

PARTITIONING OF MODERATELY VOLATILE ELEMENTS IN MAJOR ROCK FORMING MINERALS AT LOW PRESSURE: IMPLICATIONS FOR THE MOON Kathleen E. Vander Kaaden¹, David S. Draper², Francis M. McCubbin², Richard L. Rowland¹, Justin J. Reppart¹, Clive R. Neal³, David C. Burney³, and G. Jeffrey Taylor⁴. ¹Jacobs, NASA Johnson Space Center, Mail Code XI3, Houston, TX 77058, ²ARES NASA Johnson Space Center, 2101 NASA Parkway, Houston, TX 77058, ³Department of Civil Engineering and Geological Sciences, University of Notre Dame, Notre Dame, Indiana 46556. ⁴Hawaii Institute of Geophysics and Planetology, University of Hawaii, Honolulu, Hawaii 96822 (kathleen.e.vanderkaaden@nasa.gov).

Introduction: The partitioning of moderately volatile elements (50% condensation temperatures between 1300–700 K, [e.g., 1]) and highly volatile elements (50% condensation temperatures ≤ 700 K, [e.g., 1]) between silicate, metal, and sulfide phases is highly informative about lunar bulk composition, differentiation, and magmatic evolution. Although high temperature and pressure experiments to determine the partitioning of elements between these various phases have been conducted previously [e.g., 2 and references therein], the addition of volatile elements to the system complicates the experimental techniques and presents numerous experimental and analytical challenges. One of the more challenging difficulties is the retention of the volatiles in the system over the course of experimentation. Thus only a few studies have examined the partitioning of moderately and highly volatile elements, and fewer studies have been conducted at lunar-relevant pressure (P), temperature (T), oxygen fugacity, and melt compositions [e.g., 3–5]. This sparseness of data hampers the ability to know the fate of moderately and highly volatile elements during the thermochemical evolution of the Moon, including magma ocean crystallization, subsequent mantle overturn, and production of secondary magmas. This current study aims to produce new partitioning data relevant to the role and distribution of the volatile and non-volatile, yet geochemically significant, elements (Co, Ni, Zn, Se, Rb, Sr, Mo, Ag, Cd, In, Sb, Ce, Yb, Tl, Pb, Bi) during the thermal and magmatic evolution of the Moon.

Methods: Experiments are currently underway to explore the partitioning of moderately volatile elements between major rock-forming minerals and melt under lunar conditions using lunar melt compositions. Each experiment is analyzed by the electron microprobe (EPMA) and by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) in order to determine appropriate partition coefficients for the elements of interest.

Starting Materials. Starting materials were synthesized using reagent grade, powdered oxides and carbonates. For this initial study, in order to investigate later stage processes in a lunar magma ocean (particularly the formation of ilmenite), we prepared a synthetic equivalent to Apollo sample 70215, which is a high-Ti mare basalt. Phase relations for this composition have been determined in the past, which

helped to constrain the PT conditions used here [e.g., 6]. A separate trace element mix was made that contained 1000 ppm of each oxide component to allow for small, measurable variations in the trace elements of interest. From here, two final mixes were made. The first mix contained 1000 ppm of the trace element mix combined with the major and minor element mix. The second mix was a combination of the trace element mix and the major/minor element mix in proportions such that Sn will be present at 1000 ppm Sn. The two different doping concentrations will help to assess whether Henrian behavior is exhibited by the trace elements in these experiments.

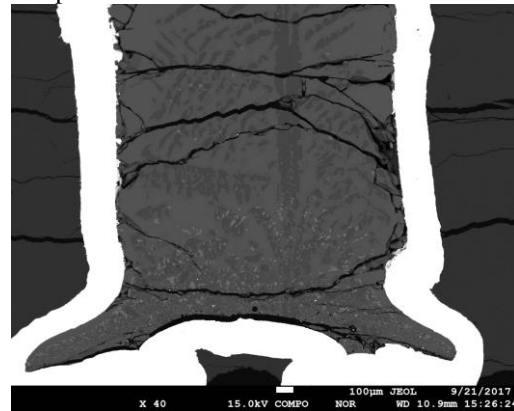


Figure 1. Example experimental charge (A17_10) run at 0.8 GPa and crystallized at 1150 °C. Smooth background is quenched glass, darker lath phases are olivine, and lighter phases are oxides (ilmenite-geikielite solid solution and chromite-ulvöspinel). The bright area around the sample is the AuPd capsule, which was triple crimped and welded at the bottom, shown at the base of the image.

Experimental. Experiments were conducted on both mixes in order to investigate various doping levels and to see if Henry's law was obeyed. All experiments were conducted using the 13 mm Quickpress piston-cylinder apparatus at Johnson Space Center (JSC). Initial experiments were conducted at 0.8 GPa, simulating comparatively shallow magma ocean depths. Each experiment was completed by first packing the starting material into a Au₇₅Pd₂₅ capsule. The capsule was then sealed using a Lambert PUK 5 welder to ensure the volatiles were contained within the capsule during the experiment. The loaded and sealed AuPd capsule was surrounded by a graphite heater and MgO inner parts,

which were placed within a barium carbonate cell (used as the *P* medium during the experimental run). All initial experiments were conducted in the absence of sulfur. The goal of these experiments is to run at *T*s corresponding to melt fractions ranging from near-liquidus to no less than 25% liquid in order to ensure the presence of reliably analyzable melt pools. Each experiment was first taken to a superliquidus *T* of 1350 °C, determined from the phase diagram by [6], and held for 12 mins to fully melt the starting materials. From here, each run was cooled to the target *T* initially at 500 °C/min and slowing to 100 °C/min upon approaching the final *T* to ensure the growth of analyzable crystals and to avoid an overshoot of the desired crystallization temperature [e.g., 7]. Experiments were held at crystallization *T* for 4 hours. An example run product is shown in Figure 1.

EPMA. All experimental run products were mounted in epoxy, polished to a 0.3 µm finish, carbon coated, and initially characterized and analyzed for major and minor elements using the JEOL 8530F microprobe at JSC. All analyses were conducted using an accelerating voltage of 15 keV and a beam current of 15 nA. A 5 µm spot size was employed for glass analyses and a focused beam was used for analyses of mineral phases. Elements analyzed include Si (VG-2 glass and olivine used as standards), Mg (olivine and diopside), Na (albite), Al (VG-2 glass), P (apatite), Ca (A99 glass), Ti (rutile), K (orthoclase), Cr (chromite), Ba (benitoite), Fe (A99 glass and olivine), and Mn (spessartine). Ba was included in the analyses to test for contamination from the *P* medium. If large quantities were detected, it would imply there was a breach in the sealed capsule.

LA-ICP-MS. All trace elements will be analyzed by LA-ICP-MS at the Midwest Isotope and Trace Element Research Analytical Center at the University of Notre Dame under the direction of C. Neal. A New Wave 213 nm laser ablation system operating at a 55 µm spot size is connected to a Thermo Finnigan Element2 High Resolution ICP-MS with a He carrier gas and an Ar plasma. Instrument drift throughout the analyses will be monitored using Mn in olivine as an internal standard and data calibrated using the NIST610 external standard. In all other phases, Ca will be used for the drift correction, and NIST612 for data calibration. An accurate and precise method of determining trace elements has been documented in [8–10] and will be adapted for the elements of interest in this study.

Results: Thus far we have conducted experiments on both compositions in order to ensure Henrian behavior is being followed based on our doping levels of moderately volatile and geochemically significant elements. We have run a time series to determine the time needed for the melting step to fully melt and

homogenize the starting materials. Experiments were run at 0.8 GPa and 1350 °C and held for 4 mins, 10 mins, and 30 mins. Based on our EPMA data, 10 mins is sufficient time to melt and homogenize the starting materials. Therefore, for all subsequent crystallization experiments, the melting step was held for 12 mins. We have completed three crystallization experiments at 0.8 GPa and 1200 °C, 1150 °C, and 1125 °C, which were all heated first to 1350 °C for 12 mins then held at their respective crystallization *T* for 4 hours. Phases present in these experiments can be found in Table 1. The lowest *T* run product with both olivine and melt present (A17_10) yields an Fe-Mg K_D value of 0.29, suggesting our experimental charges reached a steady state within 4 hours. Work is ongoing to collect LA-ICP-MS analyses of all phases present in order to determine partitioning coefficients of the volatile and geochemically significant elements of interest. Future work will include lower *T* experiments to reach a melt fraction of ~25%.

Exp #	$T_{\text{xtal}}(\text{°C})$	Phases Present
A17_7	1350	Melt
A17_18	1200	Melt, olivine, ilmenite-geikielite SS
A17_10	1150	Melt, olivine, chromite-ulvöspinel, ilmenite-geikielite SS
A17_14	1125	Melt, pyroxene, ilmenite-geikielite SS

Implications of Research: The source(s) of lunar volatiles, the timing of their incorporation into the Moon, and how they have been processed throughout lunar history are among the many unanswered questions regarding the role of volatiles in the lunar interior. This research will generate a new database of partition coefficients across the entire suite of highly volatile and geochemically significant elements relevant to lunar conditions, providing a means to assist answering these critical questions.

References: [1] Lodders K., (2003) *Astrophys. J.* 591:1220–1247. [2] Leo A.C., et al. (1971) *Chem. Rev.*, 71:52–616. [3] Kiseeva E.S. & Wood B.J. (2013) *EPSL*, 383:68–81. [4] Klemme S.D. et al., (2006) *Chem. Geo.*, 234:251–263. [5] McKay G.A. & Weill D.F. (1976) *PLSC 7th*, 2427–2447. [6] Longhi J., et al., (1974) *PLSC 5th*, 447–469. [7] Draper D.S., et al., (2006) *GCA*, 70:2400–2416. [8] Hui H., et al., (2001) *GCA* 27, 6439–6460. [9] Donohue P.D., et al., (2012) *Geostand. Geoanal. Res.* 36, 61–73. [10] Fagan, A.L., et al., (2013) *GCA* 106, 429–445.