Prediction of metal–silicate partition coefficients for siderophile elements: An update and assessment of PT conditions for metal–silicate equilibrium during accretion of the Earth

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ABSTRACT

Experimental studies of the partitioning of siderophile elements between metallic and silicate liquids have provided fundamental constraints on the early history and differentiation conditions of the Earth. With many new studies even in the last 20 yr, several models have emerged from the results, including low pressure equilibrium, high pressure equilibrium, and combined high and low pressure multi-stage models. The reasons – silicate melt composition, pressure effects on silicate melt structure, different methods for calculating metal activity coefficients, and the role of deep mantle phases – for the multitude of resulting models have not been specifically addressed before, yet are critical in evaluating the more likely and realistic models. The four reasons leading to the divergence of results will be discussed and evaluated. The behavior of the moderately siderophile elements Ni and Co will be compared using several approaches, each of which results in the same conclusion for Ni and Co. This consistency will eliminate the supposition that one or the other approaches gives a more accurate answer for element partitioning. Newly updated expressions for 11 elements are then derived and presented and applied to the early Earth to evaluate the idea of a late stage equilibration between a core forming metal and silicate melt (or magma ocean). It is possible to explain all 11 elements at conditions of 27–33 GPa, 3300–3600 K, $\Delta IW = -1$, for peridotite and a metallic liquid containing 10% of a light element. The main difference between the current result and several other recent modeling efforts is that Mn, V, and Cr are hosted in deep mantle phases as well as the core. The other elements – Ni, Co, Mo, W, P, Cu, Ga, and Pd – are hosted in core, and detailed modeling here shows the importance of accounting for oxygen fugacity, silicate and metallic liquid compositions, as well as temperature and pressure. The idea of late stage metal–silicate equilibrium at a restricted pressure and temperature range leaving a chemical finger print on the upper mantle remains viable.

Published by Elsevier B.V.

1. Introduction

Siderophile elements in planetary mantles have long been used to constrain the conditions during planetary accretion and differentiation (e.g., Ringwood, 1961; Wanke, 1981). The partition coefficient of a siderophile element between metal and silicate melt, can help to constrain the pressure, temperature, oxygen fugacity, and compositional conditions during core formation. Since ~1990, high pressure and temperature (PT) experiments on metal–silicate systems have shown that partition coefficients [D(met/sil)] for siderophile (iron-loving) elements are much different than those measured at low PT conditions (Hillgren et al., 1994; Walker et al., 1993). The high PT data have been used to argue for a magma ocean during growth of the early Earth (Li and Agee, 1996; Ohtani et al., 1997). In the ensuing decades there have been hundreds of new experiments carried out and published on a wide range of siderophile elements (>80 experiments published each for Ni, Co, Mo,

W, P, Mn, V, Cr, Ga, Cu and Pd). Despite the publication of many data for a large number of siderophile elements, there has not been agreement on the conditions existing during early differentiation of the Earth (Fig. 1). Some authors have concluded there was a shallow to intermediate depth magma ocean (Li and Agee, 1996; Ohtani et al., 1997; Righter et al., 1997). Other authors have concluded a hotter, deeper magma ocean (up to 60 GPa; Chabot and Agee, 2003; Li and Agee, 2001; Wade and Wood, 2001). Others have concluded that the Earth started accreting under reducing conditions and became progressively more oxidized as accretion continued (Wood et al., 2006, 2008), similar to heterogeneous accretion models from the 1980s (Newsom and Sims, 1991; Wanke, 1981).

Some studies have drawn conclusions based on a small subset of siderophile elements, or a set of elements that provides little leverage on the large scale differentiation (such as slightly siderophile elements Nb, Mn, Cr, and V), and very few studies have attempted to quantitatively explain more than 5 elements at a time. In addition some studies have focused on the effect of one light element (e.g., Corgne et al., 2009; Rubie et al., 2004, — oxygen; Fitoussi et al., 2009;
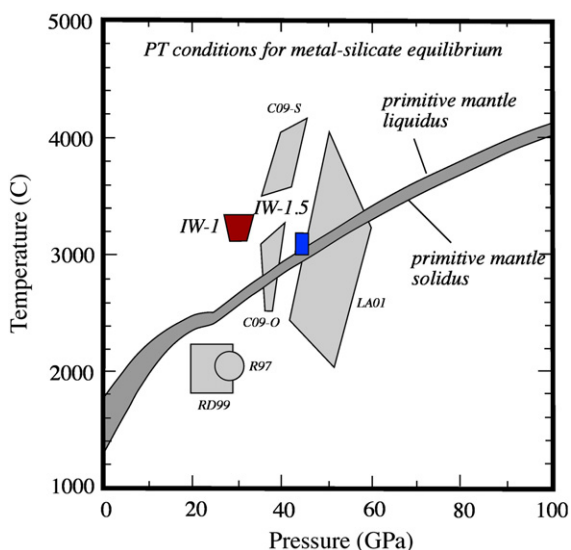
Fig. 1. Pressure and temperature diagram showing the melting curve (liquidus and solidus) for Earth's primitive upper mantle (from Walter and Tronnes, 2004). Colored fields are the pressure and temperature conditions defined by this study where Ni, Co, Mo and W concentrations in Earth's primitive upper mantle can be explained by metal–silicate equilibrium (see Section 6). Also shown are the pressure–temperature conditions for metal–silicate equilibrium proposed by a number of previous workers, including Righter et al. (1997), Righter and Drake (1999), Li and Agee (2001), and Corgne et al. (2009). The latter study proposed various PT conditions for an S-rich core and an O-rich core both of which are shown.

Wood et al., 2009 — Si; Brett, 1984 — sulfur), whereas it is widely agreed that there are likely several light elements in the Earth's core (Hillgren et al., 2000; Poirier, 1994).

The purpose of this study is to identify issues that have led to a difference in interpretation of siderophile element partitioning, including the importance of silicate melt composition, the role of pressure changes in volumetric properties of melts, the role of deep (lower) mantle phases in producing mantle depletions, and the variation of metal activities with metallic liquid composition. An assessment will be made of these issues and then updated predictive expressions for 11 siderophile elements – Ni, Co, Mo, W, P, Ga, Cu, Mn, V, Cr, and Pd – will be presented based on new experimental data available since 1999 (Righter and Drake, 1999). The resulting expressions will be applied to the siderophile element depletions in Earth's upper mantle. It will be shown that the concentrations of all 11 elements in the primitive upper mantle (Table 1) can be explained by metal-silicate equilibrium at a specific PT region, which corresponds to the latest stage of accretion of the Earth. Extremely high PT conditions or multi-stage models are not necessary, and are only required in previous studies in which the effects of silicate melt composition, deep mantle phases, fO_2 and pressure effects are not adequately addressed.

2. Previous work — sources of disagreement between models

There are a number of factors that have led to diverging interpretations of experimental data. Four of these are summarized here — their impact on the modeling results will become clear in the results section.

2.1. The importance of silicate melt composition

Silicate melt compositions used in many experimental studies cover a huge range (Fig. S1). Some studies have concluded that melt composition is not an important control on D(Ni) and D(Co) metal/silicate (Chabot et al., 2005), or have ignored this variable altogether (Kegler et al., 2008). In fact, the change in D(Ni) and D(Co) ascribed to pressure in the dataset of Kegler et al. (2008) are coupled to changes

in melt composition (see next section). The decreases observed for D(Ni) and D(Co) due to silicate melt becoming depolymerized are also observed for other elements, such as Cu, Zn and W (Righter et al., 2010). But this effect cannot be generalized, as there are just as many elements that exhibit an increase in D(met/sil) as peridotite melt compositions are approached (Righter et al., 2010).

Quantification of silicate melt compositional variation is frequently done with the standard silicate melt structural parameter, NBO/T (ratio of non-bridging oxygens to tetrahedrally coordinated cations; Mysen, 1991). Some elements show a strong affinity for CaO compared to MgO (O'Neill and Eggins, 2002; O'Neill et al., 2008), but NBO/T cannot distinguish between these two network modifiers. As a result, a more realistic modeling approach is to use oxide mole fractions which can help to unravel the competing or opposing effects of cations like Ca and Mg. It is clear that the effect of silicate melt composition is crucial to quantify for every element (e.g., Righter et al., 2010), and it needs to be understood in particular for FeO bearing systems that approach peridotite (e.g., Al- and Ca-poor, Mg-rich). In the present study, for Mo, W, and P, oxide mole fractions are used to quantify the silicate melt effects, whereas for all other elements, the smaller melt composition effects are quantified with the simpler single parameter, NBO/T. There are >100 experiments for which to employ these terms for W and P, spanning a broad compositional range for each element. For Mo, there are fewer data, but there have been several targeted studies that show variation with silicate melt composition (Righter et al., 2010; Walter and Thibault, 1995) and so the existing database is adequate for quantifying this effect for D(Mo).

An additional chemical effect that has not been previously quantified but is significant, is a complex of siderophile elements with S in silicate melt. This effect is significant for Mo, V and Ga (but not other elements) and therefore a term for S content of the silicate melt will be added for each of these elements (see Sections 4 and 5). Because some high FeO silicate melts can dissolve up to 4000 or 5000 ppm S (Righter et al., 2009a,b) this can be a large factor in some experimental studies and there must be a method to correct for the S content of the Earth's primitive mantle which is closer to 200–250 ppm and 8 wt.% FeO.

2.2. Are there silicate melt structural changes between 1 and 20 GPa?

Several recent studies (Cottrell et al., 2009, 2010; Kegler et al., 2008) have concluded that changes in D(met/sil) at higher pressure are due to structural changes in silicate melts. In the case of D(Ni) and D(Co), Kegler et al. (2008) argue that the partition coefficients decrease with increasing pressure, but there is a slope change at 5–10 GPa that is due to Ni and Co coordination changes in the silicate melt (Fig. 2a). In the case of D(W), Cottrell et al. (2009) argue that D(W) changes from a positive slope to a negative slope at higher pressures (Fig. 3), again due to a melt structural change at ~5 GPa.

There are alternate explanations for both. The Kegler et al. (2008) dataset is not for constant composition. The melt composition was changed and the change correlates with pressure (Fig. 2a); the slope change occurs at the same point where melt composition changes. What these authors overlooked or ignored is the effect of melt compositional change. If the ln Kd(Fe–Ni) data of Kegler et al. (2008) are regressed against 1/T, P/T, and NBO/T, there is a clear melt compositional term that is important when examining data from basalt to peridotite (Kegler data vary from NBO/T = 0.5 to >4; Fig. 2b). When this regression is used to calculate ln Kd (Fe–Ni) and ln Kd(Fe–Co) along an adiabat and for NBO/T = 2.8, the convergence pressure changes to a value close to 35 GPa, rather than the 60–70 GPa argued by Kegler et al. (2008) using a regression of only P and T (Fig. 3c; Table 2b). Indeed all data regressed for lnD (see below) results in a melt compositional term for lnD(Ni) that is significant, and must be accounted for in any calculations or modeling. Conclusions reached by Kegler et al. (2008) regarding the role of pressure must be reconsidered and the effects they observed are due to both