

ISOTOPIC AND ELEMENTAL ABUNDANCES OF COPPER AND ZINC IN: LUNAR BASALTS, GLASSES, AND SOILS, A TERRESTRIAL BASALT, PELÉ'S HAIRS, AND ZAGAMI. G.F.Herzog¹, Frederic Moynier^{2,3}, and Francis Albarede³, ¹ Dept. Chemistry and Chemical Biology, Rutgers U., Piscataway, NJ 08854-8087 (herzog@rutchem.rutgers.edu), ² Dept. Geology, University of California, Davis, CA 95616, ³ ENS Lyon, 46 Allée d'Italie, 69364 Lyon, France.

Introduction: The relatively high volatilities of Cu and Zn encourage speculation that their isotopic abundances might show evidence for mass-dependent fractionation. Data available for lunar samples confirm this speculation but are few and only partially understood [1]. Heavy isotopes are enriched in soils, due either to solar wind sputtering or micrometeorite impact; light isotopes are enriched in pyroclastic glass 74220, due either to Rayleigh evaporation followed by complete condensation or to partial condensation; and heavy-isotopes seem to be slightly enriched above terrestrial values in the one fully fledged basalt analyzed to date, Ti-rich 74275. We set out to obtain additional isotopic data for Zn and Cu, especially in lunar basalts, for sharper comparisons with terrestrial, martian, and other lunar samples, and to consider the origins of any differences. Secondary goals were 1) to distinguish between competing hypotheses for the origin of the heavy isotope enrichments in lunar soils; 2) to compare the isotopic compositions of orange and of black glass from Apollo 17; and to demonstrate that a surface component largely determines the bulk isotopic composition measured for the pyroclastic glasses.

Experimental methods: The following samples were analyzed: Ti-rich lunar basalts 10017, 10022, 10024, 10057, 70215, 71055, 74255, 75055, and

75075; size separated fractions of lunar soils 15021, 15231, 70181, and 79221 and of pyroclastic glasses 74001 (black) and 74022 (orange); a basalt from Piton des Neiges, Réunion Island; two samples of Pelé's hairs from the Nyiragongo volcano; and a sample of the martian meteorite Zagami.

We used nylon sieves to separate the soils and the pyroclastic glasses into size fractions. Moynier et al. [1] describe the methods for chemical separation and isotopic analysis of Cu and Zn. Powdered samples (20-70 mg) were leached in 0.2 HCl for 5 minutes in an ultrasonic bath. The samples dissolved in HNO₃/HF at 130°C in about 50 h. After separation by ion exchange, Zn and Cu were analyzed by using the MC-ICPMS P54 in Lyon. The sample external reproducibility is 50 ppm; the total blank (10 ng) represents < 1% of the total signal.

Results: Table 1 is a summary of measured elemental concentrations and of isotopic abundances given as δ values with respect to the reference isotopes ⁶⁴Zn and ⁶³Cu for Zn and Cu, respectively. Measured elemental concentrations of Zn and Cu are comparable to literature values

Discussion: Our samples include Zn from the Earth, Mars, the Moon (=Earth + large impactor?) and micrometeorites, principally carbonaceous, which contribute much of the Zn found in lunar soils. The isotopic fractionation of zinc in our samples is

Table 1. Average elemental concentrations and isotopic compositions of Cu and Zn.

	Cu (ppm)	$\delta^{65}\text{Cu}/^{63}\text{Cu}$ (‰)	Zn (ppm)	$\delta^{66}\text{Zn}/^{64}\text{Zn}$ (‰)	Cu/Zn ¹	Ref.
Lunar basalts	3.3±0.3 (6) 7.1±2.1 (5) 10±2 (19)	0.5±0.2 (6)	2.3±0.6 (8) 4.0±2.3 (5) 1.6±0.1 (33)	1.4±0.2 (8)	2.8±0.9 (5) ^a 3.8±1.0 (5) ^a 6.2 ^b	c [2] [3]
Lunar soils	6.1±1.2 (3) 12±1 (43)	3.1±0.3 (10)	26±2 (9) 28±4 (77)	4.1±0.3 (14)	0.23±0.05 ² 0.44 ²	c [3]
74001 & 74220	19±12 (3)	-0.4±0.4 (4)	165±46 (4)	-3.7±0.3 (4)	0.12±0.08	c
Orange glass	26		210		0.12	[4]
Bulk Moon	6.9		20		0.35	[5]
Orgueil (CI)	125	-0.09	315	0.49	0.40	[6-8]
Terrestrial basalts	170 (2)	-0.1 to 0 (2) 0	37 (4)	0.2 to 0.4 (4) 0 to 0.3	4.6	c [9]
Zagami			60 (2)	-0.30 (2)		c,[10]

Notes: Uncertainties are standard deviations of the mean. Numbers in parentheses indicate the number of analyses in the average. **a)** Average of ratios for individual samples. **b)** Column 2/Column 4 **c)** This work.

mass dependent within the uncertainties of the measurements (Figure 1). We infer that the zinc in all of them comes from a reservoir or reservoirs that are linkable by mass-dependent fractionation processes.

With the exception of 10017, relative to terrestrial basalts, Ti-rich lunar basalts are enriched in the heavier isotopes of both Zn and Cu: We find for lunar basalts $\delta^{65}\text{Cu}/^{63}\text{Cu}=0.5\pm 0.2$ (N=6) and $\delta^{66}\text{Zn}/^{64}\text{Zn} = 1.4\pm 0.2$ (N=8) vs. $\delta^{66}\text{Zn}/^{64}\text{Zn} \sim +0.3$ ‰ and $\delta^{65}\text{Cu}/^{63}\text{Cu} \sim 0$ ‰ for terrestrial basalts. The enrichments of heavy isotopes in the lunar samples could reflect: igneous fractionation associated with lunar differentiation; late-stage volatilization at the lunar surface; late-stage incorporation of fractionated lunar material (micrometeoritic or fumarolic) at the lunar surface; and/or volatilization associated with a giant impact. Mindful of the caution of [11], and along the same general lines as [12,13], we prefer to attribute them to condensed-phase separations that took place in the course of producing a phase, probably a sulfide, that is enriched in zinc relative to copper, in which copper is more volatile, and which may later have been the source of the coatings on the pyroclastic glasses.

Data for size separates of the pyroclastic glasses 74001 and 74220 confirm the well-known surface correlation of Cu and Zn, but reveal no sharp differences between either the Cu/Zn ratios or the isotopic composition of grain interiors and exteriors. The absence of differences suggests that measurements for bulk samples are dominated by a light-isotope-rich surface component to which we assign the values $\delta^{65}\text{Cu}/^{63}\text{Cu} = -1.3\pm 0.3$ and $\delta^{66}\text{Zn}/^{64}\text{Zn} = -4.0\pm 1.3$. It is also possible, but seems less likely, that the isotopic composition of the interiors and exteriors are identical.

Data for size separates of lunar soils confirm an enrichment of heavy isotopes [1]. Taken relative to Orgueil, we find $\delta^{65}\text{Cu}/^{63}\text{Cu}=3.2\pm 0.3$ (N=10) and

$\delta^{66}\text{Zn}/^{64}\text{Zn} = 3.6\pm 0.3$ (N=14). As with the lunar glasses, in all but lunar soil 15231 our isotopic data show no strong grain-size dependence.

When lunar samples are sorted by type, the correlation between $\delta^{65}\text{Cu}/^{63}\text{Cu}$ and $\delta^{66}\text{Zn}/^{64}\text{Zn}$ is weak (Figure 2).

The size of the isotopic fractionation inferred for the surface component in the soils is smaller by a factor of three than predicted by a published model of sputtering [14]. An alternative explanation for the isotopic fractionation invokes the energy delivered by micrometeorite impact rather than by solar particles to accelerate mass-dependent fractions of the isotopes to lunar escape velocity. Calculations of these fractions based on a hydrodynamic quenching model, however, predict isotopic fractionations that are appreciably smaller than observed in the soils, suggesting that vaporization may not suffice and that sputtering remains a viable option [15]. The disagreement between sputtering theory and observation may reflect incomplete separation of particle by size.

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