EFFECT OF PRESSURE ON THE PARTITIONING OF HIGHLY SIDEROPHILE ELEMENTS BETWEEN LIQUID FE-ALLOY AND PERIDOTITIC LIQUID.

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Introduction: The term 'highly siderophile' for the platinum group elements (Ru, Rh, Pd, Os, Ir, Pt) and Re categorizes their geochemical character observed in 1 bar partitioning experiments, which is extremely metal loving. As a consequence, these elements have metal-silicate partition coefficients of $\geq 10^4$ which would result in their almost complete removal from a molten silicate mantle equilibrating with molten metal during planetary core formation. However, in Earth's mantle, concentrations of these highly siderophile elements (HSE's) are unexpectedly high. The most widely accepted explanation for this overabundance is that these elements were added to the mantle, in chondritic ratios, following the main stage of core formation as a 'late veneer' of chondritic material [1, 2]. However, the late-veneer hypothesis may require reevaluation because improved analytical techniques have revealed that some of the HSE ratios of the PUM are non-chondritic [3]. An alternative possibility, that metal-silicate equilibration at high pressure and temperature (e.g. 30-40 GPa, >3000 K) has contributed to the current abundances of HSE's, has not been tested due to lack of experimental data. While the solubilities of some HSE's at 1 bar and moderate temperatures are quite well known, the number of high-pressure and/or high-temperature studies is limited. Existing studies cover a maximum pressure range of ≤16GPa at ≤2000°C and high-temperature experiments (≤2500°C) were performed at relatively low pressures (~ 2GPa). Moreover, these studies have often concentrated on individual elements, mainly Pt [4, 5, 6] or Pd [4, 7], whereas the relative behaviour is important for explaining HSE mantle abundances. The aim of the present study is to evaluate metal–silicate equilibration in a magma ocean as a possible explanation for the HSE inventory of the Earth's mantle by investigating the behavior of a range of HSE's in a system consisting of liquid Fe-alloy and molten peridotite at 3-25 GPa and temperatures >2000°C.

Experimental Procedure: We have performed liquid metal-liquid silicate partitioning experiments for Ru, Rh, Pd, Re, Ir and Pt at 3.5-6 GPa, 2200°C and 18 GPa, 2200-2400°C using multianvil apparatus (18-11mm assemblies with a stepped LaCrO$_3$ heater). Initially, we employed mixed powders of 60 wt% silicate phase (primitive mantle (PM) composition, FeO ~8wt%) and 40 wt% metal phase (metallic powders of Fe + HSE's) as the starting material. However, using mixed powders might result in incomplete metal-silicate separation and the formation of so-called metallic micro-nuggets – which could lead to an overestimation of the HSE concentrations in the silicate phase. Therefore, in subsequent experiments we added the HSE's as a chip of previously alloyed metal to silicate + Fe powder mixtures. In order to vary oxygen fugacity and to provide relatively oxidising conditions, the combined concentration of the HSE's in the Fe-alloy metal phase was varied from 50 to 90 wt%. In all cases we employed MgO single crystal capsules and run times of 70 - 180 s.

Results and Discussion: During the experiments, the liquid metal separates from the molten silicate and forms several spheres that vary in number and size. A typical example is shown in Fig. 1a. The metal displays coarse quench textures (2-50 µm scale) including dendritic crystals and zoned grains. Coarse quench crystals also form in the silicate phase. The back scattered electron (BSE) image of Fig. 1b shows the texture of a run product recovered from 6 GPa which is dominated by large skeletal olivine crystals. The interstitial regions consist of a brighter silicate phase in the centre and a metallic phase that is concentrated along the boundaries of the olivine crystals. We interpret this as a quench phenomenon and assume that this metal had been dissolved in the silicate melt prior to the quench.

Analytical Techniques: The metal phase was analyzed with the electron microprobe. Because of the coarse quench textures, a defocused electron beam (10-30 µm diameter) was used and single analysis points were set along rectangular grids with some overlap of the excited areas. Because of the extremely low concentrations of the HSE's, analyses of the quenched silicate liquid were carried out with the LA-ICP-MS facility at BGI consisting of a Coherent COMPexPRO 102 excimer laser combined with a Perkin Elmer ELAN DRC-e mass spectrometer. As there is a lack of appropriate standards for analysing HSE's in silicate phases we synthesized silicate glass standards of eutectic diopside-anorthite bulk composition doped with Ru, Rh, Pd, Re, Ir and Pt in the range

4-120 ppm. The HSE concentrations of the standard glasses were determined by isotope dilution ICP-MS analysis at the Freie Universität in Berlin. Additionally, we employed NIST 610 glass as an external standard for Fe, Ti, Mn and Cr. To account for the coarse quench textures we used a 70 µm spot size.
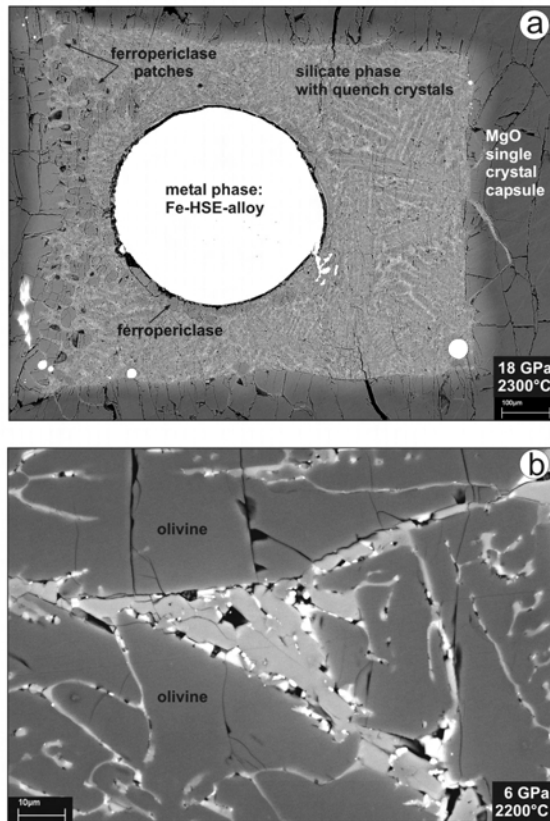

Fig 1: BSE images of run products at 6 and 18GPa.
a) The metal phase has separated to form a large sphere and the silicate phase displays large quench crystals.
b) Detail of the quenched silicate phase showing an interstitial pocket between large skeletal olivine crystals. The white phase is metal that is considered to have been dissolved in the silicate liquid.

Preliminary results for experiments using mixed metal + silicate powders as starting materials are displayed in Fig. 2. The logarithmic values of the Ru, Rh, Pd, Re, Ir and Pt metal-silicate weight concentration ratios (D) at 2200°C and at an oxygen fugacity of 2.3 log units above the Fe-FeO equilibrium (IW+2.3) are plotted as a function of pressure. HSE solubility in the silicate melt is highest for Pd and lowest for Ir at both pressures. With the possible exception of Ir, the solubility of HSE's in the silicate melt increases with increasing P, especially in the case of Pd, Rh and Ru.

When compared to 1 bar partition coefficients, which we have calculated for Rh and Pt from [8], high pressure reduces the partition coefficients by more than an order of magnitude. The large change between 1 bar and 5 GPa might result from pressure-induced structural changes in the silicate liquid, as previously proposed based on the metal-silicate partitioning behaviour of Ni and Co [9]. In addition, the difference between most of the HSE partition coefficients is relatively small at 6-18 GPa compared to the 1 bar values for Pt and Rh, which differ by two orders of magnitude.

Even though the redox conditions of these results are relatively high, we expect a similar pressure effect at oxygen fugacities that are more realistic for core formation. These data imply that there is a tendency for HSE's to become less siderophile with increasing pressure. Whether this trend continues to higher pressures, how partitioning is affected by high temperatures and consequences for planetary core formation will be the focus of further study.
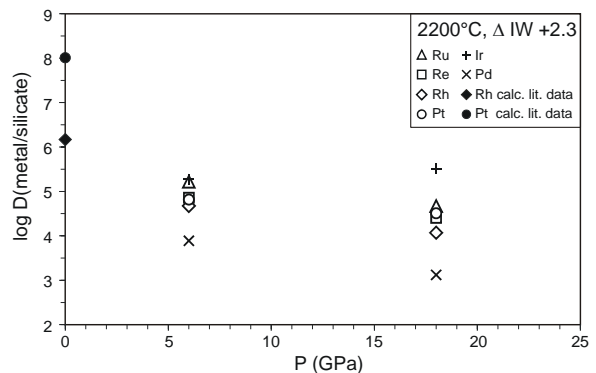

Fig 2: Logarithmic values of the Ru, Rh, Pd, Re, Ir and Pt metal - silicate concentration ratios (D) plotted against pressure (P) at 2200°C and 2.3 log units above the iron wustite buffer (Δ IW +2.3). 1 bar data for Rh and Pt are calculated using equations from [8].

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