

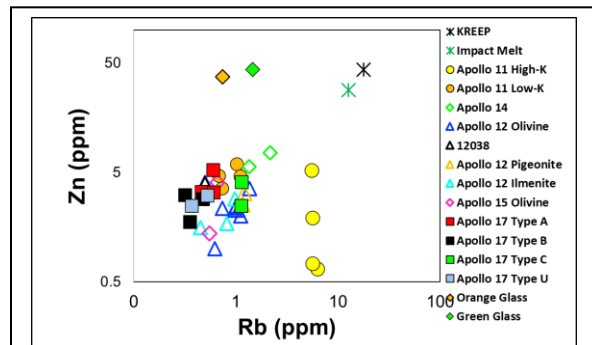
**MODERATELY VOLATILE ELEMENTS IN LUNAR BASALTS; NEW INSIGHTS ON LMO AND SOURCE REGION EVOLUTION.** Burney, D.<sup>1</sup> and Neal, C.R.<sup>1</sup> <sup>1</sup>University of Notre Dame, Notre Dame IN, 46556; dburney@nd.edu.

**Introduction:** The Giant Impact hypothesis is the most commonly accepted mechanism of formation for the Moon [1,2]. It posits that a Mars-sized body collided with early Earth, and the ejected debris (sourced from both the impactor and the Earth) subsequently coalesced and cooled to form the Moon [2]. The violence of this process would have created temperatures capable of volatilizing a great deal of material, and the Moon was hypothesized to be highly depleted in highly volatile species (H<sub>2</sub>O, CO<sub>x</sub>, F, Cl, and S) [3]. Recent analyses on olivine hosted melt inclusions, volcanic glass beads, nominally hydrous mineral phases (apatite), and nominally anhydrous minerals have shown this “dry Moon” hypothesis to be inaccurate [4-7]. Therefore, the efficiency of volatile loss during Moon formation is questioned.

Moderately volatile elements (MVEs) are defined as elements with a condensation temperature between 350 and 1100 K [8]. The concentration of MVEs in lunar basalts may provide insight into the overall level of depletion the Moon experienced, and also the heterogeneity of volatiles in the mantle due to their resistance to volatilization relative to highly volatile elements [8].

Mare basalts are the result of partial melting of compositionally distinct regions of the lunar mantle [9]. The material that coalesced after the Giant Impact would have been mostly molten, and modeling shows mineralization in the order of Bowen’s reaction series as cooling progressed [10]. Mg-rich phases (Olivine and orthopyroxene) formed first and being denser than the surrounding melt, settled to the base of the lunar magma ocean (LMO) [10]. Each phase would be progressively more Fe-rich until the ilmenite came on the liquidus [10]. The final dregs of the LMO were highly enriched in K, REE, and P (and other incompatible elements) so the products from this source region are named KREEP. Lunar basalts can be broadly categorized as low-Ti, high-Ti, and KREEP, being derived from early, late, and final stages of LMO crystallization respectively [9].

**Methods:** The MVEs analyzed are Zn, Se, Rb, Ag, Cd, In, Sb, Tl, Pb, & Bi. They have been measured in whole rock samples using solution mode inductively coupled plasma mass spectrometry (SM-ICP-MS). The trace nature of these MVEs makes them especially susceptible to spectral interferences, which occur when another element in the sample combines with an atmospheric element (e.g. O<sub>2</sub>) to form a polyatomic ion with the same mass of the element of interest. When sorting elements by mass in ICP-MS, these polyatomic interferences

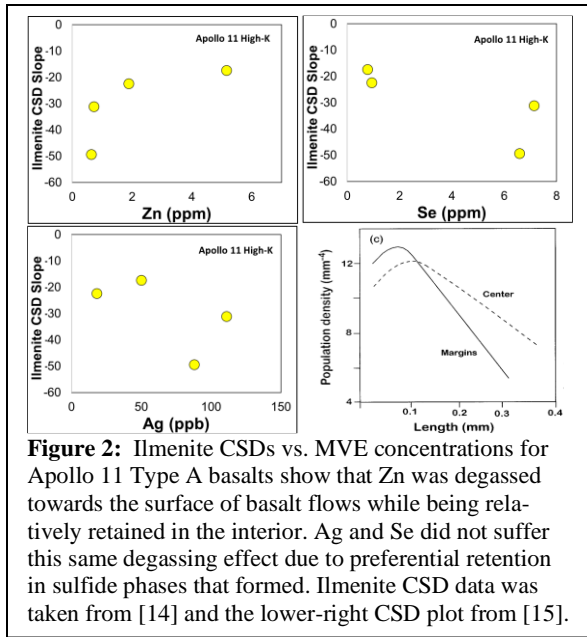


**Figure 1:** Rb vs. Zn showing the comparable concentrations of high-Ti (solid squares and circles) and low-Ti (open symbols). Yellow circles are the A11 high-K basalts showing a degassing of Zn relative to Rb, while KREEP and the impact melt are the two most enriched samples. The volcanic glass beads fall off of any mixing line between the mare basalts and KREEP compositions which reflects the unique origin of the glasses.

ences will artificially inflate the measured concentration. To mitigate this, a series of “interference solutions” were designed to quantify, and subsequently remove, the major interferences on the elements of interest [11]. This results in an “interference corrected” concentration in each sample. Standard reference materials (SRMs) BIR and BHVO were run with the samples to ensure analytical accuracy.

**Results & Discussion:** The incompatible nature of these MVEs with the crystallizing phases in the LMO means that as crystallization progressed, they should be progressively more enriched in the surrounding melt. The resulting concentrations should show an increase from low-Ti basalts to high-Ti basalts to KREEP. The opposite is seen when comparing low-Ti to high-Ti basalts (Fig. 1). This lack of enrichment in the high-Ti basalts relative to the low-Ti samples is interpreted to be evidence of a degassing event [12]. This event would have breached the early lunar crust before the LMO was fully crystallized and allowed for the loss of volatiles from these later-stage sourced lithologies. It has been shown that the late-state LMO suffered a degassing event [13,14] although isotopically some elements (e.g. Zn) may not have fractionated similarly to others (e.g. Cl) [11, 12]. These data confirm that volatiles were lost in the late stages of LMO evolution.

Evidence for degassing upon eruption is seen in correlating MVE contents with textures. Crystal size distributions (CSDs) are a quantitative petrographic analysis comparing the number of crystals present with their size



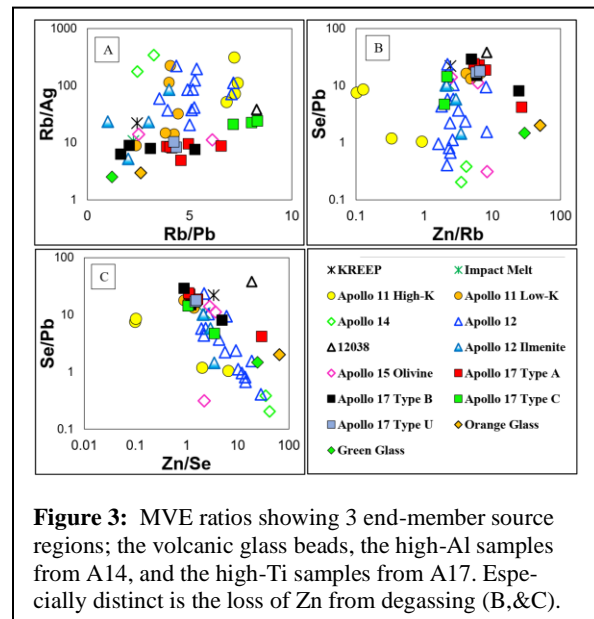
**Figure 2:** Ilmenite CSDs vs. MVE concentrations for Apollo 11 Type A basalts show that Zn was degassed towards the surface of basalt flows while being relatively retained in the interior. Ag and Se did not suffer this same degassing effect due to preferential retention in sulfide phases that formed. Ilmenite CSD data was taken from [14] and the lower-right CSD plot from [15].

[13]. Differences in the slope between these two parameters indicate relative cooling rates (and relative position in a lava flow) (Fig 2). The steeper slope and lower Zn concentrations within A11 samples shows a correlation between the margin of a flow and a loss of Zn (i.e. degassing upon eruption) (Fig 2). The opposite is seen with Ag and Se which are interpreted to have been preferentially sequestered into sulfide phases as they are the most chalcophile elements of the MVE suite (Fig 2).

Volcanic glass beads were also analyzed with high-Ti and low-Ti compositions. These glasses retain volatiles after eruption better than basalts and have shown to be some of the most volatile rich material returned by the Apollo missions [6]. These data show the orange glass is enriched in the MVEs relative to mare basalts, but not uniformly across all analyzed elements (Fig 1). They are similar to KREEP in terms of Zn, but similar to basalts with respect to Rb (Fig 1). The glasses have been modeled to have come from a deeper source region than the mare basalts and their unique MVE ratios is consistent with this [16].

Ratios of the MVEs reveal three source regions that may provide end-member compositions that the rest of the mare basalts are mixtures of (Fig 3). These are the volcanic glasses, the high-Al basalts from Apollo 14, and the high-Ti basalts from Apollo 17; specifically the Apollo 17 type C basalts, which are the most primitive basaltic compositions from Apollo 17. These end-member compositions may provide the compositions necessary to mix and create the other basaltic samples collected from the Apollo missions using cumulate overturn as a mechanism (Fig 3).

**Conclusion:** The Moon, while depleted in volatiles relative to Earth, contains significant amounts of volatile species. The MVE data from mare basalts have revealed degassing on a global scale (LMO) and during eruption (Apollo 11 Types A basalts). The unexpected depletion of high-Ti basalts with respect to low-Ti basalts shows an overall loss in volatile species in the later stage LMO cumulate source regions consistent with a crust-breaching impact(s) while the LMO was partially molten (cf. [17]). MVE ratios indicate multiple source regions for mare basalts consistent of mixing of source regions during overturn of the LMO cumulate pile.



**Figure 3:** MVE ratios showing 3 end-member source regions; the volcanic glass beads, the high-Al samples from A14, and the high-Ti samples from A17. Especially distinct is the loss of Zn from degassing (B,&C).

**References:** [1] Hartmann W.K. & Davis D.R. (1975) *Icarus* 24, 504-515. [2] Canup, R.M. & Asphaug, E. (2001) *Nature* 412, 708-712. [3] Anders, E. (1970) *Science* 169, 1309-1310. [4] Hauri E. et al. (2011) *Science* 333, 213-215. [5] McCubbin F. et al. (2015) *Amer. Mineral.* 100, 1668-1707. [6] Saal A. et al. (2008) *Nature* 454, 192-195. [7] Hui H. et al. (2013) *nat. Geosci.* 6, 177-180. [8] Palme, H. et al. (1988) *Meteorites and the Early Solar System I*, 436-461. [9] Hallis, L.J. et al. (2014) *GCA* 134, 289-316. [10] Elkins-Tanton, L.T. et al. (2011) *EPSL* 304, 326-336. [11] Burney, D.C. et al. (2017) *LPSC* 48, #1068. [12] Burney, D.C. et al. (2018) *LPSC* 49 #1274. [13] Higgins M.D. (2011) *Internat. Geol. Rev.* 53, 354-376. [14] Xue Z., et al., (2019). *LPSC* 50 #2466. [15] Higgins M.D. (1998) *J. Petrol* 39, 1307-1323. [16] Longhi, J. (1992). *PLPSC* 22, 343-353. [17] Barnes et al. (2016) *EPSL* 447, 84-94.