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Modelling siderophile elements during core formation and accretion, and the role of the

deep mantle and volatiles.

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Kevin Righter

NASA-JSC

Mailcode KT

2101 NASA Parkway

Houston, TX 77058

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18   **Abstract**

19   The last decade has seen general agreement that moderately siderophile elements (MSE) in

20   Earth's primitive upper mantle (PUM) can be explained by metal-silicate equilibrium at mid-

21   mantle depths in an early Earth magma ocean environment.   Despite the agreement, there are

22   some differences in the detailed modelling that has been carried out. This paper will examine

23   siderophile element metal/silicate partitioning with respect to three different topics: a) an

24   examination of aspects of the modelling that one might suspect leads to differences in outcomes

25   or in comparison between models, but actually are in agreement with experimental data and

26   between models, b) a discussion of the role of the deep mantle in modelling efforts, and c) the

27   role and/or fate of volatiles in magma ocean scenarios with an emphasis on where data are

28   lacking.

29   **Introduction**

30   Detailed models for the origin and accretion of the Earth grew out of early ideas

31   developed by Eucken (1944) for heterogeneous accretion, in which the material accreting to form

32   the Earth changed with time producing the layers of the Earth. These models were developed in

33   more detail by Turekian and Clark (1969), Clark (1961), Anders (1977). An alternative to

34   heterogeneous accretion –homogeneous accretion – in which the Earth accreted from a

35   homogeneous mixture of metallic and silicate grains and later differentiated into the core and

36   mantle, was proposed originally by Urey (1951), Safronov (1959), Elsasser (1963) and Birch

37   (1965) over a similar timeframe. The former models had problems explaining the light elements

38   in Earth's core, and the upper mantle compositions (with both refractory and siderophile

39   elements), whereas the latter models could not explain the elevated siderophile content of the

40   mantle, oxidized iron, and the idea that any accreting H_2O and CO_2 would be reduced to H and C

41   in the presence of metal (core) thus eliminating sources for Earths hydrosphere and atmosphere

42   (Ringwood, 1979). In particular the elevated siderophile element contents in Earth's mantle

43   were problematic but data used to evaluate their abundances was experimental data collected at

44   low pressures.

45   The development of high pressure techniques in the 1980s and 90s led to an abundance of

46   studies of siderophile elements, all of which revealed that siderophile element contents of Earth's

47   mantle could possibly be explained by metal-silicate equilibrium at elevated PT conditions

48   compared to the earlier studies at 1 bar and low temperatures (e.g., Li and Agee, 1996; Walter

49   and Thibault, 1995). As a result, Earth accretion models are now a combination of aspects of

50   heterogeneous accretion and homogeneous accretion alike, with core-mantle equilibrium able to

51   explain siderophile element contents e.g., Righter, 2011a; Wade et al., 2012), and especially if

52   the composition of the materials changes during accretion (Rubie et al., 2011). The last decade

53   has seen general agreement that moderately siderophile elements in Earth's PUM can be

54   explained by metal-silicate equilibrium at mid-mantle depths (30 to 70 GPa) in a magma ocean

55   environment (e.g., Siebert et al., 2012; Bouhifd and Jephcoat, 2011). There is some

56   disagreement over the exact PT conditions, and whether fO_2 was variable during accretion (e.g.,

57   Rubie et al., 2011; Righter and Ghiorso, 2012; Siebert et al., 2013).

58   Three topics bearing on the Earth accretion models will be discussed in this paper. First,

59   aspects of siderophile element modelling have been questioned by some, including a) the role of

60   pressure in causing coordination changes in metallic and silicate melts at 5 and 20 GPa, b) the

61   role of absolute versus relative oxygen fugacity in the calculations, and c) the choice of methods

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62   for quantifying effects of alloying elements on siderophile element activities in metallic liquid.

63   It will be shown that none of these structural effects have any bearing on the predictive

64   expressions, and that all the observed changes in partition coefficients are fully predicted by the

65   multiple linear regression expressions. It will also be shown that regressions using relative fO_2

66   (ΔIW) and absolute fO_2 predict the same behavior, albeit in two different ways. Similarly, we

67   compare two modelling approaches for activities in metallic liquids and show that there is overall

68   agreement in the nature and magnitude of the metallic compositional effects.

69   Second, modelling has not generally included deep mantle reservoirs. This has led to some

70   models that fit Nb, V and Cr via core formation. Yet the lower mantle may be most important

71   reservoir. Additional studies have revealed that a deep basal magma ocean may be relevant and

72   could harbor elements. The general role of deep mantle reservoirs in differentiation models will

73   be discussed.

74   Finally, a number of volatile elements, volatile siderophile and highly siderophile elements have

75   been studied only at a limited set of conditions relevant to a deep magma ocean scenario, and a

76   comprehensive understanding is lacking. Volatiles are typically discussed in terms of indigenous

77   versus exogenous origin, and this classic question remains open for many. For example, some

78   elements like In, As, and Sb are all poorly studied and so conclusions drawn from these studies

79   have high uncertainty. Similarly, the HSE, although notoriously difficult to study both

80   analytically and experimentally, have had a number of solid studies completed in recent years.

81   However, information such as the effect of non-metals in metallic liquid (S, C, O and Si), as well

82   as silicate melt composition, are needed for a full evaluation. It will be shown that the HSE

83   contents of all differentiated bodies have viable explanations other than late chondritic additions

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84   and multiple hypotheses should be entertained until the controlling variables are fully explored

85   by experimental studies.

86   These three topics illustrate that although a general model is emerging for the earliest

87   differentiation event for the early Earth, there remain many outstanding questions and avenues

88   for further exploration. These should lead to a better understanding of the accretion of the Earth

89   and the origin of its volatile elements.

90   **1. Evaluating models – pressure, fO_2, and metal activities**

91   The partitioning of siderophile elements between metal and silicate (core and mantle) has

92   been studied experimentally by equilibrating metal and silicate melt mixtures at high

93   temperatures and measuring the partition coefficient as D = wt% i in metal / wt% i in silicate

94   melt. Because of the strong dependency on temperature, pressures, fO_2, and metal and silicate

95   composition, efforts were made to predict the D as a function of these variables with chemical

96   thermodynamics as a guide. Predictive expressions introduced by Righter et al. (1997) and

97   Righter and Drake (1999) are based on the equilibrium (using Ni as an example):

98                              $$2 \, NiO = 2 \, Ni + O_2 \tag{1}$$

99   and have the form:

100        $$\ln D(metal/silicate) = a\ln fO_2 + b/T + cP/T + d[\ln(1-Xs)] + e[\ln(1-Xc)] + \Sigma f_i X_i + g, \tag{2}$$

101   where D is the partition coefficient (defined above), Xs and Xc are the mole fractions of S, C in

102   metallic liquid, and X_i are the mole fractions of oxide components in silicate melt. The form of

103   these expressions is guided by the thermodynamics of simple metal-oxide equilibria that control

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104   each element's partitioning and, include terms that mimic the activity coefficients of each

105   element in the metal and silicate. Absolute oxygen fugacity is calculated using the approach of

106   Righter et al. (1997) and Righter and Drake (1999) (see Righter, 2011a).

107   Other studies have used:

108     $$\ln D = a(\Delta IW) + b/T + cP/T + d[\ln(1-Xs)] + e[\ln(1-Xc)] + \Sigma f_i X_i + g \qquad (3)$$

109   where relative fO_2 is used instead of absolute fO_2, or

110     $$\ln D = \ln (X_i \text{ met}) / (X_i \text{ sil}) = a(\Delta IW) + b/T + cP/T + (\gamma_i \text{ sil})/(\gamma_i \text{ met}) \qquad (4)$$
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112
113   where γ_i is an activity coefficient for the siderophile element (i) in either metal or silicate melt.

114   In many cases the silicate melt activity is assumed equal to unity, but the activity coefficient in

115   the metal is quantified. A popular model for the metal uses the Wagner ε formalism (Wagner,

116   1962; Lupis, 1983) which represents the effects of different solutes on one another's

117   thermodynamic properties according to:

118     $$\ln \gamma_i \;=\; \ln \gamma_i^0 + \sum_{j=2}^{N} \varepsilon_i^j \, x_j \qquad (5)$$

119   where γ_i is the activity coefficient of solute i in the mixed alloy and γ_i^0 is its activity coefficient

120   when it is infinitely dilute in pure liquid Fe under the same conditions of pressure and

121   temperature.   The interaction parameters ε_i^j refer to the measured effects of component j on the

122   activity of i in the alloy and are assumed to be linearly dependent on the mole fraction of j, x_j.

123   Equations (1) through (5) will be used below to illustrate various aspects of the modelling that

124   has been carried out in recent studies.

125   *A role for metallic and silicate liquid structural changes at ~ 5 GPa?*

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126   Several metal/silicate partitioning studies have shown that at pressures near 5 GPa the

127   partition coefficient can change in slope (**Figure 1a,b**). In the case of D(Ni), the slope changes

128   from a moderately negative, to slightly negative (Kegler et al. (2008), whereas in the case of

129   D(W), the slop changes from positive to negative (Cottrell et al., 2009). Because this is not

130   behavior immediately expected of a linear dependence, the authors of both attributed the change

131   in D(metal/silicate) instead to changes in silicate melt structure at higher pressures, citing the

132   study of Keppler and Rubie (1993) on coordination change for Ni in albitic melt in this pressure

133   range. Similarly, Sanloup et al. (2011) argued that Fe-rich metallic liquid undergoes a structural

134   change in this pressure range, and showed many literature studies of D(Ni) partitioning that

135   exhibited a change near 5 GPa. In fact, neither of these explanations are necessary and the

136   changes in slope in the partition coefficients for Ni and W and any other siderophile element are

137   expected and fully predicted by the multiple linear regressions published by many authors (e.g.,

138   Righter, 2011a), as will be explained below.

139   A change in partition coefficient at this pressure range is due to the fact that the pressure

140   dependency of D(metal/silicate) is not simple linear dependence, because the pressure term is

141   'P/T' (Equations 2, 3, 4).   This link with temperature means that any variation in

142   D(metal/silicate) with pressure will be coupled with temperature changes as well, and will not be

143   a linear function. For example, the magnitude of decrease in D(Ni) with pressure changes near 5

144   GPa because the change is defined by the P/T term (**Figure 2a**). For Ni, the initial steep slope

145   could be mistaken for a linear effect below 5 GPa and a second linear effect above 5 GPa, but in

146   reality this is one continuous curve as shown by Righter et al. (2011a,b). The latter study is

147   based on experimental data that spans 1 bar to 42 GPa, 1300 to 4000 ºC, IW-5 to IW+1, basalt to

148   peridotite silicate melts, and S- and C-bearing metallic liquids. Therefore, the need to explain

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149   such a change, whether due to a structural change in silicate or metallic liquid, disappears.

150   Furthermore, the metallic liquids considered in the Sanloup et al. (2011) study are of variable

151   composition with some containing S, some C, and some no light element. Each metallic liquid

152   should have a different pressure of structural change so there is no reason why this phenomenon

153   should be connected to the change in partition coefficients seen for Ni or W.

154   In the case of W, Cottrell et al. (2009) demonstrate a slope change from positive to negative

155   at ~ 5 GPa, but this is partly attributable to the temperatures chosen for the individual pressure

156   points. For example, the lowest pressure points (0.5, 1, 2, and 6 GPa) are at T = 2100 K, while

157   the intermediate pressure point (11 GPa) is at 2400 and the highest pressure point (18 GPa) is at

158   2500 K. Such a change in slope is fully predicted by linear regressions for W (and other

159   elements as well, like Ga and P) if the temperatures are chosen to be low, intermediate and high

160   like this (**Figure 2b**). If D(W) is calculated along a liquidus, where temperature also increases

161   with pressure, at first D(W) increases, but then decreases at pressure greater than 5 GPa (Figure

162   2b).

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

164   Sanloup et al. (2013) argue that there are non-linear (with pressure) trends for D(Ni) that

165   they ascribe to silicate melt structural change at > 20 GPa, and that multi-linear regression

166   approaches can't account for. In fact, the MLR approach predicts exactly what is observed so

167   there is no missing melt structural term in the predictive expressions (**Figure 3**). This is not to

168   say that melt structure is not important, but only that the current partitioning approaches have not

169   ignored anything that can be quantified. Of course, understanding melt structure is important,

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170   but there are no effects that are required to quantify in this PT range, because the simple

171   equilibria used in linear regression analysis can fully explain all data.

172   To illustrate how D(Ni) is predicted to change with pressure, we have plotted the calculated

173   D(Ni) values along a liquidus of Andrault et al. (2011) and compared it to the data shown by

174   Sanloup et al. (2013). The resulting plot shows excellent agreement between the calculated and

175   measured partition coefficients, which indicates no additional terms are necessary to explain the

176   partitioning data for Ni.

177   *Role of relative vs. absolute fO$_2$ calculation and incorporation into partitioning expressions.*
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179   Recent geochemical models for accretion and core formation emphasize either changing fO$_2$

180   (like a classic Wänke, 1981 model of early reduced materials followed by later oxidized

181   materials), or relatively constant fO$_2$ (e.g., Rubie et al., 2011; Siebert et al., 2013; Righter and

182   Ghiorso, 2012). Because the models are based on similar partitioning studies and elements it

183   may be confusing why the results are so different.   One major difference between approaches is

184   that one (equation 3) uses relative fO$_2$ in predictive expressions (e.g., Cottrell et al., 2009; Wood,

185   2008, Kegler et al., 2008), while other (equation 2) uses absolute fO$_2$ (e.g., Righter and Drake,

186   1999; Righter, 2011a). Consideration of relative fO$_2$ is certainly convenient and sometimes is

187   the best way to estimate the fO$_2$ of an experiment or series of experiments in lieu of detailed

188   thermodynamic data.   However, the inherent assumption is that there is no pressure or

189   temperature effect on ΔIW and that an experiment, for example done on basalt and metallic FeNi

190   at 1 GPa and 1900 K has the same ΔIW value as one done at 30 GPa and 3500 K. Relative fO$_2$

191   was originally considered as a useful approximation for discussing oxygen fugacity relative to

192   buffers in magmatic system within a restricted T and P range where temperature effects were

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193   likely minimal (i.e., between 700 and 1200 °C). This may not be true at the ultra-high pressures

194   and temperatures considered in metal-silicate partitioning experiments where temperatures may

195   be between 1600 and 4000 °C (e.g., Righter and Ghiorso, 2012). Nonetheless, when using Δ IW

196   in regression analysis, the effect of pressure is lumped entirely onto the volume term (P/T) term.

197   Consideration of absolute fO_2, on the other hand, is more difficult due to the lack of

198   thermodynamic data at extreme PT conditions, but it does allow the effects of pressure to be

199   allocated to both the fO_2 term (ln fO_2) and the volume (P/T) terms as it should. That is, when

200   pressure is increased, the absolute fO_2 rises, and the volume of reaction changes – these are two

201   different effects that can be accounted for when absolute fO_2 is used in linear regression.

202   Furthermore, the volume change of metal-oxide equilibria is positive, and the regression

203   coefficients resulting from equation (2) also result in positive values of c, in agreement with

204   chemical thermodynamics. The negative c coefficient resulting from regressions using equation

205   (3) is counter intuitive and could lead to misperceptions about partitioning behavior. How

206   important is this effect? An example is illustrated for D(Ni) and D(Co) in which the same

207   datasets are used to derive regression coefficients a through g for equations (2) and (3). The

208   results show that the agreement between the two approaches is good until approximately 40 GPa,

209   where the predicted D values start to differ substantially (**Figure 4**). There is therefore, no

210   significant difference between these two approaches as long as pressure calculations do not

211   exceed 40 GPa. Which approach is used depends on what kind of information one wishes to

212   include in the modelling. The simplistic ΔIW approach makes unrealistic assumptions, but

213   allows easier prediction of D. The absolute fO_2 approach may allow a more realistic modelling

214   of accretion, and produce coefficients that are more true to chemical thermodynamics, but is

215   limited by our knowledge of fO_2 at high PT conditions.

216   *Effect of non-metallic elements in the metallic liquid*

217   The variation of trace metal activities in metallic liquids can be quite large and is

218   dependent upon metal composition, especially light elements such as C, S, and O. Two

219   fundamentally different approaches have been taken to model these activities.

220   One approach, taken by Righter and Drake (1999), is to use empirical terms that mimic

221   the Margulies parameter (W_{ij}) terms for activity coefficients. This approach fits empirical terms

222   (e.g., $\ln[1-X_s]$) by multiple linear regression of experimental data acquired at the P and T and

223   metallic liquid compositions of interest to core formation. A second approach calculates epsilon

224   interaction parameters (ε) using values obtained at 1 bar and 1400 to 1600 ºC, mainly from the

225   steelmaking industry, and applies them directly (or with a temperature extrapolation approach) to

226   experiments done at variable P and T (Wade and Wood, 2005; Corgne et al., 2008).   A positive

227   aspect of this approach is that there is a large body of data from the steelmaking literature (e.g.,

228   Lupis, 1983; Steelmaking Data Sourcebook, 1988). Because these databases are tailored for

229   steel making, and not core formation, information for all elements of interest is not available, and

230   thus some gaps for many elements. There are no corrections for ε at high pressure conditions –

231   the data have all been obtained for the low P conditions of steelmaking – whereas the d and e

232   terms of Righter (2011a) are derived from the high PT experiments that contain relevant phases

233   such as S, C-, and Si-bearing FeNi metallic liquids.

234   These two approaches can be compared for the effect of C and S on activity coefficients.

235   The d and e terms of Equation (2) measure the same effect as εC and εS in equation (5). A

236   comparison of d and e terms from Righter (2011a), Righter et al. (2011a) to epsilon values

237   complied by Lupis (1983) show that for sulfur the agreement is very good. For carbon the two

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238   approaches may yield different absolute values in a few cases, but the magnitude and sign of the

239   effects are in good overall agreement. Both approaches predict, for example, the chalcophility of

240   Sn, Cr, Cu, and V, and the anthracaphility of Mo and W (**Figure 5**).

241   *Summary for predictive expressions*

242   Assessment of temperature and pressure on metal-silicate partitioning of Ni, and W do

243   not reveal any melt structural effects either at low pressure (~ 5 GPa) or at higher pressure (20

244   GPa), as suggested in recent studies (Sanloup et al., 2011; Sanloup et al., 2013; Palme et al.,

245   2011; Kegler et al., 2008; Cottrell et al., 2009). Palme et al. (2011) and Rai and van Westrenen

246   (2014) both criticize combination of <5 GPa and > 5 GPa partitioning data due to melt structural

247   effects, but these are non-existent as experimental data can be combined and can predict the

248   changes in partition coefficients observed at 5 GPa with a single expression. The differences

249   between regressions using high and low pressure data plotted as lines by Rai and van Westrenen

250   (2014) in their Figure 2 are all within error for both sets of regressions and thus do not illustrate

251   the need to split data between the high and low pressure regimes. Indeed, the combined <5 GPa

252   and >5 GPa datasets for Ni, Co, Mo and W used by Righter and Drake (1996, 1997) to predict

253   core formation conditions in the very low pressure eucrite parent body (likely asteroid 4 Vesta)

254   predicted a core size of ~18 mass % in excellent agreement with the measurements made by the

255   Dawn spacecraft (Russell et al., 2012; McSween et al., 2014).   Furthermore, expressions of

256   Righter (2011a) for Ni, Co and W can be used to predict D at the high PT conditions investigated

257   by Siebert et al. (2012, 2013) and Bouhifd and Jephcoat (2011). Comparison of these predicted

258   values to those measured reveals good agreement (**Figure 6**), indicating that the predictive

259   ability of these expressions using both high and low pressure partitioning data.

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260   Although different approaches have been used to model fO_2 and metal activity coefficients,

261   there is good agreement between these different approaches and employment of one or the other

262   will not lead to significantly different conclusions regarding the conditions of metal-silicate

263   partitioning of Ni and Co, for example.

264   Two effects that will lead to major differences in modelling outcomes are the role of silicate

265   melt compositional variation, and the role of deep mantle phase equilibria. The former topic has

266   been the subject of a comment and response and will not be covered in detail here (Righter,

267   2011b; Palme et al., 2011). However, an independent assessment of the role of melt composition

268   on D(Ni) and D(Co) (Walter and Cottrell, 2013) supports the argument of Righter (2011a,b), as

269   does the ability of expressions of Righter (2011a) to predict high pressure (up to 80 GPa) data of

270   Siebert et al. (2012) for D(Ni) and D(Co), even with low pressure data included in the

271   regressions. The role of deep mantle phase equilibria, on the other hand, will be the focus of the

272   next section.

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274   **2. Deep mantle reservoirs and siderophile element modelling**

275   Our knowledge of the PUM comes from relatively shallow portions of the mantle - upper

276   mantle xenoliths and massifs. Mn, V, Cr, Nb and Ta have all been used in core formation

277   modelling and due to their weak siderophile behavior at low PT conditions, they require quite

278   high PT and/or reduced conditions to become siderophile enough to produce a depletion (e.g.,

279   Wade and Wood, 2001; Cartier et al., 2014). Recent work at 35-74 GPa has also shown that an

280   O-bearing metallic core may enhance the metal-silicate partition coefficients for V and Cr, thus

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281   obviating the need for a reduced stage during Earth's accretion to satisfy the Nb, V, and Cr

282   content of the mantle (Siebert et al., 2013).

283   However, the weakly siderophile elements Mn, V, and Cr offer an excellent example of

284   elements whose behavior at high PT conditions is not yet fully mature. For example, the recent

285   work of Siebert et al. (2013) argues that dissolved O enhances D(V), D(Cr), such that an O-

286   bearing metallic core might satisfy the depletions of these elements at a more modest redox state

287   rather than at reduced conditions. Isolating the effect of O may be possible by using the

288   predictive expressions of Righter (2011a) to calculate D(V), D(Cr), and D(Mn), at the

289   experimental conditions and compositions of Siebert et al. (2013). The predicted D(V) values

290   are higher (up to 5x) than measured, predicted D(Mn) values are lower (up to 8x) than measured,

291   and the predicted D(Cr) values are approximately the same. These comparisons are in agreement

292   with the conclusion of Siebert et al. (2013) that O will influence D(V), but perhaps this is a

293   weaker effect for D(Cr), and the magnitude of the effect may differ from that inferred by Siebert

294   et al. (2013). Of course it is also possible that the predictive expressions derived by Righter

295   (2011a) should not be extrapolated into the higher PT conditions of the Siebert et al. (2013)

296   study, but we have seen in previous discussion that Ni and Co results can be well predicted using

297   the approach of Righter (2011a).   Nonetheless, it is clear that core formation modelling must

298   account for dissolved Si and O (not usually included), in addition to C and S (most commonly

299   included) because these elements can have significant effects on the metal activities and

300   D(metal/silicate) values.

301   Despite the potential for explaining depletions of these elements in the mantle by core

302   formation, these elements may instead be controlled by partitioning into portions of the deep

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303   mantle, such as the lower mantle, a basal magma ocean, or recycled oceanic crust (eclogite). Mn,

304   V and Cr all have measured D(Mg-perovskite/melt) and D(ferropericlase/melt) >1 (McFarlane et

305   al., 1994; Taura et al., 2001) and thus are potentially compatible in the lower mantle. On the

306   other hand several other studies have reported D(Mg-perovskite/melt) slightly < 1, suggesting

307   these element may be weakly incompatible (Corgne et al., 2005; Liebske et al., 2005). To

308   illustrate the importance of knowing the degree of compatibility or incompatibility of V and Cr

309   in deep mantle phases, simple calculations are used to demonstrate the magnitude of the

310   depletions. For example, if V and Cr are slightly compatible in the lower mantle compared to

311   the upper mantle (e.g., D(LM/UM) = 1 to 2) the depletions of V and Cr in Earth's PUM can be

312   explained by metal-silicate equilibrium at much less reducing conditions than IW-4 as required

313   in models by Wood et al. (2008).   To illustrate the potential role of lower mantle in controlling

314   V and Cr contents of the PUM, calculations have been carried out using D(V) and D(Cr)

315   metal/silicate from Righter (2011a) (**Figure 7**). V and Cr can clearly be matched by metal-

316   silicate equilibrium at conditions of IW-2 with D (SS/LS) > 1 (Figure 6). Given this illustration,

317   additional measurements with a focus on these few elements may be important to resolve the

318   issue of lower mantle contribution to depletions in the PUM.

319   Much of the partitioning data for deep mantle phases have been obtained at conditions

320   relevant to the top of the lower mantle, rather than the bottom. Thus the compatibility of Mn, V

321   and Cr in these deep mantle phases should be examined at higher pressure conditions as well.

322   Furthermore, the isotopic fractionation of Cr between metal, deep mantle phases, and melt

323   should be investigated to allow incorporation of Cr isotopic data into this evaluation (Moynier et

324   al., 2011). In addition, the presence of a layer of post-perovskite phase in the deep mantle (Mao

325   et al., 2005) may affect element partitioning in the deepest part of Earth's mantle. Furthermore,

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326   because of the low-to-high spin-state transition in ferropericlase (Fischer et al., 2011), the

327   oxygen fugacity at this deep part of the mantle may be higher and thus create a redox reactive

328   zone that would also affect element partitioning.

329   There may have been a basal magma ocean at the beginning of Earth history (Labrosse et

330   al., 2007). The idea of Nebel et al. (2010) that Nb may reside in the material that formed this

331   basal magma ocean opens up many questions about other elements. Although the Sm-Nd system

332   may not be sensitive enough to record fractionations due to such a hidden reservoir (e.g., Jackson

333   and Carlson, 2012), the Hf-W system may offer more leverage and there are indeed larger

334   fractionations preserved in komatiitic rocks (Touboul et al., 2012). An additional reservoir

335   deserving attention is subducted crust or eclogite. Concentration of Nb and/or Ta in such

336   material could contribute to the depletions of these two elements in the PUM (Rudnick et al.

337   2000).

338   The role of the deep mantle and in particular deep trapped melts, in mantle evolution

339   must be pursued in greater detail and may offer some insights into weakly siderophile elements

340   as well.   A quantitative assessment of the effects of a basal magma ocean, subducted oceanic

341   crust (or eclogite) and the presence of deep mantle phases (postperovskite, Mg-perovskite,

342   ferripericlase) would benefit from experimentation on trace element partitioning at these deep

343   mantle pressures.

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

345   *Exogenous versus indigenous*

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346   The origin of Earth's volatiles has been debated for decades, and the theories fall into two

347   general categories – that the Earth obtained its volatile content from the materials out of which it

348   accreted (indigenous), or that it acquired its volatiles later in history during a late accretion event

349   or events such as the late veneer or late accretion (exogenous). Sources for the latter idea include

350   comets (e.g., Delsemme, 1998), carbonaceous chondrites (e.g., Chou, 1978; Dauphas and Marty

351   2002), or an un-sampled chondritic reservoir (Drake and Righter, 2002). If the early Earth

352   experienced a deep magma ocean in which a significant portion of the mantle equilibrated with

353   light element containing core metal, then this physical scenario will have an important influence

354   on the volatile content of the primitive mantle as well. Of course, the origin of Earth's volatiles

355   could be attributed to a combination of indigenous and exogenous processes. In this section

356   evidence from the classic volatile elements (C, S, H, and N), highly siderophile elements

357   (platinum group elements, Au and Re), and volatile siderophile elements will be discussed,

358   highlighting the areas where additional data and experiments are needed to fully evaluate models

359   for the origin of Earth's volatiles.

360   *Classic volatiles – C, S, H, N*

361   Sulfur partitioning between metallic liquid and silicate liquid as a good example of the

362   extent to which chemical thermodynamics exerts control on core-mantle equilibrium. Boujibar

363   et al. (2014) present a mature expression for predicting D(S) metal/silicate, which is dependent

364   on the silicate melt composition, metallic liquid composition, temperature, pressure and oxygen

365   fugacity. Most of these variables are well understood and their expression takes advantage of

366   close to a dozen studies each of which explores one or several variables. This expression can be

367   used to construct a diagram showing the expected S content of the mantle as D(S) and Earth bulk

368   S content changes (**Figure 8**). At high pressures and a modest bulk S content (intermediate

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369   between C and O chondrites, the Earth's mantle S content (~ 250 ppm) can be produced by core

370   formation with D(S) ~ 200, which is approximately the value calculated at IW-2, 40 GPa, 3473

371   K for peridotite melt. These conditions are slightly higher PT conditions than proposed for early

372   Earth metal-silicate equilibrium by Righter (2011a), but more recent updates to the expressions

373   of Righter (2011a) adding the effect of metallic Si content and additional high PT studies have

374   lead to a series of solutions between 35 and 45 GPa and ~3500 K (Righter et al., 2013; 2014a),

375   fully consistent with this result for S.

376   The current understanding of C partitioning is not as complete. For example, the work of

377   Dasgupta et al. (2013) shows that D(C) metal/silicate can be as low as ~100 at conditions of 1 to

378   5 GPa and peridotite silicate melt, but the dependence on pressure, temperature and melt

379   composition remains poorly characterized so far. However, with D(C) metal/silicate ~100 the C

380   content of the primitive mantle may be produced by metal-silicate equilibrium, so the values

381   measured at low PT conditions come close to allowing an equilibrium signature in the PUM.

382   Similarly, studies of N have led to the conclusion that D(N) metal/silicate may be 10-20 for the

383   Earth during accretion and core formation (Roskosz et al., 2013; Libourel et al., 2003), which is

384   adequate to explain the depletion of N (relative to the noble gases) in the PUM (Marty, 2012)

385   Hydrogen presents a special case due to the experimental difficulty in studying its

386   behavior at high PT conditions. Kuramoto and Matsui (1996) suggested that H and C alloying

387   into the core could explain several aspects of terrestrial geochemistry such as the density deficit

388   in the core, the volatile content of the mantle, and the oxidized nature of the upper mantle.

389   Okuchi (1997) showed that at low pressure (up to 7 GPa) H may dissolve into Fe metallic liquid,

390   and could account for a majority of the density deficit in the core. More recently, Nomura et al.

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391   (2014) showed that at the temperature of the CMB, only Fe-H alloys could remain liquid and

392   thus concluded that H may be the dominant light element in Earth's core.

393   Clearly, much additional work needs to be done on H, C, and N to understand whether

394   their contents in the PUM could be explained by an early magma ocean scenario with a metal-

395   silicate overprint. In addition, many studies have been done on simple systems, such as Fe-S,

396   Fe-C, Fe-Si (e.g., Hirose et al., 2013), but really we seek information on the complex system that

397   includes O, S, Si, C, H and N, and how they will be partitioned in a magma ocean scenario. We

398   are beginning to understand some of these elements - like S – but we still have a ways to go for

399   H, C, N. The effect of these elements on partitioning of other elements like the MSE (Ni, Co,

400   Mo, W discussed above) or the HSE and VSE (discussed below) is also of fundamental

401   importance.

402

403   *HSEs and the "need" for a late veneer*

404   HSEs have been used to constrain the style of accretion of material to Earth and other

405   differentiated bodies.   HSE have very high (>10,000) values of metal/silicate partition

406   coefficients at low pressure conditions, and expected concentrations in the mantle (if it

407   equilibrated with the core) are much lower than measured concentrations in the terrestrial PUM.

408   So these elements have traditionally been used to argue that the higher than expected levels of

409   HSE in the mantle are due to late additions of chondritic material to the Earth (Chou, 1978;

410   Morgan et al., 1981). More extensive studies of mantle materials have shown that several of the

411   HSE exhibit non-chondritic ratios in the PUM (**Figure 9**), indicating that these elements have

412   also been fractionated slightly from chondritic, much like the MSE Ni, Co and W (Becker et al.,

413   2006). Like Ni, Co and other siderophile elements, new experimental studies have shown that

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414   D(HSE) metal/silicate is lowered substantially at higher P and T conditions, such that the

415   mismatch between expected and measured HSE contents is smaller, but still not quite a large

416   enough effect to explain their concentrations in the mantle by core-mantle equilibrium.

417   Temperature, in particular, has been shown to be an important factor in lowering D(HSE)

418   metal/silicate. Some recent examples are the lowering of D(Au, Ir) metal/silicate (Brenan and

419   McDonough, 2009), D(Pt) metal/silicate (Bennett et al., 2014), and D(HSE) metal/silicate (Mann

420   et al., 2012).   These studies conclude, as did many previous studies, that HSE cannot be

421   explained by high PT equilibrium between metal and silicate melt, and must have been brought

422   in after core formation via late accretion.

423   However, there are a number of avenues that have not yet been explored that could

424   possibly and plausibly account for the HSEs in an equilibrium scenario. The effect of alloying

425   elements on HSE partitioning can be very large, and S for example can change the partition

426   coefficient for D(Ir) solid metal / liquid metal by a factor of 1000 (e.g., Chabot et al., 2003),

427   similar in magnitude to the mismatch between calculated and observed Ir abundances identified

428   in recent studies (Bennett et al., 2014; Mann et al., 2012). Sulfur is well known to be a candidate

429   for Earth's core light element, but is perhaps limited for the Earth to a few wt% rather than the

430   ~30 wt% possible in Fe-S liquids (Dreibus and Palme, 1996).   There are other elements, though,

431   whose effects are unknown, but likely to be similar to sulfur due to geochemical considerations.

432   Carbon, for example may be present in Earth's core in several wt% and is known to decrease

433   D(HSE) having large and positive interaction parameters (Righter et al., 2014b), Si may be

434   present in up to 10 wt% in Earth's core and is known to cause large decreases in D(Mo), D(W),

435   D(As) metal/silicate (Tuff et al., 2012; Nickodem et al., 2013), and O is known to influence

436   partitioning in metallic systems as well (Walker, 2000). To illustrate the potential effect of S and

20

437 C on lowering D(HSE), we calculate partition coefficients for Au and Ir along a liquidus PT path

438 (mimicking accretion), and compare S- and C-free metallic liquid to those for S- and C-bearing

439 metallic liquids. The effect of S and C is clearly important with the S- and C-free system having

440 D(Au) and D(Ir) too high to explain their contents in the mantle, but with Xs = 0.25 and Xc =

441 0.10 in the metallic liquid, both D(Au) and D(Ir) become low enough to explain the contents in

442 Earth's PUM (**Figure 10**).

443   An additional effect that is starting to be appreciated for HSE partitioning is sulfur

444 dissolved in silicate melt (Laurenz et al. 2013). Sulfur dissolved into silicate melt can cause

445 complexing with HSE such that the solubility in a S-bearing silicate melt increases, thus causing

446 D(HSE) metal/silicate to decrease. This may be especially important at reducing conditions

447 where S solubility in silicate melt is high.   So, the effects of light elements (C, S, Si, O) alloyed

448 in metallic liquids on D(HSE) metal/silicate needs to be understood but offers promise in

449 explaining the HSE content of Earth's PUM.

450

451 *Late accretion for Mars, Moon, and asteroids?*

452   Recent work on HSEs in martian meteorites, differentiated asteroids (eucrites, diogenites,

453 angrites), and the Moon have led some to argue these bodies also experienced a late veneer or

454 late chondritic additions after core formation. This idea is debatable for each body, and viable

455 alternative explanations include mixing of HSE from core into mantle by shear deformation

456 (Rushmer et al., 2005; HEDs), brecciation and contamination with chondritic material either as

457 fragmental regolith or impact melt breccia (HEDs and angrites). In addition, in some cases the

458 patterns are not sufficiently chondritic and can actually be explained by metal-silicate

459 equilibrium (Moon and Mars).

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460   The martian meteorites exhibit "broadly" chondritic ratios of HSE but they are not all

461   chondritic and can be as much as 2 to 5 x non-chondritic which is much larger variation

462   compared to even the Earth, where there are already strongly non-chondritic Au/Ir and Ru/Ir

463   ratios documented. Rai and van Westrenen (2013) applied S-free partitioning results of Mann et

464   al. (2012) to core formation in Mars, found the D(HSE) metal/silicate to be too high and argued

465   thus that Mars requires a late veneer of chondritic material added after core formation. However,

466   when metallic S and C effects are quantified as well as the fO_2, T, P and melt composition, it

467   becomes clear that a late veneer is not required for Mars (Righter et al., 2014b). In fact, HSE

468   contents observed in the martian meteorites can easily be explained by metal-silicate equilibrium

469   between the primitive martian magma ocean and a S-, and C-bearing metallic core at conditions

470   of ~ 14 GPa and 2250 K (Righter et al., 2014b).

471   The near chondritic HSEs in the HED parent body (Day et al;., 2012), coupled with the

472   evidence for a small amount of Si in the HED PB core (Pringle et al., 2014) have led to the idea

473   that the HED parent body underwent core formation at reduced conditions (IW-4) and then

474   accreted a late veneer, which brought the HSE to chondritic levels. The problem with this model

475   is that the FeO content of the HED PB mantle would have been extremely low in a scenario of

476   IW-4, and the late veneer would not provide enough FeO to reconcile the known high FeO

477   content. A more plausible explanation for the elevated HSE contents in some HEDs is that the

478   HED PB experienced some early stress which led to the mixing of core material back into the

479   shallower mantle (Rushmer et al., 2005), or that the diogenites measured by Day et al. (2012)

480   experienced some chondritic contamination due to the brecciation event that formed them.

22

481   Finally, arguments that the Moon experienced a late veneer (Day et al., 2007; Bottke et

482   al., 2010) are not consistent with the non-chondritic Au, Pd, and Ru concentrations that are

483   calculated for the post core formation lunar mantle, and the HSE content of the anorthosite

484   parent magma (Sharp et al., 2014). Even though late accretion is predicted by dynamic modelling,

485   such additions may not necessarily be seen geochemically, nor do they necessarily have to be

486   seen. Late chondritic additions can occur, but unless they either a) get oxidized so the HSE stay

487   in the mantle, or b) get mixed into mantles efficiently, a late chondritic addition will suffer the

488   same fate as any accreted metal-bearing material and mobilize to the core, especially if the

489   differentiated bodies are largely molten, but even if they are partially molten (Rushmer et al.,

490   2000).

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

492   A large group of elements exhibits both siderophile and volatile behavior and thus can be

493   used to constrain both core formation and volatility processes, and of general utility in accretion

494   models for Earth. Several of these elements have known chalcophile behavior, such as Cu and

495   Sn, whereas several are known to be sensitive to Si content of Fe alloy such as As and Sb.

496   Although some fundamental studies have established a baseline for these elements, many

497   variables remain unexplored, yet are known to be important. For example, Righter et al. (2009)

498   demonstrated that D(Sb) metal/silicate depends upon S content of silicate melt. Similarly, D(Sn)

499   metal/silicate is apparently strongly fO_2 dependent because of solubility of Sn^{4+} in silicate melts.

500   Sn may thus offer more insight into fO_2 than many other VSEs which are 1+ or 2+.   The volatile

501   siderophile elements offer a diverse range of valences (and thus fO_2 dependence) and chemical

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502   behavior with respect to S, C and Si bearing systems. Further scrutiny of their partitioning

503   behavior and application to Earth can serve to strengthen existing accretion models.

504   **Summary and implications**

505   Linear regression modelling approaches predict changes in D(i) metal/silicate due to pressure,

506   temperature, metallic liquid composition, and do not require any additional terms or variables

507   that are being neglected.

508   Deep mantle reservoirs and phases may exert control on the concentrations of weakly siderophile

509   elements, such as Mn, V, Cr, Nb and Ta, in the PUM. Modelling attempts to explain such

510   elements soley by metal-silicate equilibrium may lead to more reduced or hotter temperatures

511   than if these reservoirs are also considered.

512   Volatile elements such as S, C, H and N may be partitioned into the core, but the content in the

513   PUM may be explained by high PT metal-silicate equilibrium, as recently done for S. Much

514   information is missing to fully evaluate this idea, especially for C, H and N, but if true would not

515   require exogenous sources for Earth's volatiles. Experimental studies at deep Earth conditions

516   should focus on combinations of elements rather than simple systems that are known to be un-

517   Earth-like.

518   Studies of the HSE have demonstrated that D(HSE) metal/silicate for many of these elements

519   remain higher than 1000 approaching the high PT conditions suggested for metal-silicate

520   equilibrium in the early Earth. But a number of variables relating to metal/silicate partitioning

521   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 and 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 fO_2 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 (X_{SiO2} = 0.38; X_{Al2O3} = 0.03; X_{CaO} = 0.03; nbo/t = 2.55) and relative fO_2 of ΔIW = -2 (X_S = 0.01 and X_C = 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 fO_2 of ΔIW = -1.25 (S- and C-free metal).

34

810 **Figure 4:** Comparison of D(Ni) and D(Co) calculated with relative fO$_2$ (using ΔIW term as in

811 equation [3]) and absolute fO$_2$ (using lnfO$_2$ term as in equation [2]) approaches. Both curves for

812 both elements are calculated for conditions of ΔIW=-2, nbo/t = 2.7, and S and C-free metallic

813 liquid, along liquidus PT path for peridotite from Andrault et al. (2011). The agreement between

814 the approaches is clear, but results start to deviate at pressures > 40 GPa. Coefficients for Ni

815 using equation (2) are: a = -0.31 (0.02), b = -12380(1110), c = 132 (31), d = -2.03 (0.22), e =

816 +1.83 (0.61), f = -0.30 (0.04), and g = 7.40(0.46); standard error of regression = 0.60; r^2=0.814; n

817 = 308; Constant Variance Test: Passed   (P = 0.620). Coefficients for Ni using equation (3)

818 are: a = -0.71 (0.04), b = 7960(800), c = -240(22), d = -2.01(0.22), e = +1.84(0.61), f = -

819 0.31(0.04), and g = 2.64(0.5); standard error of regression = 0.61; r^2=0.811; n = 308; Constant

820 Variance Test: Passed (P = 0.689). Coefficients for Co using equation (2) are: a = -0.24 (0.02),

821 b = -12930 (1360), c = 208 (38), d = -0.48 (0.33), e = +0.44 (0.62), f = -0.18 (0.05), and g = 6.60

822 (0.49); standard error of regression = 0.55; r^2=0.751; n = 215; Constant Variance Test: Passed

823   (P = 0.069). Coefficients for Co using equation (3) are: a = -0.55 (0.05), b = 2620 (820),

824 c = -79 (27), d = -0.47 (0.33), e = +0.48 (0.63), f = -0.18 (0.04), and g = 2.95 (0.51); standard

825 error of regression = 0.55; r^2=0.754; n = 215; Constant Variance Test: Passed (P = 0.067).

826 Nickel and cobalt datasets are from Seifert et al. (1988), Hillgren (1993), Li and Agee (1996,

827 2001), Gaetani and Grove (1997), Jana and Walker (1997a, b), Righter et al. (1997, 2010),

828 Thibault and Walter (1995), Hillgren et al. (1994, 1996), Holzheid and Palme (1997, 2007), Ito

829 et al. (1998), Chabot et al. (2005), Bouhifd and Jephcoat (2008), Kegler et al. (2008), Wade and

830 Wood (2001, 2005), Walker et al. (1993), Peach and Mathez (1994), Corgne et al. (2008).

831 **Figure 5:** Comparison of epsilon interaction parameter (from Lupis, 1983) and d[ln(1-Xs)] and

832 e[ln(1-Xc)] terms from Righter (2011a) and Righter et al. (2011), for sulfur (A) and carbon (B).

35

833   Chalcophile (S-loving) and anthracaphile (C-loving) behavior requires negative epsilon values,

834   as demonstrated in both approaches.

835   **Figure 6**: Comparison of measured D(Ni), D(Co) and D(W) metal/silicate from the studies of

836   Siebert et al. (2012, 2013) and Bouhifd and Jephcoat (2011) with values calculated using the

837   expression of Righter (2011a). Solid line is the 1:1 line.

838   **Figure 7:** Effect of D(V) and D(Cr) SS/LS on calculated V and Cr contents of the magma ocean

839   during accretion. At low pressures V and Cr are compatible in spinel and garnet, while at high

840   pressures they are compatible in ferropericlase and MgFe-perovskite. Calculations are done

841   using the following mass balance equation (from Righter et al., 1997):

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

843   Where x is the fraction of silicate, p is the fraction of molten silicate, m is the fraction of molten

844   metal, C_{bulk}^{i} is the bulk concentration of siderophile element, C_{LS}^{i} the concentration of

845   siderophile element in the liquid silicate, $D_{SS/LS}^{i}$ is the partition coefficient between solid silicate

846   and liquid silicate, $D_{LM/LS}^{i}$ is the partition coefficient between liquid metal and liquid silicate,

847   and $D_{SM/LS}^{i}$ is the partition coefficient between solid metal and liquid silicate.   For these

848   calculations, x = 0.68. p = 0.7, and m = 1; in the case of an entirely molten core, m = 1 and the

849   last term on the right disappears. Horizontal bands are the V and Cr contents of the PUM from

850   Newsom (1995).

36

851   **Figure 8**: S content of Earth's mantle as D(S) metal/silicate and bulk S content vary. Again, the

852   following mass balance equation is used for these calculations (see Figure 6 caption for

853   definitions of terms):

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

855   For these calculations, x = 0.68. p = 0.7, and m = 1; in the case of an entirely molten core, m = 1

856   and the last term on the right disappears. In addition, D(S) SS/LS = 0.01. Sulfur content of

857   PUM and bulk S contents for H, L, LL and CI chondrites are from compilation of Newsom

858   (1995).

859   **Figure 9:** Terrestrial mantle depletions of all the HSE (values and uncertainty for each element

860   are from Becker et al., 2006) in the terrestrial mantle normalized to CI chondrites and Mg –

861   values from Newsom (1995). The heavy horizontal line with shaded box is the value for 0.0030

862   x CI chondrites with uncertainty (Becker et al., 2006); clearly five of these elements fall within

863   the CI chondritic shaded box.   However, the non-chondritic Au, Pd and Ru values (relative to

864   other HSE) suggest that simple late chondritic additions cannot explain all the HSE. Shown at

865   left edge are calculated HSE depletions expected if D(HSE) metal/silicate were 200, 300, 400,

866   500, 600, and 700.   It is clear the in order for an equilibrium scenario to explain the HSE in the

867   PUM, D(Au) metal/silicate and D(Pd) metal/silicate must be ~ 400, D(Ru) metal/silicate must be

868   ~ 600, and D(Re, Pt, Rh, Os, Ir) metal/silicate must be ~700.

869   **Figure 10:** Calculated D(Au) and D(Ir) metal/silicate using predictive expressions (equation 2)

870   presented by Righter et al. (2014b). Panel A shows the calculation along liquidus of Andrault et

871   al. (2011) out to 4000 K, for a metallic liquid with no S, or C. Panel B shows the same

872   temperature range, but for a metallic liquid that contains $X_S = 0.25$ and $X_C = 0.1$.   This

37

873   calculation is not meant to be a detailed explanation for the terrestrial PUM (Earth's core

874   contains less S and C than this example), but instead illustrates the dramatic effect of adding S

875   and C to the metallic liquid. Horizontal bands represent D(Au) and D(Ir) required for a core-

876   mantle equilibrium scenario.

877

nbo/t = 2.7; ΔIW = -1.25; Xs = Xc = 0; T varies from 2073 to 2873 K

nbo/t = 2.55; ΔIW = -2; Xs = 0.01, Xc = 0.02; T varies from 1800 to 3073 K