



The importance of sulfur for the behavior of highly-siderophile elements during Earth's differentiation

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Received 27 January 2016; accepted in revised form 8 August 2016; available online 16 August 2016

Abstract

The highly siderophile elements (HSEs) are widely used as geochemical tracers for Earth's accretion and core formation history. It is generally considered that core formation strongly depleted the Earth's mantle in HSEs, which were subsequently replenished by a chondritic late veneer. However, open questions remain regarding the origin of suprachondritic Ru/Ir and Pd/Ir ratios that are thought to be characteristic for the primitive upper mantle. In most core-formation models that address the behavior of the HSEs, light elements such as S entering the core have not been taken into account and high P – T experimental data for S-bearing compositions are scarce. Here we present a comprehensive experimental study to investigate the effect of increasing S concentration in the metal on HSE metal–silicate partitioning at 2473 K and 11 GPa. We show that the HSEs become less siderophile with increasing S concentrations in the metal, rendering core-forming metal less efficient in removing the HSEs from the mantle if S is present. Furthermore, we investigated the FeS sulfide–silicate partitioning of the HSEs as a function of pressure (7–21 GPa) and temperature (2373–2673 K). The sulfide–silicate partition coefficient for Pt increases strongly with P , whereas those for Pd, Ru and Ir all decrease. The combined effect is such that above ~20 GPa Ru becomes less chalcophile than Pt, which is opposite to their behavior in the metal–silicate system where Ru is always more siderophile than Pt. The newly determined experimental results are used in a simple 2-stage core formation model that takes into account the effect of S on the behavior of the HSEs during core formation. Results of this model show that segregation of a sulfide liquid to the core from a mantle with substantial HSE concentrations plays a key role in reproducing Earth's mantle HSE abundances. As Ru and Pd are less chalcophile than Pt and Ir at high P – T , some Ru and Pd remain in the mantle after sulfide segregation. Addition of the late veneer then raised the concentrations of all HSE to their current levels. Suprachondritic Ru/Ir and Pd/Ir ratios of the mantle can thus be explained by a combination of sulfide segregation together with the addition of a late veneer without the need to invoke unknown chondritic material.

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Keywords: HSE; Core formation; Sulfide–silicate partitioning; Metal–silicate partitioning

1. INTRODUCTION

The defining property of the highly siderophile elements (HSEs – Re, Os, Ir, Ru, Pt, Pd, Rh, Au) is their strong affinity to partition into Fe-rich metal. Therefore, the HSEs are useful geochemical tracers of processes involving metal–silicate equilibration such as the formation of the Earth's

core (e.g. Kimura et al., 1974; Wänke, 1981; O'Neill, 1991; Righter et al., 2008; Walker, 2009). It is known from 1-bar solubility experiments (e.g. O'Neill et al., 1995; Borisov and Palme, 2000; Fortenfant et al., 2003, 2006; Ertel et al., 2008) as well as high P – T metal–silicate partitioning experiments (e.g. Holzheid et al., 2000; Righter et al., 2008; Brenan and McDonough, 2009; Mann et al., 2012) that segregation of metal to the Earth's core should have left the mantle much more depleted in HSEs than what is observed for the primitive upper mantle (PUM),

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which is generally used as a proxy for the whole mantle. Most experimental data also suggest a strong fractionation among the HSEs during metal–silicate equilibration (O'Neill et al., 1995; Brenan and McDonough, 2009; Mann et al., 2012), which is also not seen. Instead, the HSEs are thought to be present in roughly chondritic proportions in the PUM (e.g. Becker et al., 2006; Barnes et al., 2015). The most accepted model to explain the apparent overabundance and chondritic ratios of the HSEs is the so-called “late veneer” concept (e.g. Kimura et al., 1974; Wänke, 1981). After core formation ceased chondritic material was accreted to the Earth's mantle, thereby establishing the absolute and relative mantle HSE abundances. Such late accretion of chondritic material has proven to be a common feature of planetary bodies in the solar system (e.g. Day et al., 2007; Walker, 2009; Dale et al., 2012). Estimates of the amount of material added to Earth's mantle range from 0.3% to 1% of the total mass of the Earth (Morgan et al., 2001; Walker, 2009; Jacobson et al., 2014; Walker et al., 2015). A caveat of this theory is that in detail PUM appears to have suprachondritic Ru/Ir and Pd/Ir ratios, which cannot be reproduced by the late accretion of any known meteorite group (e.g. Becker et al., 2006; Walker, 2009). Lunar impact melt rocks appear to display similar suprachondritic Ru/Ir and Pd/Ir ratios. Therefore, it has been suggested that the late veneer could be composed of material that is either not represented by known meteorites (Wang and Becker, 2013; Fischer-Gödde et al., 2015; Walker et al., 2015), or consists of a mixture of CI-chondrite and iron-meteorite-like material (e.g. Fischer-Gödde and Becker, 2012; Kruijjer et al., 2015).

Another possibility to explain suprachondritic Pd/Ir and Ru/Ir might be if some Pd and Ru were retained in the mantle during core-formation. While this is possible for the least siderophile element Pd, this cannot explain Ru/Ir, however, because Ru is too strongly siderophile at high P – T (at 30 GPa, 2673 K and FMQ-2 $D_{Pd} = 1.9 \times 10^3$, $D_{Ru} = 5.1 \times 10^5$ and $D_{Ir} = 2.4 \times 10^6$ – Mann et al., 2012). A potential solution could be the presence of light elements in core-forming metallic liquids. It has become increasingly apparent that light elements such as O, Si, C and S entering the core will affect the partitioning behavior of a range of trace elements (e.g. Jana and Walker, 1997a,b; Chabot and Agee, 2003; Wood et al., 2013; Righter et al., 2014; Fischer et al., 2015; Wang et al., 2016). For the behavior of the HSEs sulfur potentially plays an important role, as the HSEs are also strongly chalcophile elements (Peach et al., 1990; Fleet et al., 1991; Bezmen et al., 1994; Crocket et al., 1997; Pruseth and Palme, 2004; Fonseca et al., 2009, 2011, 2012; Mungall and Brenan, 2014). Sulfur can have an effect in two different ways: Firstly, the presence of S may influence the metal–silicate partitioning behavior of trace elements (e.g. Jana and Walker, 1997a; Cottrell et al., 2009; Mann et al., 2009; Rose-Weston et al., 2009; Righter, 2011; Wade et al., 2012; Wood et al., 2014). This may also be true for the HSEs because S^{2-} dissolved in silicate melts bonds with HSEs and thereby enhances their solubility (Laurenz et al., 2013; Mungall and Brenan, 2014), causing metal–silicate partition coefficients to decrease. Moreover, S present in the metal phase also

affects HSE partitioning. Partition coefficients for Pd reported by Righter et al. (2008) with up to 5 wt.% S in the metal phase are significantly lower than the results of Mann et al. (2012) for S-free metal. This indicates that S-bearing metals are potentially less efficient in extracting HSEs to the core.

Secondly, an immiscible sulfide melt may have exsolved from the magma ocean and segregated to the core (e.g. O'Neill, 1991; Wood and Halliday, 2005; Lee et al., 2007). This hypothesis was shown to be consistent with chalcophile element patterns of the mantle (e.g. Kiseeva and Wood, 2015) as well as its Cu-isotope signature (Savage et al., 2015). Sulfide–silicate partition coefficients of the HSEs at low P – T conditions are generally high and range between 10^3 and 10^8 (e.g. Fleet et al., 1991; Bezmen et al., 1994; Fonseca et al., 2009, 2012; Mungall and Brenan, 2014). Most recent determinations at 1 bar, 1473 K and ~FMQ-1 yield $D^{\text{sulfide-silicate}}$ between 4×10^5 for Ru and 3×10^6 for Pt and Ir (Mungall and Brenan, 2014). Although these data were generated at P – T conditions much lower than those inferred for the formation of Earth's core, they imply that HSEs could be efficiently extracted to the core by core-forming sulfide liquids (O'Neill, 1991).

The aim of this study is to assess the effect of S, either dissolved in metal or as immiscible sulfide melt, on the behavior of the HSEs during core formation. Therefore, we have investigated experimentally the effect of S on the metal–silicate partitioning behavior of the HSEs as well as their sulfide–silicate partitioning at high P – T conditions. From these experiments, we also determined the solubility of S in peridotite melts to ascertain under which conditions an immiscible sulfide melt can exsolve from a magma ocean. The results are applied to model the behavior of the HSEs during core formation, and to address the question of how the HSE abundances of the Earth's mantle were established.

2. EXPERIMENTAL PROCEDURES AND RUN PRODUCTS

Two sets of experiments were carried out to study the partitioning behavior of Pt, Pd, Ru and Ir at high temperatures and pressures. These HSEs were chosen in order to investigate the origin of possible suprachondritic Pd/Ir and Ru/Ir ratios in the Earth's mantle while maintaining a chondritic Pt/Ir ratio. These elements also include the most siderophile (Ir) as well as the least siderophile (Pd) of the HSEs. In the first set (Set 1) we equilibrated molten peridotite with a range of metal or sulfide compositions along the Fe–FeS binary join at constant P (11 GPa) and T (2473 K), to systematically study the effect of S on HSE metal–silicate partitioning. In the second set of experiments (Set 2) the sulfide–silicate partitioning of the HSEs was investigated by equilibrating FeS sulfide melt with molten peridotite at pressures from 7 to 21 GPa and temperatures between 2373 and 2673 K.

In both cases, the starting silicate composition was a synthetic peridotite corresponding to the primitive mantle composition (Palme and O'Neill, 2014). The peridotite composition was prepared from reagent-grade oxides and

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