



# Controls on the solubility of rhenium in silicate melt: Implications for the osmium isotopic composition of Earth's mantle

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## ABSTRACT

The solubility of Re and Au in haplobasaltic melt has been investigated at 1673–2573 K, 0.1 MPa–2 GPa and IW–1 to +2.5, in both carbon-saturated and carbon-free systems. Results extend the existing, low pressure and temperature, dataset to more accurately predict the results of metal-silicate equilibrium at the base of a terrestrial magma ocean. Solubilities in run-product glasses were measured by laser ablation ICP-MS, which allows for the explicit assessment of contamination by metal inclusions. The Re and Au content of demonstrably contaminant-free glasses increases with temperature, and shows variation with oxygen fugacity ( $fO_2$ ) similar to previous results, although lower valence states for Re (1+, 2+) are suggested by the data. At 2 GPa, and  $\Delta IW$  of +1.75 to +2, the metal-silicate partition coefficient for Re ( $D_{Met/Sil}$ ) is defined by the relation

$$\text{Log} D_{Met/Sil}^{Re} = 0.50(\pm 0.022) \times 10^4 / T(K) + 3.73(\pm 0.095)$$

For metal-silicate equilibrium to endow Earth's mantle with the observed time-integrated chondritic Re/Os, (and hence  $^{187}\text{Os}/^{188}\text{Os}$ ),  $D_{Met/Sil}$  for both elements must converge to a common value. Combined with previously measured  $D_{Met/Sil}$  for Os, the estimated temperature at which this convergence occurs is 4500 ( $\pm 900$ ) K. At this temperature, however, the Re and Os content of the equilibrated silicate is  $\sim 100$ -fold too low to explain mantle abundances. In the same experiments, much lower  $D_{met/sil}$  values have been determined for Au, and require the metal-silicate equilibration temperature to be  $< 3200$  K, as hotter conditions result in an excess of Au in the mantle. Thus, the large disparity in partitioning between Re or Os, and Au at core-forming temperatures argues against their mantle concentrations set solely by metal-silicate equilibrium at the base of a terrestrial magma ocean.

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## 1. Introduction

Accretion of the Earth from planetesimals of chondritic composition (McDonough and Sun, 1995; Wood et al., 2006), with concurrent differentiation into a metal core and silicate mantle, is generally thought to have occurred over the first  $\sim 30$  Myr of Earth history (e.g. Kleine et al., 2002; Yu and Jacobsen, 2011). During accretion, heat generated by the decay of short-lived isotopes and the collision of large impactors are likely to have raised global temperatures sufficiently to cause widespread melting and the formation of a magma ocean, through which more dense Fe–Ni liquid could descend (Rubie et al., 2007). It is hypothesized that this descending metal stalls at the rheological

base of the magma ocean, where it may equilibrate with molten silicate at high pressure and temperature. Subsequent gravitational instability then causes rapid segregation through the crystalline lower mantle without further significant chemical exchange (Wade and Wood, 2005; Wood et al., 2006; Rubie et al., 2007). In this scenario, siderophile (iron-loving) trace elements should be transported to the growing core, leaving a depleted silicate mantle with element ratios that depend upon the differing affinities for the metal phase. The distribution of trace elements between metal and silicate phases at equilibrium may be expressed as a partition coefficient ( $D_{Met/Sil}$ ), defined as:

$$D_{Met/Sil}^i = C_i^{Met} / C_i^{Sil} \quad (1)$$

where  $C_i$  is the concentration of element  $i$  in the superscript phase. Experiments to determine  $D_{Met/Sil}$  for the moderately siderophile elements (MSE) suggest that the silicate Earth may record a signature of equilibrium between core-forming metal and a magma ocean (e.g. Wade and Wood, 2005). Partition coefficients

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for the MSE converge to values which may explain the observed primitive upper mantle (PUM) abundances at ~27–40 GPa and 3000–3600 K, suggesting a deep (>800 km) magma ocean (Bouhifd and Jephcoat, 2011; Righter, 2011; Siebert et al., 2011). In most cases, these models also require  $fO_2$  to increase during accretion, but not exceed a value of  $\sim IW-2$  (Wade and Wood, 2005; Siebert et al., 2011). Elements with the strongest affinity for Fe-metal are termed the highly siderophile elements (HSE) and comprise Re, Ru, Rh, Ir, Os, Pt and Au. Experiments at relatively low pressure and temperature (0.1 MPa,  $\leq 1673$  K) suggest the PUM should be rendered essentially barren of HSEs by core-formation, and inter-element ratios should deviate strongly from chondritic values (e.g. Kimura et al., 1974; Borisov et al., 1994; Borisov and Palme, 1996; Ertel et al., 2001; Fortenfant et al., 2003). Instead, comparatively modest depletions are observed ( $\sim 100$  times lower than CI) and inter-element ratios are broadly chondritic (Becker et al., 2006; Fischer-Gödde et al., 2011). This disconnect between experiment and observation is often termed the ‘excess siderophile element problem’ (e.g. Capobianco et al., 1993). The most commonly posited solution to this problem is a post-core-formation accretion of chondritic material which mixed with the silicate Earth, elevating HSE concentrations but having no discernable effect on the more abundant MSEs. This so-called ‘late veneer’ is required to comprise  $\sim 0.5\%$  of the present silicate Earth mass to elevate HSE contents to the observed level. One alternative to a late veneer is that  $D_{Met/Sil}$  values for the HSE decrease and converge to a similar value at very high temperature ( $T$ ) and pressure ( $P$ ), leading to higher mantle concentrations and chondritic element ratios (Murthy, 1991). This idea has seen mixed success with some data for Pt, Pd, Re and Au suggesting equilibrium core-formation alone is sufficient to explain their observed abundance (e.g. Brenan and McDonough, 2009; Righter et al., 2008; Cottrell and Walker, 2006; Ohtani and Yurimoto, 1996). Os and Ir however, retain large  $D_{Met/Sil}$  ( $> 10^7$ ) values even under high  $P$  and  $T$  conditions (Brenan and McDonough, 2009).

A time-integrated and high precision measure of Re/Os and Pt/Os ratios is provided by radiogenic Os isotopes.  $^{187}\text{Re}$  and  $^{190}\text{Pt}$  decay to  $^{187}\text{Os}$  and  $^{186}\text{Os}$  respectively, with half lives of  $\sim 42$  Ga and  $\sim 470$  Ga. Measured upper mantle  $^{187}\text{Os}/^{188}\text{Os}$  and  $^{186}\text{Os}/^{188}\text{Os}$  are within error of the ratios determined for ordinary chondrites, suggesting identical metal-silicate partitioning for the parent and daughter elements or a PUM with Re, Pt and Os concentrations set by a process other than equilibrium core-formation (Meisel et al., 2001; Brandon et al., 2006). The high precision of these isotope measurements sets them apart from estimates of HSE element ratios obtained from the regression of mantle xenolith compositions, which rely upon a melting proxy such as  $\text{Al}_2\text{O}_3$  content, to determine their primitive element abundances. This makes estimates of Re/Os ( $0.090 \pm 0.002$ ) and to a lesser extent Pt/Os ( $2.0 \pm 0.2$ ) a key constraint on the chondritic nature of the PUM (Becker et al., 2006; Brandon et al., 2006; Meisel et al., 2001).

### 1.1. Previous experimental results

Although high  $P$  and  $T$  metal-silicate partitioning data for Re are scarce, there have been several attempts to measure Re solubility at temperatures  $\leq 1673$  K and 0.1 MPa which have seen some success. Ertel et al. (2001) used the mechanically assisted equilibration technique to measure solubility at a lower  $fO_2$  than previously possible although sample heterogeneity plagued experiments approaching the iron-wüstite buffer. They found a clear dependence of solubility on  $fO_2$  and extremely siderophile ( $D_{Met/Sil}^{\text{Re}} \approx 10^{10}$ ) behaviour under core forming conditions. This conflicts with other results at 20 GPa and 5 GPa which suggest that  $D_{Met/Sil}$  will decrease sufficiently to account for mantle HSE abundances (Ohtani and Yurimoto, 1996; Jana and

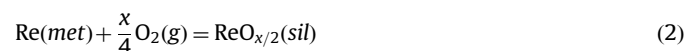
Walker, 1997). However, the partition coefficient determined by Ohtani and Yurimoto (1996) is based upon a single experiment. Also, there was no consideration of potential contamination of analyses by metal inclusions, a feature common to HSE experiments at low  $fO_2$ . The study by Jana and Walker (1997) concerned the effect of sulphur which was found to decrease the affinity of Re for Fe metal, however, the partitioning of Re between sulphur poor metal and silicate melt decreased with the run duration of these experiments. It is the metal-phase which begins Re-doped in these experiments, and this correlation with time makes the attainment of equilibrium, at least with regard to Re, somewhat ambiguous. There was also no measure or control of  $fO_2$  for those experiments, a variable demonstrated to exert strong control over partitioning behaviour (Ertel et al., 2001; O'Neill et al., 1995). An attempt was made by Righter and Drake (1997) to parameterise the dependence of Re partitioning on  $T$ ,  $P$ ,  $fO_2$ , silicate melt composition and metal sulphur content, in order to predict Re behaviour under core-forming conditions. The database of results used to construct this predictive equation includes studies where Re concentrations in the silicate phase were determined using bulk analytical techniques, allowing no direct appraisal of potential metal-inclusion contamination or separation of an ‘inclusion free’ signal from a contaminated run-product. The importance of determining sample heterogeneity by use of micro-analytical techniques was aptly demonstrated by Ertel et al. (2001) through comparison of their data, acquired by laser ablation inductively coupled mass spectrometry (LA-ICP-MS), with that obtained from neutron activation analysis. This comparison demonstrates how bulk analysis of metal-inclusion bearing glasses can indicate erroneously high metal solubilities and an artificially weak dependence of solubility on  $fO_2$ . Extrapolation of such data from  $> IW$  to core-forming conditions of  $IW-4$  to  $IW-2$ , predicts unrealistically high solubilities in silicate melt, and concomitant low  $D_{Met/Sil}$  values (Ertel et al., 2001).

In the present study we systematically assess Re solubility as a function of oxygen fugacity, temperature, and pressure with the glass phase measured by LA-ICP-MS. This serves to extend the investigated  $P$ - $T$ - $fO_2$  space to conditions with greater relevance to terrestrial accretion and core-formation. Our primary goals are to identify the  $T$  dependence of partitioning up to 2573 K, determine the presence or absence of a pressure effect in the 0.1 MPa–2 GPa region and measure Re solubility close to the IW buffer in Fe-bearing melts free of contamination by metal inclusions. Results provide a more reliable means to calculate mantle Re/Os following core-formation and allow a more accurate evaluation as to whether the estimated PUM value can be reconciled with metal-silicate equilibrium.

## 2. Theoretical background

### 2.1. Rhenium dissolution in silicate melt and calculation of metal-silicate partitioning

Re is thought to dissolve in silicate melts primarily through an oxidation reaction of the form:



The equilibrium constant for this reaction ( $K$ ) can be expressed as:

$$\log K = \log \left[ a_{\text{ReO}_{x/2}}^{\text{Sil}} \right] - \log \left[ a_{\text{Re}}^{\text{Met}} \right] - \frac{x}{4} \log [fO_2] \quad (3)$$

where  $a_{\text{ReO}_{x/2}}^{\text{Sil}}$  and  $a_{\text{Re}}^{\text{Met}}$  are the activities of Re in silicate melt and metal alloy respectively and  $fO_2$  is oxygen fugacity. At saturation in pure Re metal ( $a_{\text{Re}}^{\text{Met}} = 1$ ) and where the mole fraction of

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