ELEMENTAL AND ISOTOPIC ABUNDANCES OF FE, CU AND ZN IN LOW-TI LUNAR BASALTS. F.N. Lindsay[1], G.F. Herzog[1], F. Albarède[2], R.L. Korotev[3]. [1]Dept. Chem. & Biol. Chem., Rutgers University, New Brunswick, NJ 08854 (flindsay@rci.rutgers.edu); [2]Ecole Normale Supérieure (LST) 69364 Lyon cedex 7, France; [3]Dept. Earth Planet. Sci., Washington University, St. Louis, MO 63130.

Introduction: Isotopic measurements of moderately volatile elements, such as Cu and Zn, in basaltic rocks can help us to understand mechanisms of element mobilization, heterogeneities within planetary reservoirs and perhaps, large-scale planetary processes. For reasons not yet understood, high-Ti lunar basalts are enriched in the heavy isotopes of Cu and Zn compared with their terrestrial counterparts [1,2]. As the high-Ti basalts (>7.5 wt%) constitute only a small fraction of all lunar basalts, about 5% [3], study of the much more abundant low-Ti lunar basalts is warranted. We report here the results of isotopic analyses of a variety of geological standards and lunar samples, including three low-titanium basalts (2.3 - 3.3 TiO_2 wt%).

Analytical procedures: Though not new [4-8], δ-level isotopic analyses of Cu and Zn isotopes are not yet common either. Elemental concentrations in lunar basalts are typically less than 10 ppm and for Zn in particular laboratory contamination is endemic. For this work, chemical separations were carried out in a class 1000 clean room at Rutgers University. Samples, ranging in mass from 25 mg to 185 mg, were powdered with a mortar and pestle prior to digestion by fluxing with conc. HF and HNO_3 in closed teflon vials for two weeks at ~125°C. After drying, each sample was fluxed repeatedly – in most cases twice - with 8M HNO_3 until the solution was clear. Our procedure for the purification of Zn, Cu and Fe is based on that of [6]. Zn is separated using AGW-X8, 200-400 mesh anion-exchange resin with mixed 1.5M HBr/0.5M HNO_3; Cu and Fe are separated using AG MP-1M, 100–200 mesh anion-exchange resin with 7M and 2M HCl. A small split (≤20%) is taken for element abundance measurements. Cu and Zn were measured with an Element high-resolution, inductively-coupled plasma mass spectrometer (HR-ICP-MS); Fe was measured with a Varian ICP-optical emission spectrometer (OES). Elemental concentrations are calculated through comparison with standard solutions.

The remaining sample is analyzed isotopically using a Nu Plasma multi-collector mass spectrometer (MC-

ICP-MS) at ENS, Lyon [Moynier et al., 2006]. Isotope ratios are expressed as δ values relative to: [63]Cu and NIST 976 for Cu; [64]Zn and JMC 400882B for Zn; and [54]Fe and IRMM-14 for Fe. Terrestrial basalt standards were analyzed both to develop and to check the column chemistry.

Results: Table 1 shows the measured elemental abundances and isotopic ratios. Yields, which must be high in order to avoid fractionation in the laboratory [9], were found to be ≥ 94%. Total procedural blanks (ng) were as follows: Cu, <4.5; Zn, <7.8; Fe, <300, all of which represent <1% of the total signal.

Elemental concentrations - Most of our concentration data agree with literature values within ~10%, with the exception of those for lunar soil 66041 for which we found higher Cu, 18 ppm, and lower Zn, 15 ppm,

Table 1. Fe, Cu, and Zn concentrations and isotopic abundances (‰).

This work / Lit.	$\delta^{56}Fe$	$\delta^{57}Fe$	Fe wt%	$\delta^{65}Cu$	Cu ppm	$\dfrac{\delta^{66}Zn}{2}$	$\dfrac{\delta^{68}Zn}{4}$	Zn ppm
USGS Standards								
BIR-1								80.7±1.2
	0.10	0.14	8.2±0.3		106.3±3.5			72.0±3.9
			7.9±0.4		67.0±2.6			59.2±3.7
	0.02	0.02	7.9±0.5		89.0±2.6	0.13	0.13	63.7±2.8
	0.00-0.12	-0.02-0.10	8.0-8.5	-0.03	54-132	0.13	0.14	50-119
BCR-1	0.06	0.10		0.01	16.1±0.2	0.08	0.11	118.9±1.4
	0.14	0.20	9.4±0.4		15.6±2.1			115.8±3.5
					11.6±0.3	0.10	0.12	122.5±4.3
	0.03-0.12	0.10-0.19	9.3-9.5	0.07	11.8-41	0.1-0.3	0.16-0.2	100-145
PCC-1			5.7±0.1		7.9±0.1	0.13	0.16	33.4±1.4
			5.5±0.1		6.3±0.1	0.14	0.12	34.7±1.4
	0.03-0.04	0.02-0.04	5.75-5.83		6-11			31-55
Lunar Soils								
15231	0.30	0.43	9.1±1.2		4.4±0.3	2.90	2.89	23.4±2.6
	0.51	0.95	8.96	2.10	3.0-7.8	2.7-3.2	2.7-3.2	5.4-52
76501	0.20	0.26	8.0±1.0		17.7±2.7			29.4±0.6
	0.11	0.26	7.9-8.0	2.61	14.0-15.0	1.90	1.98	12-35
66041	0.27	0.43	4.2±0.1			1.66	1.63	15.2±1.0
	0.27	0.41	3.5-4.7	4.05	7.9	2.09	2.00	22-23.8
Lunar Basalts								
12002	0.08	0.17	16.3±1.0	1.14	5.0±0.2			2.0±0.1
	0.10	0.16	16.0-17.2		4.6-6.5			0.7-7.2
12009	0.10	0.20	16.5±1.0	-0.08	15.4±0.5	0.20	0.19	3.3±0.1
			15.6		10.4–14.0			1.8-9.7
12018	0.04	0.10	16.3±1.0	1.96	4.8±0.1	-1.04	-1.03	2.8±0.1
			16-17		4.4-8.1			1.9-2.6
74275					21.6±0.3			11.4±0.1
	0.20	0.32	12.8±0.2		15.6±1.1			53.8±3.7
			12.3±0.8		15.9±1.7	0.17	0.18	48.8±3.5
	0.14	0.16	12.9±0.7	1.02	3.3±0.3			3.9±0.6
	0.12	0.17	13.3±0.8	0.77	3.0±0.3			4.4±0.9
	0.12	0.16		0.74	3.1±0.3			11.7±0.8
	0.13	0.16	10.0-12.2	1.40	3.3-48.7	0.1-0.4	0.06-0.47	1.7-74.2

than did [1]: 7.9 ppm and 23 ppm, respectively. These differences may reflect sample heterogeneity.

Iron isotopes - Fe isotope ratios generally agree with literature values. Our measurements confirm [1] that the lunar soils are enriched in the heavy iron isotopes, with $\delta^{56}Fe \geq 0.2‰$. With current precision for $\delta^{56}Fe$, 1-σ=0.08‰, we cannot distinguish reliably between results for individual lunar basalts [10,11]. Our data do suggest larger group averages for high- than for low-Ti basalts, a trend seen clearly in the data of [10].

Cu isotopes - $\delta^{65}Cu$ values for USGS standards BCR-1 and especially BIR-1 (1-σ=0.06‰) are lighter than those in the literature. Our BIR-1 powder may have become contaminated. Compared with terrestrial basalt, two low-Ti lunar basalts are enriched in heavy Cu; one falls into the terrestrial range, ($\delta^{65}Cu$: -0.1 to +0.1; [1]). High- Ti basalt 74275 shows variation between samples, but is heavier than terrestrial.

Zn isotopes - The Zn isotope abundances for all types of samples analyzed agree with literature values (1-σ=0.11‰). The largest difference found is for lunar soil 66041 for which we measure $\delta^{66}Zn$=1.7‰ and [1] reports 2.1‰. Zinc is usually but not always isotopically heavy in lunar basalts. Like high-Ti basalt 10018 [2], low-Ti basalt 12009 is isotopically light in zinc. With data for only 2 low-Ti basalts we cannot yet assess possible systematic differences from their high-Ti counterparts. The lunar soils have the strongest enrichment of heavier Zn isotopes.

Discussion: *Mass fractionation* – Our data for Fe and Zn plot along lines concordant with mass dependent fractionation (Figure 1). They mirror previously seen arrays showing heavy isotope enrichment increasing in the order glass < basalt < soils [1,2]. Values of $\delta^{65}Cu$ show the same trend averaging -0.4/0.9/3.0 ‰ in glass/basalt/soil [1,2]. In the glasses, δ<0 reflects evaporation and condensation of volcanic fountaining processes; in the soils, micro-meteorite impact and vaporization lead to δ>0.

Basalt heterogeneity – Refs. [1,2] reported positive $\delta^{66}Zn$ for all high-Ti basalts except 10017, for which $\delta^{66}Zn$ = -5.4±0.09. Our data for low-Ti basalts provide

additional examples of such variation (i.e., from positive to negative $\delta^{65}Cu$ and $\delta^{66}Zn$) as do recent results of F. Moynier (pers. comm.). That basalts somehow preserved such variations from the era of the Moon's formation seems plausible only if Cu and Zn are distributed into different phases, which had and retained dissimilar isotope ratios. Local processes, however, such as mineral fractionation and/or contamination by soil- or glass-like components at the lunar surface, seem a more likely explanation of the variations. In absolute terms, most of the isotopic results for basalts fall within a fairly narrow range near 0 and between the ranges defined by glasses and soils, both of which have much higher elemental concentrations of Zn and Cu. Nonetheless, a lack of correlation between $\delta^{66}Zn$ and $\delta^{65}Cu$ hints at the presence of distinct components attributable to the basalts themselves.

Conclusions: We have implemented chemical procedures [6] that allow us to separate with minimal contamination Fe, Cu, and Zn from lunar samples and to measure their isotope abundances. Although the number of low-Ti basalts analyzed is still small (3), our results for Cu and Zn are compatible with averages reported for high-Ti basalts by [2, ($\delta^{65}Cu$ of 0.5‰ ; $\delta^{66}Zn$ of 1.2‰)] and by F. Moynier (pers. comm.); our results for Fe and Zn are compatible with averages for low-Ti basalts reported by [10, ($\delta^{56}Fe$ of 0.07‰ ; $\delta^{57}Fe$ 0.11‰)] and by F. Moynier (pers. comm.). The existence of appreciable variations in Cu and Zn isotope abundances in lunar basalts is clear. The reasons for them are not. From a planetary perspective, the challenge is to find and characterize the sources of Zn and Cu in the basalts.

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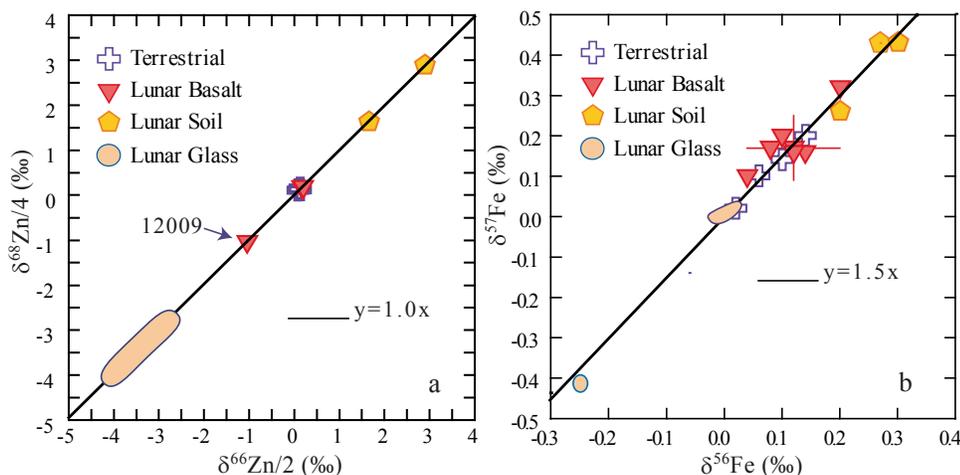

Figure 1. a) $\delta^{68}Zn/4$ ‰ *vs.* $\delta^{66}Zn/2$ ‰ and b) $\delta^{57}Fe‰$ *vs.* $\delta^{56}Fe‰$: The data show mass dependent fractionation. Data for lunar glass shown for comparison [1,12]. Error bar for $\delta^{57}Fe$ (0.08‰) is representative.