METAL–SILICATE PARTITIONING OF TUNGSTEN FROM 10 TO 50 GPa. G.A. Shofner[1], A.J. Campbell[2], L. Danielson[3], Z. Rahman[3], and K. Righter[4], [1]Towson Univ., Dept. of Physics, Astronomy and Geoscience, Towson, MD 21204, gshofner@towson.edu, [2]Univ. of Chicago, Dept. of the Geophysical Sciences, Chicago, IL 60637, [3]Jacobs Technologies, NASA JSC, Houston, TX 77058, [4]NASA Johnson Space Center, Houston, TX 77058.

Introduction: Geochemical models of core formation are commonly based on core and mantle abundances of siderophile elements that partitioned between silicate and metal in a magma ocean in the early Earth. Tungsten is a moderately siderophile element that may provide constraints on the pressure, temperature, composition, and oxygen fugacity conditions, and on the timing of core formation in the Earth. Previous experimental studies suggest that pressure exerts little to no influence over W metal–silicate partitioning up to 24 GPa[1-8], and indicate that the stronger influences are temperature, composition, and oxygen fugacity. However, core formation models based in part on W, predict metal–silicate equilibration pressures outside the available experimental pressure range, requiring extrapolation of parameterized models[3,5,6,7]. Therefore, higher pressure experimental data on W were needed to constrain this important parameter.

Experiments: We measured the partitioning behavior of W in high pressure and temperature experiments using the multi-anvil press (MAP) in the high pressure lab at NASA-JSC, and using laser-heated diamond-anvil cells in the Laboratory for Mineral Physics at the University of Maryland (UMD). Starting materials consisted of a mixture of natural peridotite and metal powders with approximately 2:1 and 5:1 wt% silicate to metal ratios for MAP and LHDAC experiments, respectively. The metals consisted of Fe and W in a ratio of approximately 5:1 wt%.

The MAP experiments were conducted using COMPRES standardized octahedral assemblies with five experiments in MgO capsules and three in graphite capsules. The experimental run temperatures ranged from approximately 2400 to 2700 K, and pressures ranged from 10 to 26 GPa.

LHDAC experiments consisted of a mixed silicate and metal foil that was approximately 5-8 microns thick, sandwiched between two insulating peridotite layers. Pressure calibration was by ruby fluorescence. Temperatures were determined by fitting measured thermal emissions to the Planck radiation function. Two experiments were at 3800 K and a third at 4400 K. Pressures ranged from 28 to 50 GPa. LHDAC samples were recovered for compositional analysis using a FEI Quanta 3D FEG focused ion beam (FIB) at NASA-JSC, yielding sample sections approximately one micron thick (Figure 1).

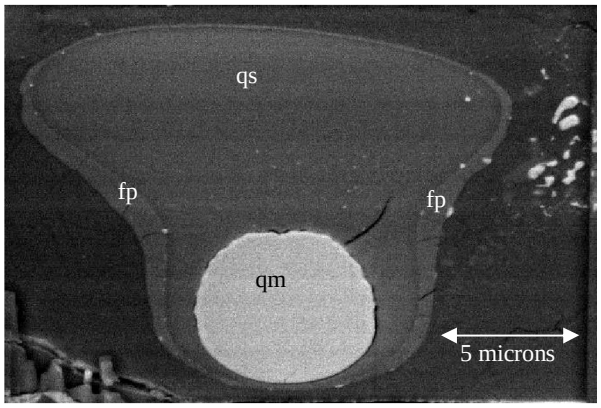

Figure 1. LHDAC sample G36; P = 28 GPa and T = 3800 K; qs-quenched silicate melt, qm-quenched metallic liquid, fp-ferropericlase.

Recovered samples were analyzed using electron microprobes at both NASA-JSC (Cameca SX-100) and UMD (JEOL JXA-8900R).

Results and Discussion: Liquid metal/liquid silicate partition coefficients (D_W) were calculated for each experiment using the mass fractions of W in the metal and silicate phases. Experimental oxygen fugacity was determined from the Fe contents of coexisting silicate and metallic melts, assuming ideal solutions.

Using the present data combined with literature data[1,2,4,5,6,7,8], the metal-silicate partitioning of W was parameterized using multiple linear regression to yield the regression equation $\log D_W (\pm 0.30) = a + b\,(\Delta IW) + c / T + d\,P / T + e\,\Sigma f_i X_i + f\,X_C + g\,X_S$; the silicate compositional parameters ($f_i X_i$) are the mole fractions of SiO_2, Al_2O_3, CaO and MgO, and the metal parameters X_C and X_S are the mole fractions of C and S. Regression coefficients and their 1-sigma uncertainties are: a = 1.07 (0.61), b = -1.41 (0.12), c = -2669 (550), d = -83 (11), e [SiO_2 = 2.49 (0.80), Al_2O_3 = 5.99 (1.63), CaO = -10.4 (1.21), MgO = -3.10 (0.79)], f = 1.78 (0.33), and g = -2.75 (0.78).

Using this regression equation, log D_W was calculated along a peridotite liquidus[9,10] with fO_2 = -2.3 ΔIW, silicate compositional terms of X_{SiO2} = 0.38, X_{Al2O3} = 0.02, X_{CaO} = 0.03, and X_{MgO} = 0.51, and metal compositional terms of X_C = 0.009 and X_S = 0.03. The result is that W is increasingly lithophile with increas-

ing pressure along a peridotite liquidus, i.e. in a deepening magma ocean. Isolating the pressure and temperature dependencies by calculation along isobars and isotherms, log D_W varies by approximately 1.4 log units over 0-60 GPa, and by approximately 1.0 log unit over 2000-4000 K. Within uncertainties, these relationships indicate that the pressure and temperature dependencies are of roughly equal importance across a P-T range applicable to probable conditions of a deep magma ocean.

Applying this parameterization, and literature parameterizations[11] for Ni and Co, to the problem of core formation in the Earth, a pressure-temperature solution of 50 GPa and 3600 K was determined along a peridotite liquidus for a single-stage, magma ocean core formation model. A total pressure–temperature solution space of 48-54 GPa and 3500-4200 K was determined (Figure 2). A continuous accretion model based on exponential planetary mass growth rate, linear mantle and core density growth rates, and homogeneous accretion resulted in a pressure-temperature solution of 59 GPa and 3900 K that represents the final depth of the magma ocean along a peridotite liquidus.

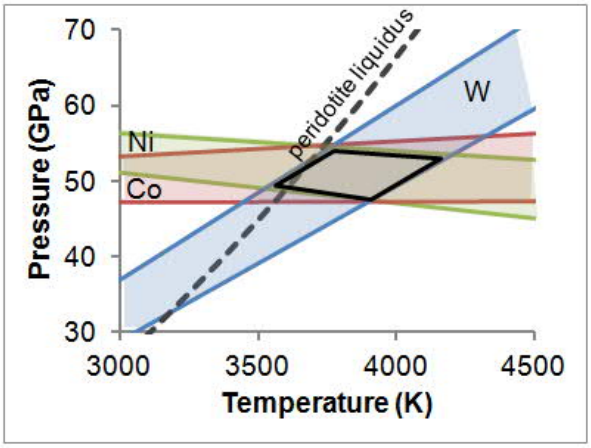

Figure 2. Pressure-temperature solution space for equilibrium core formation model. Colored regions are ranges of P-T conditions where the predicted partition coefficients equal core-mantle partition coefficients; widths of bands represent uncertainty on core and mantle abundances. Black polygon is the total solution space for W, Ni and Co. Liquidus is a fit to average of a peridotite liquidus and a chondritic mantle liquidus[9,10]. Core-mantle partition coefficients based on silicate Earth and core compositional models[12,13,14].

The timing of core formation in the Earth can be constrained using the Hf-W geochronometer. The magnitude of the W isotopic anomaly in this system is directly related to the partitioning of W into the core. Using the W parameterization of this study, the Hf/W ratio is predicted to decrease substantially with increasing pressure and depth. A primitive mantle Hf/W = 20 is predicted along a peridotite liquidus at approximately 53 GPa and 3800 K (Figure 3).

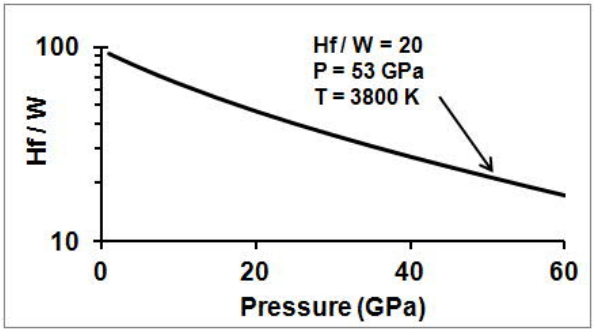

Figure 3. Evolution of Hf/W ratio during core formation, calculated along a peridotite liquidus, assuming 60% volume fraction mantle melting and 3 mol% S in the core.

Conclusions: This research has extended the experimental pressure and temperature ranges of W metal-silicate partitioning data and thereby provides better constraint on model predictions that previously required extrapolation from lower P-T data. We find that the temperature and pressure effects on W metal-silicate partitioning are essentially equal. Single-stage and continuous accretion models based on W, Ni and Co show pressure and temperature ranges indicative of equilibrium core formation in a deep magma ocean; a Hf/W ratio that is consistent with a primitive mantle value was predicted at similar pressure-temperature conditions.

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