

QUANTIFYING MODERATELY VOLATILE ELEMENTS IN MARE BASALTS: APPLICATION OF THE METHOD. D. Burney¹, C.R. Neal¹, and A. Simonetti¹. Department of Civil & Environmental Engineering & Earth Sciences, University of Notre Dame, Notre Dame, IN 46556, USA.

Introduction: The Moon was formed from a Giant impact between the proto-Earth and a Mars-sized planetesimal - Theia. This impact would have involved considerable energy that promoted melting and evaporation of a significant amount of material. Initial analyses of lunar material collected during the Apollo missions indicated that the Moon was depleted in volatiles with respect to the Earth [1]. Advancements in analytical techniques (e.g., Fourier Transform InfraRed spectroscopy – FTIR, nano-SIMS) have been able to measure trace abundances of volatile species (i.e.: CO_x, H₂O, Cl, F, & S) within lunar volcanic glasses and nominally hydrous mineral phases such as apatite [2-4]. The recent discovery of highly volatile elements has suggested a more complicated model for lunar formation than the Giant Impact Hypothesis provides [2-4]. The ability of the highly volatile species to be trapped within the lunar interior indicates that elements that condense at higher temperatures must also be present. These elements are referred to as moderately volatile elements (MVEs), and those of interest for this method (Zn, Se, Rb, Ag, Cd, In, Tl, Bi, Pb, and Sb) have condensation temperatures between 650-1350K. It is through this high temperature condensation process, that the MVEs may record fractionation events occurring early in the Moon's history [5].

Solution-mode inductively coupled plasma mass spectrometry (ICP-MS) was used to measure these MVEs in digested whole rock samples due to the instrument's high ionization efficiency and low detection limits (ppt level). Quantifying the MVEs using ICP-MS comes with two major difficulties. 1) They are generally present in very low abundances (low to mid-ppb) making them susceptible to spectral interferences, and 2) There is a lack of adequate standard reference materials (SRMs) with which to evaluate the accuracy of analyses. To mitigate these problems, this method uses two approaches. The first is to use a set of solutions designed to quantify individual spectral interferences on each MVE of interest and subsequently remove the interferences from the signal in order to create an interference corrected concentration. The second is to run two SRMs repeatedly to not only quantify their compositions, but to define the accuracy and precision of this method. BIR-1 was selected to represent a depleted MORB source, and BHVO-2 as an enriched OIB source.

Methods: SRMs were digested using an HF-HNO₃ method following [6]. Six interference solutions were mixed at 5ppb in 2% HNO₃ containing all elements that

1	2	3	4	5	6	Table 1: The elements within the 6 interference solutions. All elements are 5 ppb.
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					

could cause a major spectral interference (**Table 1**). The possible spectral interferences considered were isobaric, oxide, argide, chloride, dioxide, and hydroxide. The interference solutions were designed using two parameters; 1) The interfering element must be present at a relative isotopic abundance >10%, and 2) The elements within a single interference solution cannot cause a spectral interference on each other. All six interference solutions are run at the beginning and end of each analytical procedure bracketing the whole rock samples. The ion signals for each MVE of interest from the six interference solutions are then converted into counts/ppb. Using the concentration of the

BIR-1	This Study (ppm)	2σ	GeoReM (ppm)	2σ	n
Zn	73.7	8.7	70.4	8.5	64
Se	0.22	0.34	0.02	0.01	3
Rb	0.20	0.02	0.21	0.07	74
Ag	0.039	0.006	0.041	-	2
Cd	0.08	0.02	0.08	0.05	13
In	0.05	0.03	0.06	0.005	5
Sb	0.49	0.06	0.46	0.13	18
Tl	0.005	0.008	0.002	0.002	13
Pb	2.91	0.35	3.04	0.45	81
Bi	0.005	0.002	0.005	0.002	4
BHVO-2					
Zn	110	12.4	103.9	10.1	96
Se	1.36	0.66	0.18	0.03	3
Rb	9.5	1.04	9.3	1.08	131
Ag	0.11	0.02	0.09	0.06	6
Cd	0.12	0.04	0.15	0.22	24
In	0.08	0.04	0.12	0.09	8
Sb	0.11	0.02	0.10	0.04	28
Tl	0.02	0.01	0.02	0.01	29
Pb	1.59	0.19	1.65	0.39	105
Bi	0.013	0.005	0.015	0.014	12

Table 2: Concentrations (ppm) measured using the methods described above. The error for GeoReM [7] was calculated by the author (see text). BIR-1 n = 16, BHVO-2 n = 17.

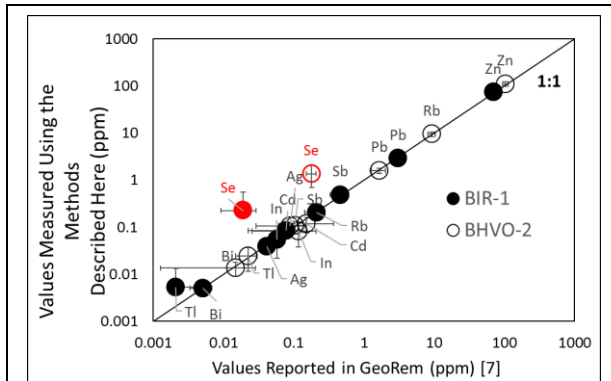


Figure 1: Concentrations of the MVEs as measured using this method vs reported in GeoReM. Values should fall along the 1:1 line. Errors are reported as 2σ .

interfering species in the samples, the contribution is removed from the MVE of interest giving an interference-corrected concentration.

Results & Discussion: The concentrations measured using this method match the values reported in the GeoReM database to a reasonable degree with the exception of Se (**Fig. 1, Table 2**). BIR-1 was analyzed a total of 16 times, and 17 times for BHVO-2. GeoReM uses a statistical method to calculate the 95% confidence level based on the standard deviation of the mean concentrations as reported by different laboratories [7]. For easier comparison, the reported GeoReM concentrations were compiled, and the 2σ reported along with the 2σ of the data gathered using this method (**Table 2**).

While the uncertainties reported using this interference solution method mostly fall at or below those calculated from the GeoReM database, there are a few exceptions. The 2σ from this interference solution method for Se, and Tl are large. The reason for this can be summarized by the methods used for each analysis. The GeoReM database uses concentrations reported by many different laboratories worldwide, which use different methods. Many of these methods are more precise than solution mode ICP-MS, such as ID-TIMS (isotope dilution thermal ionization mass spectrometry), hydride generation, and ID-MC-ICP-MS (MC = multi-collector). While these methods can yield more precise data, they also require more pre-analysis sample manipulation, and more sample mass for the analysis.

While a few of the MVEs of interest show uncertainties that are slightly above the GeoReM database, only one (Se) is not reproducing the reported concentration. Se falls on the Ar-dimer so low abundances of Se are often overwhelmed by the background measured in the blanks. The mass of one Se isotope (^{77}Se) avoids the Ar-dimer, but its relative isotopic abundance is 7.63%.

Quantifying ^{77}Se has produced concentrations that are consistently higher than the GeoReM values (**Fig. 1, Table 2**) and show high variability. This is due to the poor ionization of Se in the plasma. The best method to measure it is by hydride generation [8]. The other nine MVEs of interest are being reproduced accurately and precisely (**Fig. 1, Table 2**).

The benefits of this interference solution method is that it allows for the acquisition of a large suite of elements using small sample sizes, and no pre-analysis manipulation apart from digestion. This is especially beneficial for lunar samples which are only available for analyses in small quantities (usually <1 g).

Summary and Conclusions: The low abundance of MVEs, coupled with the lack of SRMs, make them elements that are not commonly measured. Their intermediate condensation temperatures, between refractory common mineral forming elements and highly volatile species, may prove useful as tracers during early planetary condensation and differentiation [5]. The method described here quantifies any spectral interferences on the 10 MVEs of interest using six interference solutions, and subsequent interference removal from the signal allows for an interference corrected concentration to be obtained. While other methods could be used, the large amount of sample material or pre-analysis manipulation makes these alternative methods less viable for precious lunar material.

This method provides accurate and precise concentrations for 9 of the 10 MVEs of interest, with the exception being Se due to its poor ionization efficiency and low isotopic relative abundance (**Fig. 1 and Table 2**) [5]. All other elements are reproduced to within associated uncertainties as reported by the GeoReM database [7].

References: [1] Anders E. et al. (1971) *PLSC 2*, 1021-1036. [2] Hauri E. et al. (2011) *Science* 333, 213-215. [3] McCubbin, F., et al. (2015) *Amer. Mineral.* 100, 1668–1707. [4] Saal, A., et al. (2008) *Nature* 454, 192-195. [5] Palme, H. et al. (1988) *Meteorites and the Early Solar System I*, 436-461. [6] Bellucci, J., et al. (2014) *Chem. Geol.*, 365, 69-86. [7] Jochum K. et al. (2016) *Geostand. Geoanal. Res.*, 40, 333-350. [8] Townsend, A. (1999) *J. Anal. Chem.*, 364, 521-526.