

# Activity coefficients of siderophile elements in Fe-Si liquids at high pressure

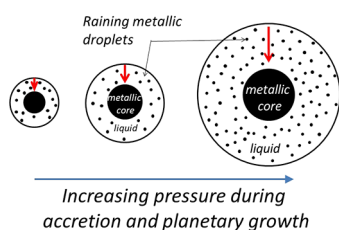
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## Abstract

### Thermodynamics of metal-silicate equilibration



cients for application to higher pressure processes (at least to 10 GPa).

Metallic core formation in differentiated bodies in the inner solar system can take place between low pressures (near 1 bar) to much higher pressures (up to 100 GPa). Most thermodynamic models of metal-silicate equilibria utilise activity coefficients for metallic tracers in Fe liquids, nearly all of which have been carried out at low pressures. This study focuses on the effect of pressure on activity coefficients for Au, P, V, Mn, Ga, Zn, Cd, Sn, W, Pb, and Nb in liquid Fe-Si alloys. From a series of experiments at 10 GPa, 2373 K containing variable Si content in a metallic liquid we have derived epsilon interaction parameters in Fe-Si liquids ( $\epsilon_M^{Si}$ ). Comparison of 1 GPa and 10 GPa data shows no difference except for Nb. Epsilon parameters derived from low pressure experiments can thus be used to calculate activity coefficients for application to higher pressure processes (at least to 10 GPa).

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## Introduction

Light elements can alloy with Fe in the cores of terrestrial planetary bodies. Due to density considerations, Earth's core likely contains ~10 % of a light element, which could be a combination of S, C, Si, and O with Si probably being the most abundant (Hirose *et al.*, 2013). The dissolution of these elements, and in particular Si, is dependent upon oxygen fugacity (Righter *et al.*, 2020), which also controls the solubility of trace elements in metallic and silicate melts. Because Si is a major alloying agent in metallic cores, its solution in Fe metallic liquids can have a significant influence on the activity coefficients of siderophile elements, and thus the partitioning behaviour of those elements between the core and mantle (Tuff *et al.*, 2011; Righter *et al.*, 2018).

The Earth's core is estimated to have formed at pressures between 40–60 GPa (Wade and Wood, 2005; Righter, 2011; Siebert *et al.*, 2011). Pressure is known to influence volumetric properties of metallic and silicate liquids (e.g., Armstrong *et al.*, 2019), and also affect oxygen fugacity (e.g., Righter, 2016), but less is known about the effect of pressure on activity coefficients (e.g., Steenstra *et al.*, 2020). If, for example, the activity coefficient of a moderately siderophile element (like W) in metallic Fe doubled, the corresponding concentration of that element in the silicate melt would nearly double as well. Thus even a modest change in activity coefficient will have a significant effect on mantle concentrations of siderophile element modelling outcomes. Understanding the effect of pressure on activity coefficients in the Fe-Si system, and in metallic liquids in general, is

thus important for modelling core formation in the Earth and other terrestrial-like planets.

In this work, we carried out a series of experiments (See Supplementary Information Part 1, Fig. S-1, and Table 1) at 10 GPa to investigate the effect variable Si content has on the activity coefficients of Au, P, V, Mn, Ga, Zn, Cd, Sn, W, Pb, and Nb in Fe-Si alloys at 10 GPa and 2373 K. We derive interaction parameters for Fe-Si liquids for comparison to behaviour already investigated at 1 GPa, using the same starting materials (Righter *et al.*, 2018).

## Results

**Determination of epsilon interaction parameters.** The epsilon interaction parameter ( $\epsilon_M^{Si}$ ) is a measure of the interaction between a trace element M and the solute Si in a Fe metallic liquid. The  $\epsilon_M^{Si}$  approach for calculating activity coefficients allows effects of solutes like Si, S, and C to be quantified for a multi-component metallic liquid (Supplementary Information Part 3). Positive  $\epsilon_M^{Si}$  values indicate dissolved Si causes a decrease in partition coefficients, whereas negative values indicate an increase. Mn is the only element to exhibit a negative  $\epsilon_M^{Si}$  of  $-1.1 \pm 5.0$  (standard error), and even this value is only marginally negative when error is considered. V and Zn have small, positive  $\epsilon_M^{Si}$  of  $3.5 \pm 6.6$  and  $6.2 \pm 3.3$ , respectively. Cd, Pb, Nb, and W all have positive but slightly lower  $\epsilon_M^{Si}$  of  $8.1 \pm 1.3$ ,  $6.4 \pm 1.8$ ,  $7.0 \pm 8.3$  and  $14.3 \pm 6.7$ , respectively (Figs. 1, S-2). Au, Ga, and Sn have moderate, positive  $\epsilon_M^{Si}$  of  $16.9 \pm 3.7$ ,

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**Table 1** Silicate and metal compositions and partition and exchange coefficient summary (values in parentheses represent 2 $\sigma$  error).

<i>Experiment</i>	2	3	5	6	7
<i>Silicate</i>					
SiO <sub>2</sub>	34.1(7)	37.4(7)	40.0(8)	41.0(8)	25.8(5)
TiO <sub>2</sub>	2.14(2)	2.52(3)	2.58(3)	2.76(3)	1.27(1)
Al <sub>2</sub> O <sub>3</sub>	6.5(1)	8.2(2)	6.8(1)	9.4(2)	8.3(2)
FeO	3.00(3)	1.39(1)	0.170(2)	0.180(2)	0.070(1)
MnO	0.090(1)	0.060(1)	0.050(1)	0.040(1)	0.030(1)
MgO	42.1(8)	36.1(7)	38.0(8)	35.2(7)	54.6(1.1)
CaO	8.73(9)	10.63(11)	9.79(10)	9.05(9)	5.27(5)
Na <sub>2</sub> O	1.15(2)	1.43(3)	1.76(4)	1.54(3)	1.05(2)
K <sub>2</sub> O	1.04(1)	1.34(1)	1.60(2)	1.39(1)	0.75(1)
P <sub>2</sub> O <sub>5</sub>	0.060(3)	0.029(2)	0.024(2)	0.014(1)	0.016(1)
Total	98.87	99.04	100.75	100.54	97.19
Au (ppm)	1.5(1)	2.2(1)	25.5(1.3)	16.1(8)	14.4(7)
Ga	1.20(6)	1.40(7)	1.90(10)	1.20(6)	0.80(4)
Zn	21.5(1.1)	8.9(4)	11.2(6)	8.2(4)	4.1(2)
V	128.8(6.4)	45.8(2.3)	19.2(1.0)	13.1(0.7)	5.1(0.3)
Mn	697(35)	465(23)	387(19)	310(16)	155(8)
Cd	0.6(0(3)	0.50(3)	0.40(2)	0.30(2)	0.10(1)
Pb	0.50(3)	0.20(1)	0.10(1)	0.10(1)	0.10(1)
Sn	0.10(1)	0.20(1)	0.10(1)	0.10(1)	0.10(1)
Nb	29.3(1.5)	11.7(6)	1.5(1)	1.0(1)	0.20(1)
W	15.4(8)	0.60(3)	0.10(1)	0.10(1)	0.20(1)
<i>Metal</i>					
Si	0.04(1)	3.20(6)	7.31(15)	10.27(21)	11.62(23)
Fe	94.5(1.9)	91.1(1.8)	84.0(1.7)	81.1(1.6)	78.1(1.6)
P	0.38(1)	0.63(1)	0.73(1)	0.89(2)	0.85(2)
Au	4.12(8)	3.24(6)	5.64(11)	5.53(11)	4.97(10)
Total	99.04	98.12	97.68	97.81	95.59
Ga (ppm)	39(2)	38(2)	58(3)	47(2)	81(4)
Zn	361(18)	534(27)	609(30)	702(35)	867(43)
V	42(2)	655(33)	486(24)	576(29)	215(11)
Mn	175(9)	2600(130)	4000(200)	4534(227)	2950(148)
Cd	28.0(1.4)	49.0(2.5)	86.0(4.3)	43.0(2.2)	28.0(1.4)
Pb	23.0(1.2)	27.0(1.4)	50.0(2.5)	18.0(9)	47.0(2.4)
Sn	9.4(5)	12.3(6)	21.5(1.1)	19.8(1.0)	17.4(9)
Nb	4.4(2)	166(8)	58(3)	148(7)	48(2)
W	12.3(6)	5.9(3)	2.4(1)	5.2(3)	3.4(2)
X(Fe)	0.98	0.91	0.83	0.77	0.75
X(FeO)	0.022	0.010	0.0012	0.0013	0.0005
$\Delta$ IW	-3.31	-3.90	-5.66	-5.53	-6.38
ln (1-XSi)	0.000	-0.066	-0.154	-0.216	-0.250
D(Au)	27500(3800)	14700(2000)	2210(300)	3440(480)	3450(480)
D(Fe)	31.5(4.4)	65.5(9.2)	494(69)	451(63)	1120(157)
D(Ga)	32.5(4.6)	27.1(3.8)	30.5(4.3)	39.2(5.5)	101.3(14.2)
D(Zn)	16.8(2.4)	60.0(8.4)	54.4(7.6)	85.6(12.0)	211.5(29.6)
D(V)	0.33(5)	14.3(2.0)	25.3(3.5)	44.0(6.2)	42.2(5.9)
D(Mn)	0.25(4)	5.6(8)	10.3(1.4)	14.6(2.0)	19.0(2.7)
D(Cd)	46.7(6.5)	98(14)	215(30)	143(20)	280(39)
D(Pb)	46(6)	134(19)	497(70)	182(25)	471(66)
D(Sn)	94(14)	62(9)	215(30)	198(28)	174(24)
D(Nb)	0.15(2)	14.2(2.0)	38.7(5.4)	148(21)	240(34)
D(W)	0.80(10)	9.8(1.4)	24.0(3.0)	52.0(7.0)	17.0(2.0)
ln Kd Au	7.72(1.08)	6.70(94)	3.73(52)	4.18(59)	3.67(51)
ln Kd Ga	-2.73(38)	-3.92(55)	-6.84(96)	-6.37(89)	-6.84(96)

Table 1 (Continued)

Experiment	2	3	5	6	7
ln Kd Zn	-1.54(25)	-0.969(16)	-3.12(50)	-2.55(41)	-2.61(42)
ln Kd V	-7.34(1.03)	-4.56(64)	-7.03(98)	-6.25(88)	-7.71(1.08)
ln Kd Mn	-5.74(86)	-3.28(49)	-4.71(71)	-4.25(64)	-4.95(74)
ln Kd Cd	-0.517(83)	-0.474(76)	-1.74(28)	-2.04(33)	-2.32(37)
ln Kd Pb	-0.523(73)	-0.169(24)	-0.904(13)	-1.79(25)	-1.81(25)
ln Kd Sn	-3.53(49)	-5.27(74)	-8.03(1.12)	-7.79(1.09)	-9.79(1.37)
ln Kd Nb	-11.8(1.7)	-8.89(1.24)	-12.9(1.8)	-11.1(1.6)	-13.0(1.8)
ln Kd W	-8.29(1.16)	-7.10(99)	-10.2(1.4)	-9.12(1.27)	-12.1(1.7)
ln Kd P	-14.47(2.02)	-16.28(2.28)	-25.68(3.60)	-23.85(3.34)	-28.38(3.97)

17.1 ± 3.8, and 23.1 ± 3.5, respectively, whereas P yielded the highest value of  $\epsilon_M^{Si}$  at 55.0 ± 11.4 (Figs. 1, S-2).

## Discussion

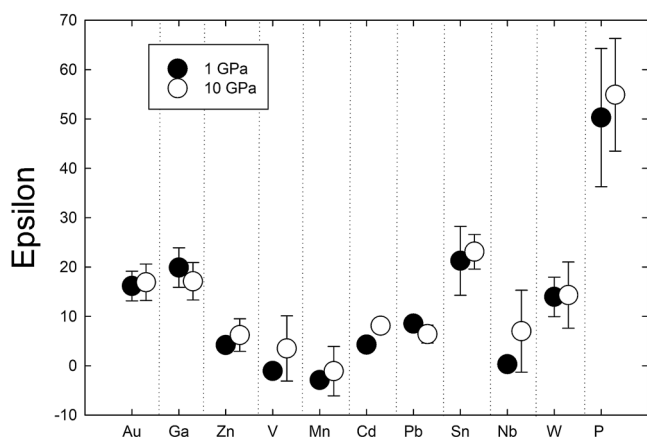
**Comparison to low pressure epsilon parameters.** Comparison of our newly determined 10 GPa  $\epsilon_M^{Si}$  to values at 1 GPa (re-calculated to 2373 K using the following equation:  $\epsilon_i^{2373} = \epsilon_i^{1873} \frac{1873}{2373}$ ) from previous studies) shows very similar values at both pressures (Fig. 1). Zn, V, Cd, and Nb are all shifted to higher values at 10 GPa, but the differences are within error. Similarly, Pb is slightly lower than the 1 GPa value, but still within error. Nb has the largest difference in measured epsilon values at low pressure and 10 GPa (albeit still within error), suggesting there might be a measurable pressure effect at even higher pressures. However, the low pressure value in Figure 1 was taken from the *Steelmaking Data Sourcebook* (1988) and is a value of -0.66, compared to our 10 GPa value of 7.0 ± 8.3. These experimental differences in the two studies are likely important and thus make difficult a comparison between low and high pressure values to assess a pressure effect. Despite these small differences for a few elements, our 10 GPa data are largely indistinguishable

from the 1 GPa data and indicate that activity coefficients are not strongly dependent upon pressure.

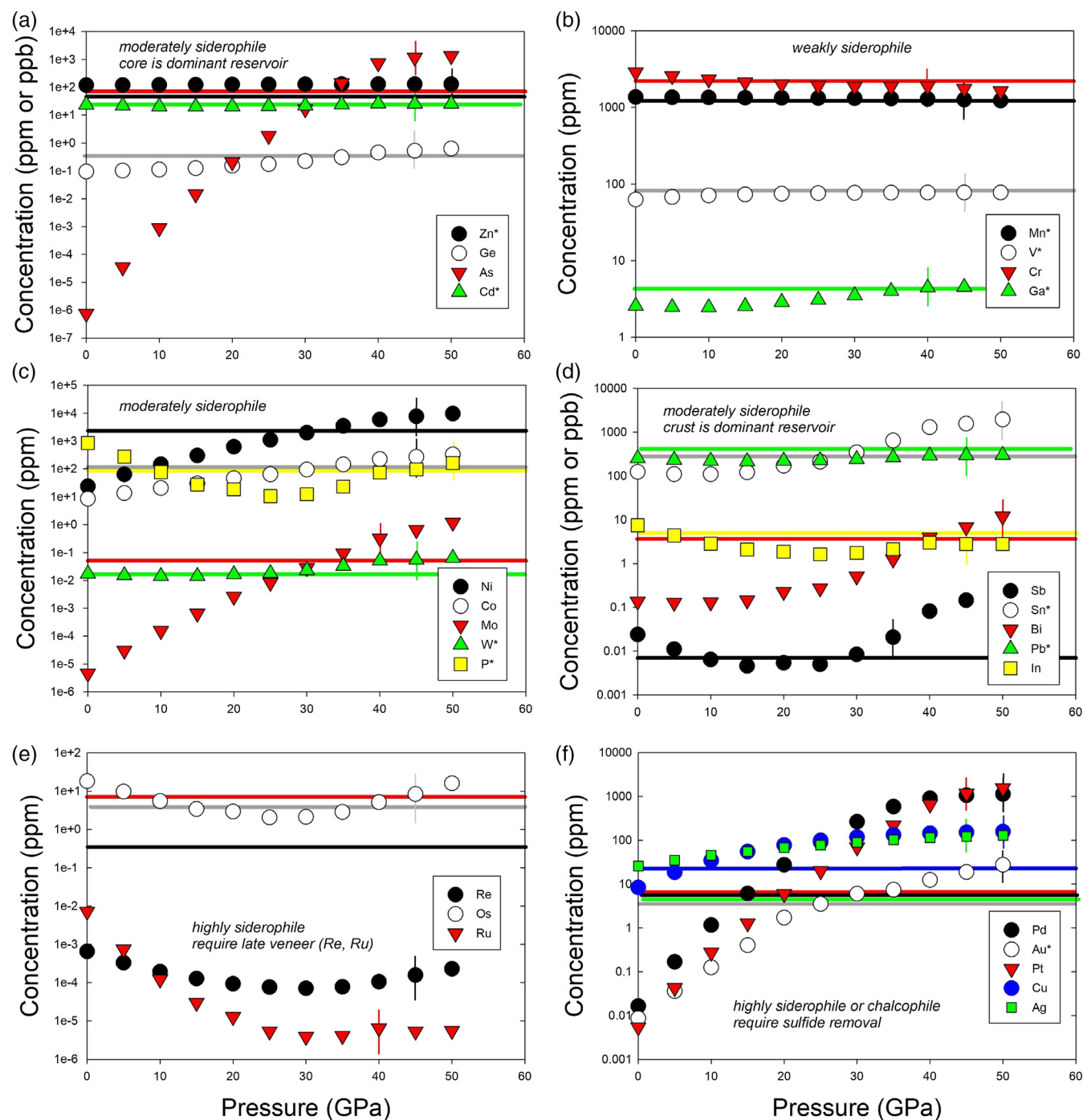
Steenstra *et al.* (2020) examine the effect of pressure on  $\epsilon_M^{Si}$  combining their data at 1 to 4 GPa with 11 GPa data from Vogel *et al.* (2018), for 12 elements, some of which we have examined here. Our results for Cd, Pb, Mn, V, and Sn are in overall agreement – none of these elements shows discernable change between 1 and 10 GPa. Steenstra *et al.* (2020) also present some evidence for change at high pressure for  $\epsilon_M^{Si}$  for Ni, In, As and Sb, but change in those series occurs between 1 and 2 GPa and change above that is negligible (*i.e.*, 2 GPa = 11 GPa values for As, Sb, Sn). Pb, Cu, Cr, Mn, V, and Cd  $\epsilon_M^{Si}$  all show no trend at higher pressures, similar to most elements we have examined here.

**Implications.** The accretion of terrestrial planets is a process that begins in the earliest Solar System as differentiated bodies form within a few million years after the start of the Solar System or  $T_0$  (Kleine *et al.*, 2009; Levison *et al.*, 2015). The process continues with oligarchic growth of planetesimals (Kokubo and Ida, 1998) and then transitions to growth by merging and impact of planetesimals into planets (*e.g.*, Chambers, 2013). As this process unfolds, the energetics of accretion increase steadily providing sufficient energy to melt – either partially or completely – planetary mantles and metal-silicate mixtures (*e.g.*, de Vries *et al.*, 2016). The equilibration of metal and silicate melts is rapid and complete during this process (Kendall and Melosh, 2016; Lherm and Deguen, 2018) and thus the siderophile element content of the molten portion of the planet will change as the depth and associated pressure of metal-silicate equilibrium increases (*e.g.*, Rubie *et al.*, 2003). Modelling of siderophile element contents of molten upper mantle melts in equilibrium with Fe-Si-S-C metallic liquids during accretion now includes 26 elements (Fig. 2), including moderately siderophile and refractory (Ni, Co, Mo, and W), moderately siderophile and volatile (P, Ga, Cu, Ge, Sb, As, In, Bi, Sn, Ag, Cd, and Pb), weakly siderophile (Mn, Cr, V, Zn), and highly siderophile (Au, Pd, Pt, Re, Os, Ru) elements. The number of elements that can be modelled for Fe-Si-S-C liquids using this approach has nearly tripled since 2016.

A complete understanding of this large group of elements is desirable for a number of reasons. First, some of these elements are critical to biochemical processes and the origin of life, being part of energetically favourable enzymes or participants in chemical processes (*e.g.*, W, Mo, P, Ni, Co; Falkowski *et al.*, 2008; Kim *et al.*, 2013; Benner *et al.*, 2019), taking part in biochemical processes at black smokers, or involved in respiration (V, Cu, and Zn). For example, enhanced concentration of P in terrestrial or extrasolar planetary mantles is expected in equilibrium with Fe-Si liquids (Richter *et al.*, 2018). Higher concentrations in the mantle would aid the eventual transfer of P to the crust



**Figure 1** Comparison of 1 GPa and 10 GPa epsilon interaction parameters, with the 1 GPa values re-calculated from 1873 to 2373 K as discussed in the text. P, Au, Ga, Sn, Cd, Pb, Nb, W, Zn and V all have positive  $\epsilon_M^{Si}$ , indicating that Si will cause a decrease in D metal/silicate with Si present in the metallic liquid. Mn has a negative  $\epsilon_M^{Si}$ , indicating that Si will cause a very slight increase in D(Mn) metal/silicate with Si present in the metallic liquid. Nb exhibits the largest difference in measured  $\epsilon_M^{Si}$  at low pressure and 10 GPa, suggesting there might be a measurable pressure effect at even higher pressures.

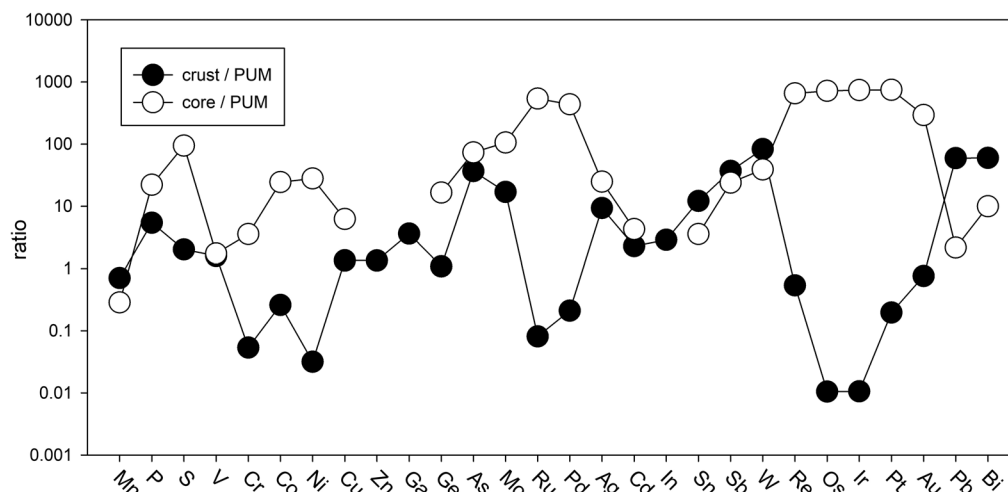


**Figure 2** Evolution of siderophile element content of a terrestrial magma ocean as accretion proceeds and the PT conditions of metal-silicate equilibrium increase. Primitive upper mantle (PUM) siderophile element concentrations (from [Palme and O'Neill, 2014](#)) are horizontal lines with colour matching the symbols of the calculated values in each panel. The concentrations of 19 elements can be explained by metal-silicate equilibrium in a near 30–40 GPa magma ocean (Ni, Co, Mo, W, P, Mn, V, Cr, Ga, Zn, In, Ge, Sb, As, Sn, Bi, Cd, and Pb). Calculated concentrations of some elements such as Ag, Cu, Au, Pd, Pt become higher than PUM values, indicating the need for a removal mechanism such as a sulfide matte or late metallic segregation (see [Righter et al. 2018](#), for detailed discussion). These 5 elements, together with Re, Os, and Ru, ultimately have their mantle concentrations set by addition of chondritic material after core formation and sulfide segregation.

([Supplementary Information Part 4](#)), thus influencing the stability of P-bearing biochemicals such as ADP, RNA, and DNA in habitable planets. Second, the highly siderophile elements (e.g., Au, Ru, Ir, Os), chalcophile elements (Cu, Ag), and volatile trace metals are frequently employed in constraining post core formation and late accretion processes (e.g., [Walker, 2009](#)) as well as how Earth (and other bodies) acquired volatiles in general (e.g., [Halliday, 2013](#); [Righter et al., 2019](#)). And third, the

distribution of most siderophile elements between core, mantle and crust is dominated by the core, but the distribution of several exceptional elements is actually dominated by the crust (e.g., Bi, Sn, As, Sb, Mo, W, Pb, In; [Fig. 3](#)). All of these elements exhibit positive  $\epsilon_M^{Si}$  values, indicating their mantle concentrations would be elevated by equilibration with Fe-Si core-forming alloy. The higher mantle concentrations would also enhance the ultimate transfer of these elements to the crust and produce





**Figure 3** Concentrations of siderophile elements in the crust (Rudnick and Gao, 2014) and core (McDonough, 2003) of the Earth, normalised to values in the primitive upper mantle (PUM) (Palme and O'Neill, 2014). This diagram demonstrates that most siderophile elements are concentrated into the core, but there is an important and significant subset that is more highly concentrated into the crust, including Mn, Bi, Pb, In, Sn, Sb, and W.

similar or higher concentrations in the crust compared to the core (Fig. 3). Thus, a complete understanding of how all these siderophile elements became established in the primitive mantle and ultimately in the crust is essential to understanding the basic geochemistry of the early Earth.

The current work includes moderately siderophile and refractory (W), moderately siderophile and volatile (P, Cd, Sn, Pb), weakly siderophile (Mn, V, Ga, Zn, Nb), and highly siderophile (Au) elements. Most elements in these 4 groups exhibit no pressure effect on the activity coefficients in Fe-Si liquids, perhaps a surprising result because some have argued that structural changes in metallic liquids in this pressure range may lead to changes in partitioning behaviour in the Fe-C and Fe-Si liquids (5.2 GPa in Fe-C; Sanloup *et al.*, 2011, and 1-4 GPa in Fe-Si; Shibazaki *et al.* 2015). Although one might expect changes in epsilon parameters (and thus activity coefficients) due to such structural changes, our results suggest that there is no effect up to 10 GPa. It is possible that Fe-Si liquids do not undergo such structural changes below 10 GPa (*e.g.*, Sanloup *et al.*, 2004), and thus we do not see a change in activity coefficients. Some changes are proposed at higher pressures (*e.g.*, Morard *et al.*, 2007; Fe-S), and so detection of changes in activity coefficients at higher pressures should be pursued as well. In the meantime, because our results show no evidence for such structural changes in Fe-Si liquids below 10 GPa, the epsilon parameters can be employed in modelling equilibria at pressures up to 10 GPa.

Further studies of other siderophile elements at 10 GPa should be undertaken for comparison to the current results and to measure potential pressure effects on activity coefficients. Most elements should also be studied to pressures higher than 10 GPa and up to 70 GPa – pressures more applicable to those during the accretion of larger terrestrial planets. In particular, Cu, Mo, Bi, As, Sb, as well as the highly siderophile elements (HSE) Pt and Pd all exhibit pressure dependence, and thus pressure effects on activity coefficients must be thoroughly understood and studied in more detail. Additionally, a better understanding of the effect of pressure on Nb would be important to evaluating the Nb content of the mantle of differentiated bodies and the overall distribution cores and mantles in differentiated bodies (*e.g.*, Nebel *et al.*, 2010; Münker *et al.*, 2017).

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## Additional Information

Supplementary Information accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2034>.



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