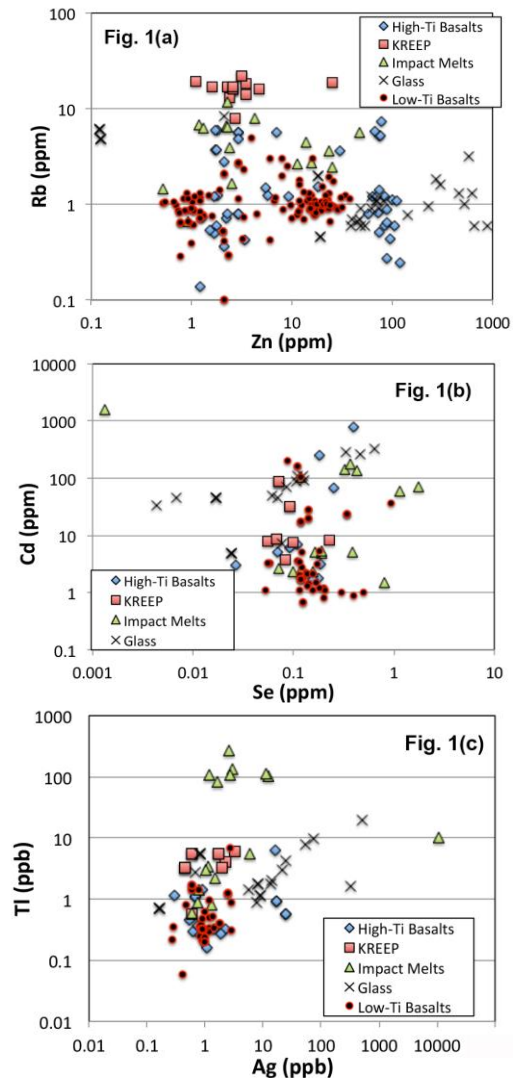


ACCOUNTING FOR THE VOLATILE ELEMENTS: A METHOD FOR QUANTIFYING TRACE VOLATILE ELEMENTS USING SOLUTION MODE ICP-MS. P. T. Lowe^{1,2}, C. R. Neal^{1,2}, and A. Simonetti¹,
¹Department of Civil and Environmental Engineering and Earth Science, University of Notre Dame, 156 Fitzpatrick Hall, Notre Dame, IN 46556, USA (plowe1@nd.edu; neal.1@nd.edu), ²SSERVI Center for Lunar Science and Exploration, Lunar & Planetary Institute, Houston, TX 77058.

Introduction: Trace volatile elements, namely Zn, Se, Rb, Ag, Cd, In, Tl, Bi, Pb, and Sb, from lunar samples are known to be depleted (relative to Earth's mantle) ([1] and references therein), consistent with the Giant Impact hypothesis for the origin of the Moon (e.g., [2])... Data available for these elements were derived by time-consuming radiochemical neutron activation analysis (RNAA) and microbeam techniques (e.g., [3-8]). Few techniques can determine the full suite of volatile elements on the same sample, and the relatively small sample sizes used bring into question whether the analysis is representative of the bulk rock.

Previous data characterized elements in different Apollo sample suites. This non-systematic approach means that, for example, the effects of crystal fractionation, assimilation, etc., that have subsequently been shown to affect different mare basalt suites, cannot be evaluated on the distribution of these elements. Some important inferences can be made from the current sample suite. On the basis of Zn data (Fig. 1a) two broad groups of low-Ti and high-Ti basalts are defined, with KREEP samples being enriched in Rb. Both groups of low- and high-Ti basalts trend towards KREEP (Fig. 1a) consistent with source contamination and/or magmatic assimilation. Volcanic glasses have the highest Zn, but average Rb abundances (Fig. 1a). Two groups of low- and high-Ti basalts are also defined, albeit not as clearly, on the basis of Cd data, but here KREEP samples plot with the mare basalts, and the volcanic glasses with the basalt groups with highest Cd contents (Fig. 1b). In terms of Ag and Tl abundances (Fig. 1c), the volcanic glasses form a positive trend, only one group of low-Ti basalts is seen, although two groups of high-Ti basalts are evident. Two groups of impact melts are evident (Fig. 1c).

It appears that the presence of two basalt groups in Figure 1 a,b and two impact melt groups in Figure 1c is an analytical artifact. The lower abundance group is generally comprised of RNAA data, whereas the higher abundance group contains data generally obtained by other methods. A systematic re-examination of Apollo samples is required to define any analytical artifacts and/or confirm the validity of previous data. We present a solution mode inductively coupled plasma mass spectrometry (ICP-MS) method to quantify the abundances of volatile elements noted above. This method homogenizes approximately ~50mg of sample in solu-



tion to minimize sample heterogeneity resulting from coarse grain sizes.

Notable hinderances solution mode ICP-MS has in determining volatile abundances in lunar samples are isobaric and polyatomic interferences. We have developed a new method for monitoring and correcting the critical interferences so as to determine the ultra low abundance of these trace volatile elements.

Methods: The method is a variation of the protocol presented in [9]. Samples are processed in a Class 1000 clean lab. 200mg of sample is crushed and ground to a fine powder using an agate mortar and pestle, which have been cleaned by soaking in ultra pure 8N HNO₃ and rinsed with ultra pure 18MΩ water and

dried. 50 mg of the sample is then placed in a 15 mL Savillex Teflon beaker and dissolved using 1mL of concentrated double distilled (DD) 16 N HNO₃ and 4 mL of DD HF, and placed on a 110°C hot plate for 48 hours. The sample was then cooled and placed uncapped on a 150°C hot plate until the sample was dried. Next, 40 drops of DD 16N HNO₃ were added to the dried sample, the beakers capped, and placed on a hotplate at 110°C overnight. Once again the sample beakers were cooled, uncapped, and dried on a 150°C hotplate. This process was repeated three times to ensure all fluorides (and potential polyatomic interferences) were eliminated. The sample was then transferred to clean 125 mL polypropylene bottles as 100 g of DD 2% HNO₃.

	Isobaric	Oxide (¹⁶ O)	Hydroxide (¹⁶ OH)
Zn	Ni	Ti, Cr	Ti, V, Cr
Se	Ge	Fe, Ni, Zn	Fe, Cu, Ni
Rb	Sr	Ga	Zn, Ge
Mo	Zr, Ru	Ge, Se, Kr, Br,	As, Se, Kr, Br,
Ag		Zr, Nb	Zr, Mo
Cd	Sn, In	Zr, Mo, Ru	Y, Zr, Nb, Mo, Ru
In	Cd, Sn	Mo, Ru	Zr, Mo, Ru
Sb	Te	Ag	Ru, Pd, Cd
Tl		Re, Os	W, Os
Pb	Hg	Os, Pt, Ir	Re, Os, Pt, Ir
Bi		Ir	Os, Pt

Table 1 – Potential Interferences.

The elements of interest have potential interferences that could possibly affect the elemental abundances derived (Table 1).

Interference solutions were made in order to define the magnitude of each interference. Where more than one interfering species affects a given isotope of interest five interference solutions were made (Table 2) to allow each interference to be quantified. Each interfer-

Interference Solution	Potential elements of interest receiving counts from the interference solutions
1. V, Fe, Y, Te, W, Hg	⁶⁶ Zn, ⁶⁷ Zn, ⁶⁸ Zn, ⁷⁰ Zn, ⁷⁴ Se, ¹⁰⁶ Cd, ¹⁰⁸ Cd, ¹²³ Sb, ²⁰³ Tl, ²⁰⁴ Pb
2. Ni, Nb, Sn, Ir	⁶⁴ Zn, ⁷⁴ Se, ⁷⁶ Se, ⁷⁷ Se, ⁷⁸ Se, ⁸⁰ Se, ¹⁰⁷ Ag, ¹⁰⁹ Ag, ¹¹⁰ Cd, ¹¹² Cd, ¹¹⁴ Cd, ¹¹⁵ In, ¹¹⁶ Cd, ²⁰⁷ Pb, ²⁰⁸ Pb, ²⁰⁹ Ir
3. Ti, Ge, Ru, Os	⁶⁴ Zn, ⁶⁶ Zn, ⁶⁷ Zn, ⁷⁰ Zn, ⁷⁴ Se, ⁷⁶ Se, ⁹⁸ Mo, ¹⁰⁰ Mo, ¹¹² Cd, ¹¹³ Cd, ¹¹⁴ Cd, ¹¹⁵ In, ¹¹⁶ Cd, ¹²¹ Sb, ²⁰³ Tl, ²⁰⁵ Tl, ²⁰⁶ Pb, ²⁰⁷ Pb, ²⁰⁸ Pb, ²⁰⁹ Bi
4. Cu, Ga, Pd, Pt	⁸⁰ Se, ⁸² Se, ⁸⁵ Rb, ¹⁰⁶ Cd, ¹⁰⁸ Cd, ¹¹⁰ Cd, ¹²¹ Sb, ²⁰⁶ Pb, ²⁰⁷ Pb, ²⁰⁸ Pb, ²⁰⁹ Bi
5. Cr, Sr, Br, Zr, Re	⁶⁶ Zn, ⁶⁷ Zn, ⁶⁸ Zn, ⁷⁰ Zn, ⁸⁷ Rb, ⁹⁵ Mo, ⁹⁷ Mo, ⁹⁸ Mo, ¹⁰⁰ Mo, ¹⁰⁶ Cd, ¹⁰⁷ Ag, ¹⁰⁹ Ag, ¹¹⁰ Cd, ¹¹¹ Cd, ¹¹² Cd, ¹¹³ Cd, ¹¹³ In, ²⁰⁴ Pb, ²⁰⁶ Pb

Table 2 - Interference solutions

ence solution was made to a 10 ppb concentration.

Certain elements of interest have the potential to interfere with others we wish to quantify. For example, Zn can potentially cause interferences on Se and Rb, Se on Mo. Four separate standard solutions (Table 3) are made to separate these elements to prevent interference when determining each elements individual contributions. With these “standard” solutions, we can quantify the interference these elements potentially have on each other. The four standard solutions are defined in (Table 3).

Standard Solution	Elements
A	Cd, Se, Rb, Pb
B	Ag, In, Bi
C	Mo, Zn
D	Tl, Sb

We also used external calibration to convert counts from the ICP-MS to ppb. We made concentration solutions of 0.5 and 2.5 ppb containing all the elements of interest.

We made one stock solution with each element diluted to 5 ppb in 2% HNO₃.

A spike stock solution containing approximate concentrations of each of our elements of interest is also made. The solution is made to contain the concentrations: 100 ppb Zn, Mo, Cd; 4 ppb Rb, Pb; 2 ppb Se, In, Ag, Sb; 1 ppb Tl. Samples were analyzed in duplicate –one unspiked and one spiked. All solutions were analyzed on a Nu Instruments AttoM HR-ICP-MS using the sequence in Table 5.

Bracket	Analytes
1	AB 1, Std. A, Std. B, Std. C, Std. D
2	AB 2, IS 1, 2, 3, 4, 5
3	AB 3, 0.5 Concentration Std.
4	AB 4, 2.5 Concentration Std.
5	AB 5, IS 1, 2, 3, 4, 5
6	AB 6, Std. A, Std. B, Std. C, Std. D
7	AB 7, Procedural Blank Unsp, Sp
8	AB 8, Unknown Sample 1 Unsp, Sp
9	AB 9, Unknown Sample 2 Unsp, Sp
10	AB 10, Unknown Sample 3 Unsp, Sp
11	AB 11, IS 1, 2, 3, 4, 5
12	AB 12, Std. A, Std. B, Std. C, Std. D, AB 13

Table 4 - Sequence of Analysis. (AB - Acid Blank, Std. - Standard, IS - Interference Solution, Sp - Spiked, Unsp - Unspiked)

References: [1] Heiken G. et al. (1991) Camb. Uni. Press, 736 pp. [2] Hartmann W. & Davis D. (1975) *Icarus* 24, 504-515. [3] Chou C. et al. (1975) *PLSC* 6, 1701-1727. [4] Ganapathy R. et al. (1973) *PLSC* 4 1239-1261. [5] Anders E. et al. (1971) *PLSC* 2, 1021-1036. [6] Morgan J. et al. (1972) *PLSC* 3, 1377-1395. [7] Shearer C. et al., (1990) *GCA* 54, 851-867. [8] Shearer C. et al. (1991) *EPSL* 102, 134-147. [9] Neal, C. (2001) *JGR* 106, E11, 27865-27885