Modelling siderophile elements during core formation and accretion, and the role of the deep mantle and volatiles.

Revision 1

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Abstract

The last decade has seen general agreement that moderately siderophile elements (MSE) in Earth’s primitive upper mantle (PUM) can be explained by metal-silicate equilibrium at mid-mantle depths in an early Earth magma ocean environment. Despite the agreement, there are some differences in the detailed modelling that has been carried out. This paper will examine siderophile element metal/silicate partitioning with respect to three different topics: a) an examination of aspects of the modelling that one might suspect leads to differences in outcomes or in comparison between models, but actually are in agreement with experimental data and between models, b) a discussion of the role of the deep mantle in modelling efforts, and c) the role and/or fate of volatiles in magma ocean scenarios with an emphasis on where data are lacking.

Introduction

Detailed models for the origin and accretion of the Earth grew out of early ideas developed by Eucken (1944) for heterogeneous accretion, in which the material accreting to form the Earth changed with time producing the layers of the Earth. These models were developed in more detail by Turekian and Clark (1969), Clark (1961), Anders (1977). An alternative to heterogeneous accretion – homogeneous accretion – in which the Earth accreted from a homogeneous mixture of metallic and silicate grains and later differentiated into the core and mantle, was proposed originally by Urey (1951), Safronov (1959), Elsasser (1963) and Birch (1965) over a similar timeframe. The former models had problems explaining the light elements in Earth’s core, and the upper mantle compositions (with both refractory and siderophile elements), whereas the latter models could not explain the elevated siderophile content of the
mantle, oxidized iron, and the idea that any accreting H₂O and CO₂ would be reduced to H and C in the presence of metal (core) thus eliminating sources for Earth's hydrosphere and atmosphere (Ringwood, 1979). In particular, the elevated siderophile element contents in Earth's mantle were problematic but data used to evaluate their abundances was experimental data collected at low pressures.

The development of high pressure techniques in the 1980s and 90s led to an abundance of studies of siderophile elements, all of which revealed that siderophile element contents of Earth's mantle could possibly be explained by metal-silicate equilibrium at elevated PT conditions compared to the earlier studies at 1 bar and low temperatures (e.g., Li and Agee, 1996; Walter and Thibault, 1995). As a result, Earth accretion models are now a combination of aspects of heterogeneous accretion and homogeneous accretion alike, with core-mantle equilibrium able to explain siderophile element contents e.g., Righter, 2011a; Wade et al., 2012), and especially if the composition of the materials changes during accretion (Rubie et al., 2011). The last decade has seen general agreement that moderately siderophile elements in Earth's PUM can be explained by metal-silicate equilibrium at mid-mantle depths (30 to 70 GPa) in a magma ocean environment (e.g., Siebert et al., 2012; Bouhifid and Jephcoat, 2011). There is some disagreement over the exact PT conditions, and whether fO₂ was variable during accretion (e.g., Rubie et al., 2011; Righter and Ghiorso, 2012; Siebert et al., 2013).

Three topics bearing on the Earth accretion models will be discussed in this paper. First, aspects of siderophile element modelling have been questioned by some, including a) the role of pressure in causing coordination changes in metallic and silicate melts at 5 and 20 GPa, b) the role of absolute versus relative oxygen fugacity in the calculations, and c) the choice of methods.
for quantifying effects of alloying elements on siderophile element activities in metallic liquid.

It will be shown that none of these structural effects have any bearing on the predictive expressions, and that all the observed changes in partition coefficients are fully predicted by the multiple linear regression expressions. It will also be shown that regressions using relative fO$_2$ ($\Delta$IW) and absolute fO$_2$ predict the same behavior, albeit in two different ways. Similarly, we compare two modelling approaches for activities in metallic liquids and show that there is overall agreement in the nature and magnitude of the metallic compositional effects.

Second, modelling has not generally included deep mantle reservoirs. This has led to some models that fit Nb, V and Cr via core formation. Yet the lower mantle may be most important reservoir. Additional studies have revealed that a deep basal magma ocean may be relevant and could harbor elements. The general role of deep mantle reservoirs in differentiation models will be discussed.

Finally, a number of volatile elements, volatile siderophile and highly siderophile elements have been studied only at a limited set of conditions relevant to a deep magma ocean scenario, and a comprehensive understanding is lacking. Volatiles are typically discussed in terms of indigenous versus exogenous origin, and this classic question remains open for many. For example, some elements like In, As, and Sb are all poorly studied and so conclusions drawn from these studies have high uncertainty. Similarly, the HSE, although notoriously difficult to study both analytically and experimentally, have had a number of solid studies completed in recent years. However, information such as the effect of non-metals in metallic liquid (S, C, O and Si), as well as silicate melt composition, are needed for a full evaluation. It will be shown that the HSE contents of all differentiated bodies have viable explanations other than late chondritic additions.
and multiple hypotheses should be entertained until the controlling variables are fully explored by experimental studies.

These three topics illustrate that although a general model is emerging for the earliest differentiation event for the early Earth, there remain many outstanding questions and avenues for further exploration. These should lead to a better understanding of the accretion of the Earth and the origin of its volatile elements.

1. Evaluating models – pressure, fO$_2$, and metal activities

The partitioning of siderophile elements between metal and silicate (core and mantle) has been studied experimentally by equilibrating metal and silicate melt mixtures at high temperatures and measuring the partition coefficient as $D = \text{wt}\% \ i \ \text{in metal} / \text{wt}\% \ i \ \text{in silicate melt}$. Because of the strong dependency on temperature, pressures, fO$_2$, and metal and silicate composition, efforts were made to predict the D as a function of these variables with chemical thermodynamics as a guide. Predictive expressions introduced by Righter et al. (1997) and Righter and Drake (1999) are based on the equilibrium (using Ni as an example):

$$2 \text{NiO} = 2 \text{Ni} + \text{O}_2 \quad \quad (1)$$

and have the form:

$$\ln D(\text{metal/silicate}) = a \ln fO_2 + b/T + cP/T + d[\ln(1-Xs)] + e[\ln(1-Xc)] + \sum f_iX_i + g, \quad \quad (2)$$

where D is the partition coefficient (defined above), Xs and Xc are the mole fractions of S, C in metallic liquid, and $X_i$ are the mole fractions of oxide components in silicate melt. The form of these expressions is guided by the thermodynamics of simple metal-oxide equilibria that control
each element's partitioning and, include terms that mimic the activity coefficients of each
element in the metal and silicate. Absolute oxygen fugacity is calculated using the approach of

Other studies have used:

\[ \ln D = a(\Delta IW) + b/T + cP/T + d[\ln(1-Xs)] + e[\ln(1-Xc)] + \Sigma f_i X_i + g \]  

(3)

where relative fO₂ is used instead of absolute fO₂, or

\[ \ln D = \ln \left( \frac{X_i \text{ met}}{X_i \text{ sil}} \right) = a(\Delta IW) + b/T + cP/T + \left( \frac{\gamma_i \text{ sil}}{\gamma_i \text{ met}} \right) \]  

(4)

where \( \gamma_i \) is an activity coefficient for the siderophile element (i) in either metal or silicate melt.

In many cases the silicate melt activity is assumed equal to unity, but the activity coefficient in
the metal is quantified. A popular model for the metal uses the Wagner ε formalism (Wagner,
1962; Lupis, 1983) which represents the effects of different solutes on one another’s
thermodynamic properties according to:

\[ \ln \gamma_i = \ln \gamma_i^0 + \sum_{j=2}^{N} \epsilon_i^j x_j \]  

(5)

where \( \gamma_i \) is the activity coefficient of solute i in the mixed alloy and \( \gamma_i^0 \) is its activity coefficient
when it is infinitely dilute in pure liquid Fe under the same conditions of pressure and
temperature. The interaction parameters \( \epsilon_i^j \) refer to the measured effects of component j on the
activity of i in the alloy and are assumed to be linearly dependent on the mole fraction of j, \( x_j \).

Equations (1) through (5) will be used below to illustrate various aspects of the modelling that
has been carried out in recent studies.

A role for metallic and silicate liquid structural changes at ~ 5 GPa?
Several metal/silicate partitioning studies have shown that at pressures near 5 GPa the partition coefficient can change in slope (Figure 1a,b). In the case of D(Ni), the slope changes from a moderately negative, to slightly negative (Kegler et al. (2008), whereas in the case of D(W), the slope changes from positive to negative (Cottrell et al., 2009). Because this is not behavior immediately expected of a linear dependence, the authors of both attributed the change in D(metal/silicate) instead to changes in silicate melt structure at higher pressures, citing the study of Keppler and Rubie (1993) on coordination change for Ni in albitic melt in this pressure range. Similarly, Sanloup et al. (2011) argued that Fe-rich metallic liquid undergoes a structural change in this pressure range, and showed many literature studies of D(Ni) partitioning that exhibited a change near 5 GPa. In fact, neither of these explanations are necessary and the changes in slope in the partition coefficients for Ni and W and any other siderophile element are expected and fully predicted by the multiple linear regressions published by many authors (e.g., Righter, 2011a), as will be explained below.

A change in partition coefficient at this pressure range is due to the fact that the pressure dependency of D(metal/silicate) is not simple linear dependence, because the pressure term is ‘P/T’ (Equations 2, 3, 4). This link with temperature means that any variation in D(metal/silicate) with pressure will be coupled with temperature changes as well, and will not be a linear function. For example, the magnitude of decrease in D(Ni) with pressure changes near 5 GPa because the change is defined by the P/T term (Figure 2a). For Ni, the initial steep slope could be mistaken for a linear effect below 5 GPa and a second linear effect above 5 GPa, but in reality this is one continuous curve as shown by Righter et al. (2011a,b). The latter study is based on experimental data that spans 1 bar to 42 GPa, 1300 to 4000 ºC, IW-5 to IW+1, basalt to peridotite silicate melts, and S- and C-bearing metallic liquids. Therefore, the need to explain
such a change, whether due to a structural change in silicate or metallic liquid, disappears. Furthermore, the metallic liquids considered in the Sanloup et al. (2011) study are of variable composition with some containing S, some C, and some no light element. Each metallic liquid should have a different pressure of structural change so there is no reason why this phenomenon should be connected to the change in partition coefficients seen for Ni or W.

In the case of W, Cottrell et al. (2009) demonstrate a slope change from positive to negative at ~ 5 GPa, but this is partly attributable to the temperatures chosen for the individual pressure points. For example, the lowest pressure points (0.5, 1, 2, and 6 GPa) are at T = 2100 K, while the intermediate pressure point (11 GPa) is at 2400 and the highest pressure point (18 GPa) is at 2500 K. Such a change in slope is fully predicted by linear regressions for W (and other elements as well, like Ga and P) if the temperatures are chosen to be low, intermediate and high like this (Figure 2b). If D(W) is calculated along a liquidus, where temperature also increases with pressure, at first D(W) increases, but then decreases at pressure greater than 5 GPa (Figure 2b).

A role of silicate liquid structural changes at >20 GPa?

Sanloup et al. (2013) argue that there are non-linear (with pressure) trends for D(Ni) that they ascribe to silicate melt structural change at > 20 GPa, and that multi-linear regression approaches can't account for. In fact, the MLR approach predicts exactly what is observed so there is no missing melt structural term in the predictive expressions (Figure 3). This is not to say that melt structure is not important, but only that the current partitioning approaches have not ignored anything that can be quantified. Of course, understanding melt structure is important,
but there are no effects that are required to quantify in this PT range, because the simple
equilibria used in linear regression analysis can fully explain all data.

To illustrate how D(Ni) is predicted to change with pressure, we have plotted the calculated
D(Ni) values along a liquidus of Andrault et al. (2011) and compared it to the data shown by
Sanloup et al. (2013). The resulting plot shows excellent agreement between the calculated and
measured partition coefficients, which indicates no additional terms are necessary to explain the
partitioning data for Ni.

Role of relative vs. absolute fO2 calculation and incorporation into partitioning expressions.

Recent geochemical models for accretion and core formation emphasize either changing fO2
(like a classic Wänke, 1981 model of early reduced materials followed by later oxidized
materials), or relatively constant fO2 (e.g., Rubie et al., 2011; Siebert et al., 2013; Righter and
Ghiorso, 2012). Because the models are based on similar partitioning studies and elements it
may be confusing why the results are so different. One major difference between approaches is
that one (equation 3) uses relative fO2 in predictive expressions (e.g., Cottrell et al., 2009; Wood,
2008, Kegler et al., 2008), while other (equation 2) uses absolute fO2 (e.g., Righter and Drake,
1999; Righter, 2011a). Consideration of relative fO2 is certainly convenient and sometimes is
the best way to estimate the fO2 of an experiment or series of experiments in lieu of detailed
thermodynamic data. However, the inherent assumption is that there is no pressure or
temperature effect on ΔIW and that an experiment, for example done on basalt and metallic FeNi
at 1 GPa and 1900 K has the same ΔIW value as one done at 30 GPa and 3500 K. Relative fO2
was originally considered as a useful approximation for discussing oxygen fugacity relative to
buffers in magmatic system within a restricted T and P range where temperature effects were
likely minimal (i.e., between 700 and 1200 °C). This may not be true at the ultra-high pressures and temperatures considered in metal-silicate partitioning experiments where temperatures may be between 1600 and 4000 °C (e.g., Righter and Ghiorso, 2012). Nonetheless, when using Δ IW in regression analysis, the effect of pressure is lumped entirely onto the volume term (P/T) term.

Consideration of absolute fO₂, on the other hand, is more difficult due to the lack of thermodynamic data at extreme PT conditions, but it does allow the effects of pressure to be allocated to both the fO₂ term (ln fO₂) and the volume (P/T) terms as it should. That is, when pressure is increased, the absolute fO₂ rises, and the volume of reaction changes – these are two different effects that can be accounted for when absolute fO₂ is used in linear regression. Furthermore, the volume change of metal-oxide equilibria is positive, and the regression coefficients resulting from equation (2) also result in positive values of c, in agreement with chemical thermodynamics. The negative c coefficient resulting from regressions using equation (3) is counter intuitive and could lead to misperceptions about partitioning behavior. How important is this effect? An example is illustrated for D(Ni) and D(Co) in which the same datasets are used to derive regression coefficients a through g for equations (2) and (3). The results show that the agreement between the two approaches is good until approximately 40 GPa, where the predicted D values start to differ substantially (Figure 4). There is therefore, no significant difference between these two approaches as long as pressure calculations do not exceed 40 GPa. Which approach is used depends on what kind of information one wishes to include in the modelling. The simplistic ΔIW approach makes unrealistic assumptions, but allows easier prediction of D. The absolute fO₂ approach may allow a more realistic modelling of accretion, and produce coefficients that are more true to chemical thermodynamics, but is limited by our knowledge of fO₂ at high PT conditions.
Effect of non-metallic elements in the metallic liquid

The variation of trace metal activities in metallic liquids can be quite large and is dependent upon metal composition, especially light elements such as C, S, and O. Two fundamentally different approaches have been taken to model these activities.

One approach, taken by Righter and Drake (1999), is to use empirical terms that mimic the Margulies parameter ($W_{ij}$) terms for activity coefficients. This approach fits empirical terms (e.g., $\ln(1-X_{s})$) by multiple linear regression of experimental data acquired at the $P$ and $T$ and metallic liquid compositions of interest to core formation. A second approach calculates epsilon interaction parameters ($\varepsilon$) using values obtained at 1 bar and 1400 to 1600 °C, mainly from the steelmaking industry, and applies them directly (or with a temperature extrapolation approach) to experiments done at variable $P$ and $T$ (Wade and Wood, 2005; Corgne et al., 2008). A positive aspect of this approach is that there is a large body of data from the steelmaking literature (e.g., Lupis, 1983; Steelmaking Data Sourcebook, 1988). Because these databases are tailored for steel making, and not core formation, information for all elements of interest is not available, and thus some gaps for many elements. There are no corrections for $\varepsilon$ at high pressure conditions – the data have all been obtained for the low $P$ conditions of steelmaking – whereas the $d$ and $e$ terms of Righter (2011a) are derived from the high $PT$ experiments that contain relevant phases such as S, C-, and Si-bearing FeNi metallic liquids.

These two approaches can be compared for the effect of C and S on activity coefficients. The $d$ and $e$ terms of Equation (2) measure the same effect as $\varepsilon C$ and $\varepsilon S$ in equation (5). A comparison of $d$ and $e$ terms from Righter (2011a), Righter et al. (2011a) to epsilon values compiled by Lupis (1983) show that for sulfur the agreement is very good. For carbon the two
approaches may yield different absolute values in a few cases, but the magnitude and sign of the
effects are in good overall agreement. Both approaches predict, for example, the chalcophilicity of
Sn, Cr, Cu, and V, and the anthracaphility of Mo and W (Figure 5).

Summary for predictive expressions

Assessment of temperature and pressure on metal-silicate partitioning of Ni, and W do
not reveal any melt structural effects either at low pressure (~ 5 GPa) or at higher pressure (20
GPa), as suggested in recent studies (Sanloup et al., 2011; Sanloup et al., 2013; Palme et al.,
2011; Kegler et al., 2008; Cottrell et al., 2009). Palme et al. (2011) and Rai and van Westrenen
(2014) both criticize combination of <5 GPa and > 5 GPa partitioning data due to melt structural
effects, but these are non-existent as experimental data can be combined and can predict the
changes in partition coefficients observed at 5 GPa with a single expression. The differences
between regressions using high and low pressure data plotted as lines by Rai and van Westrenen
(2014) in their Figure 2 are all within error for both sets of regressions and thus do not illustrate
the need to split data between the high and low pressure regimes. Indeed, the combined <5 GPa
and >5 GPa datasets for Ni, Co, Mo and W used by Righter and Drake (1996, 1997) to predict
core formation conditions in the very low pressure eucrite parent body (likely asteroid 4 Vesta)
predicted a core size of ~18 mass % in excellent agreement with the measurements made by the
Dawn spacecraft (Russell et al., 2012; McSween et al., 2014). Furthermore, expressions of
Righter (2011a) for Ni, Co and W can be used to predict D at the high PT conditions investigated
by Siebert et al. (2012, 2013) and Bouhifd and Jephcoat (2011). Comparison of these predicted
values to those measured reveals good agreement (Figure 6), indicating that the predictive
ability of these expressions using both high and low pressure partitioning data.
Although different approaches have been used to model fO\(_2\) and metal activity coefficients, there is good agreement between these different approaches and employment of one or the other will not lead to significantly different conclusions regarding the conditions of metal-silicate partitioning of Ni and Co, for example.

Two effects that will lead to major differences in modelling outcomes are the role of silicate melt compositional variation, and the role of deep mantle phase equilibria. The former topic has been the subject of a comment and response and will not be covered in detail here (Righter, 2011b; Palme et al., 2011). However, an independent assessment of the role of melt composition on D(Ni) and D(Co) (Walter and Cottrell, 2013) supports the argument of Righter (2011a,b), as does the ability of expressions of Righter (2011a) to predict high pressure (up to 80 GPa) data of Siebert et al. (2012) for D(Ni) and D(Co), even with low pressure data included in the regressions. The role of deep mantle phase equilibria, on the other hand, will be the focus of the next section.

2. Deep mantle reservoirs and siderophile element modelling

Our knowledge of the PUM comes from relatively shallow portions of the mantle - upper mantle xenoliths and massifs. Mn, V, Cr, Nb and Ta have all been used in core formation modelling and due to their weak siderophile behavior at low PT conditions, they require quite high PT and/or reduced conditions to become siderophile enough to produce a depletion (e.g., Wade and Wood, 2001; Cartier et al., 2014). Recent work at 35-74 GPa has also shown that an O-bearing metallic core may enhance the metal-silicate partition coefficients for V and Cr, thus...
obviating the need for a reduced stage during Earth’s accretion to satisfy the Nb, V, and Cr content of the mantle (Siebert et al., 2013).

However, the weakly siderophile elements Mn, V, and Cr offer an excellent example of elements whose behavior at high PT conditions is not yet fully mature. For example, the recent work of Siebert et al. (2013) argues that dissolved O enhances D(V), D(Cr), such that an O-bearing metallic core might satisfy the depletions of these elements at a more modest redox state rather than at reduced conditions. Isolating the effect of O may be possible by using the predictive expressions of Righter (2011a) to calculate D(V), D(Cr), and D(Mn), at the experimental conditions and compositions of Siebert et al. (2013). The predicted D(V) values are higher (up to 5x) than measured, predicted D(Mn) values are lower (up to 8x) than measured, and the predicted D(Cr) values are approximately the same. These comparisons are in agreement with the conclusion of Siebert et al. (2013) that O will influence D(V), but perhaps this is a weaker effect for D(Cr), and the magnitude of the effect may differ from that inferred by Siebert et al. (2013). Of course it is also possible that the predictive expressions derived by Righter (2011a) should not be extrapolated into the higher PT conditions of the Siebert et al. (2013) study, but we have seen in previous discussion that Ni and Co results can be well predicted using the approach of Righter (2011a). Nonetheless, it is clear that core formation modelling must account for dissolved Si and O (not usually included), in addition to C and S (most commonly included) because these elements can have significant effects on the metal activities and D(metal/silicate) values.

Despite the potential for explaining depletions of these elements in the mantle by core formation, these elements may instead be controlled by partitioning into portions of the deep
mantle, such as the lower mantle, a basal magma ocean, or recycled oceanic crust (eclogite). Mn, V and Cr all have measured $D(\text{Mg-perovskite/melt})$ and $D(\text{ferropericlase/melt}) > 1$ (McFarlane et al., 1994; Taura et al., 2001) and thus are potentially compatible in the lower mantle. On the other hand several other studies have reported $D(\text{Mg-perovskite/melt})$ slightly $< 1$, suggesting these element may be weakly incompatible (Corgne et al., 2005; Liebske et al., 2005). To illustrate the importance of knowing the degree of compatibility or incompatibility of V and Cr in deep mantle phases, simple calculations are used to demonstrate the magnitude of the depletions. For example, if V and Cr are slightly compatible in the lower mantle compared to the upper mantle (e.g., $D(\text{LM/UM}) = 1$ to $2$) the depletions of V and Cr in Earth’s PUM can be explained by metal-silicate equilibrium at much less reducing conditions than IW-4 as required in models by Wood et al. (2008). To illustrate the potential role of lower mantle in controlling V and Cr contents of the PUM, calculations have been carried out using $D(\text{V})$ and $D(\text{Cr})$ metal/silicate from Righter (2011a) (Figure 7). V and Cr can clearly be matched by metal-silicate equilibrium at conditions of IW-2 with $D(\text{SS/LS}) > 1$ (Figure 6). Given this illustration, additional measurements with a focus on these few elements may be important to resolve the issue of lower mantle contribution to depletions in the PUM.

Much of the partitioning data for deep mantle phases have been obtained at conditions relevant to the top of the lower mantle, rather than the bottom. Thus the compatibility of Mn, V and Cr in these deep mantle phases should be examined at higher pressure conditions as well. Furthermore, the isotopic fractionation of Cr between metal, deep mantle phases, and melt should be investigated to allow incorporation of Cr isotopic data into this evaluation (Moynier et al., 2011). In addition, the presence of a layer of post-perovskite phase in the deep mantle (Mao et al., 2005) may affect element partitioning in the deepest part of Earth’s mantle. Furthermore,
because of the low-to-high spin-state transition in ferropericlase (Fischer et al., 2011), the oxygen fugacity at this deep part of the mantle may be higher and thus create a redox reactive zone that would also affect element partitioning.

There may have been a basal magma ocean at the beginning of Earth history (Labrosse et al., 2007). The idea of Nebel et al. (2010) that Nb may reside in the material that formed this basal magma ocean opens up many questions about other elements. Although the Sm-Nd system may not be sensitive enough to record fractionations due to such a hidden reservoir (e.g., Jackson and Carlson, 2012), the Hf-W system may offer more leverage and there are indeed larger fractionations preserved in komatiitic rocks (Touboul et al., 2012). An additional reservoir deserving attention is subducted crust or eclogite. Concentration of Nb and/or Ta in such material could contribute to the depletions of these two elements in the PUM (Rudnick et al. 2000).

The role of the deep mantle and in particular deep trapped melts, in mantle evolution must be pursued in greater detail and may offer some insights into weakly siderophile elements as well. A quantitative assessment of the effects of a basal magma ocean, subducted oceanic crust (or eclogite) and the presence of deep mantle phases (postperovskite, Mg-perovskite, ferropericlase) would benefit from experimentation on trace element partitioning at these deep mantle pressures.

3. **Is late accretion necessary to account for HSEs and volatiles?**

*Exogenous versus indigenous*
The origin of Earth’s volatiles has been debated for decades, and the theories fall into two general categories – that the Earth obtained its volatile content from the materials out of which it accreted (indigenous), or that it acquired its volatiles later in history during a late accretion event or events such as the late veneer or late accretion (exogenous). Sources for the latter idea include comets (e.g., Delsemme, 1998), carbonaceous chondrites (e.g., Chou, 1978; Dauphas and Marty 2002), or an un-sampled chondritic reservoir (Drake and Righter, 2002). If the early Earth experienced a deep magma ocean in which a significant portion of the mantle equilibrated with light element containing core metal, then this physical scenario will have an important influence on the volatile content of the primitive mantle as well. Of course, the origin of Earth’s volatiles could be attributed to a combination of indigenous and exogenous processes. In this section evidence from the classic volatile elements (C, S, H, and N), highly siderophile elements (platinum group elements, Au and Re), and volatile siderophile elements will be discussed, highlighting the areas where additional data and experiments are needed to fully evaluate models for the origin of Earth’s volatiles.

**Classic volatiles – C, S, H, N**

Sulfur partitioning between metallic liquid and silicate liquid as a good example of the extent to which chemical thermodynamics exerts control on core-mantle equilibrium. Boujibar et al. (2014) present a mature expression for predicting D(S) metal/silicate, which is dependent on the silicate melt composition, metallic liquid composition, temperature, pressure and oxygen fugacity. Most of these variables are well understood and their expression takes advantage of close to a dozen studies each of which explores one or several variables. This expression can be used to construct a diagram showing the expected S content of the mantle as D(S) and Earth bulk S content changes (**Figure 8**). At high pressures and a modest bulk S content (intermediate
between C and O chondrites, the Earth’s mantle S content (~ 250 ppm) can be produced by core formation with D(S) ~ 200, which is approximately the value calculated at IW-2, 40 GPa, 3473 K for peridotite melt. These conditions are slightly higher PT conditions than proposed for early Earth metal-silicate equilibrium by Righter (2011a), but more recent updates to the expressions of Righter (2011a) adding the effect of metallic Si content and additional high PT studies have lead to a series of solutions between 35 and 45 GPa and ~3500 K (Righter et al., 2013; 2014a), fully consistent with this result for S.

The current understanding of C partitioning is not as complete. For example, the work of Dasgupta et al. (2013) shows that D(C) metal/silicate can be as low as ~100 at conditions of 1 to 5 GPa and peridotite silicate melt, but the dependence on pressure, temperature and melt composition remains poorly characterized so far. However, with D(C) metal/silicate ~100 the C content of the primitive mantle may be produced by metal-silicate equilibrium, so the values measured at low PT conditions come close to allowing an equilibrium signature in the PUM. Similarly, studies of N have led to the conclusion that D(N) metal/silicate may be 10-20 for the Earth during accretion and core formation (Roskosz et al., 2013; Libourel et al., 2003), which is adequate to explain the depletion of N (relative to the noble gases) in the PUM (Marty, 2012).

Hydrogen presents a special case due to the experimental difficulty in studying its behavior at high PT conditions. Kuramoto and Matsui (1996) suggested that H and C alloying into the core could explain several aspects of terrestrial geochemistry such as the density deficit in the core, the volatile content of the mantle, and the oxidized nature of the upper mantle. Okuchi (1997) showed that at low pressure (up to 7 GPa) H may dissolve into Fe metallic liquid, and could account for a majority of the density deficit in the core. More recently, Nomura et al.
(2014) showed that at the temperature of the CMB, only Fe-H alloys could remain liquid and thus concluded that H may be the dominant light element in Earth’s core.

Clearly, much additional work needs to be done on H, C, and N to understand whether their contents in the PUM could be explained by an early magma ocean scenario with a metal-silicate overprint. In addition, many studies have been done on simple systems, such as Fe-S, Fe-C, Fe-Si (e.g., Hirose et al., 2013), but really we seek information on the complex system that includes O, S, Si, C, H and N, and how they will be partitioned in a magma ocean scenario. We are beginning to understand some of these elements - like S – but we still have a ways to go for H, C, N. The effect of these elements on partitioning of other elements like the MSE (Ni, Co, Mo, W discussed above) or the HSE and VSE (discussed below) is also of fundamental importance.

**HSEs and the “need” for a late veneer**

HSEs have been used to constrain the style of accretion of material to Earth and other differentiated bodies. HSE have very high (>10,000) values of metal/silicate partition coefficients at low pressure conditions, and expected concentrations in the mantle (if it equilibrated with the core) are much lower than measured concentrations in the terrestrial PUM. So these elements have traditionally been used to argue that the higher than expected levels of HSE in the mantle are due to late additions of chondritic material to the Earth (Chou, 1978; Morgan et al., 1981). More extensive studies of mantle materials have shown that several of the HSE exhibit non-chondritic ratios in the PUM (Figure 9), indicating that these elements have also been fractionated slightly from chondritic, much like the MSE Ni, Co and W (Becker et al., 2006). Like Ni, Co and other siderophile elements, new experimental studies have shown that
D(HSE) metal/silicate is lowered substantially at higher P and T conditions, such that the mismatch between expected and measured HSE contents is smaller, but still not quite a large enough effect to explain their concentrations in the mantle by core-mantle equilibrium. Temperature, in particular, has been shown to be an important factor in lowering D(HSE) metal/silicate. Some recent examples are the lowering of D(Au, Ir) metal/silicate (Brenan and McDonough, 2009), D(Pt) metal/silicate (Bennett et al., 2014), and D(HSE) metal/silicate (Mann et al., 2012). These studies conclude, as did many previous studies, that HSE cannot be explained by high PT equilibrium between metal and silicate melt, and must have been brought in after core formation via late accretion.

However, there are a number of avenues that have not yet been explored that could possibly and plausibly account for the HSEs in an equilibrium scenario. The effect of alloying elements on HSE partitioning can be very large, and S for example can change the partition coefficient for D(Ir) solid metal / liquid metal by a factor of 1000 (e.g., Chabot et al., 2003), similar in magnitude to the mismatch between calculated and observed Ir abundances identified in recent studies (Bennett et al., 2014; Mann et al., 2012). Sulfur is well known to be a candidate for Earth’s core light element, but is perhaps limited for the Earth to a few wt% rather than the ~30 wt% possible in Fe-S liquids (Dreibus and Palme, 1996). There are other elements, though, whose effects are unknown, but likely to be similar to sulfur due to geochemical considerations. Carbon, for example may be present in Earth’s core in several wt% and is known to decrease D(HSE) having large and positive interaction parameters (Righter et al., 2014b), Si may be present in up to 10 wt% in Earth’s core and is known to cause large decreases in D(Mo), D(W), D(As) metal/silicate (Tuff et al., 2012; Nickodem et al., 2013), and O is known to influence partitioning in metallic systems as well (Walker, 2000). To illustrate the potential effect of S and
C on lowering $D(\text{HSE})$, we calculate partition coefficients for Au and Ir along a liquidus PT path (mimicking accretion), and compare S- and C-free metallic liquid to those for S- and C-bearing metallic liquids. The effect of S and C is clearly important with the S- and C-free system having $D(\text{Au})$ and $D(\text{Ir})$ too high to explain their contents in the mantle, but with $X_s = 0.25$ and $X_C = 0.10$ in the metallic liquid, both $D(\text{Au})$ and $D(\text{Ir})$ become low enough to explain the contents in Earth’s PUM (Figure 10).

An additional effect that is starting to be appreciated for HSE partitioning is sulfur dissolved in silicate melt (Laurenz et al. 2013). Sulfur dissolved into silicate melt can cause complexing with HSE such that the solubility in a S-bearing silicate melt increases, thus causing $D(\text{HSE})$ metal/silicate to decrease. This may be especially important at reducing conditions where S solubility in silicate melt is high. So, the effects of light elements (C, S, Si, O) alloyed in metallic liquids on $D(\text{HSE})$ metal/silicate needs to be understood but offers promise in explaining the HSE content of Earth’s PUM.

Late accretion for Mars, Moon, and asteroids?

Recent work on HSEs in martian meteorites, differentiated asteroids (eucrites, diogenites, angrites), and the Moon have led some to argue these bodies also experienced a late veneer or late chondritic additions after core formation. This idea is debatable for each body, and viable alternative explanations include mixing of HSE from core into mantle by shear deformation (Rushmer et al., 2005; HEDs), brecciation and contamination with chondritic material either as fragmental regolith or impact melt breccia (HEDs and angrites). In addition, in some cases the patterns are not sufficiently chondritic and can actually be explained by metal-silicate equilibrium (Moon and Mars).
The martian meteorites exhibit “broadly” chondritic ratios of HSE but they are not all chondritic and can be as much as 2 to 5 x non-chondritic which is much larger variation compared to even the Earth, where there are already strongly non-chondritic Au/Ir and Ru/Ir ratios documented. Rai and van Westrenen (2013) applied S-free partitioning results of Mann et al. (2012) to core formation in Mars, found the D(HSE) metal/silicate to be too high and argued thus that Mars requires a late veneer of chondritic material added after core formation. However, when metallic S and C effects are quantified as well as the fO₂, T, P and melt composition, it becomes clear that a late veneer is not required for Mars (Righter et al., 2014b). In fact, HSE contents observed in the martian meteorites can easily be explained by metal-silicate equilibrium between the primitive martian magma ocean and a S-, and C-bearing metallic core at conditions of ~ 14 GPa and 2250 K (Righter et al., 2014b).

The near chondritic HSEs in the HED parent body (Day et al., 2012), coupled with the evidence for a small amount of Si in the HED PB core (Pringle et al., 2014) have led to the idea that the HED parent body underwent core formation at reduced conditions (IW-4) and then accreted a late veneer, which brought the HSE to chondritic levels. The problem with this model is that the FeO content of the HED PB mantle would have been extremely low in a scenario of IW-4, and the late veneer would not provide enough FeO to reconcile the known high FeO content. A more plausible explanation for the elevated HSE contents in some HEDs is that the HED PB experienced some early stress which led to the mixing of core material back into the shallower mantle (Rushmer et al., 2005), or that the diogenites measured by Day et al. (2012) experienced some chondritic contamination due to the brecciation event that formed them.
Finally, arguments that the Moon experienced a late veneer (Day et al., 2007; Bottke et al., 2010) are not consistent with the non-chondritic Au, Pd, and Ru concentrations that are calculated for the post core formation lunar mantle, and the HSE content of the anorthosite parent magma (Sharp et al., 2014). Even though late accretion is predicted by dynamic modelling, such additions may not necessarily be seen geochemically, nor do they necessarily have to be seen. Late chondritic additions can occur, but unless they either a) get oxidized so the HSE stay in the mantle, or b) get mixed into mantles efficiently, a late chondritic addition will suffer the same fate as any accreted metal-bearing material and mobilize to the core, especially if the differentiated bodies are largely molten, but even if they are partially molten (Rushmer et al., 2000).

Volatile siderophile elements or VSE (Sn, As, Sb, Ge, Ga, In, Zn)

A large group of elements exhibits both siderophile and volatile behavior and thus can be used to constrain both core formation and volatility processes, and of general utility in accretion models for Earth. Several of these elements have known chalcophile behavior, such as Cu and Sn, whereas several are known to be sensitive to Si content of Fe alloy such as As and Sb. Although some fundamental studies have established a baseline for these elements, many variables remain unexplored, yet are known to be important. For example, Righter et al. (2009) demonstrated that D(Sb) metal/silicate depends upon S content of silicate melt. Similarly, D(Sn) metal/silicate is apparently strongly fO₂ dependent because of solubility of Sn⁴⁺ in silicate melts. Sn may thus offer more insight into fO₂ than many other VSEs which are 1⁺ or 2⁺. The volatile siderophile elements offer a diverse range of valences (and thus fO₂ dependence) and chemical
behavior with respect to S, C and Si bearing systems. Further scrutiny of their partitioning behavior and application to Earth can serve to strengthen existing accretion models.

Summary and implications

Linear regression modelling approaches predict changes in D(i) metal/silicate due to pressure, temperature, metallic liquid composition, and do not require any additional terms or variables that are being neglected.

Deep mantle reservoirs and phases may exert control on the concentrations of weakly siderophile elements, such as Mn, V, Cr, Nb and Ta, in the PUM. Modelling attempts to explain such elements solely by metal-silicate equilibrium may lead to more reduced or hotter temperatures than if these reservoirs are also considered.

Volatile elements such as S, C, H and N may be partitioned into the core, but the content in the PUM may be explained by high PT metal-silicate equilibrium, as recently done for S. Much information is missing to fully evaluate this idea, especially for C, H and N, but if true would not require exogenous sources for Earth’s volatiles. Experimental studies at deep Earth conditions should focus on combinations of elements rather than simple systems that are known to be un-Earth-like.

Studies of the HSE have demonstrated that D(HSE) metal/silicate for many of these elements remain higher than 1000 approaching the high PT conditions suggested for metal-silicate equilibrium in the early Earth. But a number of variables relating to metal/silicate partitioning have not yet been explored, such as the effect of light elements alloying with Fe.
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**Figure Captions**

**Figure 1a:** Change in slope of Kd (Ni-Fe) and Kd(Co-Fe) data from Kegler et al. (2008), where slope changes between 1 and 5 GPa data. **Figure 1b:** D(W) behavior (from Cottrell et al., 2009) where data < 5 GPa show an increase with pressure, whereas those at >5 GPa show a decrease with pressure.

**Figure 2a:** Predicted D(Ni) behavior showing that the distinct change in slope between 1 and 5 GPa demonstrated by Kegler et al. (2008) is fully accounted for by the multiple linear regression equation for D(Ni) of Righter (2011a) (using form of equation 2). These D(Ni) values are calculated along the liquidus of mantle peridotite taken from Andrault et al. (2011), and for peridotite (nbo/t = 2.7) and relative fO2 of ΔIW = -1.25 (S- and C-free metal). **Figure 2b:** Predicted D(W) behavior showing that the distinct change in slope near 5 GPa is fully predicted by the multiple linear regression equation for D(W) of Shofner et al. (2014) and Shofner (2011) (using form of equation 3). These D(W) values are calculated along the liquidus of mantle peridotite taken from Andrault et al. (2011), and for peridotite (XSiO2 = 0.38; XAl2O3 = 0.03; XCaO = 0.03; nbo/t = 2.55) and relative fO2 of ΔIW = -2 (XS = 0.01 and XC = 0.02 in Fe metal).

**Figure 3:** Predicted behavior of D(Ni) using Righter (2011a) multiple linear regression equation, compared to data plotted by Sanloup et al. (2013). Data plotted are from studies of Tschauner et al. (2001), Thibault and Walter (1995), Siebert et al. (2012), Li and Agee (1996), O’Neill et al. (1998), and Ohtani and Yurimoto (1996). D(Ni) curve is calculated along liquidus PT path for peridotite from Andrault et al. (2011), and for peridotite (nbo/t = 2.7) and relative fO2 of ΔIW = -1.25 (S- and C-free metal).
**Figure 4:** Comparison of D(Ni) and D(Co) calculated with relative fO2 (using ΔIW term as in equation [3]) and absolute fO2 (using lnfO2 term as in equation [2]) approaches. Both curves for both elements are calculated for conditions of ΔIW=-2, nbo/t = 2.7, and S and C-free metallic liquid, along liquidus PT path for peridotite from Andrault et al. (2011). The agreement between the approaches is clear, but results start to deviate at pressures > 40 GPa. Coefficients for Ni using equation (2) are: \(a = -0.31 \pm 0.02\), \(b = -12380 \pm 1110\), \(c = 132 \pm 31\), \(d = -2.03 \pm 0.22\), \(e = +1.83 \pm 0.61\), \(f = -0.30 \pm 0.04\), and \(g = 7.40(0.46)\); standard error of regression = 0.60; \(r^2=0.814\); \(n = 308\); Constant Variance Test: Passed \((P = 0.620)\). Coefficients for Ni using equation (3) are: \(a = -0.71 \pm 0.04\), \(b = 7960 \pm 800\), \(c = -240 \pm 22\), \(d = -2.01 \pm 0.22\), \(e = +1.84(0.61)\), \(f = -0.31(0.04)\), and \(g = 2.64(0.5)\); standard error of regression = 0.61; \(r^2=0.811\); \(n = 308\); Constant Variance Test: Passed \((P = 0.689)\). Coefficients for Co using equation (2) are: \(a = -0.24 \pm 0.02\), \(b = -12930 \pm 1360\), \(c = 208 \pm 38\), \(d = -0.48 \pm 0.33\), \(e = +0.44 \pm 0.62\), \(f = -0.18 \pm 0.05\), and \(g = 6.60 \pm 0.49\); standard error of regression = 0.55; \(r^2=0.751\); \(n = 215\); Constant Variance Test: Passed \((P = 0.069)\). Coefficients for Co using equation (3) are: \(a = -0.55 \pm 0.05\), \(b = 2620 \pm 820\), \(c = -79 \pm 27\), \(d = -0.47 \pm 0.33\), \(e = +0.48 \pm 0.63\), \(f = -0.18 \pm 0.04\), and \(g = 2.95 \pm 0.51\); standard error of regression = 0.55; \(r^2=0.754\); \(n = 215\); Constant Variance Test: Passed \((P = 0.067)\). Nickel and cobalt datasets are from Seifert et al. (1988), Hillgren (1993), Li and Agee (1996, 2001), Gaetani and Grove (1997), Jana and Walker (1997a, b), Righter et al. (1997, 2010), Thibault and Walter (1995), Hillgren et al. (1994, 1996), Holzheid and Palme (1997, 2007), Ito et al. (1998), Chabot et al. (2005), Bouhifd and Jephcoat (2008), Kegler et al. (2008), Wade and Wood (2001, 2005), Walker et al. (1993), Peach and Mathez (1994), Corgne et al. (2008).

**Figure 5:** Comparison of epsilon interaction parameter (from Lupis, 1983) and \(d[\ln(1-Xs)]\) and \(e[\ln(1-Xc)]\) terms from Righter (2011a) and Righter et al. (2011), for sulfur (A) and carbon (B).
Chalcophile (S-loving) and anthracophile (C-loving) behavior requires negative epsilon values, as demonstrated in both approaches.

**Figure 6:** Comparison of measured D(Ni), D(Co) and D(W) metal/silicate from the studies of Siebert et al. (2012, 2013) and Bouhifd and Jephcoat (2011) with values calculated using the expression of Righter (2011a). Solid line is the 1:1 line.

**Figure 7:** Effect of D(V) and D(Cr) SS/LS on calculated V and Cr contents of the magma ocean during accretion. At low pressures V and Cr are compatible in spinel and garnet, while at high pressures they are compatible in ferropericlase and MgFe-perovskite. Calculations are done using the following mass balance equation (from Righter et al., 1997):

\[
C_{bulk}^i = x(C_{LS}^i + (1-p)D_{SS/LS}^i) + (1-x)(mD_{LM/LS}^i + (1-m)D_{SM/LS}^i)
\]

Where \(x\) is the fraction of silicate, \(p\) is the fraction of molten silicate, \(m\) is the fraction of molten metal, \(C_{bulk}^i\) is the bulk concentration of siderophile element, \(C_{LS}^i\) the concentration of siderophile element in the liquid silicate, \(D_{SS/LS}^i\) is the partition coefficient between solid silicate and liquid silicate, \(D_{LM/LS}^i\) is the partition coefficient between liquid metal and liquid silicate, and \(D_{SM/LS}^i\) is the partition coefficient between solid metal and liquid silicate. For these calculations, \(x = 0.68\), \(p = 0.7\), and \(m = 1\); in the case of an entirely molten core, \(m = 1\) and the last term on the right disappears. Horizontal bands are the V and Cr contents of the PUM from Newsom (1995).
Figure 8: S content of Earth’s mantle as D(S) metal/silicate and bulk S content vary. Again, the following mass balance equation is used for these calculations (see Figure 6 caption for definitions of terms):

\[
C_{\text{bulk}}^i = x \{ C_{LS}^i \left[ p + (1-p)D_{SS/LS}^i \right] + (1-x) \{ C_{LS}^i [mD_{LM/LS}^i + (1-m)D_{SM/LS}^i] \} \}
\]

For these calculations, \( x = 0.68 \), \( p = 0.7 \), and \( m = 1 \); in the case of an entirely molten core, \( m = 1 \) and the last term on the right disappears. In addition, \( D(S) SS/LS = 0.01 \). Sulfur content of PUM and bulk S contents for H, L, LL and CI chondrites are from compilation of Newsom (1995).

Figure 9: Terrestrial mantle depletions of all the HSE (values and uncertainty for each element are from Becker et al., 2006) in the terrestrial mantle normalized to CI chondrites and Mg – values from Newsom (1995). The heavy horizontal line with shaded box is the value for 0.0030 x CI chondrites with uncertainty (Becker et al., 2006); clearly five of these elements fall within the CI chondritic shaded box. However, the non-chondritic Au, Pd and Ru values (relative to other HSE) suggest that simple late chondritic additions cannot explain all the HSE. Shown at left edge are calculated HSE depletions expected if D(HSE) metal/silicate were 200, 300, 400, 500, 600, and 700. It is clear the in order for an equilibrium scenario to explain the HSE in the PUM, D(Au) metal/silicate and D(Pd) metal/silicate must be ~ 400, D(Ru) metal/silicate must be ~ 600, and D(Re, Pt, Rh, Os, Ir) metal/silicate must be ~700.

Figure 10: Calculated D(Au) and D(Ir) metal/silicate using predictive expressions (equation 2) presented by Righter et al. (2014b). Panel A shows the calculation along liquidus of Andrault et al. (2011) out to 4000 K, for a metallic liquid with no S, or C. Panel B shows the same temperature range, but for a metallic liquid that contains \( X_S = 0.25 \) and \( X_C = 0.1 \). This
calculation is not meant to be a detailed explanation for the terrestrial PUM (Earth’s core contains less S and C than this example), but instead illustrates the dramatic effect of adding S and C to the metallic liquid. Horizontal bands represent D(Au) and D(Ir) required for a core-mantle equilibrium scenario.
$nbo/t = 2.7; \Delta IW = -1.25; Xs = Xc = 0; T$ varies from 2073 to 2873 K

$nhb/n = 2.55; \Delta IW = -2; Xs = 0.01, Xc = 0.02; T$ varies from 1800 to 3073 K
$D(\text{Ni})$ data plotted by Sanloup 2013

$D(\text{Ni})$ predicted using Righter 2011

$nbo/t = 2.7; \Delta IW = -1.25; X_S = X_c = 0; T \text{ varies from } 2073 \text{ to } 4273 \text{ K}$
HSEs in Earth's mantle

Depletion (rel. CI, Mg)

D(HSE) met/sil

Au  Re  Pd  Pt  Rh  Ru  Ir  Os

700 600 500 400 300 200

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