



# Accretion and core formation: The effects of sulfur on metal–silicate partition coefficients

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## Abstract

The accretion of the Earth was marked by the high-pressure segregation of the core, accompanied by dissolution of about 10% of one or more “light” elements into the metal. Cosmochemical data suggest that, of these 10% “light” elements, the core contains ~1.7% S (Dreibus and Palme, 1996) and there is evidence that volatile elements such as S accreted to the Earth late in planetary growth, plausibly as a sulfide “matte” (O’Neill, 1991). Given that metallurgical data indicate that dissolution of even small amounts of sulfur in liquid Fe can have profound effects on the activities of some trace components, we have undertaken a study of the affect of S on the metal–silicate partitioning of a number of the most important chalcophile and siderophile elements.

We performed experiments at 1.5 GPa and 1460–1650 °C on metal–silicate partitioning of W, Mo, Ni, Co, Cu, Ag, Mn, Cd, Tl, Cr, Sb, In, Pb, Ga, Ge, V and Zn under conditions where the S content of the metal was varied from 0 to 37 wt%. Mn and Ag were found to exhibit the highest ratio of chalcophile to siderophile behaviour while W, Ga and Sb are the most “chalcophobic” of the elements studied. In terms of the 1-parameter epsilon model (Wagner, 1962) we derived values for each element at 1600 °C as follows (negative values indicate chalcophile behaviour):  $\epsilon_{\text{Cu}}^{\text{S}} = -2.57$ ;  $\epsilon_{\text{Mn}}^{\text{S}} = -6.41$ ;  $\epsilon_{\text{Ag}}^{\text{S}} = -4.15$ ;  $\epsilon_{\text{Sb}}^{\text{S}} = 4.36$ ;  $\epsilon_{\text{Cd}}^{\text{S}} = -3.78$ ;  $\epsilon_{\text{In}}^{\text{S}} = -0.24$ ;  $\epsilon_{\text{Tl}}^{\text{S}} = -6.21$ ;  $\epsilon_{\text{Ga}}^{\text{S}} = 6.54$ ;  $\epsilon_{\text{Pb}}^{\text{S}} = -3.73$ ;  $\epsilon_{\text{Cr}}^{\text{S}} = -3.70$ ;  $\epsilon_{\text{Ge}}^{\text{S}} = 7.03$ ;  $\epsilon_{\text{V}}^{\text{S}} = -3.14$ ;  $\epsilon_{\text{Zn}}^{\text{S}} = -1.68$ ;  $\epsilon_{\text{Mo}}^{\text{S}} = 2.27$ ;  $\epsilon_{\text{W}}^{\text{S}} = 6.47$ ;  $\epsilon_{\text{Ni}}^{\text{S}} = 2.17$ ;  $\epsilon_{\text{Co}}^{\text{S}} = 2.40$ .

We use these new data in conjunction with published pressure–temperature dependences of metal–silicate partitioning to test the effects of accreted S on the calculated trace element concentrations in bulk silicate Earth. The approach employs a continuous accretion model in which the oxidation state of the Earth and pressure of core segregation both increase during accretion. We find that, without addition of S in the latter stages of accretion, the Mo/W ratio of silicate Earth would be several times larger than that observed. Addition of ~2% S accompanied by small amounts of carbon in the last 15% of accretion, however, enables us to match the observed concentrations of these elements in silicate Earth. This confirms an earlier conclusion that the Mo/W ratio of silicate Earth requires late sulfide addition to the core (Wade et al., 2012).

Further support for late sulfide addition to the core comes from the depletion factors of volatile chalcophile elements Cu, Ga, Sb, Ag, Zn, Pb, Cd, In and Tl in silicate Earth relative to lithophile elements of similar volatility. We find that depletions of these elements are well correlated with their partition coefficients into sulfide (FeS) liquids at 1.5 GPa and temperatures of 1460–1650 °C. In contrast there is essentially no correlation between their depletion factors and sulfur-free liquid Fe–silicate partition coefficients.

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## 1. INTRODUCTION

The isotopic and trace element compositions of silicate Earth provide a wealth of constraints on the processes and timescales of terrestrial accretion and differentiation. In order to apply these constraints most usefully, however, it is necessary to know the chemical compositions of the silicate Earth and of the bulk Earth. Detailed analysis of mantle peridotites and their melting products (after Ringwood, 1966) shows that primitive upper mantle (or bulk silicate Earth, BSE) has approximately CI chondritic ratios of refractory lithophile elements (Allègre et al., 1995; McDonough and Sun, 1995), an observation implying that refractory element ratios in the bulk Earth approximate those in CI chondrites and that depletions of siderophile elements in the mantle are due to their partitioning into the core. A simple mass balance calculation based on a bulk volatile-free CI composition yields a mantle with a major element composition approximating that observed and an Fe-rich core of approximately the correct mass (Ringwood, 1966). Ringwood noted, however, that the Earth's mantle had concentrations of Ni, Co and Cu, which appeared to be too high to be explained by simple equilibration between mantle and core, the “excess siderophile” problem.

As the earth accreted and the core segregated, elements were partitioned between the Fe-rich metallic phase and the silicate mantle according to partition coefficients  $D_i$  defined as follows:

$$D_i = \frac{[i]_{\text{metal}}}{[i]_{\text{silicate}}} \quad (1)$$

where  $[i]$  is the weight concentration of element  $i$  in the phase of interest. Experimental measurements of  $D_i$  for many refractory elements of varying degrees of siderophile character (Ni, Co, W, Mo, V, Cr, Nb, Ta for example) have been obtained over wide ranges of temperature and pressures to about 25 GPa. Recently the pressure range has been extended to 74 GPa in the diamond anvil cell (Siebert et al., 2013). These measurements have shown that the “excess siderophile” problem can be largely eliminated if core-mantle equilibration took place at high pressures (Thibault and Walter, 1995; Li and Agee, 1996; Wade and Wood, 2005; Kegler et al., 2008; Cottrell et al., 2009; Wade et al., 2012). In addition to pressure and temperature, metal-silicate partitioning of some elements (notably Mo and W, Wade et al., 2012) has been found to be sensitive to composition of the silicate melt and there is an obvious partitioning dependence of all elements on  $fO_2$ , since transfer of an element (M) of valence  $n$  from silicate to metal involves reduction:



Given the current concentration of FeO in the mantle of about 8 weight% and of Fe in the core of 80% (Allègre et al., 1995) reaction (2) yields an apparent  $fO_2$  of core segregation approximately 2 log  $fO_2$  units below Fe-FeO (iron-wüstite, IW) equilibrium. Assuming that this oxygen fugacity applied throughout accretion, measured partition coefficients for Ni, Co, Mo and W combined with current mantle abundances of these elements imply pressures of core-mantle equilibration of >30 GPa (e.g. Li and Agee, 1996). If we make the reasonable assumption that the pres-

Table 1  
Experimental conditions.

Expt No.	Composition	T, °C	Capsule type	Duration (min)
KK18-2 (A312)	50%CMAS + 50%Fe + TR	1565	MgO	30
KK19-1 (A314)	30%CMAS + 70%FeS + TR	1515	MgO	30
KK19-2 (A319)	30%CMAS + 70%FeS + TR	1565	MgO	30
KK20-1 (A315)	30%CMAS + 55%FeS + 15%Fe + TR	1565	MgO	30
KK20-2 (A318)	30%CMAS + 55%FeS + 15%Fe + TR	1565	MgO	30
KK21-1 (A316)	30%CMAS + 35%FeS + 35%Fe + TR	1565	MgO	30
KK22-1 (A317)	30%CMAS + 20%FeS + 50%Fe + TR	1565	MgO	30
KK23-1 (A321)	30%CMAS + 50%FeS + 20%Fe + TR	1565	MgO	30
KK23-2 (A322)	30%CMAS + 50%FeS + 20%Fe + TR	1565	MgO	30
A232	25%CMAS + 75%Fe + Co, Ni	1650	SiO <sub>2</sub>	20
A239	CMAS + FeS + Fe + Co, Ni	1650	SiO <sub>2</sub>	20
A242	25%CMAS + 75%FeS + Co, Ni	1650	SiO <sub>2</sub>	20
BW1210-1	25%CMAS + 35%Fe + 35%FeS + 5%FeO + W, Mo	1650	MgO	30
BW1214	25%CMAS + 37%Fe + 37%FeS + W, Mo	1650	MgO	20
BW1215	25%CMAS + 75%Fe + W, Mo	1650	MgO	30
BW1216	25%CMAS + 30%Fe + 45%FeS + W, Mo	1650	MgO	30
BW1220	25%CMAS + 50%Fe + 25%FeS + Co, Ni	1650	SiO <sub>2</sub>	20
BW1046	40%CMAS + 60%Fe + Co, Ni	1650	SiO <sub>2</sub>	40
750	22%Di + 8%An + 15%SiO <sub>2</sub> + 5%FeO + 50%FeS + TR1	1460	MgO	90

Pressure of all experiments was 1.5 GPa.

CMAS is a composition close to the 1.5 GPa eutectic composition in the system anorthite–diopside–forsterite (An<sub>50</sub>Di<sub>28</sub>For<sub>22</sub>) (Presnall et al., 1978).

Trace element (TR) mixture included: Cu, Ag, Tl, In, Cr, Mn, V, Ga, Ge, Cd, Sb, Zn, Pb.

Trace element (TR1) mixture contains same elements as TR but without Ge, Cd, In and Sb and with additional Nb.

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