

Zinc isotopic composition of lunar high- and low-titanium mare basalts G. Florin¹, P. Gleißner¹ and H. Becker¹,
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Introduction: Moon and Earth are depleted in volatile elements when compared to chondrites. The significantly stronger depletion in volatile elements in most lunar samples has evolved to a key aspect to understand the formation of the Earth-Moon system. The most widely accepted Moon-formation hypothesis suggests that the Moon formed after a giant impact of a Mars-sized impactor on to the proto-Earth. The apparent strong volatile depletion of the lunar interior estimated from mare basalts [1] then could be one of the consequences of this giant impact. This interpretation is also supported by the consistent heavy isotopic compositions of some moderately volatile elements (*e.g.*, K, Rb, and Zn) in lunar rocks [2-4]. However, recent detection of water and elevated volatile contents in different lunar lithologies as well as of water at its surface (*e.g.*, [5-7]) might indicate a Moon mantle much less depleted in volatiles than previously argued. Following these arguments, variable isotopic composition of lunar materials was interpreted as indicative of strong magmatic degassing during the lunar magma ocean stage or later magmatic differentiation [*e.g.*, 8-10]. However, because results from different measurement methods and different lunar lithologies not always agree, the extent of lunar volatile depletion and volatile loss processes are a matter of active debate.

Because the magnitude of the lunar volatile depletion has important consequences for our understanding of Moon's formation and differentiation, its elemental and isotopic compositions need to be more precisely defined. Here we present the first results of our ongoing effort to produce a comprehensive data set for mass dependent stable isotope fractionation of Zn and other volatile elements in lunar samples.

Samples: In this study we analyzed 11 low-Ti and 6 high-Ti mare basalts from Apollo missions 11, 12, 15, and 17. Samples were chosen to reflect various basaltic suites (different source regions in the lunar mantle), compositions and textures (different cooling histories). We analyzed vitrophyric low-Ti basalts, interpreted as unfractionated basalt liquidus compositions (*e.g.*, 12009, 15016, 15555) [12]; high-MgO partial cumulate rocks (*e.g.*, 12020, 12040) [13]; highly vesicular basalts (*e.g.*, 15016, 15556); high-Ti olivine-porphyrific and plagioclase-poikilitic basalts (70035, 70215, 70275, 75055); and high-Ti, low-K ilmenite basalts (10020, 10058).

Method: Sample preparation, digestion, chemical separation, and analyses were conducted in the Geochemistry laboratories at Freie Universität Berlin, Germany. Samples have been gently crushed in an agate mortar, digested in HF-HNO₃ and then converted into HCl. We adopted the chemical procedure of Freymuth *et al.* (2020) [14].

The Zn stable isotope composition of lunar basalts was analyzed by the state-of-the-art Thermo Scientific Neoma Multicollector ICP-MS. To correct for external and internal mass fractionation (*e.g.*, chemistry, MC-ICP-MS behavior), a double spike (⁶⁷Zn-⁷⁰Zn) was added to samples prior to column chemistry. Sample solutions were introduced with an ESI Apex Omega desolvator and a 50µl/min PFA nebulizer, and data were acquired in medium resolution ($m/\Delta m > 4000$) to resolve the Zn signals from polyatomic interferences. With this configuration we report an intensity of 1.5V on mass ⁶⁴Zn for a 20 ng/g solution. The standard error on ⁶⁶Zn/⁶⁴Zn ratio over a cycle of 60 scans is 7 ppm and the 2SD reproducibility on the delta value was better than 0.04 ‰. We report a Zn blank of 0.5 ng, negligible compared to the >200 ng Zn processed for analyzed samples. The isotope ⁴⁸Ti was measured in each sample before stable isotope analysis to make sure that Ti/Zn < 0.01 [15]. Nickel was monitored during the measurements to correct for ⁶⁴Ni interference (<10⁻⁴ V) if needed. Germanium was not monitored because it fully evaporates during the digestion procedure due to the use of HCl [16].

Results and discussion: We report the first zinc elemental and isotopic composition of Apollo mare basalt samples obtained via double spike technique and using the Thermo Scientific Neoma Multicollector ICP-MS. Data is given in per mille and calculated as delta value with respect to the IRMM3702 isotope standard:

$$\delta^{66/64}\text{Zn} (\text{‰}) = \left(\left(\frac{{}^{66}\text{Zn}/{}^{64}\text{Zn}_{\text{sample}}}{{}^{66}\text{Zn}/{}^{64}\text{Zn}_{\text{IRMM3702}}} - 1 \right) * 1000 \right)$$

In order to ease comparison to earlier data $\delta^{64/66}\text{Zn}_{\text{IRMM3702}}$ values are then converted to JMC-Lyon by adding $\Delta_{\text{IRMM3702}-\text{JMC Lyon}}$ (+0.28 ‰ [14]), errors are in 2SD.

Low Ti mare basalts are characterized by a large range of variations in isotopic composition from $\delta^{66/64}\text{Zn} = -3.41 \pm 0.24 \text{ ‰}$ to $+1.91 \pm 0.04 \text{ ‰}$ with the

majority of the data lying between $+1.27 \pm 0.06$ ‰ and $+1.91 \pm 0.04$ ‰ and a limited range of Zn mass fractions (from 0.87 ppm to 1.21 ± 0.01 µg/g). In comparison analyzed high-Ti mare basalts $\delta^{66/64}\text{Zn}$ range from $+1.19 \pm 0.03$ ‰ to 0.70 ± 0.03 ‰ and have generally higher and more variable mass fractions of Zn (from 1.40 to 2.28 ± 0.03 µg/g).

Our new data generally agree with older data [e.g., 4, 17, 18] (Figure 1), but our typical uncertainties reported for $\delta^{66/64}\text{Zn}$ are 2 to 3 times lower than in previous studies [e.g., 3-4, 17-18]. Excluding the three low $\delta^{66/64}\text{Zn}$ outliers (12005, 12009, 15016), our current data show a difference between low-Ti ($+1.56 \pm 0.51$ ‰) and high-Ti ($+0.89 \pm 0.34$ ‰) mare basalt samples. Hence, the lunar interior might be heterogeneous in Zn stable isotopes and in average could be somewhat isotopically lighter than previously suggested [e.g., 18] with a $\delta^{66/64}\text{Zn} = +1.26 \pm 0.78$ ‰.

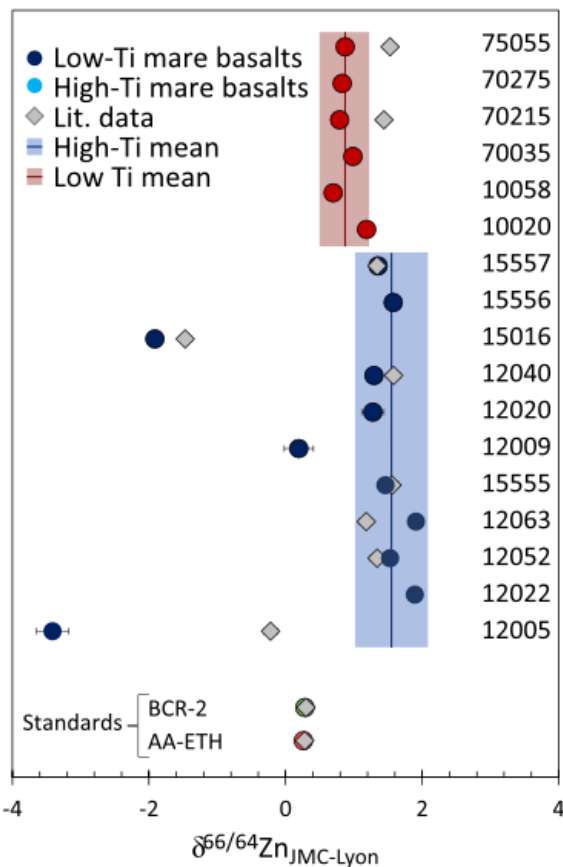


Figure 1: $\delta^{66/64}\text{Zn}$ isotopic composition for low (blue circles) and high (red circles) titanium mare basalts. Blue and red shades represent their respective mean.

Samples of 4 different low-Ti mare basalt suites (A12 Ilm, Pig, Ol basalts and A15 Ol normative basalts) fall in the restricted range of $+1.27 \pm 0.06$ ‰ to $+1.91 \pm$

0.04 ‰. Indicating a homogeneous mean source composition of $+1.56 \pm 0.51$ ‰.

Isotopically light Zn in lunar mare basalt samples (down to -3.1 ‰) have been reported in previous studies [5, 17]. Such compositions which strongly deviate from the narrow range of most low-Ti mare basalts most likely reflects re-condensation of isotopically light Zn from a gas phase previously evaporated on the lunar surface [2, 18].

Finally, higher mass fractions of Zn in high-Ti mare basalts are most likely related to their extensive fractional crystallization history [e.g., 19]. Samples analyzed in our study align on a linear regression and show an evolution toward lower $\delta^{66/64}\text{Zn}$ and higher [Zn]. If this relationship can be confirmed by other samples it might indicate a yet unknown fractionation process which affects high-Ti mare basalts and/or their mantle sources. Together with previously published data on mare basalts [e.g., 4] and magnesian suite rocks [20], lunar magmatic rocks display a large range of $\delta^{66/64}\text{Zn}$ values. Such heterogeneity is not consistent with an isotopically homogeneous lunar interior, instead it supports variably volatile depleted lunar source regions.

Acknowledgments: The authors gratefully acknowledge the Lunar Sample Curator and the CAPTEM for the allocation of Apollo samples. Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – Project-ID 263649064 – TRR 170.

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