DEVELOPING A METHOD FOR MEASURING MODERATELY VOLATILE ELEMENTS IN LUNAR BASALT USING SOLUTION MODE ICP-MS. Burney, D.[1], Neal, C.R.[1], and Simonetti, A.[1] [1]University of Notre Dame, Notre Dame IN, 46556 (dburney@nd.edu; neal.1@nd.edu; simonetti.3@nd.edu).

Introduction: The depletion of volatiles on the Moon relative to Earth is consistent with its formation due to a Mars-sized body colliding with the early proto-Earth. A collision of this magnitude would create very high temperatures that would deplete any moderately volatile to volatile elements in the resulting Moon. Early analyses of lunar material brought back by the Apollo missions generally agreed that the Moon was essentially volatile depleted [1,2]. Recently, newer analytical methods (e.g., Fourier Transform InfraRed spectroscopy - FTIR, nano-SIMS) have quantified trace volatile elements in olivine hosted melt inclusions, volcanic glasses, and apatite grains [1-3]. These studies have shown that endogenous volatiles are present within the lunar interior, which is dichotomous with the large impact model. While modifications to this model have been suggested (e.g., [4,5]), large gaps in the lunar geochemical database means that these changes cannot be fully tested.

The impact hypothesis posits that moderately volatile elements (MVEs) that have a condensation temperature ~750 K such as Zn, Se, Rb, Ag, Cd, In, Tl, Bi, Pb, and Sb, would also be depleted along with the highly volatile elements. Quantifying these elements may provide insight into fractionation events that occurred early in the Moon's formation.

Methods: The low concentration and lack of reference materials for these elements makes careful analysis of the lunar samples challenging. A solution mode-ICP-MS methodology was employed in this study given its relatively high ionization efficiency, low detection limits (ppt level), and relative spectral simplicity. A clear understanding of potential interferences, the quantification and removal of their effects, and replication of data is of the utmost importance for this study. To quantify potential interferences on the MVEs, six interference solutions were used. The potential interference types are isobaric, oxides, hydroxides, dioxides, chlorides, or argides that have masses overlapping those of the MVEs (Table 1). All interference solutions were prepared at 5 ppb in 2% ultrapure HNO_3, and pertinent elements were distributed throughout the interference solutions in a
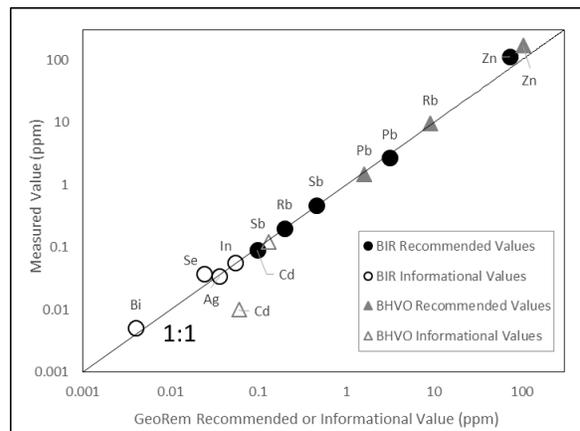

Figure 1: A comparison of GeoRem preferred (closed symbols) and informational (open symbols) values vs. the values measured here for reference materials BIR and BHVO.
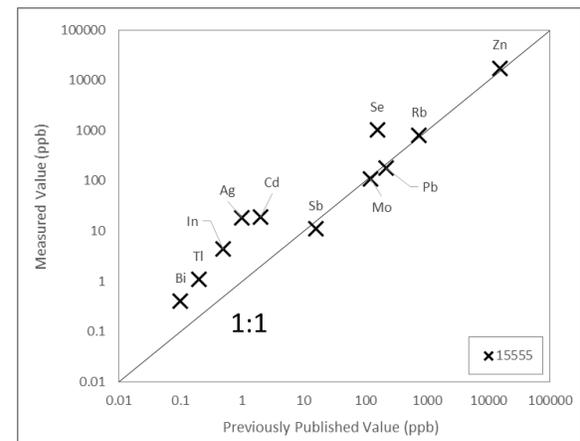

Figure 2: A comparison of previously published values [6-9] of 15555 vs. values measured using the methods above.

very specific manor using two parameters (Table 2): 1) each interference for a single isotope of an element of interest was mixed into a different solution to allow for the isolation of specific interference contributions. For example, ^{68}Zn has oxide (Cr), argide (Si), and hydroxide (V) interferences, therefore Cr, Si, and V are allocated into separate interference solutions; 2) all elements in an individual interference solution cannot interfere with

Isotope	Zn64	Zn66	Zn68	Se76	Se78	Se80	Rb85	Rb87	Ag107	Ag109	Cd110	Cd111	Cd112	Cd113	Cd114	In115	Sb121	Sb123	Tl203	Tl205	Bi209
Isobaric								Sr													
Oxide (16)	Ti		Cr	Ni		Zn	Ga	Ga	Zr	Nb	Zr	Mo			Mo			Ag			
Argide (40)	Mg	Mg	Si			Ar	Sc	Ti		Ga	Ge	Ga	Ge		Ge			Kr	Dy	Ho	Tm
Chloride (35)		P				Sc		Cr	Ge	Ge			Se			Se	Kr	Sr	Er	Er	Yb
Dioxide (32)					Ti	Ti	Cr	Mn			Se		Se		Kr	Kr	Y	Zr	Yb	Yb	Hf
Hydroxide (17)	Ti	Ti	V	Co		Cu	Zn	Ge	Zr	Zr,Mo	Nb	Zr	Mo	Mo		Mo					

Table 1: The types of interferences on each element of interest. Colors correspond to the six interference solutions mixed (Table 2).

1	2	3	4	5	6
Mn	Ga	Sr	Ti	Cr	Ge
Zr	Se	Mo	Nb	Dy	Yb
Zn	Mg	Tm	Co	Y	Sc
Hf	V	P	Er	Ag	Ni
Ho	Cu	Si			

Table 2: The elements present in each of the six inter-ference solutions were mixed at 5 ppb each.

each other such as is the case for the isobaric interferences of ^{50}Ti and ^{50}Cr. The ion signals for these two elements overlap, and therefore must be in separate solutions. The interference solutions, and potential interferences they are quantifying can be found in Tables 1 and 2.

These 6 solutions are always analyzed in tandem with the unknowns, and are used to quantify the interferences at the time of the analytical run. The interferences produced by the 5 ppb solutions can then be used to calculate a counts-per-ppb of interference for every isotope of interest and these are applied to correct sample analyses.

Results & Discussion: A comparison between trace element GeoRem recommended values and the values measured in this study for BIR and BHVO whole rock reference matereials show a strong agreement (Fig. 1). This significant correlation shows that the methodology employed here is capable of replicating well defined data. Multiple analyses of these standards yield standard deviations within reported uncertainty, and their analyses will continue in conjunction with lunar samples to ensure accuracy and precision of previsouly unanalyzed material. Informational values (Fig. 1, open symbols) are not as robust as recommended values (Fig. 1 solid symbols), so informational values typically show a larger deviation from the published abundance. Although all possible major interferences were monitored, no evidence of chloride production shows that not all interferences will play a strong roll in future analyses.

Lunar sample 15555 has been previously analyzed for at least some of the MVEs [6-9] thus giving the opportunity to duplicate concentrations in lunar material as well as international standards. A comparison between the previously published data from 15555 and this study shows some scatter, especially in the lowest concentration elements. However, the duplication of these same trace elements within two basaltic reference materials that were analyzed with 15555 shows the robustness of the method described here. Future replicate analyses of lunar material will constrain the variability seen at lower concentrations.

Summary & Conclusions: MVEs present in lunar basalts may hold the signature of geologic processes occurring during the early formation of the Moon. These

elements (Zn, Se, Rb, Ag, Cd, In, Sb, Tl, Bi, & Pb) have a condensation temperature of ~750 K. Presence of these elements in significant relative abundances in the source regions of mare basalts (which formed from the lunar magma ocean), would place constraints on the giant impact hypothesis or may negate it altogether. Threfore, quantification of these MVEs is a critical element in understanding the origin and evolution of the Moon, and the processing of these elements during planetary differentiation. The measurement of highly volatile elements in lunar volcanic glasses and basalts in recent years [1,2] shows that these elements were not lost entirely during formation of the Moon, and brings the assumption that MVEs should also be present. Initial analyses (e.g., [6-8]) indicate low absolute abundances of these elements, so a precise and accurate method is required to expand this database. While intricate, solution mode ICP-MS is a relatively fast analytical technique for quantifying the MVEs detailed here. All possible interferences must be quantified so their contributions can be removed from the signal therby revealing the true concentration of the elements of interest. The method presented here isolates, and quantifies the most common interferences for these elements of interest using six strategically designed interference solutions. Interfering elements have been dispersed throughout the 5 ppb interference solutions, and when run in conjunction with samples, the interferences are quantified into counts per ppb and subtracted from the sample signal. These methods have been applied to reference materials BIR and BHVO in order to determine the viability of the method on lunar basalts. Samples have been run in duplicate to show that this method yields reproducible results that can be used to quantify the moderately volatile trace elements in lunar basalts.

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