Isotopic composition of zinc, copper, and iron in lunar samples

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Abstract

We determined by ICP-MS the concentrations and isotopic ratios of Fe, Cu, and Zn in the Ti-rich lunar basalt 74275, in the lunar orange glass 74220, and in up to 10 lunar soils, namely, 14163, 15231, 64501, 66041, 68841, 69941, 70011, 72501, 75081, and 76501. Two analyses of zinc in lunar basalt 74275 give $\delta^{66}Zn = 0.17‰$ and $0.75‰$, values within the range of those measured in terrestrial basalts; copper in lunar basalt 74275 has $\delta^{65}Cu \sim +1.4‰$, which is isotopically heavier than values observed in terrestrial basalts. In the orange glass, we measured $\delta^{56}Fe = -0.24‰$, $\delta^{65}Cu = -0.42‰$, and $\delta^{66}Zn \sim -3.6‰$. These values of δ are more negative than those obtained for 74275 and for typical lunar basalts, but for Cu, comparable to those observed in terrestrial sulfides and meteorites. In lunar soils we found $0.11‰ \leqslant \delta^{56}Fe \leqslant 0.51‰$, $2.6‰ \leqslant \delta^{65}Cu \leqslant 4.5‰$, and $2.2‰ \leqslant \delta^{66}Zn \leqslant 6.4‰$. Insofar as we can generalize from a small sample set, S, Fe, Cu, Zn, and Cd show similar trends in isotopic fractionation on the Moon. Lunar basalts have nearly terrestrial isotopic ratios. Relative to the lunar basalt 74275, the pyroclastic glass 74220 is enriched in the lighter isotopes of Fe, Cu, and Zn, and the soils are enriched in the heavier isotopes of Fe, Cu, and Zn. The patterns in the basalts are likely inherited from the source material; the light-isotope enrichments seen in the orange glass originated during lava fountaining or, less probably, during partial condensation of vapor; and the heavy-isotope enrichments in the lunar soils were likely created by a combination of processes that included micrometeorite vaporization and sputtering. In the orange glass, the light-isotope enrichments (relative to lunar basalts) of Zn are larger than those of Cu. If these enrichments reflect accurately the isotopic composition of the gas, they suggest that Cu is more volatile than Zn in the liquid from which the gas derived. A simple model built on the known flux of micrometeorites to the lunar surface and a published estimate that micrometeorites generate 10 times their own mass of vapor, predicts heavy-isotope enrichments comparable to those observed in soils but only if the regolith gardening rate is set at about one twentieth of the generally accepted value of 1 cm/My. This discrepancy may reflect the difference in the time constants for micrometeorite milling and decimeter-scale gardening, or the importance of sputtering.
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Analyses of numerous lunar samples have established that additions of extralunar meteoroid debris have provided most of the vapor-mobilized elements now found in lunar surface materials. Nevertheless, the observed patterns of concentrations of vapor-mobilized elements cannot be explained, even to a first approximation, by the simple mixing of indigenous lunar material . . . with meteoroid material similar to CI-carbonaceous chondrites.

Haskin and Warren (1991).

1. Introduction

In their treatment of lunar geochemistry, Haskin and Warren (1991) identified 17 lunar trace or minor elements (Fig. 1) as "vapor-mobilized" based on high relative volatility and overall low abundances relative to those in CI chondrites. We focus on two elements in the group, Cu and Zn, and the less volatile element, Fe. Lunar glasses and soils often contain higher concentrations of vapor-mobilized elements than do the lunar basalts (Haskin and Warren, 1991; Warren, 2004). For example, Zn concentrations of ∼200 ppm measured in the orange glass 74220 (e.g., Wasson et al., 1976) are ∼40 times larger than typically found in lunar basalts and almost 2/3 the value

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																	F
																S	Cl
										Cu	Zn			As	Se	Br
										Ag	Cd	In			Te	I
										Hg	Tl	Pb	Bi			

Fig. 1. Vapor mobilized elements on the Moon.

for CI chondrites (Lodders and Fegley, 1998). Copper concentrations in the orange glass (26 ppm; Taylor et al., 1991, p. 266) are perhaps five times the size of those in basalts (Haskin and Warren, 1991, p. 468) and ~1/5 the value for CI chondrites (Lodders and Fegley, 1998). Zinc concentrations in lunar soils typically exceed those of mare basalts by factors of 6–10. Data for Cu in soils are scarcer and any enhancement over lunar basalts less clear-cut. Overall, soils seem at most slightly richer than basalts in Cu, 1.2 ± 0.1 ppm vs. 1.0 ± 0.2 ppm (data from Haskin and Warren, 1991, Fig. 8.25c).

Haskin and Warren (1991) discuss the explanations for the generally higher concentrations of vapor-mobilized elements in glasses and soils. The source of enrichment in the glasses is likely pyroclastic lunar volcanism. After volatile elements vaporized from fountaining lavas, the vapor condensed on the surfaces of grains sprayed outward from the source region. For the soils, on the other hand, several lines of evidence point to a continual influx to the lunar surface of volatile-rich CI-like micrometeoroids as the source of the excesses.

Isotopic analyses add to the understanding of how the vapor-mobilized elements move on the lunar surface. For example, Ding et al. (1983) found mass-dependent enrichments of the light sulfur isotopes in selected samples of orange glass 74220. Preferential evaporation of the lighter isotopes from lava followed by condensation without isotopic fractionation is consistent with the picture developed to account for the elemental abundances alone.

Soils, in contrast to the orange glass, tend to be isotopically heavy relative to lunar (and terrestrial) basalts. Heavy-isotope enrichments are seen for several elements including O (Epstein and Taylor, 1971, 1972), Si (Clayton et al., 1974), K (see Humayun and Clayton, 1995) Cd (Sands et al., 2001), with smaller values for Mg (Esat and Taylor, 1992; Warren et al., 2005), Ca (Russell et al., 1977), and Fe (Wiesli et al., 2003; Poitrasson et al., 2004). The data set for sulfur, however, is the most extensive and the most illuminating (see McEwing et al., 1980). Kerridge et al. (1975a) demonstrated that $\delta^{34}S$ increases slowly with the sulfur concentration in lunar soils. They

explained this otherwise enigmatic correlation with a model in which lunar soils gain sulfur through micrometeorite bombardment, but also lose it either when meteorite impacts eject atoms in the target material or when high-energy particles or photons (Yakshinskiy and Madey, 1999) from the Sun interact with surfaces. These processes favor retention of the heavier isotopes.

If the vapor-mobilized elements are not the only ones subject to isotopic alteration on the Moon, they are nonetheless especially good examples for study, in part because the isotopic effects can be large even in bulk samples. Moreover, little is known about the isotope abundances of Zn and Cu in lunar materials. Zn and Cu are moderately volatile and at least partly chalcophile elements (Wai and Wasson, 1977; Kallemeyn et al., 1989; Johnson and Prinz, 1991; Brearley et al., 1995; Wulf et al., 1995). Reasoning by analogy, we speculated that isotope abundances of Zn and Cu in different kinds of lunar samples might show patterns similar to those shown by Cd, which is both volatile and chalcophile, and by S itself. We set out to test this idea by measuring Zn and Cu isotope abundances in a lunar basalt, in the orange glass, and in several lunar soils. Our broader goals were to use the results to learn more about Zn and Cu transport on the lunar surface and to compare the behavior of Zn and Cu to those of other vapor-mobilized elements, especially S and Cd.

After the completion of our work on Cu and Zn, we developed the ability to make high precision isotope measurements for iron. Although iron does not belong to the vapor-mobilized group of elements, we thought it would be worthwhile to see if we could reproduce in our samples the trends reported by Wiesli et al. (2003) and Poitrasson et al. (2004).

2. Experimental methods

2.1. Samples

We obtained samples from one lunar rock, 74275, from the Apollo 17 orange glass, and from several lunar soils

(Table 1). Lunar rock 74275 is a high-Ti basalt (see Taylor et al., 1991). It is considered to represent a primary, rapidly quenched magma that formed at a depth of $\geqslant 230$ km (Taylor et al., 1991, p. 208) and a pressure of ~ 11 kb (Green et al., 1975) and to typify Ti-rich material that covers a lunar area extending over 500,000 km^2 (Head, 1974). We analyzed two chips from the interior with masses of 15 and 80 mg, respectively.

The lunar orange glass 74220 formed about 3.7 Gy ago (Alexander et al., 1980), probably in a lunar lava fountain (Meyer et al., 1975). The material is thought to have originated under a pressure of 20 kb (Green et al., 1975) at a depth of 400 km (Taylor et al., 1991, p. 208) and to be relatively pristine (Delano, 1986). Arguments against significant re-processing in the regolith include a very low maturity index ($I_s/FeO = 1.0$; Morris et al., 1983). The maturity index is calculated as the specific ferromagnetic resonance intensity, I_s, normalized to the FeO concentration of the sample (for discussion, see Housley et al., 1975; Morris, 1976; McKay et al., 1991, p. 315). Additional arguments against significant reprocessing are a relatively short lunar surface exposure age (~ 30 My; see Heiken et al., 1974), and low concentrations of meteoritic siderophiles (Morgan et al., 1974). The composition of the orange glass resembles those of high-Ti basalts such as 74275 (Taylor et al., 1991, p. 204).

We analyzed 10 soils samples in all, 1 from Apollo 14, 1 from Apollo 15, and 4 each from Apollo 16 and 17. All our soil samples were collected from with a few centimeters of the lunar surface and had been sieved to retain only particles with sizes of less than 1 mm. Soil 70011, the "fuel products contamination sample," was collected under the landing module. Morris et al. (1983) and references therein describe the lunar soils studied.

2.2. Chemical separation of zinc, copper, and iron

The experimental procedures were adapted from those described by Maréchal et al. (1999) and Luck et al. (2005). Powdered samples weighing 20–70 mg were leached in 0.2 M HCl for 5 min in an ultrasonic bath. The leaching solution was removed and then the residue was dissolved over a period of several days in HNO_3/HF at 130 °C. Zn was first purified on AG1X8 anion-exchange resin in HBr/HNO_3. Cu and Fe were further purified on AGMP1 anion-exchange resin in HCl. As anion-resins fractionate both Cu and Zn isotopes (Maréchal et al., 2003) complete recovery is necessary. The yield was checked and found to be better than 99% for Cu, Zn, and Fe.

Isotopic ratios of Zn and Cu in all samples were analyzed with the MC-ICP-MS VG Plasma 54 as described by Maréchal et al. (1999). Isotopic ratios of Fe were analyzed in pseudo-high resolution mode (closed source slits and open collector slits) on a Nu plasma 500 HR coupled with a desolvating nebulizer Nu DSN-100. This mode of operation allows interferences, $^{40}Ar^{14}N$ at mass 54 and $^{40}Ar^{16}O$ at mass 56, to be resolved. Isotope ratios are expressed as relative deviations, δ, from the standard NIST 976 for Cu, from the standard JMC 3-0749 L for Zn, and from the standard IRMM-14 for Fe. Tanimizu et al. (2002) demonstrated that the isotopic compositions of JMC and NBS 683 Zn standards are indistinguishable within errors. Our reported values of δ may be converted to absolute isotope ratios by using the terrestrial isotope ratios. For reference, we quote the terrestrial atomic abundances for Cu given by Coplen et al. (2002): ^{63}Cu, 0.69174 and ^{65}Cu, 0.30826. Although absolute abundances for Zn are not precisely known, a precise and consistent set of isotopic abundances is provided by Tanimizu et al. (2002): ^{64}Zn, 0.49188; ^{66}Zn, 0.27792; ^{67}Zn, 0.04041; ^{68}Zn, 0.18378; ^{70}Zn, 0.00600.

Table 1
Isotope and elemental abundances of Zn and Cu in lunar materials

Sample ID	Type	$\delta^{56}Fe$	$\delta^{57}Fe$	Fe (wt%)	$\delta^{65}Cu$	Cu (ppm)	$\delta^{66}Zn$	$\delta^{67}Zn$	$\delta^{68}Zn$	Zn (ppm)
74275	Basalt						0.17	0.49	0.24	
74275.318					1.40	3.4	0.75	1.10	1.88	6.0
14163.868	Soil	0.19 ± 0.06	0.50 ± 0.12	5.0	3.70		2.59	3.71	5.24	33.0
14163.159[a]	soil				1.03	10.0				
15231.200	Soil	0.51 ± 0.07	0.95 ± 0.17		4.51		6.39	9.52	12.69	
64501.226	Soil	0.11 ± 0.06	0.22 ± 0.12	2.7	3.20		4.41	6.51	8.54	23.8
66041.131	Soil	0.27 ± 0.08	0.41 ± 0.18		4.05		4.17	6.09	7.99	
68841.47	Soil						2.18	3.22	4.25	
69941.53	Soil						3.40	6.55	7.08	
70011.209	Soil				2.96		3.44	5.14	6.88	27.6
72501.226	Soil				4.08	7.3	4.45	6.70	8.89	31.0
75081.688	Soil	0.19 ± 0.05	0.33 ± 0.05		2.84		4.07	6.05	8.14	24.8
76501.184	Soil	0.11 ± 0.06	0.26 ± 0.12	7.3	2.61		3.79	5.77	7.91	
74220.793	Glass				−0.50		−3.47	−5.21	−6.87	230.9
74220.849		-0.24 ± 0.05	-0.41 ± 0.14	11.8	−0.42	32.1	−3.83	−5.72	−7.40	140.0

Notes: Values of $\delta(\permil)$ calculated from the definition shown at the right with $n = 54$ for Fe, $n = 63$ for Cu, and $n = 64$ for Zn.

$$\delta^m Y = \left\{ \frac{(^m Y/^n Y)_{unknown}}{(^m Y/^n Y)_{standard}} - 1 \right\} \times 1000.$$

[a] Barnes et al. (1972), calculated relative to SRM 976, $^{63}Cu/^{65}Cu = 2.2440 \pm 0.0021$. Uncertainties are $\pm 0.05\permil$ for $\delta^{65}Cu$, $\delta^{66}Zn$, and $\delta^{68}Zn$, ± 0.2–$0.3\permil$ for $\delta^{67}Zn$, $\pm 0.06\permil$ for $\delta^{56}Fe$, and $\pm 0.13\permil$ for $\delta^{57}Fe$.

The total blank (<10 ng for Zn and Fe and <1 ng for Cu) represents <1% of the total signal. In replicate analyses of the same samples carried out during different sessions, we obtained an external reproducibility of $\pm 0.05‰$ for $\delta^{65}Cu$, $\delta^{66}Zn$, and $\delta^{68}Zn$. The inset of Fig. 2 shows that the spread of $\delta^{67}Zn$ around the mass fractionation line is larger, about ± 0.2–$0.3‰$; possible reasons are discussed in Section 3.1. For iron, the amount of lunar material allowed us to replicate the analyses. The average external reproducibility on each sample is $\pm 0.06‰$ for $\delta^{56}Fe$ and $\pm 0.13‰$ for $\delta^{57}Fe$. As Zn, Cu, and Fe concentrations are

comparable within a factor of 2 for all solutions analyzed, we believe that these estimates of uncertainty apply to all the results.

2.3. Elemental analysis of iron, copper, and zinc

We calculated the elemental concentrations of Fe, Cu, or Zn in our samples from the measured concentrations of ^{54}Fe, ^{64}Zn, and ^{63}Cu, respectively, through a comparison with standard solutions. For the Lyon instruments, the VG Plasma 54 and the Nu plasma 500, the uncertainties associated with this technique are on the order of 5%. The assumption that the samples have the same isotopic composition as the standard is inconsequential (<1%) with respect to the measurement uncertainties.

3. Results

3.1. Mass-dependent fractionation of Fe and Zn isotopes in lunar soils and orange glass 74220

Isotope abundances are presented in Table 1 in the standard δ notation. To a first approximation, for a system undergoing mass-dependent fractionation, we expect that $\frac{\delta^m Y}{\Delta m_m} \approx \frac{\delta^l Y}{\Delta m_l}$, where m is an isotope mass, $\Delta m_m = m_m - m_n$, and $\Delta m_l = m_l - m_n$, and the index n denotes the reference isotope (see notes to Table 1). Thus, for Fe we expect $\delta^{57}Fe = 1.5 \times \delta^{56}Fe$, and for Zn, $\delta^{67}Zn = 1.5 \times \delta^{66}Zn$ and $\delta^{68}Zn = 2.0 \times \delta^{66}Zn$. With one exception, the data follow these relations within the experimental uncertainties (Fig. 2). For the soil 69941, $\delta^{67}Zn$ is larger than expected: we observe $\delta^{67}Zn/1.5 = 4.4‰$ rather than $\sim 3.4‰$. An unidentified isobaric interference may have been present at mass 67. Alternatively, the increased uncertainties at mass 67 may be due to reflections of Ar molecular compounds in the flight tube, reflections that would have affected the baseline around mass 67. It is also conceivable that we have observed a real anomaly in ^{67}Zn here; Kitts et al. (2003) reported observed non-mass-dependent fractionation of Cr isotopes in two different lunar soils. In any case, we conclude that for most lunar samples the fractionation of iron and of zinc isotopes is mass dependent.

Copper has only two stable isotopes and we cannot be sure that the observed isotope fractionations ($\delta^{65}Cu \neq 0$) are mass dependent.

3.2. Isotope fractionation of Cu, Zn, and Fe in lunar samples

Fig. 3 shows the measured values of $\delta^{56}Fe$, $\delta^{65}Cu$, and $\delta^{66}Zn$ plotted against values of $\delta^{34}S$ taken from the literature. We consider Zn first. When calculated relative to terrestrial isotope abundances, values of $\delta^{66}Zn$ range from $-3.6‰$ in the orange glass 74220 to distinctly positive values, from $+2.6‰$ to $+6.4‰$, in the lunar soils. We find $\delta^{66}Zn = +0.5 \pm 0.3‰$ for the basalt 74275. The uncertainty for 74275 exceeds the internal reproducibility by nearly an order of magnitude and probably indicates variability in
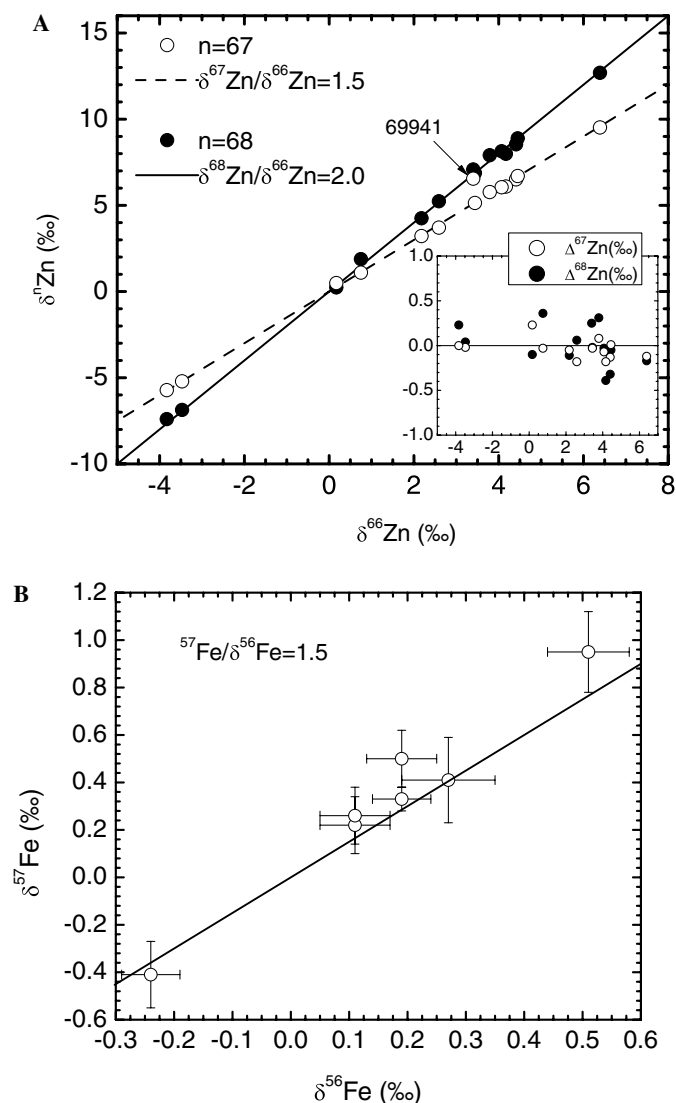
Fig. 2. If the fractionation factors α for isotopes j and k relative to isotope n are mass-dependent, i.e., follow the proportionality $\alpha \propto (m_{j,k}/m_n)^\beta$, then we have approximately $\delta_j \sim \frac{\Delta m_k}{\Delta m_j} \delta_k + \frac{1}{2} \left(\frac{\Delta m_k}{\Delta m_j}\right)^2 \frac{\delta_k^2}{1000} + \cdots$ where $\Delta m_{j,k} = m_{j,k} - m_n$. For our largest value of $\delta^{68}Zn = 6.39‰$, we find $\delta^{68}Zn = 2 \times (6.39 + 0.04)‰$, i.e., that the second-order term can be neglected. Thus, to within the uncertainties of our measurements we can test for mass-dependent fractionation by checking whether $\delta^{57}Fe = 1.5 \times \delta^{56}Fe$, $\delta^{67}Zn = 1.5 \times \delta^{66}Zn$, and $\delta^{68}Zn = 2 \times \delta^{66}Zn$. The plots show that these relations hold. The inset shows $\Delta^{67}Zn$ (except for 69941; see text) and $\Delta^{68}Zn$ calculated *with* the second order corrections.
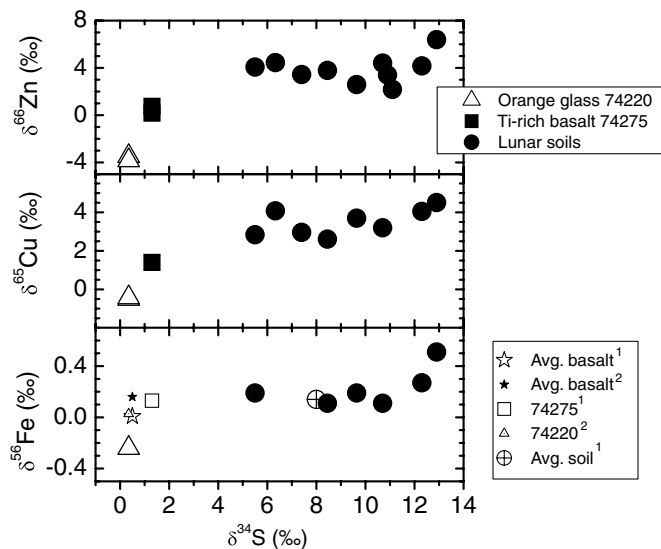
Fig. 3. Relative to lunar basalts, the heavy isotopes of Fe, Cu, and Zn are enriched in lunar soils and the lighter isotopes of Cu and Zn are enriched in the orange glass 74220. Data for sulfur are from the following sources: Kerridge et al. (1975a,b), Rees and Thode (1972, 1974), Petrowski et al. (1974), Kaplan et al. (1976), and Thode and Rees (1976). Iron data are from (1) Wiesli et al. (2003) and (2) Poitrasson et al. (2004).

the replicates. The variations that we observe from soil to soil are also much larger than the analytical error.

To our knowledge, only Xue et al. (1995) have previously reported isotope abundances of Zn in lunar samples. Xue et al. gave the following results (sample number, Zn concentrations in ppm (wt), $\delta^{66}Zn$ in ‰) for four lunar soils: 64801, 22.7, 4.4; 68841, 25, 3.8; 69941, 30, 5.4; 69961, 20, 7.6. These results are in the same range as those reported here but appear to be somewhat higher; the uncertainties of the measurements of Xue et al. are $\sim \pm 2‰$.

Values of $\delta^{65}Cu$ follow the same general pattern as those for $\delta^{66}Zn$, but in a smaller range. The lowest values, $-0.5‰$, are observed for the lunar glass; the results for the soils are again positive, ranging from $+2.6‰$ to $+4‰$; and the result for the basalt 74275 is intermediate between those for the glass and the soils, $+1.4‰$. Also as observed for $\delta^{66}Zn$, $\delta^{65}Cu$ varies from soil to soil by amounts that exceed the experimental uncertainty.

To our knowledge, Barnes et al. (1972) made the only two previous analyses of Cu isotopes in lunar samples, one for the breccia 14321 ($^{63}Cu/^{65}Cu$ (atom/atom) = 2.2458) and the other for the soil 14163, also analyzed here, ($^{63}Cu/^{65}Cu = 2.2417$). Barnes et al. quote the results relative to the standard SRM 976 (2.2440). These values translate to $\delta^{65}Cu = -0.8‰$ and $+1.0‰$ for the breccia and the soil, respectively, with uncertainties on the order of $\pm 1.4‰$. We regard the agreement for 14163 as satisfactory.

Turning to iron, we first compare our results for soils and rock samples with those of Wiesli et al. (2004). For our six lunar soil samples we find $0.11‰ \leqslant \delta^{56}Fe \leqslant 0.51‰$ and an average of $0.23 \pm 0.12‰$. Wiesli and co-workers reported $\delta(^{56}Fe/^{54}Fe)$ and $\delta(^{57}Fe/^{54}Fe)$ relative to values

measured for a set of terrestrial igneous volcanic and plutonic rocks. Their results may be converted to the IRMM-014 scale, the one that we use here, with the definition of δ and the additional information that $\delta(^{56}Fe/^{54}Fe) = -0.09 \pm 0.05$ and $\delta(^{57}Fe/^{54}Fe) = -0.11 \pm 0.07$ for IRMM-014 measured relative to the igneous volcanic and plutonic rocks (Beard et al., 2003). Wiesli et al. (2004) analyzed various grain size fractions of 6 different lunar soils. The soil samples from their work best suited for comparisons with ours are their $<45\,\mu m$ fractions. For these samples, their data correspond to $0.15‰ \leqslant \delta^{56}Fe \leqslant 0.29‰$ on the IRMM-014 scale with an average of $0.23 \pm 0.05‰$. Averaging their data for 17 samples from 8 lunar basalts and one impact-melt rock, we obtain $0.098 \pm 0.025‰$; for the 8 lunar basalts only, the average is $0.12 \pm 0.04‰$ (uncertainty = $2 \times \sigma_{mean}$). In short, and as pointed out by Wiesli et al. (2003), lunar soils are enriched in the heavy isotopes of iron relative to lunar basalts.

In the orange glass, we measured $\delta^{56}Fe = -0.24 \pm 0.05‰$. Poitrasson et al. (2004) reported $\delta(^{57}Fe/^{56}Fe)$ and $\delta(^{57}Fe/^{54}Fe)$ for orange glass, green glass, 10 lunar basalts of various kinds, 1 norite, 3 ferroan anorthosites, and two mineral separates, all relative to IRMM-014. We calculated values of $\delta(^{56}Fe/^{54}Fe)$, or in short $\delta^{56}Fe$, from their data and the relation

$$\delta^{56}Fe = \left[\frac{\frac{\delta\left(^{57}Fe/^{54}Fe\right)}{1000} + 1}{\frac{\delta\left(^{57}Fe/^{56}Fe\right)}{1000} + 1} - 1 \right] \times 1000.$$

Their results for the orange glass give $\delta^{56}Fe = 0.027 \pm 0.06‰$. Here we have set the uncertainty equal to the smaller of the average of the uncertainties that Poitrasson et al. (2004) quote for $\delta(^{57}Fe/^{56}Fe)$ and $\delta(^{57}Fe/^{54}Fe)$. The significance of their result for the orange glass emerges from a comparison with their average for lunar rocks, $\delta^{56}Fe = +0.16 \pm 0.04‰$. Relative to lunar rocks, their orange glass has $\delta^{56}Fe \sim -0.13‰$. Our result and that of Poitrasson et al. (2004) for the orange glass agree on the *direction* of the fractionation relative to lunar rocks (enrichment of light isotopes), but disagree by about 2 standard deviations with respect to the *magnitude* of the fractionation in 74220. Considering the small sizes of δ and the likely natural variability of the sample, we consider this absolute difference unsurprising.

4. Discussion

To summarize, the isotopic abundances of Fe, Cu, and Zn vary with the type of sample studied. In the orange glass, the isotopic variations are mass dependent and show light-isotope-enrichments; in the lunar basalt 74275 the isotopic abundances are fractionated to only a small degree compared to terrestrial standards; in the lunar soils the isotopic variations are mass dependent and heavy-isotope-enriched. This general pattern resembles what Sands et al. (2001) and de Laeter et al. (2005) report for Cd. As noted

in the Introduction and consistent with these observations, mass-dependent, heavy-isotope enrichments of several other elements (notably O, K, Si, S, Fe, and Cd) are known in lunar soils, and Warren et al. (2005) have recently reported isotopically light Mg in Apollo-17 black glass (δ^{26}Mg mostly in the range from $-0.2‰$ to $-0.9‰$).

In the sections to follow we will compare the isotopic results for Zn and Cu for the lunar samples with published results for terrestrial materials and meteorites. Wiesli et al. (2003) and Poitrasson et al. (2005) have already done so for Fe. We focus on Cu and Zn in the orange glass 74220 and in the lunar soil samples with the primary aim of investigating how Cu and Zn move on the lunar surface.

4.1. Comparing Cu and Zn isotope abundances in lunar basalts and in terrestrial samples

In most terrestrial rocks (marine deposits are an exception), δ^{66}Zn varies little: $-0.19 \leqslant \delta^{66}$Zn (‰) $\leqslant +0.82$, with most igneous rocks being tightly grouped around $+0.25 \pm 0.10$ ‰ (Coplen et al., 2002; Albarède, 2004). As our results for 74275 lie within the terrestrial range (Fig. 4), we conclude that the lunar zinc is not visibly fractionated isotopically relative to the Earth. The isotope abundances of other volatile elements such as K and S are also close to terrestrial values. In particular, from the data of Humayun and Clayton (1995) we calculate an average value for δ^{41}K = 0.6 ± 0.2 (standard deviation of the mean) for six lunar basalts. According to the Rayleigh equation (given explicitly in Section 4.3.2), this value corresponds to either a failure to condense or loss through evaporation of only a small part of the K originally present, 2.4%. Using data from several sources (Appendix A), we find an average value of δ^{34}S $\sim +0.5 \pm 0.2‰$ for about 20 lunar rocks, a value similar to the one quoted by Haff et al. (1977) and typical of mid-range terrestrial
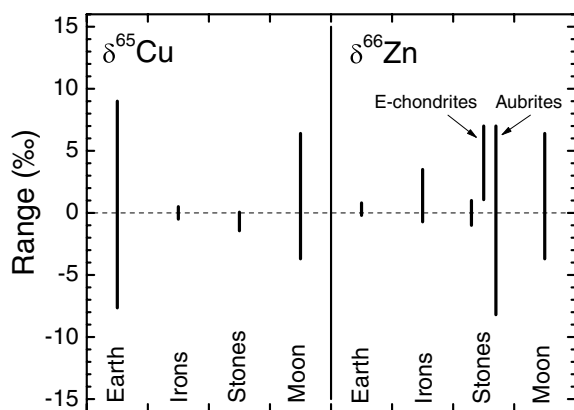
Fig. 4. Ranges of isotope abundances of Cu and Zn in lunar samples compared with those in terrestrial and meteoritic samples. Sources of data for meteorites of all classes: Gawinowski et al. (1989); Loss and Lugmair (1990); Völkening and Papanastassiou (1990); Luck et al. (2001a,b,c); Luck et al. (2003); Russell et al. (2003). Data for E-chondrites and aubrites only from Mullane et al. (2005a,b), respectively. Terrestrial data from Coplen et al. (2002) and Albarède (2004).

values reported for fresh submarine ocean basalts and glasses and for related minerals (Gurenko et al., 2001). If little loss and fractionation of K and S took place, then it seems reasonable that loss of Zn should also be small, at least on the Moon.

The results δ^{65}Cu = 1.4‰ and δ^{66}Zn = +0.75‰ suggest that the second chip of 74275 analyzed contained a mineral phase in which Cu and Zn were fractionated with respect to terrestrial igneous rocks (δ^{65}Cu $-0.1‰$ to $+0.1‰$, see Coplen et al., 2002; Albarède, 2004; Luck et al., 2003). Terrestrial copper-bearing chlorides tend to be lighter ($-7.65‰ \leqslant \delta^{65}$Cu $\leqslant -1.6‰$) and carbonates heavier ($-1‰ \leqslant \delta^{65}$Cu $\leqslant 9‰$), but these substances form under aqueous conditions on Earth and seem an inappropriate reference for lunar mare basalts. Terrestrial sulfides and native metal are, on average, unfractionated within the uncertainties ($-4.5‰ \leqslant \delta^{65}$Cu $\leqslant 6‰$ and $-3.0‰ \leqslant \delta^{65}$Cu $\leqslant +2.0‰$, respectively).

4.2. Comparing Zn and Cu isotope abundances in lunar basalts and in meteorites

In the CI-chondrite Orgueil, δ^{66}Zn is +0.48‰ (Luck and Ben Othman, 2005) and δ^{65}Cu $-0.09‰$ (Luck et al., 2003). CI chondrites are of interest here because among all meteorite classes, their compositions provide the best estimate for the composition of the early solar system. In ordinary and other carbonaceous chondrites, Luck et al. (2001a,b,c) found $0.17‰ \leqslant \delta^{66}$Zn $\leqslant 0.67‰$ and $-0.1‰ \leqslant \delta^{66}$Zn $\leqslant 0.8‰$, respectively. With one possible exception for a FUN inclusion, these ranges subsume within the uncertainties earlier results for Allende and Murchison (Völkening and Papanastassiou, 1990; Loss and Lugmair, 1990; Loss et al., 1990). Both these ranges also include our result for 74275. In closing this comparison of lunar and meteoritic Zn, we note the impressively large range of zinc isotope fractionation recently reported for enstatite achondrites, $1‰ \leqslant \delta^{66}$Zn $\leqslant 7‰$, and for E-chondrites $-8‰ \leqslant \delta^{66}$Zn $\leqslant 6‰$ (Mullane et al., 2005a,b).

For copper in ordinary and carbonaceous chondrites, Luck et al. (2003) reported $-0.51‰ \leqslant \delta^{65}$Cu $\leqslant +0.10‰$ and $-1.44‰ \leqslant \delta^{65}$Cu $\leqslant -0.09‰$, respectively. Thus, copper in stony meteorites is isotopically similar to copper in terrestrial basalts and slightly lighter than what we observe for 74275. An evaporative loss of about 10% of the Cu in a well-stirred lava could explain the systematic difference in δ^{65}Cu of 1.4‰ between lunar basalts on the one hand and terrestrial basalts and meteorites on the other; the percentage would be higher if stirring were poor. It is interesting that Cu (and S; see Appendix A) but not Zn seem to show this effect, perhaps because Zn has stronger lithophile tendencies. A provocative alternative would be that the Moon acquired isotopically heavy Cu when it formed. We emphasize, however, that we have data for only one sample and that the results for Cu in 74275 require independent confirmation in other lunar basalts.

4.3. Lunar orange glass

4.3.1. Integrity, cause, and size of light-isotope enrichments

The light isotopes of Fe, Cu, and Zn are enriched (Table 1) in bulk 74220. In principle, heating due to micrometeorite impacts could have affected these elemental and isotopic signatures. The immaturity and short lunar exposure age of the orange glass argue against such changes for Fe, Cu, and Zn. Whether the more volatile Cd also escaped such modification is unclear, and we will not consider it further in this section.

We compare the sizes of δ in 74220 (δ^{56}Fe = −0.24‰; δ^{65}Cu = −0.46‰; δ^{66}Zn = −3.65‰) with likely *ranges* of δ for lunar basalts. For iron in lunar basalts we have $0.08‰ \leqslant \delta^{56}$Fe $\leqslant 0.26‰$ (Poitrasson et al., 2004) and $0.05‰ \leqslant \delta^{56}$Fe $\leqslant 0.22‰$ (Wiesli et al., 2003). We have only our own Cu and Zn data for the one lunar basalt 74275: δ^{65}Cu = 1.4‰ and δ^{66}Zn = 0.17‰ and 0.75‰. To be conservative, we assume that isotopes of Cu and Zn are not fractionated in other lunar basalts and therefore adopt as plausible ranges $0‰ \leqslant \delta^{55}$Cu $\leqslant 1.4‰$ and $0‰ \leqslant \delta^{66}$Zn $\leqslant 0.75‰$. These choices correspond to the following ranges of light-isotope *enrichment* relative to lunar basalts for 74220: $−0.40‰ \leqslant \delta^{56}$Fe $\leqslant −0.24‰$, $−1.9‰ \leqslant \delta^{65}$Cu $\leqslant −0.5‰$, and $−4.4‰ \leqslant \delta^{66}$Zn $\leqslant 3.6‰$. From these results, it is clear that the magnitude of the fractionation increases in the order Fe < Cu < Zn.

What caused the light-isotope enrichments in 74220? Chang et al. (1974) and Thode and Rees (1976) reported enrichments of ^{32}S relative to ^{34}S in some samples of 74220. Ding et al. (1983) attributed them to preferential evaporation of lighter isotopes from lunar lava. The isotopically light vapor then condensed on the surfaces of the ejected beads and eventually formed sulfide mounds. In this picture, variations in δ^{34}S among glass samples result from varying the amounts of an isotopically light, sulfur-rich condensate. Following Ding et al. (1983), we suggest that the light isotopes of Fe, Zn, and Cu were enriched in the same way as those of S. Our observed *net* isotope fractionations in bulk orange glass imply that the vapor and future glass substrates traveled independently and combined in varying proportions, a conclusion reached previously from elemental analyses alone (see, Haskin and Warren, 1991). Had it been otherwise, we would expect little or no net fractionation in bulk 74220. This apparently straightforward observation raises a question, however: Where on the Moon is the isotopically heavy counterpart of the Fe, Zn, and Cu in 74220? Other lunar volcanic glasses are one place to search. Our disparate results for 74275 suggest that minerals separated from basalts are another.

4.3.2. Relative volatility of Cu and Zn

Here we will argue that the relative sizes of the isotopic enrichments of Cu and Zn in 74220 imply greater volatility for Cu than for Zn for the conditions associated with volcanism on the Moon. The argument requires three assumptions.

Assumption 1. Most, but not necessarily all, of the Cu and Zn in 74220 are on grain surfaces. Direct observation demonstrates the existence of surface condensates on 74220. Meyer et al. (1975) showed images of "micromounds" on the glass grain surfaces of 74220, that is, micrometer-size heaps of material thought to have condensed from vapor and to have survived mostly intact. About half the sulfur (Thode and Rees, 1976) and most of the zinc and the cadmium (Wasson et al., 1976) analyzed in the bulk glass reside in the micromounds. The semi-quantitative analyses of Meyer et al. (1975) suggest that most of the Cu is there, too.

Assumption 2. The respective isotopic compositions of Cu and Zn in 74220-grain interiors differ little from those of lunar basalts. If Assumptions 1 and 2 are true, they imply that the measured values for bulk 74220 reflect mainly, although not solely, the extent of light isotope enrichment in the coatings.

The experimental evidence bearing on Assumption 2 is inconclusive for S (see Ding et al., 1983) and non-existent for Cu and Zn. While isotopically heavy interiors might seem plausible on mass-balance grounds, we repeat that the orange glass did not form in a closed system. Thus, the length scale of any interior enrichment is essentially unconstrained. We will not consider the possibility of highly fractionated interiors further, although we regard it as an interesting subject for future study.

If correct, Assumptions 1 and 2 imply that the measured isotopic composition for the bulk sample should be a weak function of the grain size distributions. This conclusion does not apply to iron, whose distribution between interior and surface differs from that of Zn and Cu (Butler and Meyer, 1976; Butler, 1978).

Assumption 3. The coatings on 74220 formed by the condensation without further fractionation of an ambient gas that had been enriched in light isotopes as a result of a free (Rayleigh) expansion. We discuss the basis for this assumption further in Section 4.3.3.

The familiar Rayleigh equation for the liquid remaining after a free evaporation has the form

$$R(\text{residual}) = R_0 f_n^{\alpha-1} \tag{1}$$

where f_n is the fraction of reference isotope n left in the liquid after the evaporation, R is an isotope ratio, α is the isotope fractionation factor, and the subscript 0 refers to the initial state. We assume mass-dependent isotope fractionation and make the conventional assumption that $\alpha = \sqrt{m_n/m_j}$, where m is the mass and the index n denotes the reference isotope. In this picture, the isotopic data for 74220 pertain not to the residual phase, but to the complementary gas phase, which, by hypothesis, separated from the liquid and condensed without further fractionation. The mean isotopic ratio, $R(\text{gas})$, of the gas at any point in the evaporation is

$$R(gas) = R_0 \frac{1 - f_n^\alpha}{1 - f_n} \quad (2)$$

The important qualitative result from Eq. (2) is that the gas phase is isotopically lightest ($\delta < 0$) at the very start of the evaporation and becomes progressively heavier ($\delta \to 0$) with time. Thus a small degree of evaporation from the liquid corresponds to a large (negative) degree of fractionation in the corresponding gas.

As noted above, we assume that the fractionation factor $\alpha = \sqrt{m_n/m_j}$ depends on mass. Although we do not know the form(s) in which Cu and Zn evaporated, it seems safe to assume that the masses of the evaporating species of Zn and Cu and hence the fractionation factors were similar. This statement would hold, for example, for evaporation of both elements as the metals, the sulfides, or the chlorides (Chou et al., 1975). It would fail if the chemical forms of the evaporants differed.

We note in passing that any escape of light atoms from the Moon prior to condensation would have made δ more positive. As temperature and mass control the velocity distribution in the vapor, lunar escape should affect Zn and Cu isotopic ratios similarly and should not affect their apparent *relative* volatility.

Given Assumptions 1–3 we can conclude that Cu was more volatile than Zn where the orange glass formed. In particular, $|\delta^{65}Cu| < |\delta^{66}Zn|$ implies that a larger fraction of the Cu evaporated from the source liquid. From cosmochemical/nebular condensation temperatures: 684 K for Zn and 1170 K for Cu (Lodders and Fegley, 1998) we would have expected Zn to be the more volatile element. Although grain-size distributions of the samples analyzed have some influence on the measured values of δ, we do not believe that they could have changed the inferred order of volatility because the measurements for Zn and Cu refer to the same samples. A more likely reason for the higher volatility of Cu is simply that physical conditions and chemical speciation of the elements were different in the nebula and during lunar volcanism. In particular, one might expect Cu to be more volatile based on either the boiling points of the chlorides (CuCl$_2$, 778 K; ZnCl$_2$, 1006 K; Chou et al., 1975) or the melting points of the sulfides (Cu$_2$S, 1100 °C; ZnS, 1700 °C).

4.3.3. Condensation without fractionation?

Our third assumption, that condensation occurs without further fractionation, can be challenged for under certain conditions condensation enriches the light isotopes in accordance with Eq. (2) (see, Davis and Richter, 2003). In principle, then, the light-isotope enrichments observed for the orange glass could reflect the condensation with fractionation of an isotopically normal gas. In this picture, the larger absolute value of $\delta^{66}Zn$ relative to $\delta^{65}Cu$ signifies that Zn is *more* rather than *less* volatile than Cu, contrary to the conclusion of Section 4.3.2, but consistent with the higher vapor pressure of metallic Zn. We argue here, however, that the primary isotopic fractionation occurs during the evaporation of the liquid, rather than during the condensation of the gas.

Eq. (2) describes the isotopic evolution of the condensate only if it collects atoms from a single, well-defined parcel of gas, and if certain other conditions, not discussed, are met. As we imagine orange glass formation (see also Meyer et al., 1975, p. 1691), it seems unlikely that the condensate evolved in this way. Instead, we envision droplets of melt ejected from a lunar vent cooling radiatively and following ballistic trajectories while lava evaporates more or less continuously from the surface below. The atoms of gas may emanate from several locations and follow their own ballistic trajectories. The observed isotopic composition for the condensate then depends on *when* condensation starts and for how long it goes on. For specificity we imagine a bead launched at the end of an exhalation. Its accompanying vapor has passed on and dissipated. At about the same time and somewhere nearby, a parcel of lava vaporizes completely. On average, the lighter isotopes travel faster and reach the location of the bead before the heavier isotopes do. The question then becomes when the bead starts and stops collecting atoms from the 'vapor stream.' Only if the bead was in place from the beginning, and fell out early, will the coating be isotopically light. Similarly, only if the bead entered the vapor stream late will the coating may be isotopically heavy. If an isotopically normal stream of vapor bathed the bead throughout (gas transit times short compared to available condensation times), then the bead coating should have the isotopic composition of the vapor. In summary, we expect the fractionation due to kinetically controlled condensation to be small or random depending on the history of the particular particle.

4.4. Lunar soils

In all 10 of the lunar soil samples analyzed for Cu and Zn, the heavy isotopes are enriched (Table 1). Possible mechanisms include heating and vaporization due to micrometeorite milling, ion sputtering, and electron- or photon-stimulated desorption. For reference we calculate the nominal average fractions of Cu and Zn that the soils retained, f, assuming (1) a simple Rayleigh distillation; and (2) that the masses needed to calculate α are those of the atoms, Zn or Cu. The results follow: $f_{Zn} = 0.77 \pm 0.06$; $f_{Cu} = 0.80 \pm 0.04$ (uncertainties are standard deviations of the averages for the 12 soil measurements). If the dominant volatile species were the sulfides ZnS and Cu$_2$S (see McEwing et al., 1980), the fractions would only change by a few percent with $f_{ZnS} = 0.68 \pm 0.08$ and $f_{Cu_2S} = 0.76 \pm 0.04$. From published data, we can make analogous calculations for sulfur assuming that it evaporates either as S$_2$ ($f_{S_2} = 0.45 \pm 0.10$) or FeS ($f_{FeS} = 0.73 \pm 0.06$). Within the uncertainties and except for f_{S_2}, all the values agree fairly well, regardless of the choice of evaporating mass.

Rayleigh-type calculations for the Cd fractions retained by lunar soils 15041, 60501, 65701, and 72161 (14163

excluded because of contamination; see de Laeter et al. (2005)) lead, respectively, to $f_{CdS} = 0.24$, 0.40, 0.31, and 0.16 and $f_{Cd} = 0.33$, 0.50, 0.40, and 0.24. It seems clear that Cd is more volatile than S, Zn, and Cu in lunar soils.

4.4.1. Isotope fractionation and soil maturity

Kerridge et al. (1975a) demonstrated that $\delta^{34}S$ increases slowly with the sulfur concentration of lunar soils. These authors explained the correlation with a model in which carbonaceous meteorites deliver sulfur and other elements to the lunar regolith. Impact-related processes and ion sputtering cause the loss and isotopic fractionation of some of the sulfur added and some of the sulfur already present. To examine the behavior of Zn and Cu in this framework, we use the I_S/FeO ratio as an index of soil maturity (Morris et al., 1983).

Fig. 5 shows $\delta^{34}S$, $\delta^{56}Fe$, $\delta^{65}Cu$, and $\delta^{66}Zn$ plotted against I_S/FeO. $\delta^{34}S$ correlates weakly but perceptibly with I_S/FeO: R^2 is 0.32 for our samples and rises to 0.70 with soil 72501 excluded. While $\delta^{65}Cu$ also correlates weakly with I_S/FeO ($R^2 = 0.33$), $\delta^{56}Fe$ and $\delta^{66}Zn$ do not ($R^2 = 0.02$). Thus, in lunar soils, Cu and S behave more similarly to each other than to Zn and Fe. The weak correlation for Fe in different *bulk* soil samples (see Wiesli et al., 2003 for a discussion of *intra*sample correlations) may reflect buffering by a relatively high concentration of unfractionated, indigenous Fe in the lunar regolith, or perhaps differences in the grain size distributions.
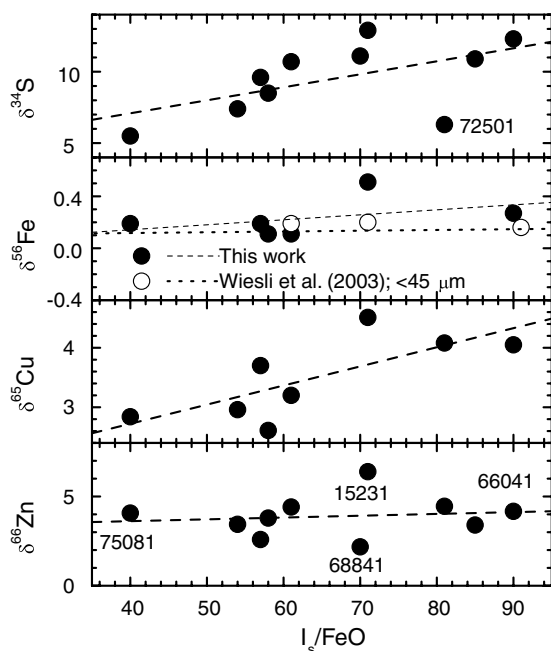
Fig. 5. In lunar soils, $\delta^{34}S$ and $\delta^{65}Cu$ correlate reasonably well with the lunar soil maturity index I_S/FeO. For $\delta^{34}S$, R^2 is only 0.32 for all our samples but 0.70 if the outlier 72501 is excluded. For $\delta^{65}Cu$, R^2 is 0.56. In contrast, neither $\delta^{56}Fe$ nor $\delta^{66}Zn$ correlates with the maturity index. The linear fit to the data of Wiesli et al. (2003) (<45 μm samples) includes three points that plot off scale.

In principle, possible differences between the grain-size distributions of our samples and those taken for the determination of the I_S/FeO ratios introduce an unwelcome complication, particularly for sulfur. Four observations argue that our approach does not appreciably distort the true trends. First, we reproduce the expected relation for S; second, the results for Cu and S are similar; and third, the samples taken for Fe, Cu, and Zn are aliquots. Finally our results for Fe are consistent with those of Wiesli et al. (2003).

4.4.2. Mass balance—elemental considerations

The Cu and Zn in lunar soils come from rocks, lavas, and micrometeoroids (see, Haskin and Warren, 1991). The rocks contribute a volume-correlated component, which to first order should have the elemental composition of mare basalts and highland monomict rocks (Table 2). Micrometeorites contribute a component that is initially surface correlated (because the projectile vaporizes and then fully or partially re-condenses), but which further micrometeorite bombardment may re-work by vaporizing some target material and by folding grains into agglutinates. Sputtering of surfaces may also drive off the lighter isotopes preferentially leaving an isotopically heavy component. Finally, lunar magmas have contributed both condensed vapor, likely to be isotopically light, at least initially, and droplets of glass (as in 74220). This material may also be re-worked and becomes isotopically heavier with time as the lighter isotopes escape the Moon.

In Table 2 we compare the concentrations of S, Cu, Zn, and Cd measured in soils with those expected from mixing extralunar, CI-like material with native lunar basaltic grains. We choose 2% for the size of the CI-like contribution based on the Ir concentrations of the soils studied (Wänke et al., 1972; Krähenbühl et al., 1973; Laul and Schmitt, 1973; Baedecker et al., 1973, 1974; Laul et al., 1974; Chou and Pearce, 1976) and the generally accepted view that virtually all the Ir in lunar soils derives from meteoritic bombardment of the lunar surface (see Haskin and Warren, 1991, pp. 404–405). A mixture of average basalts and 2% CI-like micrometeorites provides more than enough S atoms to account for the S in lunar soils and also too much Cu. In contrast, the 2% addition of CI like material cannot account for all the observed Cd and Zn. Admixture of up to 5% orange glass (we choose 2% for illustration in Table 2) does not change the pattern. Compositional considerations indicate that some Apollo 17 soils contain still larger percentages of orange glass component (see, Korotev and Kremser, 1992), but we expect the fractions to be smaller in the other materials that contribute to our average "soil" values in Table 2. As have many previous workers (see, Haskin and Warren, 1991), we therefore appeal to a separate, vapor mobilized component—from a nearby volcanic vent perhaps—to make up the balance of Cd and Zn. Taking the compositions of the coatings on the orange glass as a guide, we believe that some S and Cu accompanied the Cd and Zn in our hypothetical vapor, but were lost

Table 2
Typical elemental concentrations and ranges (in parentheses) in lunar soil constituents

	S (%)	Cu (ppm)	Zn (ppm)	Cd (ppb)
Lunar basalt[a]	0.13[b] (0.03–0.3)	10 (3–22)	3 (0.1–20)	5 (0.7–100)
CI chondrite[c]	5.4	125	315	690
Sub-total 1[d]	0.24 (0.14–0.40)	12.3 (5–24)	9.2 (6–26)	19 (14–112)
Orange glass[h]	0.0725	26	210	150 ± 100
Green glass[h]	0.0330	5.4	16	58
Sub-total 2[i]	0.23 (0.14–0.40)	13 (6–24)	13 (10–30)	21 (17–113)
Soils	0.076 ± 0.017[e]	7[e] (1.5–22)[g]	25 ± 6.5[e,f]	50 ± 22[e]

[a] Haskin and Warren (1991, pp. 416–418).
[b] See Appendix A.
[c] Lodders and Fegley (1998).
[d] Lunar basalt + 2% CI chondrite.
[e] Data from the literature for the soils analyzed in this work.
[f] This work.
[g] Haskin and Warren (1991, p. 469).
[h] Haskin and Warren (1991, pp. 266–267).
[i] Sub-total 1 + 2% orange glass.

partially as the lunar soils evolved. The pattern of isotope abundances, considered next, reinforces this conclusion.

4.4.3. A model for isotopic evolution of lunar soil under micrometeorite bombardment

We can model how the concentration, $N(t)$ [atom/cm^3], of a volatile isotope changes with time, t, in the topmost layer (thickness, $G(t)$ [cm]) of the lunar soil column under a micrometeorite bombardment with flux ϕ_μ [g/cm^2 My^{-1}]. We assume that three processes change the total number of atoms of interest, $G(t)N(t)$, in the mixed layer, i.e., that

d/dt{$(G(t)N(t))$ = micrometeorite addition

$-$ vaporization loss

$+$ gardening addition

Details are given in a separate electronic archive. This formulation leads to the differential equation

$$\frac{d}{dt}\{G(t)N(t)\} = A - BN(t) + \frac{dG(t)}{dt}D \qquad (3)$$

Terms are defined in Table 3. The equation has the solution for each isotope

$$N(t) = \frac{A + D\beta}{B + \beta} \times \left(1 - \left[\frac{\gamma + \beta t}{\gamma}\right]^{-\frac{B+\beta}{\beta}}\right) + D \times \left[\frac{\gamma + \beta t}{\gamma}\right]^{-\frac{B+\beta}{\beta}} \qquad (4)$$

Fig. 6 shows the results of applying Eq. (4) with the following assumptions: (1) the soils retained a fraction $f_N = 0.70$ of the ^{32}S and of the ^{64}Zn whether supplied by micrometeorites or originally present in the lunar target material; (2) S evaporated as S_2 and Zn as Zn; (3) the initial lunar concentrations ($C_\mathbb{C}$ in Table 3) of S and Zn were 800 ppm and 25 ppm, respectively; (4) the micrometeorite component had CI abundances of S (5.4%) and Zn (315 ppm); and (5) a gardening rate, dG/dt of 0.1 cm My^{-1}, applied. Most

lunar soils have nominal exposure times of 1 Gy or less. Over this period the model calculations show an 80% and a 10% increase in the S and the Zn concentrations, respectively. The difference arises because the initial concentration ratio C(micrometeorite)/C(Moon) is larger for S than for Zn so that the micrometeorite bombardment has a larger relative effect on S. After 1 Gy, the calculated values of δ^{34}S and δ^{66}Zn reach 1.2‰ and 3.0‰, respectively, much less than observed values.

In the context of our model, the easiest way to improve agreement with observed values of δ^{34}S and δ^{66}Zn is ad hoc (1) to decrease the gardening rate β by a factor of 20, from 0.15 to 0.0075 g/cm^2 My^{-1} and (2) to assume that different fractions of Zn and S were retained (Fig. 7). As impacts of larger masses do most of the stirring of the regolith (Arnold, 1975), it is at least conceivable that much of the isotopic evolution of soils occurs during relatively long intervals of slow micrometeorite gardening between large impacts. As to the second adjustment, differences in chemical speciation of S and of Zn in the Moon and the micrometeorite components, respectively, give reason for assigning different fractions retained to Zn and S. In carbonaceous micrometeorites, for example, S occurs in various organic and inorganic forms with different isotopic composition (e.g., Gao and Thiemens, 1993; Garvie and Buseck, 2003). Some Zn in carbonaceous chondrites occurs in the silicate phase (Wulf et al., 1995). With β set equal to 0.0075 g/cm^2 My^{-1}, f_{64Zn} to 0.7, and f_{32S} to 0.5 in our model, the Zn concentration increases by a factor of 1.7 as δ^{66}Zn rises to 6.0‰ in 500 My, an exposure age typical for our soils. In Fig. 8, we show that we can approximate the Apollo 16 data of Kerridge et al. (1975a) by starting with a relatively low intrinsic S content, 125 ppm, for lunar basalts and by assuming 0.35 retention of S.

The model can be applied to other elements. Smaller effects for nonvolatile major elements in bulk samples would

Table 3
Terms and parameters for model equation

Term	Definition	Value	Refs.
$A[\text{atom cm}^{-2}\text{My}^{-1}] = \phi_\mu(C_\mu N_{\text{Avo}}/\mathcal{M})I_N f_N$	Input from micrometeorites		
$\phi_\mu\ (\text{g cm}^{-2}\ \text{My}^{-1})$	Micrometeorite mass flux	$\sim 3 \times 10^{-3}$	1,2
$C_\mu\ (\text{g/g})$	Elemental conc. in CI chondrites		3
$N_{\text{Avo}}\ (\text{atom/mol})$	Avogadro's number		
$\mathcal{M}\ (\text{g/mol})$	Molar mass of volatile element		
I_N	Abundance of isotope N		
f_N	Fraction isotope N retained	*	
$B[\text{cm s}^{-1}] = \phi_\mu\ (F/\rho)\ (1 - f_N)$	Stripping rate due to impact volatilization		
$F[\text{g Moon/g micrometeorite}]$	Lunar mass volatilized per unit mass micrometeorite input	10	2,4
$\rho[\text{g cm}^{-3}]$	Density of lunar soil	1.5	5
$G(t)[\text{cm}] = \gamma + \beta t$	Thickness of mixed layer		6
$\gamma\ [\text{cm}]$	Thickness of surficial disturbed layer	4	
$\beta[\text{cm/My}]$	Gardening/mixing rate	*	
$D\ [\text{atom cm}^{-3}] = C_{\mathbb{C}}\ (\rho N_{\text{Avo}}/\mathcal{M})\ I_N$	Initial isotope conc. in lunar soil		
$C_{\mathbb{C}}\ [\text{g/g}]$	Initial elemental conc. in lunar soil	*	

Note. *Parameter.
Refs. (1) Gault et al. (1972), Halliday et al. (1989), Peucker-Ehrenbrink and Ravizza (2000), Taylor et al. (2000). (2) Zook (1975). (3) Lodders and Fegley (1998). (4) Housley (1979), Pierazzo et al. (1997). (5) McKay et al. (1991). (6) Arnold (1975).
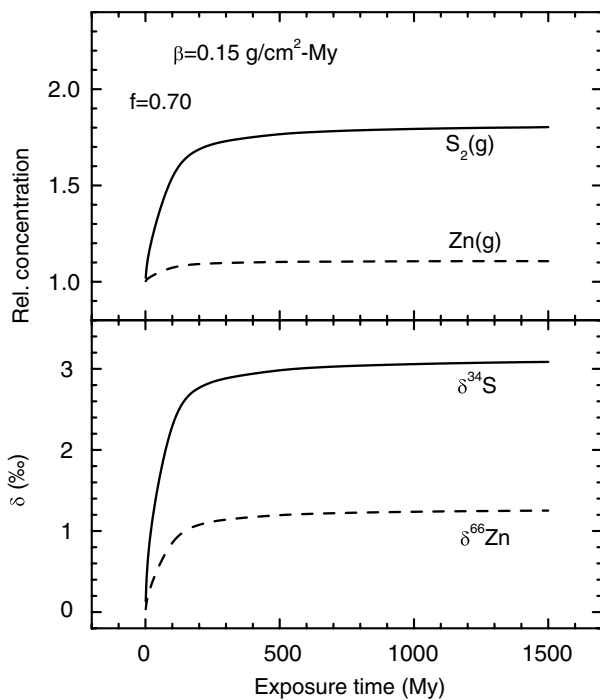
Fig. 6. Model calculations showing the evolution in lunar soils of Zn and S concentrations and of δ^{34}S and δ^{66}Zn. The calculations assume a steady micrometeorite bombardment with lunar gardening parameters taken from the literature (see text).
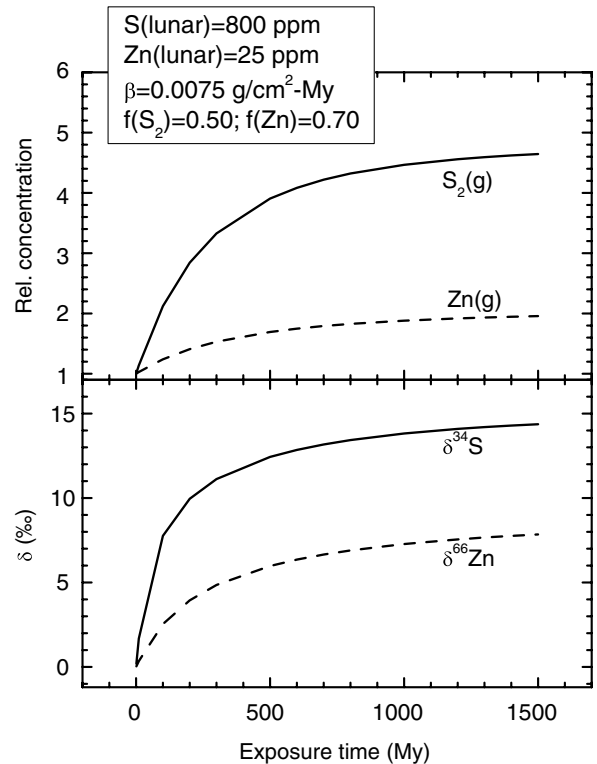

Fig. 7. Model calculations as in Fig. 6 but with the lunar gardening rate lowered in order to approximate experimental measurements for S and Zn.

be expected as the consequence of higher values of f and smaller differences between the elemental concentrations in incoming meteorites and the bombarded lunar basalts.

4.4.4. Sputtering of lunar soils

Haff et al. (1977) developed a microscopic model for treating the isotopic evolution of a thin layer of material coating lunar soils. In their model, isotopes fractionate first during sputtering and then again when lighter, fast-er-moving atoms escape from the Moon. We calculated expected values of Φ from their equations and compare them with selected measured values in Fig. 9. As no experimental measurement pertains strictly to a surface layer, in preparing Fig. 9 we settled instead for the largest values of δ that we could find. These maxima mostly refer to analyses of leaches or of fine fractions with large surface contributions. For Zn, Cu, and Cd, however, the data refer to bulk soils only, so that these three
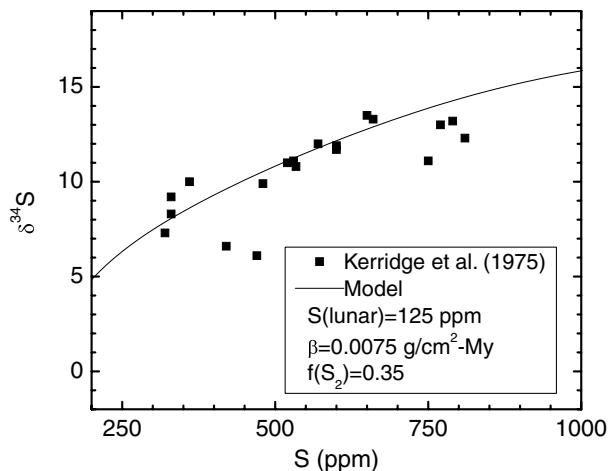
Fig. 8. Model calculations adjusted to match approximately the experimental measurements of Kerridge et al. (1975a,b).
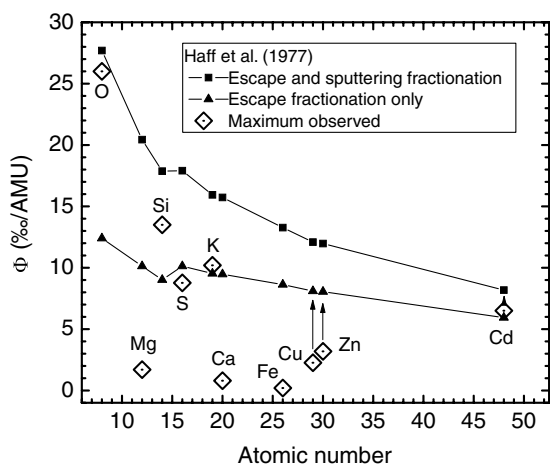

Fig. 9. Isotope fractionation calculated from the model of Haff et al. (1977) for surface layers coating grains of lunar soil compared with maximum measured values in lunar samples. Sources of data are as follows: O, Epstein and Taylor (1972); Mg, Esat and Taylor (1992); Si, Epstein and Taylor (1971); S, Thode and Rees (1979); K, Church et al. (1976); Ca, Russell et al. (1977); Fe, Wiesli et al. (2003); Cu, this work; Zn, this work; Cd, Sands et al. (2001); and de Laeter et al. (2005). The quantity Φ is the mass-dependent fractionation per unit mass.

experimental values are lower bounds. The observations match theoretical predictions for only two elements, O and perhaps Cd, a point made and considered by numerous other authors (e.g., Esat and Taylor, 1992; Keller and McKay, 1997). We will not rehearse the discussion, but suggest that better understanding is unlikely until modern microprobes are brought to bear on the disagreements that are most problematic for the model of Haff et al. (1977), namely, the ones for Mg, Ca, and Fe.

5. Conclusions

(1) The isotope abundances of Zn in Ti-rich basalt 74275 are close to normal, terrestrial values for igneous rocks. The Cu in this basalt appears to be slightly

heavier than the terrestrial value: $\delta^{65}Cu = +1.4‰$. This single observation needs confirmation for if general it suggests that volatility-related processes were important in determining the behavior of lunar copper.

(2) Zn and Cu in our sample of lunar glass 74220 are isotopically light, slightly so for Cu and decidedly so for Zn. Relative to published isotopic abundances for lunar basalts, Fe in 74220 is also isotopically light. These observations likely reflect light-isotope enrichments in an Fe-, Zn-, and Cu-bearing vapor that condensed on the exterior of orange glass grains. The *difference* in the degree of fractionation of Zn and Cu may result from either (1) a larger relative concentration of isotopically normal Cu in the interior of the orange glass; (2) kinetically favored condensation of light isotopes; or as we would prefer (3) an intrinsic difference in the volatilities of the two elements in the source of the gas, presumably a lava, with Cu being the more volatile. Possibility (1) could be checked by direct measurement. If possibility (3) should prove true, it would suggest that evaporation rates from the source are controlled by the properties of chlorides or sulfides.

(3) The heavy isotopes of Fe, Zn, and Cu are enriched in bulk lunar soils. The degrees of enrichment for Zn and Cu are similar. That of Fe is smaller, either because of lower volatility or the presence of a larger fraction of unfractionated, indigenous lunar iron. The enrichments are observed to be mass dependent in Fe and Zn and supposed to be likewise mass dependent in Cu. By analogy to S, we surmise that the isotope fractionation is surface correlated for Zn and Cu; Wiesli et al. (2003) showed directly that it is surface correlated for Fe. The absolute fractionations of Zn and Cu for bulk samples correspond to nominal evaporative losses of ~30% but are likely much larger close to grain surfaces. If the vapor-mobilized component of Zn in lunar soils were originally as light isotopically as measured for *bulk* 74220 ($\delta^{66}Zn \sim -4‰$), then $\delta^{66}Zn$ in soils must have increased over time by nearly 8‰. That *all* the soils analyzed so far are isotopically heavy in Zn and Cu suggests that the enrichments are pervasive on the lunar surface and that the light isotopes must have escaped from the Moon.

(4) The heavy-isotope enrichments of Cu in lunar soils increase slowly with soil maturity, as expected. In contrast, the values of $\delta^{66}Zn$ do not for reasons that are not understood,

(5) Our data do not speak directly to the relative importance of micrometeorite-induced vaporization and sputtering in producing the isotopic fractionations observed in soils. A simple model based on micrometeorite-induced vaporization with accepted gardening rates gives isotopic fractionations smaller than those observed. We can explain the differences

Table A.1
Sulfur contents and isotope abundances in lunar basalts

Sample	Type	S (ppm)	$\delta^{34}S$ (‰)	Ref.
10049	Fine grained rock	2200	1.25	1
10057	Fine grained rock	2280	1.2	1
12002	Olivine dolerite	632	0.46	2
12018	Olivine dolerite	549	0.68	2
12021	Pigeonite dolerite	781	0.53	2
12022	Olivine dolerite	914	−0.228	2,3
12053	Olivine basalt	722.5	0.575	2
15016	Olivine basalt	825	−0.45	4,5
15058	Porphyritic subophitic olivine basalt	719	−0.55	5
15076	Porphyritic subophitic olivine basalt	970	−1.2	5
15085	Porphyritic subophitic olivine basalt	855	−1.3	5
15499	Vitrophyric qz normative mare basalt	767	0.1667	4,5
15555	Olivine normative mare basalt	753	0.2	4,5
15556	Olivine normative mare basalt	965	0.9	5
61016	Impact melt with pristine anorthite	534	0.9	6,7
65015	Poikilitic impact melt	589	1.3	6
66095	Basaltic impact melt	903	1.8	6
70017	High Ti mare basalt	2283	1.4	8
70035	High Ti mare basalt	1580	−0.2	5
70215	High Ti mare basalt	1827	0.7	5,7,8
74275	High Ti mare basalt	1399	0.88	5,7–9
75035	High Ti mare basalt	2310	1.15	5,8
75055	High Ti mare basalt	2210	−0.2	5
75075	High Ti mare basalt	1708	1.8	8
Average		1220 ± 130	0.5 ± 0.2	
w/o 16xxx		1300 ± 140	0.4 ± 0.2	

Refs. (1) Kaplan et al. (1970). (2) Rees and Thode (1972). (3) Kaplan and Petrowski (1971). (4) Kaplan et al. (1976). (5) Gibson et al. (1975). (6) Kerridge et al. (1975b). (7) Rees and Thode (1974). (8) Petrowski et al. (1974). (9) Des Marais (1983).

by adopting smaller gardening rates, which may be appropriate for micrometeorites. It is also possible, however, that the model gives low results because sputtering of re-deposited micrometeoritic material (e.g., Kerridge and Kaplan, 1978) causes much of the fractionation.

Appendix A

See Table A.1.

Appendix B. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2006.02.030.

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