MODELLING OF EQUILIBRIUM BETWEEN MANTLE AND CORE: REFRACTORY, VOLATILE, AND HIGHLY SIDEROPHILE ELEMENTS.
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Introduction: Siderophile elements have been used to constain conditions of core formation and differentiation for the Earth, Mars and other differentiated bodies [1]. Recent models for the Earth have concluded that the mantle and core did not fully equilibrate and the siderophile element contents of the mantle can only be explained under conditions where the oxygen fugacity changes from low to high during accretion and the mantle and core do not fully equilibrate [2,3]. However these conclusions go against several physical and chemical constraints. First, calculations suggest that even with the composition of accreting material changing from reduced to oxidized over time, the fO_2 defined by metal-silicate equilibrium does not change substantially, only by approximately 1 $logfO_2$ unit [4]. An increase of more than 2 $logfO_2$ units in mantle oxidation are required in models of [2,3]. Secondly, calculatons also show that metallic impacting material will become deformed and sheared during accretion to a large body, such that it becomes emulsified to a fine scale that allows equilibrium at nearly all conditions except for possibly the length scale for giant impacts [5] (contrary to conclusions of [6]). Using new data for D(Mo) metal/silicate at high pressures, together with updated partitioning expressions for many other elements, we will show that metal-silicate equilibrium across a long span of Earth's accretion history may explain the concentrations of many siderophile elements in Earth's mantle. The modeling includes refractory elements Ni, Co, Mo, and W, as well as highly siderophile elements Au, Pd and Pt, and volatile elements Cd, In, Bi, Sb, Ge and As.

New data for Mo: We have carried out experiments focused on D(Mo) metal/silicate across a wide range of pressures, and also including metallic liquids containing Si. Low pressure experiments were carried out in a piston cylinder apparatus, and higher pressure experiments in a multi-anvil apparatus both at NASA-JSC, and some of the latter from the study of [7]. Run products, which were typically large metallic spheres surrounded by silicate melt, were analyzed for major and minor elements using electron microprobe (UMd) and for Mo in the silicate portion using laser ablation ICP-MS at Rice University (Table 1).

Ni, Co, Mo, W modelling: Droplets of metallic liquid falling through molten silicate equilibrate rapidly, and because a convecting magma ocean will have an isentropic thermal gradient from the base of the ocean to the surface, metal-silicate equilibrium will likely occur near the base of the ocean. Thus we can examine the scenario of metal-silicate equilibrium at increasing depths in a magma ocean, near the liquidus of peridotite [8]. Using expressions derived by [9], augmented with newly published data [10,11,12], we have calculated the concentrations of Ni, Co, Mo, and W in a deep magma ocean that has equilibrated with metal. For each figure, the effect of light elements is shown for pure S, C, Si and then a mixture of all three (Figure 1). It is clear that the concentrations of all four elements can be explained by equilibrium between peridotite and metallic liquid at a depth near 1200 km, and the metallic liquid must have all three light elements.

Table 1: Experimental run conditions and D(Mo)

Run	T (°C)	P (GPa)	Mo met (%)	Mo silicate (ppm)	D(Mo)
GN23	2244	16.0	0.83	34.0	244
GN24	2140	16.0	1.17	55.1	212
GN25	2154	12.0	0.85	89	96
GN26	2094	12.0	0.86	72.2	119
BJJB 185	2100	19.0	5.17	185	279
Cow B1	1600	1.0	2.13	0.155	137400
Cow C2	1600	1.0	2.19	0.29	75500
Cow D1	1600	1.0	1.67	0.5	33900

Cd, In, Bi, Sb, Ge and As modelling: The volatile siderophile elements are less well understood than the four refractory siderophile elements. However, new studies [13, 14, 15] have revealed some important systematic behavior. First, all of these elements show a significant decrease in D metal/silicate at higher temperatures. Second, the dissolution of Si into the metal phase causes a substantial decrease in D metal/silicate as well. The combination of these two effects means that some of these elements, which have very high (10^6 to 10^8) D metal/silicate at low temperature and Si-free metals, become more lithophile at higher temperature

conditions. Therefore the concentrations of these elements in Earth's mantle are also consistent with a deep magma ocean metal-silicate equilibrium.

Au, Pd and Pt modelling: Several of the highly siderophile elements have been studied in detail, allowing predictive expressions to be derived for D metal/silicate. All three of these elements have much smaller D metal/silicate at conditions of a deep magma ocean for the Earth, with values approaching 500 to 1000. Although a late veneer or late chondritic addition to Earth after core formation is commonly invoked to explain their high concentrations in Earth's mantle, all three of these elements can be explained by metal-silicate equilibrium near the base of a deep magma ocean.

Conclusions: Heterogeneous accretion models have successfully explained siderophile elements in Earth's mantle for several decades, but are non-unique and can be applied to a very wide range of accretion conditions and temperatures, and compositions. In addition, such models are at odds with what we know about fO_2 in deep magma oceans, and the kinetics of equilibration of metal-silicate. A more difficult problem has been to identify a P-T-fO_2-composition condition that could explain the siderophile element contents in a simpler scenario. Equilibrium models, though easily ruled out across a wide low PT range, can explain many elements in a simple scenario in a narrow high PT range (35-45 GPa near the peridotite liquidus). This equilibration may have occurred at the base of a magma ocean, or could represent some dynamic boundary in the early Earth such as a suspension of metallic droplets, or boundaries of a convective cell.

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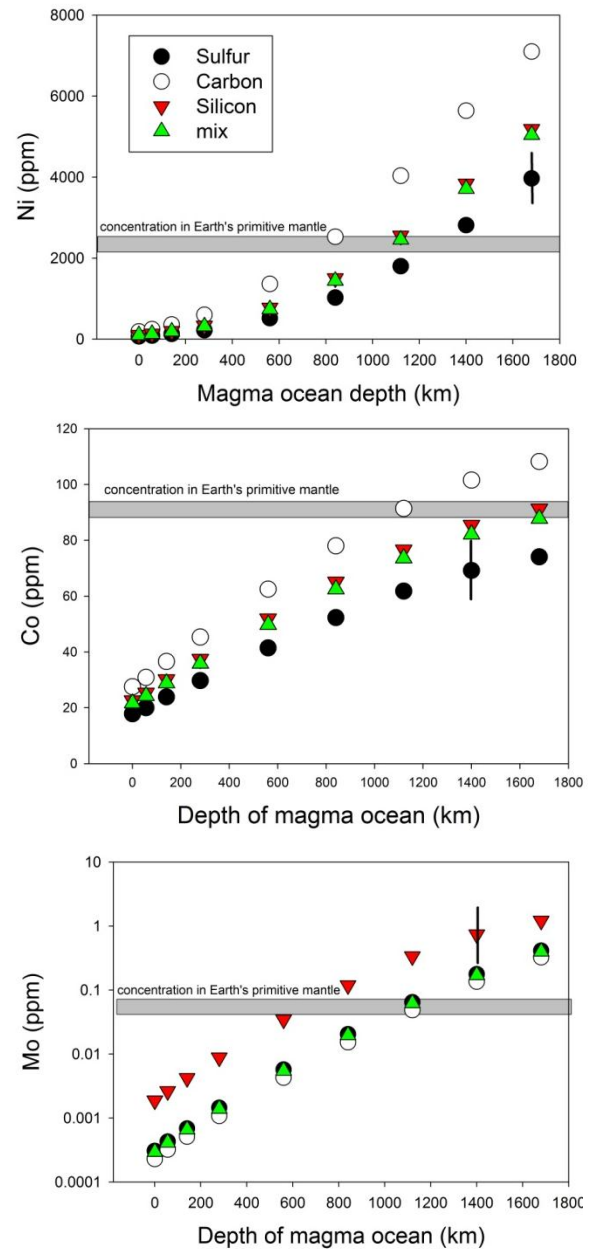

Figure 1: Ni, Co, and Mo contents of hypothetical magma oceans that have equilibrated with metallic liquids of various light element content, Fe-Ni-S, Fe-Ni-C, Fe-Ni-Si, and Fe-Ni-S-C-Si. Gray shaded boxes are the mantle concentrations in Earth's primitive upper mantle (PUM); typical error bar on calculations is shown as a vertical line. Note that pure C and S as light elements affect Ni and Co significantly, whereas Si affects Mo. An alloying mixture of S, C and Si can provide a match to the PUM concentrations at a depth of approximately 1200 km.