MAGNITUDE OF STABLE ISOTOPE FRACTIONATION IN LUNAR BASALTS.

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Introduction: Numerous investigations of traditional and nontraditional stable isotopes in lunar basalts have been carried out. At least two differences have been discovered in isotopes of volatile elements when lunar basalts are compared with terrestrial basalts. One is that the average stable isotope ratio in lunar basalts for a given volatile element may be offset with heavy isotope enrichment. For example, lunar mare basalts have a mean $\delta^{66}Zn/^{64}Zn$ value of 1.4 ± 0.5‰ [1], whereas terrestrial basalts have a mean of 0.28 ± 0.05‰ [2,3], with an offset of 1.1‰. For $^{65}Cu/^{63}Cu$, there is likely a similar enrichment in lunar basalts compared with terrestrial basalts [4]. For $^{41}K/^{39}K$, lunar basalts are about 0.4‰ more enriched than terrestrial basalts [5]. For $^{87}Rb/^{85}Rb$, lunar basalts appear to be 0.17‰ more enriched than terrestrial basalts [6]. The overall enrichment of heavy isotopes in the Moon relative to the Earth is often attributed to the global depletion of volatiles in the Moon relative to the Earth [1,5,6].

Another difference in stable isotope ratios is the much larger spread (variability) of stable isotope ratios of some volatile elements in lunar basalts compared with terrestrial basalts (note that lunar impact melts, lunar soil samples and condensates on the Moon are not considered here because the purpose is to examine the effect of post-eruptive loss of volatiles on the isotope ratios). It has been shown that stable isotope fractionation is much larger in lunar basalts than terrestrial basalts for at least the following elements: H [7], Cl [8-10], Zn [11-13], Cu [11,14], and Ga [15,16]. One key question is: what controls the difference in the magnitude of stable isotope fractionation in lunar basalts relative to terrestrial basalts?

In this work, I show that the magnitude of isotope fractionation in lunar basalts is largely controlled by volcanic degassing rather than the global volatile loss.

Magnitude of Stable Isotope Fractionation: To quantify the magnitude of stable isotope fractionation for different elements and different isotopes, a parameter Z (referred to as the normalized magnitude of isotope fractionation) is defined as the relative isotope fractionation ($\ln(R_{max}/R_{min})$, where R_{max} and R_{min} are the measured maximum and minimum isotope ratios) divided by the relative mass difference ($\ln(m_{heavy}/m_{light})$ where m_{heavy} and m_{light} are the masses of the heavy and light isotopes in the isotope ratio):

$$Z = \frac{\ln\dfrac{R_{max}}{R_{min}}}{\ln\dfrac{m_{heavy}}{m_{light}}}.$$

With the above definition, the parameter Z is independent of the isotope ratio used for the same element (such as $^{68}Zn/^{64}Zn$ versus $^{67}Zn/^{64}Zn$ versus $^{66}Zn/^{64}Zn$) for mass-dependent fractionations and it also accounts for the fact that the isotope ratio of a lighter element can fractionate more that that of a heavier element. Available data [7-16] show that the normalized magnitude of isotope fractionation in lunar basalts is largest for H ($Z \approx 4.2$), followed by Cl ($Z \approx 0.8$), Zn ($Z \approx 0.2$), Cu ($Z \approx 0.09$), and Ga ($Z \approx 0.03$).

Possible Control of the Magnitude of Isotope Fractionation in Lunar Basalts: One might first think that the large stable isotope fractionation in lunar basalts is due to "volatility" of volatile elements, possibly inversely related to the 50% condensation temperature T_c [17]. T_c for the interested elements from low to high is: H ($T_c = 182$ K), Zn (724 K), Cl (948 K), Ga (968 K) and Cu (1037 K) [17]. However, the normalized magnitude of stable isotope fractionation Z is not inversely related to the condensation temperature. For example, Cl is less volatile (higher T_c) than Zn but has a much greater normalized magnitude of stable isotope fractionation than Zn. Hence, it does not seem that the condensation temperature is the main control for the larger isotope fractionation in lunar basalts than in terrestrial basalts.

An alternative is that the larger stable isotope fractionation in lunar basalts compared with terrestrial basalts is related to post-eruptive loss of volatiles. This loss has been quantified by [18] using the ratio C_{OHMI}/C_{GB}, where C_{OHMI} is the concentration of a volatile element in olivine-hosted melt inclusions (representing pre-eruptive volatiles) and C_{GB} is that in glass beads (representining post-eruptive volatiles) in Apollo sample 74220. The ratio has been re-calculated in this work by using volatile/refractory elemental ratios to account for crystal fractionation. A larger C_{OHMI}/C_{GB} ratio means more severe post-eruptive loss of the element. Use only the data for elements with $C_{OHMI}/C_{GB} > 3$ (which are more reliably determined). The relation between Z and C_{OHMI}/C_{GB} is shown in Fig. 1: There exists an excellent positive correlation

between the normalized magnitude of isotope fractionation (Z) and the post-eruptive depletion factor of the volatile element (C_{OHMI}/C_{GB}). The relation can be fit well by $Z \approx 0.0146(C_{OHMI}/C_{GB})$ with $r^2 = 0.9963$. The excellent correlation line shown in Fig. 1 suggests that the much larger isotope ratio variation in lunar basalts compared with terrestrial basalts is mainly due to isotope fractionation during post-eruptive degassing of the volatile elements. Much of the fractionation might be due to diffusive loss, which is able to generate large isotope fractionations [19]. Jiang et al. [20] showed that $\delta^{68}Zn/^{64}Zn$ in tektites also exhibits large variability (–0.79‰ to 4.16‰), indicating that high-temperature degassing of Zn from a melt, similar to lunar volcanic degassing, can indeed fractionate Zn isotopes significantly.
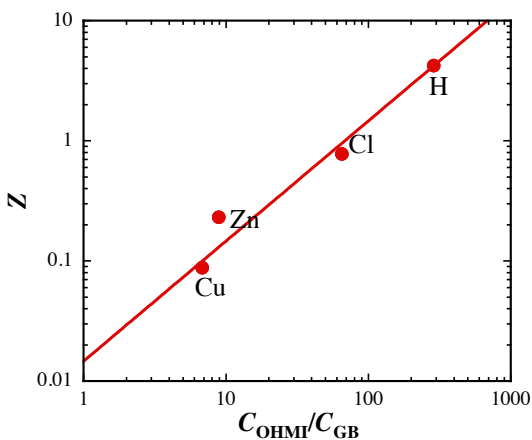

Fig. 1. Normalized magnitue of stable isotope fractionation (Z) versus depletion factor C_{OHMI}/C_{GB}.

Discussion: In summary, the large isotope ratio variability in lunar basalts is related to volcanic degassing on the Moon, rather than to the global depletion of volatiles in the Moon relative to the Earth. It appears that the global depletion of volatiles has shifted lunar stable isotope ratios to higher heavy/light ratios. For example, K and Rb are depleted in the Moon relative to the Earth by a factor of 2 to 4 [21,22] and the $^{41}K/^{39}K$ and $^{87}Rb/^{85}Rb$ isotope ratios are shifted to higher values globally by 0.4‰ [5] and 0.2‰ [6], respectively. On the other hand, the variability of the $^{41}K/^{39}K$ and $^{87}Rb/^{85}Rb$ isotope ratios in lunar basalts is only slightly larger than that in terrestrial basalts probably due to the small degrees of degassing loss in from lunar basalts [18].

Post-eruptive degassing of volatiles (a local process or secondary process) appears to be able to produce large variability of isotope ratios in H, Cl, Zn, and Cu.

Local isotope fractionation may also arise from condensation of volatiles onto glass beads as well as during impact, which are not included in the discussion here.

The data in Fig. 1 are limited and more data are needed to confirm and quantify the relation between the magnitue of isotope fractionation and the volatiles depletion factor during lunar volcanic degassing. A systematic examination of degassing loss of all volatiles (including H, C, F, Cl, S, Cu, Zn, Pb, Cs, Rb, K, Na, Li, N, Hg, Tl, I, In, Br, Cd, Se, Sn, Te, Bi, Ge, B, Sb, Ag, Au, and As) would provide key information in future assessment of loss of volatiles by volcanic degassing, as well as stable isotope ratio variability in lunar basalts if the element has two or more stable isotopes. Assessing degassing loss of volatiles is essential not only for understanding stable isotope ratio variations, but more importantly for accurate determination of the abundances of volatile elements in the Moon. Such determination is critical for understanding the origin of the Moon.

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