

Investigating the Zn Isotopic Composition of Mare Basalts; Implications for Zn systematics on the Moon.

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Introduction: The Moon is well known to be depleted in volatile elements relative to the bulk Earth and chondritic meteorites [e.g. 1, 2]; this is hypothesized to be a consequence of the Moon-forming Giant Impact [e.g. 3, 4]. Recently, there have been attempts to constrain the degree of this volatile element loss on the Moon by characterizing the isotopic composition of moderately volatile elements, such as Zn, that undergo kinetic isotopic fractionation during evaporative loss [5, 6]. Results demonstrate that lunar samples contain Zn with highly fractionated isotopic compositions relative to the bulk silicate earth (BSE) $\delta^{66}\text{Zn}$ value of +0.28‰ [7]. The general enrichment in isotopically heavy Zn in lunar basalts ($\delta^{66}\text{Zn} \sim +1.4 \pm 0.5\%$) has been proposed to reflect the composition of the mare-basalt source region [5, 8]. Because Zn isotopes do not fractionate significantly during magmatic processes [9, 10] this $\delta^{66}\text{Zn}$ value is assumed to be representative of the bulk lunar crust and ultimately to have derived from the planetary scale loss of Zn during the Giant Impact [8].

While the $\delta^{66}\text{Zn}$ values of lunar basalts are typically around +1.4‰, published values range from -5.4 to +1.9‰ [5, 6]. Several outliers can be excluded due to the likely presence of isotopically light vapor condensate on their surface (e.g. 10017, 12018). Even so, the remaining basalts span a range of $\delta^{66}\text{Zn}$ values of over 1.4‰, far outside of analytical constraints and in excess of the range attributed to magmatic processes in terrestrial systems [9, 10]. While this range in $\delta^{66}\text{Zn}$ values could be caused by surficial processes, it could also reflect heterogeneities in the basalt source reservoir, or chemical evolution of the melt during magma degassing and basalt eruption. To investigate this in more detail we present new Zn isotope data from a series of 14 mare basalts and 2 Mg-suite rocks. We aim to confirm that mare basalts are enriched in isotopically heavy Zn relative to terrestrial values, and evaluate whether, on average, they have $\delta^{66}\text{Zn}$ values close to +1.4 ± 0.5‰. New analyses of two Mg-suite rocks will help establish whether the lunar crust contains isotopically distinct Zn to the mare basalts. Because both basalt and Mg-suite samples have previously been characterized for major and trace elements [11], Sm-Nd and Rb-Sr systematics we will have a unique opportunity to interpret the Zn isotope data based on broader geochemical constraints related to petrogenesis.

Methods: We analysed 5 high-Ti basalts from Apollo 11 and 9 low-Ti basalts from Apollo 12 and 15.

In addition we analysed two Mg-suite rocks (76335 and 78238). All samples were dissolved using Parr bombs with a combination of HF-HNO₃ acid to ensure complete digestion.

Isotopic analyses were performed using a ⁶⁸Zn-⁶⁶Zn double-spike technique at LLNL. Spiked samples were purified using anion exchange resin. The total procedural blank through dissolution and purification was between 0.1-2ng of Zn; <2% of the processed Zn. Isotopic measurements were performed by MC-ICP-MS using the Thermo Neptune-plus instruments at LLNL and UC Davis. Internal precision on $\delta^{66}\text{Zn}$ values was typically < 0.02‰. Final $\delta^{66}\text{Zn}$ values are presented relative to the Zn isotope standard JMC-Lyon. To ascertain the accuracy and external precision of the technique we processed the USGS basalt standards BCR-2 and BHVO-2 multiple times through multiple digestions. We obtained $\delta^{66}\text{Zn}$ values of $0.25 \pm 0.05\%$ and $0.26 \pm 0.04\%$ respectively, which are within uncertainty of literature values [7].

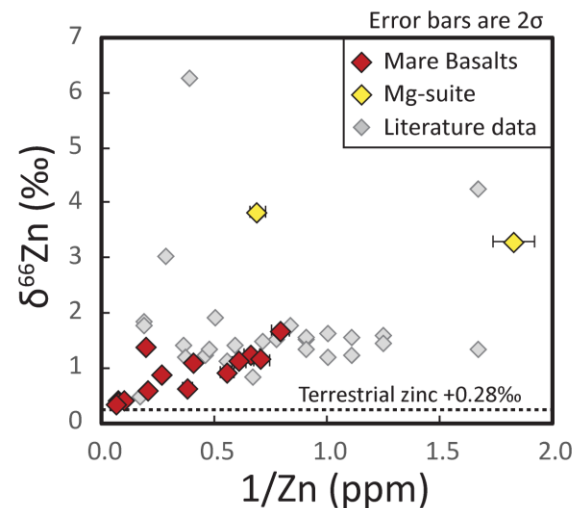


Fig. 1 – Relationship between $\delta^{66}\text{Zn}$ and Zn concentration in 14 mare basalts and 2 Mg-suite rocks. Literature data for mare basalts and lunar crust is also provided [5, 6].

Results: Zn concentrations in the mare basalts range from 1.27 to 16.76 ppm, while $\delta^{66}\text{Zn}$ values range from +0.34‰ to +1.66‰. If $\delta^{66}\text{Zn}$ is plotted vs Zn concentration there is a clear relationship in which the samples with highest $\delta^{66}\text{Zn}$ have the lowest Zn concentration and vice versa (Fig. 1). A similar relationship is also observed between $\delta^{66}\text{Zn}$ and the concentration of other chalcophile elements such as Pb and Cu. Though the samples with highest $\delta^{66}\text{Zn}$ values plot in the same $\delta^{66}\text{Zn}$ vs 1/Zn field as published work, the

linear relationship between $\delta^{66}\text{Zn}$ and $1/\text{Zn}$ has not previously been observed.

The two Mg-suite rocks, 76335 and 78238, have Zn concentrations of 0.55 and 1.45 ppm, and $\delta^{66}\text{Zn}$ values of +3.29 and 3.83‰ respectively. In general, these data are consistent with lunar crustal rocks having higher $\delta^{66}\text{Zn}$ values than mare basalts [5, 6].

Discussion: The relationship between $\delta^{66}\text{Zn}$ and Zn concentration in lunar mare basalts and Mg-suite rocks (Fig. 1) represents a two-component mixture between a source with a near terrestrial $\delta^{66}\text{Zn}$ value and another that is significantly enriched in isotopically heavy Zn. In theory, this mixing relationship could arise through several different mechanisms; these will be discussed in the following.

The simplest explanation is external addition of Zn with a $\delta^{66}\text{Zn}$ value of $\sim 0.3\%$ to each sample. This could be caused by terrestrial contamination or input of chondritic material to the lunar surface. Our procedural blanks allow us to discount anthropogenic input. Input of chondritic material is inconsistent with the observation that $\delta^{66}\text{Zn}$ does not correlate with concentrations of trace elements that are typically enriched in chondritic meteorites.

If external input is discounted, then we must next consider isotopic fractionation related to magmatic processes such as partial melting and crystallization. Mg-suite rocks and mare basalts are thought to derive from partial melting of magma ocean cumulates [e.g. 12]. While Zn isotopes fractionate during terrestrial melt extraction, the degree of fractionation is too low ($<0.2\%$, [10]) to generate the 6‰ range of $\delta^{66}\text{Zn}$ values in lunar crustal rocks and mare basalts. Furthermore, isotopic variation of $\delta^{66}\text{Zn}$ due to fractionation processes associated with magma ocean solidification are ruled out by the fact that $\delta^{66}\text{Zn}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ of the mare basalt source regions do not correlate. This is supported further by the observation that concentration of incompatible trace elements such as the REE's also do not correlate with $\delta^{66}\text{Zn}$.

Evaporative loss seems the most likely mechanism to generate %-level fractionation of Zn isotopes in lunar rocks, and has previously been demonstrated in terrestrial systems [13, 14] and invoked for lunar samples [5, 6]. Here, we consider two scenarios that could generate the data array in Fig. 1. In the first, the lunar mantle is characterized by an isotopically heavy Zn composition, as measured in FAN, Mg- and alkali suite rocks (3-6.2‰, [5, 6]). During magmatic ascent degassing results in percolation of a sulphur rich gas that contains relatively high concentrations of isotopically light Zn, as well as other volatile chalcophile elements Cu and Pb. Gas-rich magma is erupted, and some of

the volatiles (including Zn), are retained on surfaces, driving the resulting basalts to isotopically lighter $\delta^{66}\text{Zn}$ values. The alternative scenario is that the bulk Moon is relatively Zn-rich and has a $\delta^{66}\text{Zn}$ value close to the terrestrial value. In this scenario Zn is degassed during solidification of the magma ocean and is therefore not retained. Because the $\delta^{66}\text{Zn}$ value of gas is lighter than the bulk Moon, the magma ocean cumulates become progressively heavier as solidification progresses and Zn is lost to the system. Thus, the erupted mare basalts would reflect the isotopic composition of the evolving magma ocean cumulates. Such evolution can be modeled by assuming the most Zn-rich basalt has a similar composition to the basalt source (Fig. 2). If we assume that the $\delta^{66}\text{Zn}$ value of the mare basalts evolved from this composition then the Zn isotope data would be consistent with a fractionation factor (α) of 0.9997. This is similar to α values calculated for terrestrial systems [13, 14].

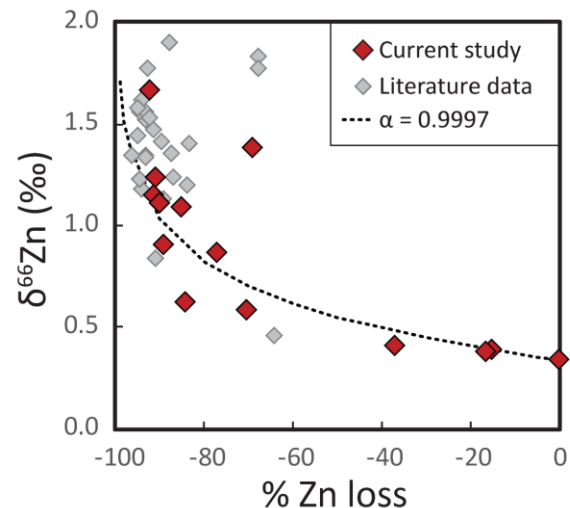


Fig. 2 – Relationship between $\delta^{66}\text{Zn}$ and % Zn loss in mare basalts. Literature data is provided for comparison [5, 6].

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