

NICKEL PARTITIONING BETWEEN LIQUID METAL AND LIQUID SILICATE IN THE LHDAC: TECHNIQUES FOR ACHIEVING RELIABLE PARTITION COEFFICIENTS. Elizabeth Cottrell¹, Yingwei Fei², Angele Ricolleau², and Vitali Prakapenka³. ¹Department of Mineral Sciences, National Museum of Natural History, Smithsonian Institution, Washington, DC, 20560, ²Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC, 20015. ³GSECARS, Advanced Photon Source, Argonne National Laboratory, IL, 60439.

Introduction: Vast expanses of pressure-temperature space in the Earth lie beyond the reach of the piston cylinder and multi-anvil, yet more and more the Earth science community identifies these deep regions as key players in the early stages of Earth's evolution as well as major influences on modern mantle chemistry and dynamics. Interpretation of geochemical observations that constrain ancient and modern mantle processes require experimental element partitioning data at static pressures only obtainable through the use of the laser-heated diamond anvil cell (LHDAC). The use of LHDAC for element partitioning has been limited because there has been no systematic demonstration that reproducible partition coefficients can be obtained. Efforts are inhibited by the technical difficulty of the experiments, sample recovery, and analysis at small spatial scales, as well as ambiguity regarding the attainment of chemical equilibrium. Here we suggest a litmus test for equilibrium partitioning studies in the LHDAC and present new techniques to obtain reliable partition coefficients. As a test case, we choose to look at Ni partitioning between liquid metal and liquid silicate because (1) it is one of the most well studied systems [1-5] (2) D_{Ni} (met/sil) depends strongly on pressure, and (3) extension of the pressure range would be of direct use in modeling a Hadean magma ocean on Earth.

Methods: Use of LHDAC for element partitioning requires extensive, systematic tests to prove its viability. Our strategy is to apply the same experimental rigor to the DAC that we apply to partitioning experiments in the multi-anvil (MA): (1) Start with systems that are well characterized at low P and compare LHDAC results to MA for overlapping P, T, X and fO_2 (2) Test for equilibrium *at all PT conditions* by performing "reversals" (3) Test for reproducibility by performing "replicates" of each experiment. (4) Monitor phase assemblage and melting using X-ray diffraction (XRD). (5) Characterize products appropriately – while EMPA may be too coarse a tool for the fine spatial scales of LHDAC, ATEM may be too fine to probe quench products. Here we report preliminary results from NanoScanning electron micro-probe (nanoSEM) and electron microprobe (EMP); analysis with nano secondary ion microprobe (nanoSIMS) is underway.

Experimental. Two starting materials homogeneous at the $<10\mu\text{m}$ scale with bulk compositions approximately equal to chondritic composition C1-C from [6] were created. Glasses in the system FeO-CaO-SiO₂-

Al₂O₃-MgO \pm saturation with NiO were equilibrated in a rapid-quench gas mixing furnace. The non-NiO bearing glass was finely ground with Fe and Ni metal powders ($3\mu\text{m}$) while the NiO saturated glass was mixed with Fe powder alone. Both starting materials were hot sintered in a piston-cylinder, double-side polished to $13\mu\text{m}$ thickness, and loaded into each experiment such that the former approached equilibrium from the "normal" or "oxidation" direction while the latter approached equilibrium from the "reverse" direction of reduction. In this manner every cell contained a pair of "reversal" experiments to test for equilibration (Figure 1).

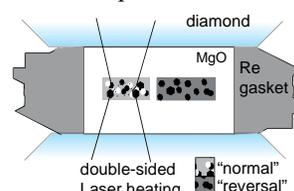


Figure 1. Experimental schematic.

Experiments presented here used uniform $15\mu\text{m}$ thickness MgO insulators, Re gaskets, and 275-350 μm culet anvils.

Experiments were conducted at the Advanced Photon Source (APS) sector 13-IDB with double-sided heating using the recently installed diode pumped fiber laser system. 1-3 spots were heated on each sample in the cell. The laser heating system delivered exceptional stability and a flat top profile; this enabled us to generate complete melt in each experiment. After converting the starting glass to a crystalline mantle assemblage at low temperature, we confirmed melting by the disappearance of all diffraction lines (save the pressure medium) and the appearance of diffuse scattering. Temperature was measured on both sides by fitting the Planck radiation function to the thermal radiation spectrum. All experiments presented here equilibrated within $\pm 250\text{K}$ of their target temperature, *as a melt*, for 30 seconds to 3 minutes on *both* the "upstream" and "downstream" sides before laser power was shut off for the quench. Time series and reversal experiments demonstrate that equilibrium partitioning in this system is achieved in ≤ 5 seconds in the MA [6]. Pressure was determined from the unit cell parameters of the MgO pressure medium [7]. Experimental pressures ranged from 15 GPa (within the MA range) to nearly 60 GPa and super-liquidus temperatures ranged from 2750-5450K.

Analytical. Samples were recovered and finely polished for X-ray mapping analysis (Figures 2, 3) with Smithsonian's FEI NOVA nanoSEM600 FEG Variable Pressure Scanning Electron Microscope. Ideally all heated spots would be exposed in a single polish,

but in reality, 1-2 spots in a cell must be fully analyzed before further polishing is needed to expose new spots. At 15kV and 730pA we achieve 350, 500, and 750nm spatial resolutions for Ni, Al, and Fe respectively. For an alloy with 20% Ni, precision is <2% and we reproduce EMP analyses to within 0.1%.

Experiments are in the process of being analyzed with Smithsonian's JEOL JXA-8900 microprobe and Carnegie's new NanoSIMS 50L ion microprobe which is being developed for trace element analysis. With the NS50L we achieve similar precision and lateral spatial resolution to the NanoSEM, with the additional benefit of nanometer scale resolution with depth as there is no excitation volume.

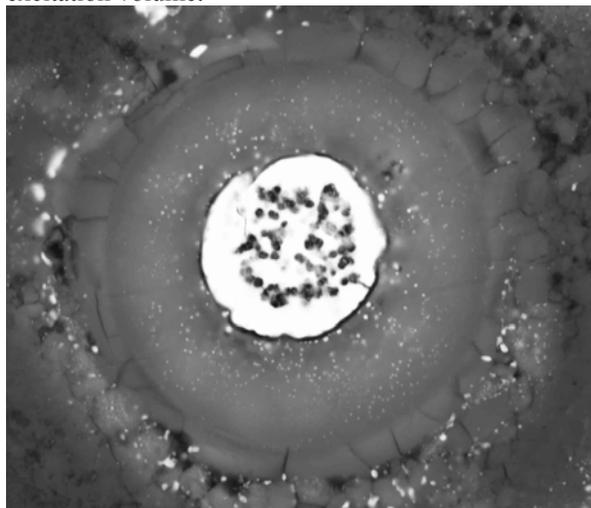


Figure 2: BSE image of experiment c23585c. Field of view is 14 μ m across.

Results and Discussion: All experiments quenched to a homogenous silicate glass with a central immiscible FeNi alloy blob (Figure 2, 3). The glass is rimmed with a magnesio-wüstite reaction halo, as would be found in an equivalent MA experiment. The quenched liquid alloys have central dark spots in back scattered (BSE) images on the order of 50-500nm which in some cases appear to be carbon-rich (from the hot sinter in graphite capsule), or some combination of Fe \pm Si \pm O-rich, however characterization is still ongoing. The quenched liquid metals are all FeNi alloys, though we note that none of them started as such. The silicate glasses all have between 1 and 6 wt% Ni though, again, glasses were originally 8% Ni or Ni-free.

Table 1 presents mostly EDS results from the nanoSEM as described above. We estimated the oxygen fugacity of the experiments relative to the iron-wüstite buffer as $\Delta IW = 2\log(X_{FeO-g}/X_{Fe-alloy})$. Experiments recorded oxygen fugacities from IW to IW-0.8.

Preliminary weight-based partition coefficients (D) for experiments in the range of the MA provide a good

match to those expected for the same conditions from the analysis of [1] – both for “normal” and “reversal” experiments. At the highest pressure (60GPa) our measured D is slightly more siderophile than would be predicted from extrapolation of the MA data (Table 1).

Table 1: EDS Results

expt	N/R	T(K)	P(GPa)	ΔIW	lnD meas.	lnD predicted
c23585c	R	4000	20	-0.68	2.51*	2.49
c50B	N	5450	58	-0.79	1.70	1.18
c35B	N	2750	16	0.03	2.43	2.49
c33C	R	4000	42	-0.39	1.36	1.29

N/R = “normal” or “reversal” expt.

lnD predicted from the regression coefficients of [1]

*From EMP which confirmed EDS

While preliminary, these results are a promising first step toward establishing LHDAC as a tool for measuring equilibrium partition coefficients.

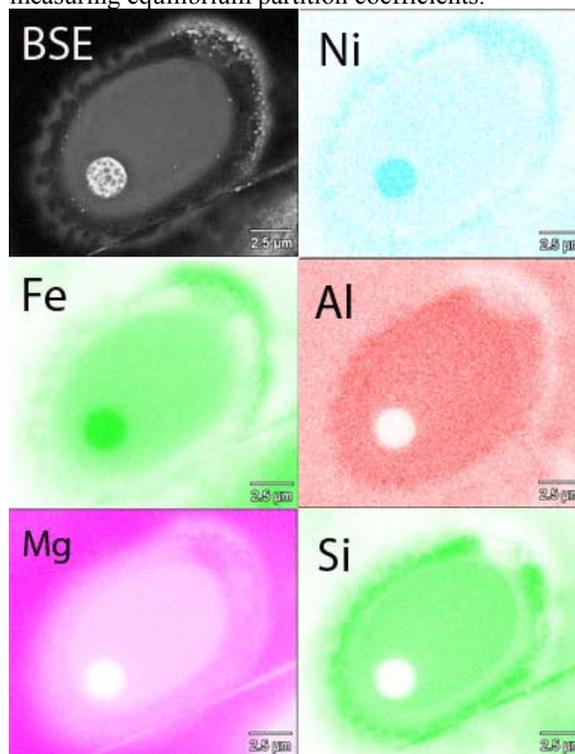


Figure 3: BSE and X-ray EDS mapping of experiment c33C. Scale bar is 2.5 μ m.

Acknowledgements: E.C. thanks T. Gooding for sample prep. and T. Komabayashi for help at APS.

References:

- [1] Chabot, et al. GCA, 2005. [2] Li and Agee. GCA, 2001. [3] Li and Agee. Nature, 1996. [4] Bouhifd and Jephcoat. EPSL, 2003. [5] Tschauner, et al. Nature, 1999. [6] Thibault and Walter. Geochim. Cosmochim. Acta, 1995. [7] Speziale, et al. JGR B: Solid Earth, 2001.