

A SYNTHESIS OF EXPERIMENTAL DATA DESCRIBING THE PARTITIONING OF MODERATELY VOLATILE ELEMENTS IN MAJOR ROCK FORMING MINERALS: IMPLICATIONS FOR THE MOON

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Introduction: Highly volatile elements [condensation temperatures below about 700 K, e.g., 1] and water are highly informative about lunar bulk composition (hence origin), differentiation and magmatic evolution, and the role of impacts in delivering volatiles to the Moon. Fractionation of volatile elements compared to moderately volatile and refractory elements are informative about high-temperature conditions that operated in the proto-lunar disk. Existing data show clearly that the Moon is depleted in volatile elements compared to the bulk silicate Earth. For example, K/Th is ~400–700 in the Moon [e.g., 2] compared to 2800–3000 in Earth [e.g., 3]. A complicating factor is that the abundances of the highly volatile elements in major lunar lithologies vary by approximately two orders of magnitude. Perhaps most interesting, H₂O is not correlated with the concentration of volatile elements, indicating a decoupling of highly volatile elements from the even more volatile H₂O. We contend that this decoupling could be a significant tracer of processes operating during lunar formation, differentiation, and bombardment, and the combination of analyzing both volatile elements and water is likely to provide significant insight into lunar geochemical history. This variation and lack of correlation raises the question: what were the relative contributions of crystallization in the magma ocean, subsequent mantle overturn, production of secondary magmas, and addition of volatiles by large impacts in producing this apparently large range in volatile abundances? This current study will 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.

Literature Review: Literature data were compiled using the Geochemical Earth Reference Model Partition Coefficient Database (earthref.org/KDD) for the elements of interest (Figure 1). Partition coefficients are the weight ratios of the element of interest between the phases under consideration (e.g. mineral/melt). Assuming henrian behavior, a D value at a given pressure and temperature remains constant, regardless of the concentration of X in the system. Data were compiled strictly for natural and synthetic lunar compositions (e.g., basalts, KREEP basalts, mare basalts, low-K Fra Mauro basalts) and partition

coefficients were found only for Co, Zn, Rb, Sr, Mo, Sb, Ce, and Yb [4–10]. Minerals of interest for this study included oxides (i.e. ferropseudobrookite, ilmenite, karrooite, and spinel), olivine, plagioclase, pyroxene, and garnet.

The combined literature data (Figure 1) show that Co is incompatible (i.e. $D < 1$) in oxides and pyroxene. Zn is incompatible in pyroxene, compatible (i.e. $D > 1$) in some oxides and incompatible in others, a discrepancy that may be reconciled in the current study. Rb, Mo, and Sb are incompatible in oxides, but there is only one experimental study for each of these elements looking at lunar compositions. Sr is compatible in plagioclase and incompatible in pyroxene, garnet, and oxides. Ce is consistently incompatible in plagioclase, pyroxene, olivine, and oxides. Yb is compatible in garnet but incompatible in plagioclase, pyroxene, olivine and oxides. Not only are there discrepancies present in the literature (e.g. Zn has been shown to be both compatible and incompatible in ilmenite), there are no data available for Ni, Se, Ag, Cd, In, Tl, Pb, or Bi in lunar compositions under lunar relevant conditions.

Approach: Experiments are currently underway using two starting materials that were synthesized using reagent grade oxides and carbonates. First, in order to explore magma ocean processes, specifically late in magma ocean crystallization when Fe/Mg is elevated, we are using a mix similar to the Apollo 12002 sample that is an olivine-bearing, low-Ti mare basalt. To investigate later stage processes, in particular the formation of ilmenite, we are also using a synthetic equivalent to sample 70215, which is a high-Ti mare basalt. Phase relations for both of these compositions have been determined in the past, which will help to constrain the *PT* conditions used here [e.g., 11, 12].

All experiments will be conducted using the 13 mm Quickpress piston-cylinder apparatus at Johnson Space Center (JSC). Initial experiments are being conducted at 1 GPa, simulating comparatively shallow magma ocean depths. Once the starting material is packed into the AuPd capsule, the capsule is sealed using a Lambert PUK 5 welder to make sure the volatiles are contained within the capsule during the experiment. The loaded and sealed AuPd capsule are placed within a barium carbonate cell, which is used as the pressure medium during the experimental run, surrounded by a graphite heater and MgO inner parts (e.g. spacers, sheaths). All

initial experiments are being conducted in the absence of sulfur. We are in the process of conducting experiments at temperatures 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 is taken to superliquidus temperatures, determined through use of the compositions respective phase diagram [e.g., 11, 12], and held for several minutes to fully melt the starting materials. From here, each run is cooled to the target temperature to ensure the growth of analyzable crystals [e.g., 13].

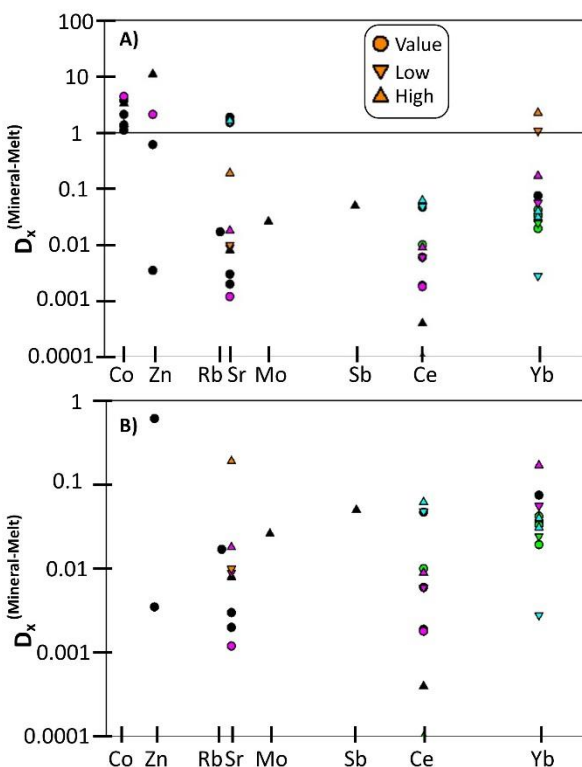


Figure 1. Partition coefficients available in the literature for lunar compositions. A) All available data. B) All available data with a D value less than 1. Olivine is green, plagioclase is cyan, pyroxene is pink, garnet is orange, and oxides are black. High and low refer to the maximum and minimum of values, respectively when a range of partition coefficients was reported.

All experimental run products are initially characterized and analyzed using the JEOL 8530F microprobe at JSC. Due to the low concentrations of trace elements, only major elements are analyzed using the microprobe. All trace elements will be analyzed by LA-ICP-MS at the Midwest Isotopes and Trace Element Research Analytical Facility at Notre Dame under the

direction of C. Neal. An accurate and precise method of determining trace elements has been documented in [14–16] and will be adapted for the elements of interest in this study.

Implications of Research: The topic of lunar volatiles has gained significant attention over the last decade [e.g., 17, 18]. Where these volatiles came from, when they were incorporated into the Moon, how they have been processed throughout lunar history, and many other questions regarding the role of volatiles in the lunar interior remain unanswered. The proposed research will generate a database of partition coefficients across the entire suite of highly volatile and geochemically significant elements relevant to lunar conditions, a set of data that is crucial to our understanding of volatiles during lunar history and one that does not yet exist. Furthermore, this database, combined with sample studies currently underway, will provide a new dimension towards understanding fundamental questions regarding the role of volatile elements in the thermal and magmatic evolution of the Moon.

References: [1] Lodders, K., (2003) *The Astrophysical Journal*, 591: p. 1220–1247. [2] Taylor, S.R., (1982) *Lunar and Planet. Inst. Houston, TX*. p. 307. [3] Sun, S.S. and W.F. McDonough, (1989) *Magmatism in the Ocean Basins*, S. A.D. and M.J. Norry, Editors. *Geol. Soc. Spec. Publ.* p. 313–345. [4] Dwarzski, R.E., et al., (2006) *American Mineralogist*, 91: p. 1536–1546. [5] Klemme, S., et al., (2006) *Chemical Geology*, 234: p. 251–263. [6] McKay, G.A., (1986) *Geochimica et Cosmochimica Acta*, 50: p. 69–79. [7] McKay, G.A. and D.F. Weill. (1976) *Proc. 7th Lunar Sci. Conf: Petrogenetic studies of mare and highland rocks*. Pergamon Press, New York. [8] McKay, G.A. and D.F. Weill. (1977) *Proc. 8th Lunar Sci. Conf*. Pergamon Press, New York. [9] Ringwood, A.E., (1970) *Journal of Geophysical Research*, 75(32): p. 6453–6479. [10] Weill, D.F. and G.A. McKay. (1975) *Proc of the 6th Lun. Sci. Conf*. Pergamon Press, New York. [11] Longhi, J., et al., (1974) *Proc. Lunar Sci. Conf.*, 5th: p. 447–469. [12] Walker, D., et al., (1976) *Geol. Soc. Am. Bull.*, 87: p. 646–656. [13] Draper, D.S., et al., (2006) *Geochimica et Cosmochimica Acta*, 70: p. 2400–2416. [14] Hui H., et al., (2001) *Geochimica et Cosmochimica Acta* 27, 6439–6460. [15] Donohue, P.D., et al., (2012) *Geostandards & Geoanalytical Research* 36, 61–73. [16] Fagan, A.L., et al., (2013) *Geochimica et Cosmochimica Acta* 106, 429–445. [17] Barnes, J.J., et al., (2016) *Nature Communications*, 7: p. 11684. [18] McCubbin, F.M., et al., (2010) *PNAS*, 107(25): p. 11223–11228.