an additional tool to reduce the Nanonugget influence on elemental concentration determinations. Subsequently, elemental concentrations determined by the combination of the two methods results in the lowest solubilities of HSEs in AnDi determined up to date, and in consequence, partition coefficients calculated from these 1 atm experiments show much higher D-values than obtained by any other method. Calculated metal/silicate partition coefficients are therefore up to 13 orders of magnitude higher D-values than observed in upper mantle samples.

As visible from Figure 1 [8], obtained solubilities of HSEs extrapolated to oxygen fugacity conditions relevant for core mantle segregation, do not converge at a certain oxygen fugacity. This would be, however, necessary to establish relative chondritic element ratios as observed in upper mantle samples. The elemental solubilities of Re, Os, Pt, and Rh, and, in consequence, the metal/silicate partition coefficients vary over

several orders of magnitude, which is not coherent with equilibrium core formation.

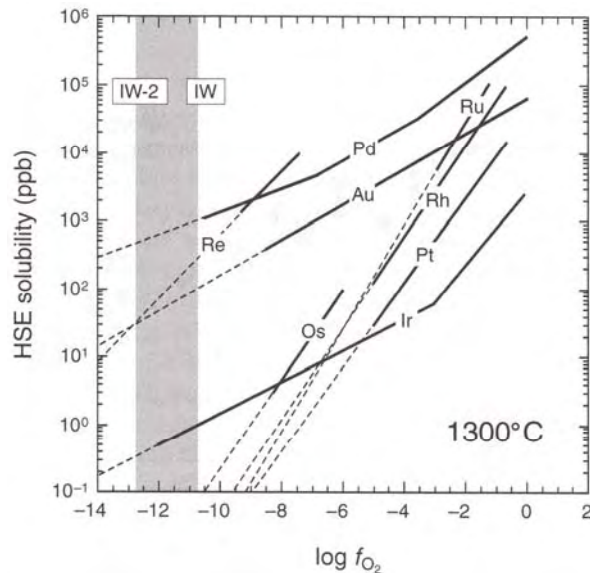


Figure 1: Experimentally determined solubilities of HSEs in AnDi in dependence of oxygen fugacity recalculated to 1300°C (from [8]).

However, it has to be stated clearly that 1 atm AnDi composition does not correspond to a mantle peridotite, investigated temperatures are much lower than temperatures discussed in latest magma ocean scenarios (>3000K), and - beside other variables (like melt composition, sulfur fugacity and activity relationships at low and high pressure) not taken into account - elemental concentrations in a magma ocean were not established at 1 atm total pressure.

Given their vastly different partitioning behavior at low temperature and pressure, it would stretch credibility, however, if there would exist any set of conditions under which all HSE partition coefficients converge to a single value. These considerations strongly reinforce the argument that, subsequent to core segregation, the addition of a late veneer of oxidized, HSE-enriched material with chondritic relative element abundances set the stage for the present day upper mantle highly-siderophile element scenario while moderately-siderophile element abundances had been established already in an HT/HP-equilibrium event during one or more magma ocean scenarios.

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