W PARTITIONING BETWEEN LIQUID METAL AND LIQUID SLICATE AS A FUNCTION OF P, T, fO$_2$, X$_{CARBON}$, AND MELT STRUCTURE: IMPLICATIONS FOR THE EARTH, MOON, MARS AND VESTA.

Elizabeth Cottrell[1], Michael Walter[2], and David Walker[3]. [1]Department of Mineral Sciences, National Museum of Natural History, Smithsonian Institution,Washington, DC, 20560, [2]Dept. of Earth Sciences, Univ. of Bristol, Bristol, UK BS8 1RJ, [3]Dept. of Earth and Environmental Sciences, Lamont-Doherty Earth Observatory, Columbia University, Palisades, NY 10964.

Introduction: Tungsten (W) has several attributes which make it especially attractive for determining whether or not an equilibrium model can be applied to core formation: (1) W is highly refractory and requires no volatility correction; (2) W is only moderately siderophile so its mantle abundance is not easily displaced by the late additional of meteoritic material (3) W is only moderately fractionated from its "geochemical twin," molybdenum (Mo), providing a geochemical pair conducive to testing models of core formation, and (4) [182]W is the daughter of lithophile element [182]Hf, and their fractionation yields temporal information about lunar and core formation as well [1-3]. Tungsten has therefore emerged as one of the key elements constraining the model terrestrial magma ocean [e.g. 4, 5].

Despite a wealth of study, a compilation of W metal/silicate partitioning data published prior to 2008 (11 studies consisting of 114 experiments) reveals a spread of over 3 orders of magnitude in D_w (met/sil) – even when oxygen fugacity and melt composition are accounted for. Moreover, regression of the compiled data in T, P, fO$_2$, or composition space across these studies yields dependencies that, on closer inspection, are in conflict with those reported within individual data sets in isolation. Here we present 103 experiments (30 published previously by [6]) at high pressure that constrain W's partitioning as a function of P, T, fO$_2$, X$_{silicate}$, and X$_{metal}$ (carbon content) by varying each of these parameters in isolation.

Experimental and Analytical Methods: Experiments in the piston-cylinder and multi-anvil were conducted the Geophysical Laboratory, Carnegie Institution of Washington, the Institute for Study of Earth's Interior (ISEI), Okayama University, and at Lamont-Doherty Earth Observatory from 0.5-18 GPa, and from 1723-2673K. Experimental assemblies were similar to [6, 7]. We employed a wide range of synthetic and natural silicate compositions that spanned a wide range of silicate melt structure (nbo/t = 0.5-4.0). Critically, experiments were run with and without carbon present. Run durations varied between 300 seconds to over 10 hours including time series experiments which indicate that all experiments reached equilibrium partitioning values. Experiments were carefully examined with scanning electron microprobe and analyzed via electron microprobe at the Smithsonian Institution and ISEI. Checks for experimental and analytical inter-laboratory bias revealed neither.

Results and Implications: Experiments quenched to Fe-W±C alloy + silicate glass or Fe-W-C alloy + carbide + silicate glass. Metal phase equilibria in our carbon-bearing and carbon-free experiments can be understood in terms of the ternary system Fe-W-C and the binary Fe-W respectively. The presence of carbon in liquid iron-alloy reduces D by about one order of magnitude, comparable in magnitude to the effects observed for oxygen content and melt composition [8]. The considerable influence of carbon in the metal-silicate system is unsurprising when one considers documented strong interaction between W and C in solid metal / liquid metal systems [9-11].

To account for solute-solute interactions in the carbon-bearing iron alloy, we employed the algorithm of Wade and Wood [5], coded as program METAL, to calculate the activities of Fe, W, and C in the carbon-bearing experiments. We have confidence in the METAL activities, first because calculated X$_C$ varies from ~0.2 to 0.35 over the temperature range of our C-bearing experiments, which is in acceptable agreement with the carbon solubility measurements of [12]. Second, and most importantly, the C-corrected partition coefficients are in agreement with the C-free (uncorrected) partition coefficients both in absolute magnitude and in their dependence on intensive parameters.

We regressed sets of C-corrected partition coefficients using least squares multi-variable linear regression to an equation of the general form:

$$\log D = \alpha + \beta(\Delta IW) + \chi(nbo/t) + \delta(1/T) + \varepsilon(P)$$

Isobaric data sets reduce to three variables, and isobaric, isothermal data sets reduce to only two variables (Table 1). All data, both C-bearing and C-free experiments lie within 0.20 standard deviations of the regression plane, and the inclusion of the C-free experiments in the regression (n=57, R^2=0.95) does not change the regression coefficients within error. This underscores the point that the C-corrected fugacities and partition coefficients faithfully reproduce the C-free experiments.

Our key findings are that: (1) Temperature has no discernable effect on D_W whatsoever in a buffer reference frame over the 1000 degree range investigated. Previously reported positive temperature effects [4, 13, 14] are either due to the conflation of temperature and

X_C in multivariate regressions, or only hold if absolute fO_2 is held constant. (2) Depolymerization of the silicate melt structure and increasing fO_2 both cause W to become more lithophile, consistent with previous studies[6, 13, 15-17]. (3) Below 3 GPa, increasing pressure causes W to become more siderophile, but above 5 GPa W becomes more lithophile with increasing pressure. This change in slope in the pressure dependence might occur as a result of changes in silicate melt structure with pressure. (4) Saturation of the alloy with Carbon causes W to become more siderophile – reducing the activity of W to approximately 0.01 ($\gamma_W \sim 0.1$) the activity of iron in the alloy to 0.4-0.5 ($\gamma_{Fe} \sim 0.7$). These activity-composition relationships result in two important shifts: a shift to lower calculated partition coefficients and to higher calculated oxygen fugacities relative to the iron-wüstite buffer than are calculated from the raw data.

Table 1. Results of multivariate regression

P (GPa)	T (K)	n	α	β (ΔIW)	χ (NBO/T)	δ (T)	ε (P)	R^2	valence
0.5	2100	5	2.85 (24)	-1.37 (17)	-1.31 (11)	-	-	0.98	5.5 (7)
1	2100	12	1.77 (25)	-1.17 (13)	-0.79 (6)	-	-	0.97	4.7 (5)
2	2300	15	2.13 (23)	-1.23 (13)	-0.85 (6)	-	-	0.97	4.9 (5)
2	2450	8	2.05 (17)	-1.13 (9)	-0.83 (4)	-	-	0.99	4.5 (4)
2	2600	14	1.95 (31)	-1.36 (17)	-0.83 (7)	-	-	0.97	5.4 (7)
2	2300 - 2600	37	1.88 (40)	-1.21 (9)	-0.86 (4)	642 (1010)	-	0.96	4.8 (4)
6	2300	12	2.78 (20)	-1.01 (7)	-0.98 (5)	-	-	0.99	4.0 (3)
6	2700	6	1.9 (1.1)	-1.24 (43)	-0.77 (26)	-	-	0.94	4.9 (1.7)
6	2300 - 2700	18	2.21 (46)	-1.05 (12)	-0.92 (8)	782 (841)	-	0.97	4.2 (5)
11	2400	4	1.90 (35)	-0.85 (24)	-0.74 (7)	-	-	0.99	3.4 (1.0)
18	2500	6	1.32 (40)	-1.13 (23)	-0.68 (12)	-	-	0.94	4.5 (9)
0.5 - 2	2100 - 2700	54	1.75 (16)	-1.18 (7)	-0.85 (3)	-	0.21 (3)	0.97	4.7 (3)
6 - 18	2300 - 2700	28	2.56 (27)	-1.09 (11)	-0.85 (7)	-	-0.05 (1)	0.95	4.4 (4)

Errors in brackets listed as one standard error in the least significant digits

Discussion: The siderophile element geochemistry of the modern mantle can accurately reflect the conditions of core formation if the process achieved equilibrium. The experimental partitioning results showing that high pressure and temperature can apparently account for Ni and Co abundances in Earth's mantle still provide the most robust geochemical evidence for a deep, Hadean magma ocean. Here we model core formation scenarios with constraints provided by Ni, Co, and now W.

Figure 1 shows the effect of pressure and fO_2 (relative to the IW buffer) on the W partition coefficient, as well as the value of D needed for bulk equilibrium of the core and mantle of the Earth, Mars, and Vesta. We have fixed the nbo/t parameter to reflect complete melting of a peridotite magma ocean (nbo/t = 2.6). We did not include a temperature term as we were unable to detect a statistically significant effect. Also plotted on Figure 1 are appropriate representations of the pressure and fO_2 conditions predicted in a number of siderophile element models, including those based on elements other than W [19, 20], as well as multi-element models that involved W [4, 5, 21].

For the Earth we find that Ni, Co and W experiments at equilibrium provide "fits" to the Earth's mantle abundances within an fO_2 range of IW-2 to -2.4, consistent with estimates for bulk Earth Fe/FeO. Our data allow high pressure equilibration (35-45 GPa), and do not place any further constraints on temperature, such that our solutions are consistent with those for Ni and Co [22]. Higher pressures are allowable if carbon is a light element in the core, and a range of cosmochemically consistent S contents are permissible.

For a Martian magma ocean at 6 GPa, fO_2's in the range of IW-1 to -2 provide the best fits, and this range is increased through the addition of S and C – consistent with cosmochemical estimates. Fits for Vesta (<0.5 GPa) occur in a similar fO_2 range to Mars and can accommodate a range of S and C contents. Such small bodies may not melt completely, and so nbo/t could vary significantly from peridotitic; fits for Vesta are also easily obtained at nbo/t = 2.0 and IW-1. The moon is the least constrained of the bodies modeled here because of its unknown core size; however, for reasonable estimates, it seems that more oxidizing conditions (IW-0.5 to -2) are most appropriate, but a smaller core would dictate more reducing conditions.
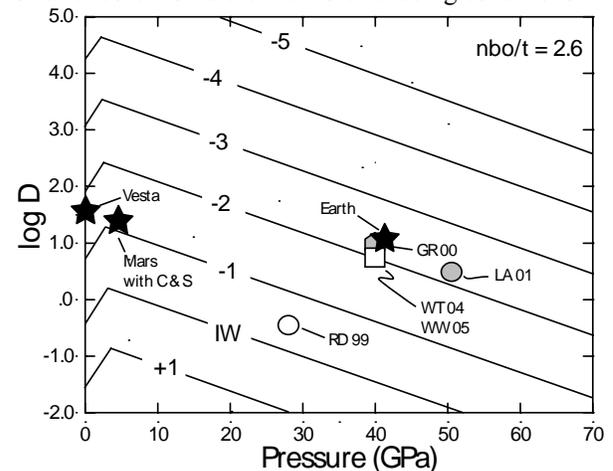

Figure 1: Magma ocean conditions consistent with equilibrium partitioning for Ni, Co, and W for several bodies (stars) as well as previously suggested magma ocean conditions from the literature.

References: [1] *Halliday, Nature, 2004* [2] *Yin, et al. Nature, 2002* [3] *Kleine et al. Nature, 2002* [4] *Righter & Drake, EPSL, 1999* [5] *Wade & Wood, EPSL, 2005* [6] *Walter & Thbault, Science, 1995* [7] *Cottrell & Walker, GCA, 2006* [8] *Cottrell & Walker, EOS Trans. AGU, 2006* [9] *Uhrenius, Caphad, 1980* [10] *Ueshima et al. JISIJ, 1980.* [11] *Chabot et al. GCA, 2006* [12] *Dasgupta & Walker, EPSL, subm.* [13] *Ertel et al. GCA, 1996* [14] *Righter, Annu.Rev.EarthPlanet.Sci., 2003* [15] *Jana & Walker, EPSL, 1997* [16] *Schmit, et al. GCA, 1989* [17] *Jaeger & Drake, GCA, 2000* [19] *Li & Agee, GCA, 2001* [20] *Gessmann & Rubie, EPSL, 2000* [21] *Walter & Trones, EPSL, 2004* [22] *Chabot, et al. GCA, 2005.*