MODERATELY VOLATILE ELEMENTS (MVEs) IN THE MARTIAN AND LUNAR MANTLES Burney, D.[1], Neal, C.R.[1], and Day, J.M.D.[2] [1]University of Notre Dame, Notre Dame IN, 46556; [2]University of California San Diego, La Jolla, CA 92093 dburney@nd.edu, neal.1@nd.edu.

Introduction: Moderately volatile elements (MVEs) are those with condensation temperature of 650-1350K [1]. They potentially contain information lost by their highly volatile counterparts (H_2O, CO_x, F, Cl, and S) regarding high temperature processes that occur during planetary formation, differentiation, or large impacts. They are incompatible in most mantle mineral phases, and have a trace abundance (low-ppm to low-ppb) in mantle-derived basalt samples. Quantification of the MVEs gives an indication of the overall volatility of a planetary body, or reservoirs within that body, as they are less likely to be completely lost during high temperature evolutionary events and are potentially fractionated to allow fingerprinting of such events [1].

The Moon was formed as the result of a Giant Impact between a Mars-sized body and the early Earth [2-4]. This collision ejected material from Earth into orbit to create a proto-lunar disc. This material either fell back to Earth, or gravitationally coalesced to form the Moon [3,4]. The heat from these processes had the capability of volatilizing a large amount of material, and the early Moon was mostly, if not entirely, molten. As this lunar magma ocean (LMO) cooled it began to crystallize a predictable sequence of minerals [5]. Early crystallizing Mg-rich phases such as olivine and orthopyroxene sank to the bottom of the LMO to produce a cumulate mantle. Later phases were more enriched in Fe, and contained ilmentite ($FeTiO_3$) as incompatible Ti became enriched in the melt [4]. The last dregs of the LMO is urKREEP due to being enriched in incompatible elements such as K, Rare Earth Elements, and Phosphorus [6]. This mantle cumulate was gravitationally unstable and caused a mantle-wide overturn event that mixed early- and late-stage cumulates [7]. The resulting compositional heterogeneity of the lunar mantle is still debated, but the diverse lunar basalt compositions are modeled to be partial melts from distinct mantle reservoirs [8]. Generally speaking, the very-low- and low-Ti basalts are derived from sources dominated by early mantle cumulates, while the high-Ti basalts are derived from sources dominated by late-stage cumulates [8].

Mars was formed through a process of accretion between 0 and 15 Myr after Solar System formation [9,10]. This accretionary model is similar to both the Earth and Moon in that material was gravitationally attracted to each other, and gravitational heating resulted in a molten proto-planet. Both the Earth and Mars are thought to have experienced magma oceans as their initial stage of differentiation [11,12]. For reasons that are still debated Mars is smaller than Earth, which has had an effect on its thermal evolution [9,13,14]. Evidence of volcanism on Mars is ubiquitous in the form of flood basalts, lava flows, and volcanos, but Mars appears to be no longer volcanically active and has no liquid core or magnetic field [15,16]. This past volcanism was driven by the loss of heat from the martian interior, and was not accompanied by large scale plate tectonics [15]. The tectonic features seen on Mars are due to contraction as the planet cooled, and not to mantle convection which is estimated to have been minimal [15].

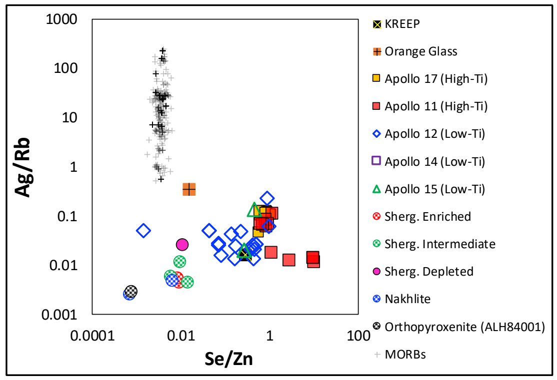

Figure 1: Se/Zn vs. Ag/Rb in lunar and martian samples. Open symbols = low-Ti lunar basalts, closed symbols = high-Ti.

Mars has been shown to have a high volatile content relative to the Moon, which may be due to the absence of a Giant Impact event in its history [17-19]. While fluvial features can be seen on the martian surface, they were created early in Mars history and are no longer being produced on a large scale [20]. While the MVE budget of Mars is not well constrained, the few analyses available show that it is more enriched in certain MVEs (i.e. Rb & Zn) than Earth. This study attempts to constrain the MVEs within the martian mantle and compare these with the Earth-Moon system.

Methods: Solution mode inductively coupled plasma mass spectrometry (SM-ICP-MS) was chosen for its broad elemental spectrum, and its high resolution capabilities. The trace nature of these MVEs makes them especially susceptible to interferences that occur when another element in the sample forms polyatomic interferences that will artificially inflate the measured concentration. To mitigate this, a series of "interference solutions" were designed to quantify, and correct for, the major interferences on the elements of interest [10]. This results in an "interference corrected" concentration in each sample. Standard reference materials (SRMs)

BIR and BHVO were run in conjunction with the lunar samples to ensure analytical accuracy.

Samples: The MVEs chosen for this study are Zn, Se, Rb, Ag, Cd, In, Sb, Tl, Pb, & Bi, and have been measured in 10 powdered whole rock samples comprised of 7 shergottites (Dar Al Gani 476, Shergotty, EETA 79001 Lithologies A & B, Los Angeles, ALH 77005, Zagami), 2 nakhlites (MIL03346, Nakhla), and orthopyroxenite (ALH84001).

Results and Discussion: Zinc is commonly used as a proxy for the entire suite of MVEs due to its relatively high concentrations (low ppm), but it is elevated in martian meteorites relative to lunar samples, and terrestrial MORBs. While this is empirically true for some MVEs (Zn & Rb), the enrichment is not as prevalent in others (Ag & Se) (**Fig 1**). This shows that the MVEs are not behaving uniformally, and using Zn to represent all of them is not warrented.

Shergottites are classified as basalts, and have been subdivided into enriched, intermediate, and depleted categories [21]. Nakhlites are more evolved, and show more cumulate textures [22]. Along with Shergottites, they show evidence of open system metasomatism. ALH 84001 has been identified as an orthopyroxenite cumulate, and has been categorized as distinct from the SNC groups [22]. The MVEs reflect the cumulate nature of the Nakhlites and the orthopyroxenite with respect to Se and Ag (Figs 1 & 2), but show an enrichment in Cd (Fig 2), which may indicate an interaction with a Cd compatible mineral phase such as garnet.

The high- and low-Ti lunar basalt suites, which represent melts derived from late and early stage LMO cumulates respectively, both show distinct compositions relative to the martian suite. This distinction cannot be uniformally categorized as an enrichment or depletion, but may reflect unique geologic partitioning of the MVEs within each respective mantle source. This could indicate that Mars has both volatile enriched reservoirs,

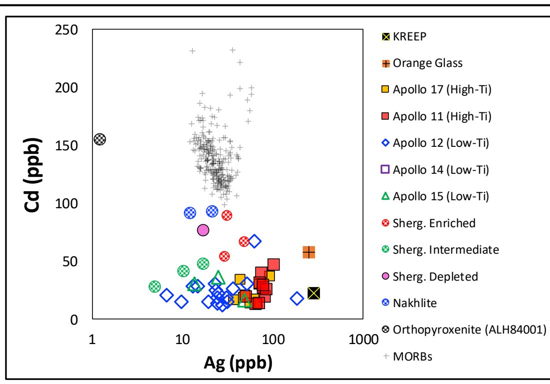

Figure 2: Ag vs. Cd. The martian samples are enriched in Cd relative to Ag, but the Nakhlite and orthopyroxenite samples are the most enriched.

as well as regions that have been degassed, and samples my be sourced these distinct reservoirs. The MVEs show the three Shergottie groups, with the highest values being in the enriched samples, and the lowest values being in the intermediate and depleted samples (**Fig 2**). Some elements (Zn & Cd) appear to have avoided any degassing events and are almost uniformally enriched relative to lunar values. The volatility of martian samples may reflect formation mechanism of each lithology; erupted material has had a chance to degass, while shallow intrusions have the ability to retain volatiles [11]. The type of Shergottite must also be taken into consideration, as the MVEs may not have been affected by degassing as much as the depletions that affect the other elements. Relative to MORB concentrations, both the Moon and Mars basalts show broad depletions. Exceptions to this are Zn, Ag, and Rb which are not always enriched but can show compariable values (Fig 1&2).

Conclusions: Fundamental planetary forming processes effected the volatile distribution in the solar system. While Mars is shown to have volatile rich reservoirs and has been broadly labeled as enriched based on Zn concentrations, these data show a more complicated behavior of the MVE suite. The geochemical spectrum seen in the basaltic shergottites indicate the variation of MVEs in the Martian mantle. Martian geology also introduces the capability of redistributing elements through processes such as metasomatism which has not occurred on the Moon to the same extent.

References: [1] Palme, H. et al. (1988) *Meteorites and the Early Solar System 1*, 436-461. [2] Hartmann W.K. & Davis D.R. (1975) *Icarus 24*, 504-515. [3] Canup, R.M. & Asphaug, E. (2001) *Nature 412*, 708-712. [4] Canup R. (2014) PTRSAA 372, 20130175. [5] Snyder, G. et al. (1992) *GCA 56*, 3809-3823. [6] Warren P.H. (1985) AREPS 13, 201-240. [7] Zhang, N. et al. (2013) *JGR 118*, 1789-1804. [8] Hallis, L.J. et al. (2014) *GCA 134*, 289-316. [9] Dauphas, N. & Pourmand, A. (2011) *Nat 473*, 489-492. [10] Nimmo, F. & Kleine, T. (2007) *Icarus 191*, 497-504. [11] McCulloch M.T. (1986) Geol. Soc. Australia Spec. Pub. 14, 864-876. [12] Elkins-Tanton L. et al. (2003) MaPS 38, 1753-1771. [13] Guest, A. & Smrekar, S.E. (2007) *Physics of the Earth and Planetary Interiors 164*, 161-176. [14] Schubert, G. et al. (1990) *Origin and Thermal Evolution of Mars*, 147-183. [15] Lison, L. & Head, J.W. (1994) *Reviews of Geophysics 32*, 221-263. [16] Dehang, V. et al. (2007) *Space Sci Rev 129*, 279-300. [17] Dreibus, G. & Wanke, H. (1977) *Meteoritics 20*, 367-381. [18] McCubbin, F.M. et al. (2010) *EPSL 292*, 132-138. [19] Usui, T. et al. (2012) *EPSL 357-358*, 119-129. [20] Irwin, R.P. et al. (2005) *JGR 110*, E12 1-38. [21] Wood, C.A. & Ashwal, L.D. (1981) *LPSC*, 1359-1375. [22] Sautter, V. et al. (2012) *MaPS Nr 3*, 330-344.