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Assessing the Behavior of Moderately Volatile Elements on the Moon in order to Constrain Processes of Magmatic Evolution and Planetary Accretion

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1. Project Goals

The main goals for this project were as follows:

- *Year-1.* Analyze the Zn and Ga isotopic composition of rocks from the mare basalt suite and discuss implications for current estimates of moderately volatile elements (MVEs) in the bulk silicate Moon (BSM).
- *Year-2.* Characterize the isotopic compositions of Zn and Ga in samples from the lunar highlands (FAN and Mg-suite) and compare/contrast with lunar basalts. Discuss implications for the processes that control MVE isotopic fractionation in lunar rocks.
- *Year-3.* Separate and process samples of picritic green glass from bulk lunar soil (15426) and characterize its elemental and MVE isotopic composition. Given its status as a relatively primitive product of mantle melting, this may provide the most robust method to estimate the initial Zn and Ga isotopic composition of the Moon.
- Produce manuscripts detailing the behavior of Ga and Zn isotopes in lunar mare basalts and highlands rocks.

2. Executive Summary

Heterogeneous isotopic compositions of Zn and Ga in lunar basalts and highlands rocks indicate that secondary processing affected the stable isotopic composition of major lunar reservoirs. It follows that these fractionating processes must be identified and characterized in order to make robust estimates for the isotopic composition of the mare basalt source regions or the bulk silicate Moon (BSM). Contrary to previous assertions (e.g., Kato & Moynier, 2017), MVEs such as Zn and Ga do not behave similarly on the Moon, in line with differences in their chemical behavior and volatility. There is clear evidence that impact reworking fractionates zinc isotopes but, in addition, zinc isotopes are also highly sensitive to the formation of Ti-bearing oxides such as ilmenite. In contrast, gallium is far less susceptible to volatile reworking, but its isotopic composition is fractionated during incorporation into plagioclase (Wimpenny et al., 2022; Render et al., 2023). Based on these findings we conclude that current isotopic compositions of Zn and Ga in lunar rocks, such as those measured for the mare basalt suite, are unlikely to be representative of the bulk Moon when it accreted. As such, estimates for the MVE isotopic composition of the BSM derived from mare basalts may not be accurate, which may have implications for the incorporation of these data into dynamical models of the Moon’s formation.

In the following, we discuss the main findings from this project in more detail, focusing on the behaviour of zinc and gallium isotopic systematics in lunar rocks and the processes that control their isotopic fractionation on the Moon.

3. Controls over Ga isotope systematics in lunar rocks.

For this task, we obtained a comprehensive set of Ga isotope data for rocks from the mare basalt suite and rocks from the lunar highlands. The combined data sets indicate that Ga isotope ratios in lunar rocks are sensitive to magmatic differentiation processes and largely controlled by the crystallization and extraction of plagioclase from the lunar magma ocean. There are several lines of evidence that support this hypothesis. The first is the behaviour of Ga isotopes in the lunar mare basalt suite. The Ga isotopic compositions (δ^{71}Ga) of these samples ranged from 0.17 to 0.53‰, which are higher than the estimated composition of the BSE (0.00 ± 0.06‰, Kato et al., 2017). To a first order, this appears consistent with the inference that the Moon accreted from volatile depleted material that was relatively enriched in heavy isotopes of Ga. However, δ^{71}Ga values are higher in samples derived from later-formed LMO cumulates/source regions with the KREEP-rich sample, 14310, having the heaviest δ^{71}Ga value of all. Furthermore, δ^{71}Ga values correlate with trace element systematics, most notably the europium anomaly, which is an indicator of plagioclase crystallization and extraction from the LMO. Given that Ga is incompatible in olivine and orthopyroxene and compatible in plagioclase the trend towards increasingly isotopically heavy Ga in rocks with larger Eu* anomalies is consistent with plagioclase incorporating relatively isotopically light Ga and thereby driving residual magmas to isotopically heavier values. This is described in more detail in Wimpenny et al., 2022 (*EPSL*).

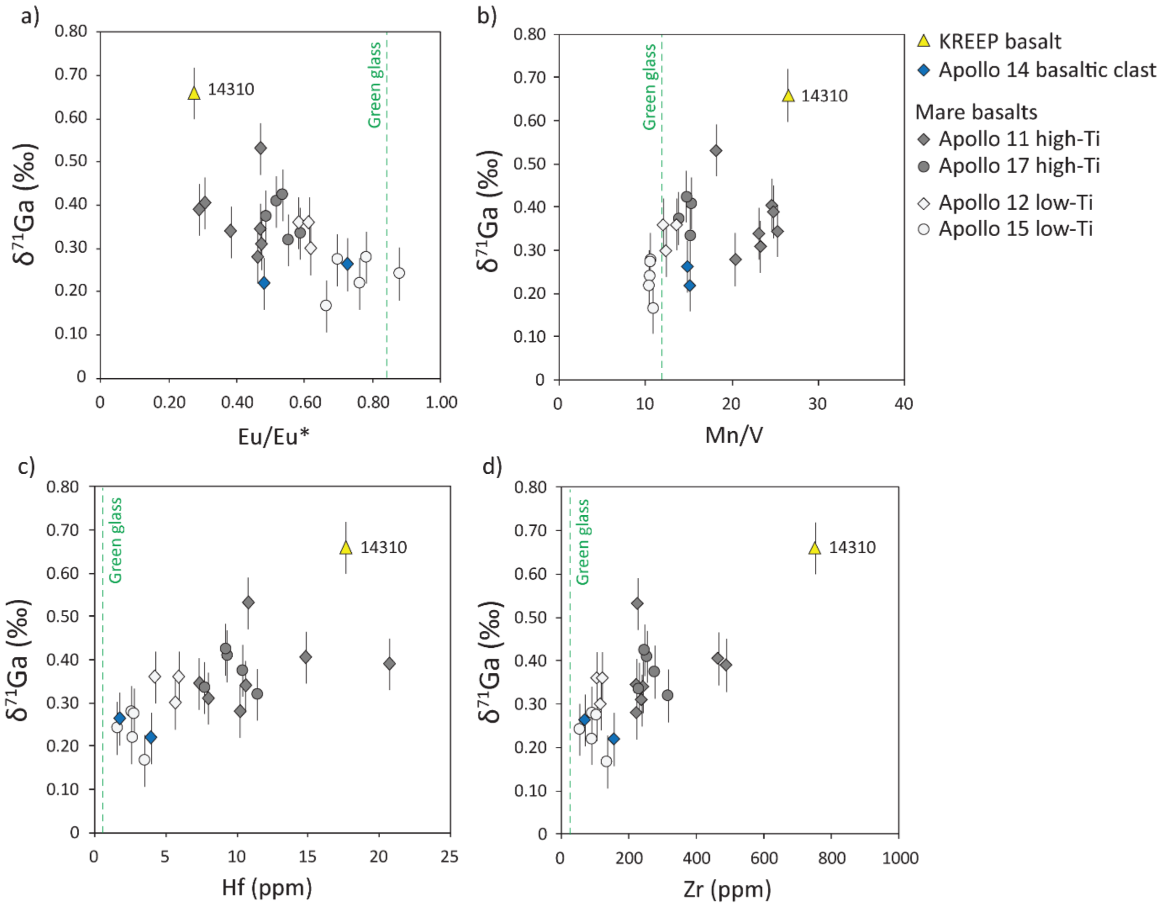

Fig. 1 – Plot of δ^{71}Ga vs trace element systematics in mare basalts, Apollo-14 clasts and KREEP rich sample 14310. Figure from Wimpenny et al., (2022).

The second line of evidence comes from the lunar highlands, specifically the isotopic composition of Ga in rocks from the ferroan anorthosite suite (FAS). These rocks have highly variable Ga isotope ratios that are either similar to, or lighter than, Ga isotope ratios in mare basalts, with a spread of δ^{71}Ga values between -0.27 and +0.22‰ (Render et al., 2023, *EPSL*). Correlations between δ^{71}Ga values and trace element ratios such as La/Sm and Ca/Mg cannot be ascribed to volatilization given the refractory nature of these elements. Neither can they be explained by varying incorporation of mafic magmas, given the low compatibility of Ga in the common mafic minerals olivine and pyroxene. Instead, the observation that δ^{71}Ga values of these rocks correlate with anorthite numbers (Fig. 2) indicates that the Ga isotopic composition of FAS rocks reflects evolution of the melt phase from which plagioclase crystallized. As anorthite numbers decrease with continued plagioclase crystallization, this indicates that FAS rocks with lower δ^{71}Ga values crystallized from less evolved magmas. The evolution to increasingly heavy δ^{71}Ga values is consistent with the inference from the mare basalt suite that plagioclase incorporates isotopically light Ga from the melt phase.

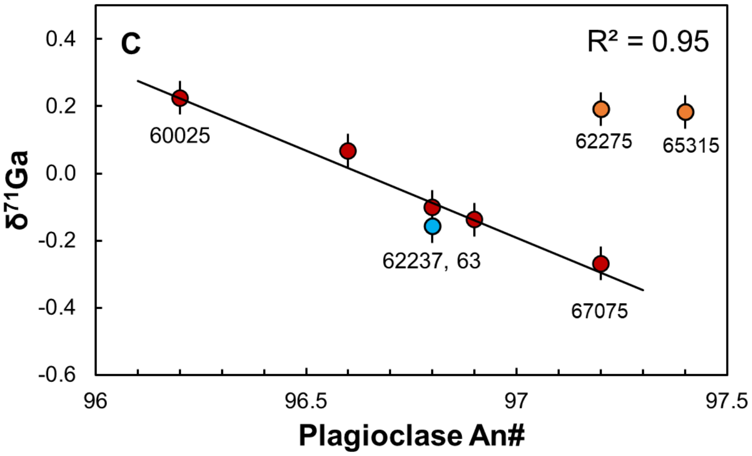

Fig. 2 – Relationship between δ^{71}Ga and anorthite number in FAS rocks (Render et al., 2023)

Based on Ga isotope systematics in the mare basalt suite and rocks from the lunar highlands it is clear that their δ^{71}Ga values were fractionated by magmatic differentiation processes and hence cannot be used directly to estimate the Ga isotopic composition of the Moon. Instead, relationships between δ^{71}Ga and trace element abundances can be used to estimate the isotopic composition of the parent magmas and large-scale lunar reservoirs from which these rocks derived. By regressing the correlation between δ^{71}Ga and Eu* in rocks from the mare basalt suite it is possible to obtain an isotopic composition in the residual LMO prior to plagioclase hitting the liquidus (i.e. prior to 78-80 PCS). Based on this, we estimated that the 'pre-plagioclase' composition of the LMO was 0.14 ± 0.10‰ (Wimpenny et al., 2022). A similar estimate can be made from Ga isotope ratios in FAS rocks. If early formed FAS, with higher An#, had δ^{71}Ga values of -0.3‰ (Fig. 2) and the fractionation factor between plagioclase and melt ($\Delta^{71}\mathrm{Ga}_{\mathrm{plagioclase\text{-}melt}}$) is between -0.3 and -0.4‰ (Fig. 3), then the δ^{71}Ga value of the 'pre-plagioclase' LMO must have been between 0.03 and 0.13‰, which is in line with estimates from mare basalts (Render et al., 2023). A third and final estimate for the isotopic composition of the primitive LMO can be obtained from the composition of picritic green glass beads from 15426, which are often considered a close analog for the low-Ti parent magmas. After leaching to remove any surficial volatiles, the residual glass contains a δ^{71}Ga value of 0.12 ± 0.03‰, which is lower than any value measured in mare basalts and within the range of δ^{71}Ga values estimated for the pre-plagioclase composition of the LMO.

Thus, three lines of evidence agree that the isotopic composition of Ga in the LMO, prior to plagioclase becoming a liquidus phase, was lower than the composition measured in most mare basalts and more similar to current estimates for the composition of the BSE (~0‰, Kato & Moynier 2017). Whether it is also representative of the δ^{71}Ga value of the Moon when it accreted cannot be ascertained. The similarity in Ga isotopic composition between the Moon and Earth most likely indicates that their precursor bodies (Theia and proto-Earth) were also isotopically similar. This removes the requirement for significant Ga loss from the accreting Moon during and/or after the Giant Impact. Instead, it is likely that Theia was already significantly depleted in Ga (and potentially other volatiles) prior to the Giant Impact, as recently proposed from Rb-Sr systematics (Borg et al., 2022). We hypothesize that the proto-Earth and Theia accreted from regions of the inner solar system with relatively homogenous Ga isotopic compositions.

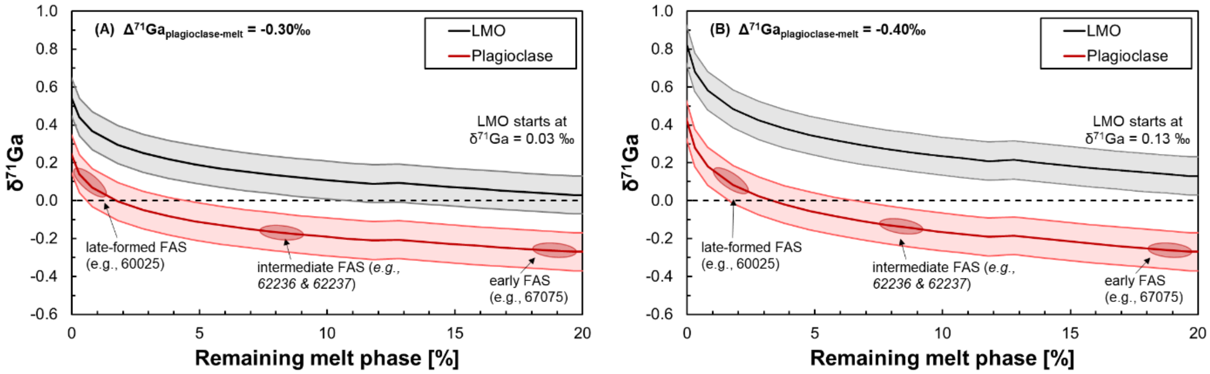

Fig. 3: Two scenarios modeling the partitioning of light Ga isotopes into plagioclase: a) $\Delta^{71}\mathrm{Ga}_{\mathrm{plagioclase\text{-}melt}}$ is assumed to be -0.30‰, requiring the LMO to start with a Ga isotope composition akin to the BSE, b) $\Delta^{71}\mathrm{Ga}_{\mathrm{plagioclase\text{-}melt}}$ is assumed to be -0.40‰, with a Ga isotopic composition of the LMO that is slightly heavier compared to the BSE and indistinguishable from a previous estimate extrapolated from lunar mare basalts (Wimpenny et al., 2022). Shaded areas represent 0.10‰ error envelopes on the modeled compositions of the LMO and plagioclase cumulates. Red ellipses indicate putative events of plagioclase crystallization, which was incorporated into the FAS investigated in this study. Taken from Render et al., (2023).

4. Controls over Zn isotope systematics in lunar rocks

The Zn isotope ratio in lunar basalts and highlands rocks span a ~15‰ range within and between the major lunar lithologies (this study, Paniello et al., 2012; Kato et al., 2015). This contrasts with igneous rocks on Earth that are relatively isotopically homogeneous (e.g., Chen et al., 2013). Thus, the observed Zn isotopic heterogeneities in lunar rocks must be produced by geologic processes occurring after accretion of the Moon. Given the relative volatility of Zn, and the propensity of Zn isotopes to undergo kinetic isotopic fractionation during evaporative processes (Moynier et al., 2009; Wimpenny et al., 2019), it is likely that some of this isotopic variation reflects the evaporative redistribution of Zn associated with impact events and magmatic outgassing. Rocks that have experienced severe secondary alteration (e.g., the 'rusty rock' 66095, Day et al., 2017) are rich in vapor-condensates and characterized by relatively high Zn abundances, up to ~400 ppm, and highly fractionated δ^{66}Zn values down to -13.7‰. Such extreme enrichments in isotopically light Zn are less common in the later formed mare basalt suite, probably reflecting the reduce impact rate at the time the basalts crystallized. Nevertheless, ~10% of the current mare basalt population (7 out of 57) contain Zn with negative δ^{66}Zn values (this study, Lindsay et al., 2011; Herzog et al., 2009; Paniello et al., 2012; Kato et al., 2015; Gargano et al., 2022). These anomalous mare basalts derive from all Apollo landing sites except Apollo-16, indicating that the interaction of basaltic rocks with an isotopically light Zn reservoir was widespread within the broader PKT region and not associated with a certain lithology or eruptive age.

If basaltic rocks with negative δ^{66}Zn values reflect the addition of isotopically light Zn at or close to the Moons surface, then their isotopic compositions are not representative of their primary magmas. It follows that these data should be excluded when estimating the primary Zn isotopic composition of the lunar mantle and/or BSM, consistent with previous Zn studies (Paniello et al., 2012; Kato et al., 2015; Day et al., 2020; Gargano et al., 2022). Similarly, Zn systematics in FAS rocks are unlikely to preserve primary mantle signatures (Kato et al., 2015). Instead, to ascertain the isotopic composition of Zn in the Moon we focus on two lunar lithologies: i) mare basalts with δ^{66}Zn values between 0.57 and 2.12‰, and ii) KREEP-rich samples, including the MGS, with δ^{66}Zn values between 1.8 and 3.8‰. Both sample suites have significant ranges in δ^{66}Zn that must be explained to estimate the isotopic composition of their parent magmas.

4.1. Zn systematics in the mare basalt suite

The low-Ti mare basalts have δ^{66}Zn values that average 1.25 ± 0.38‰ (2σ), consistent with recent δ^{66}Zn values measured in low-Ti mare meteorites (1.23 ± 0.05‰, Day et al., 2020) and slightly lower, but within uncertainty, of previously published data for the low-Ti mare basalts (1.42 ± 0.53‰, n = 21, Paniello et al., 2012; Kato et al., 2015; Gargano et al., 2022). The low-Ti parent magmas underwent fractional crystallization of an assemblage dominated by olivine and pigeonite (Neal et al., 1994), causing Co concentrations in the residual magmas to decrease as fractional crystallization proceeded. The absence of correlation between Co and δ^{66}Zn in the low-Ti mare basalts (Fig. 4a), indicates that progressive fractional crystallization of olivine and pigeonite did not cause resolvable fractionation of Zn isotope ratios in the residual magma. Assuming that the Zn isotopic composition of these samples was not affected by secondary heating processes associated with impacts, it follows that their average δ^{66}Zn value of 1.25‰ is representative of the initial parent magmas. This is unlikely to be representative of the δ^{66}Zn value of their cumulate source regions as observations from terrestrial peridotites indicate that mantle melt products (i.e., Mid Ocean Ridge Basalts, or MORB) contain Zn with δ^{66}Zn values that are ~0.15‰ heavier than Zn in the residuum (Wang et al., 2017; Sossi et al., 2018; Day et al., 2022). This isotopic effect is magnified at lower extents of partial melting (<10%), similar to those estimated to generate the low-Ti mare basalts (3-10%, Snyder et al., 1997; Borg et al., 2009). Thus, if the δ^{66}Zn value of the parent magmas were ~1.25 ± 0.4‰, then the δ^{66}Zn value of the low-Ti mare basalt source regions may have been ~1.1‰ or lower.

In contrast to the low-Ti mare basalts, the δ^{66}Zn values of the high-Ti mare basalts negatively correlate with Hf concentrations and positively correlate with Co (Fig. 4a, c). These relationships are difficult to reconcile with simple degassing of the parent magmas alone because these elements are not volatile (e.g. Lodders 2003; Wood et al., 2019). Instead, it is more likely that they reflect the isotopic fractionation of Zn in the high-Ti parent magmas prior to eruption, or mixing between chemically and isotopically distinct endmembers.

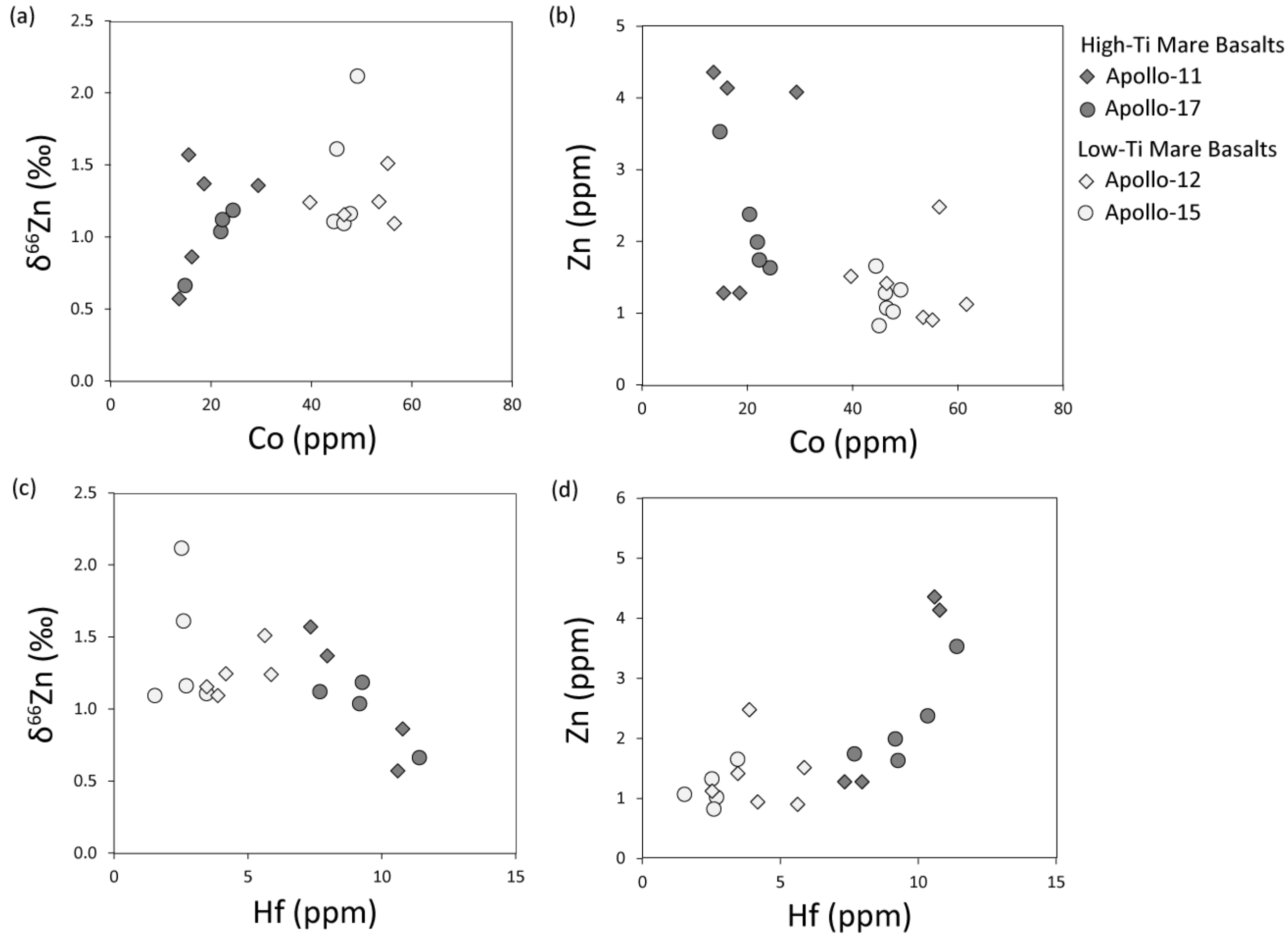

Fig. 4 – Zn systematics in rocks from the low- and high Ti mare basalt suite, plotted as a function of Co concentration (a, b) and Hf concentration (c, d). Typical uncertainties on the δ^{66}Zn values (2σ) are ~0.05‰, which is smaller than the symbols.

The most likely explanation is that the Zn isotopic composition of high-Ti mare basalts is controlled by the variable addition of late-stage IBCs to the parent magmas/source cumulates. Although the Zn isotopic fractionation factors between ilmenite or armalcolite and melt have not been constrained, recent work indicates Fe-Ti-Cr oxides can have $\Delta^{66}\text{Zn}_{\text{mineral-melt}}$ values between -0.18 and -1.43‰ (Wang et al., 2023). Because Zn is octahedrally coordinated in ilmenite (Akaogi et al., 2015), it is reasonable to infer that ilmenite also partitions Zn with a negative $\Delta^{66}\text{Zn}_{\text{mineral-}}$

$_{\text{melt}}$ value. The observation that Hf concentrations negatively correlate with δ^{66}Zn values and positively correlate with Zn abundance (Fig. 4c, d) is consistent with ilmenite playing an important role in controlling Zn systematics, based on the relatively high compatibility of Hf in ilmenite (Klemme et al., 2006; Munker 2010) and incompatibility in spinel (Wijbrans et al., 2015).

Variation in the Zn chemical and isotope compositions of the high-Ti mare basalts could result from either i) heterogeneous distribution of IBC materials in the source regions, ii) variations in the extent of partial melting or iii) variations in the proportion, or composition, of assimilated IBC materials. Although IBC is likely comprised of clinopyroxene, spinel, and ilmenite (Elkins-Tanton et al., 2011; Snyder et al., 1992), constraints from concentrations of high field strength elements indicate that preferential melting/dissolution of ilmenite would have occurred (Wagner & Grove 1997; Munker 2010). Thus, the available geochemical evidence, together with information about high-Ti mare basalt petrogenesis, suggest that ilmenite is the most likely mineral to impart isotopically light δ^{66}Zn values to the high-Ti mare basalts. The observation that the compatible element Co positively correlates with δ^{66}Zn and negatively correlates with Zn concentration (Fig. 4 a, b) is consistent with the predicted evolution of LMO residual magmas in which compatible elements are depleted by the time IBCs start crystallizing at >95 PCS (Snyder et al., 1992).

If isotopically light Zn from the LMO is incorporated into ilmenite in IBCs, it is reasonable to assume that the initial isotopic composition of Zn in the high-Ti parent magmas was heavier than in the corresponding basalts that accumulated ilmenite. If the chemical evolution of the high-Ti parent magmas was simply controlled by variable melting or addition of late-stage IBC material, then the chemical composition of the initial parent magma can be estimated from linear correlations between δ^{66}Zn and [Co] and [Hf] (Fig. 5a, c). In this case, these correlations suggest that parent magmas had Co and Hf concentrations of ~30 and 7 ppm respectively, which are consistent with estimates from petrogenetic modelling (Neal et al., 1994b). However, it is also plausible that assimilation of IBC material followed, or took place concurrently with, fractional crystallization of an assemblage dominated by olivine (Neal et al., 1990; Munker 2010). If so, it is possible that the Zn isotopic evolution of the high-Ti parent magmas followed a two-step trajectory (Fig. 5). If the high-Ti parent magmas assimilated IBC material after fractional crystallization of olivine, the abundances of compatible trace elements such as Co would have initially decreased without affecting the Zn isotopic composition or incompatible element abundances. Hence, initial Co concentrations in the high-Ti parent magmas could have been as high as Co concentrations in green and orange picritic glasses (50-70 ppm, this study; Shearer & Papike 1993). Better constraints over the chemical composition of the high-Ti parent magmas would be needed to distinguish between these scenarios.

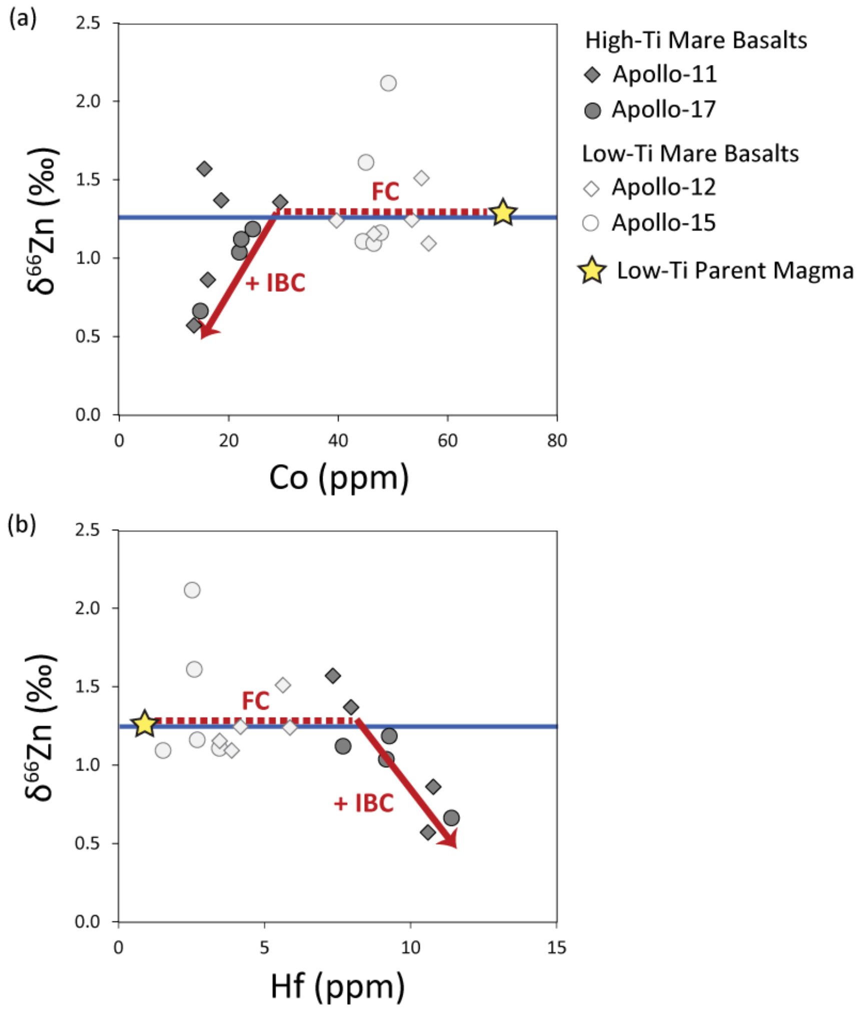

Fig. 5 – Plot showing the evolution of the Zn isotopic composition in the lunar mare basalt suite as a function of a) Co and b) Hf concentration. Here, we assume that low-Ti basaltic parent magmas initially had a δ^{66}Zn value of 1.25‰ and Co and Hf concentrations of ~70 and 0.5µg/g respectively, based on concentrations in picritic glass beads from 15426 (Borg et al., 2019). Fractional crystallization (FC) of olivine from low-Ti magmas changes the Co and Hf concentrations in the residual melt while having no effect on δ^{66}Zn. High-Ti magmas either initially contained lower Co and higher Hf concentrations (~30 and 7µg/g respectively, Neal et al., 1994b) or underwent a two-step evolution in which fractionation crystallization of olivine occurred during, or was followed by, addition of ilmenite bearing cumulates (IBC).

4.2. Zinc systematics in KREEP rich rocks

The new Zn isotope data demonstrate that KREEP-rich rocks, including those from the MGS, are strongly enriched in isotopically heavy Zn compared to rocks from the mare basalt suite (Fig. 6), and that their δ^{66}Zn values positively correlate with the Zn/Fe (Fig. 6a) and La/Sm ratios (Fig. 6b). The observation that rocks with higher La/Sm ratios typically have higher δ^{66}Zn values cannot be explained by a solid-state degassing process, as proposed by van Kooten et al., (2020), as the REEs are highly refractory (Lodders 2003; Wood et al., 2019) and would not volatilize at 1600-1800K, the estimated temperature of MVE evaporative loss (Tartese et al., 2021). Furthermore, if these correlations were controlled by varying extents of degassing we would expect the Zn/Fe ratio to decrease with increasing δ^{66}Zn, opposite to our observation. Instead, we hypothesize that covariations between δ^{66}Zn, La/Sm and Zn/Fe in KREEP-rich rocks represent two-component mixing between a primitive mafic component, with sub-chondritic La/Sm ratio, low Zn/Fe ratio of ~5×10^{-6} (Albarede et al., 2015), and mare basalt-like δ^{66}Zn value (~1.25‰), and urKREEP with a suprachondritic La/Sm ratio, high Zn/Fe ratio of ~6×10^{-5} (Warren 1989) and δ^{66}Zn value that must be higher than 3.82‰ (Fig. 6).

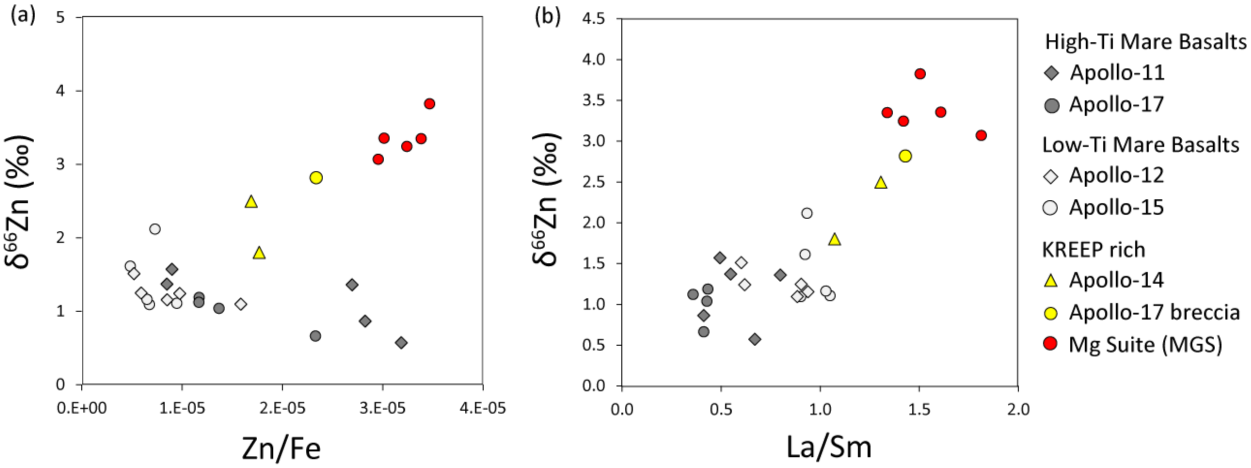

Fig. 6 – Zn isotope ratios plotted as a function of a) Zn/Fe and b) La/Sm. Typical uncertainties on the δ^{66}Zn values (2σ) are ~0.05‰, which is smaller than the symbols.

The full extent of Zn isotopic fractionation in urKREEP cannot be directly constrained without analyzing a pure endmember sample, which currently does not exist in Apollo sample collections. Recent experimental work has calculated that MGS mantle source regions must contain 25-50% urKREEP in order to generate melts that match the Mg# and REE abundances of the parent magmas to the MGS troctolites (Elardo et al., 2020). Based on their derivation from such KREEP-rich magmas, the δ^{66}Zn values of MGS rocks can be used to estimate the δ^{66}Zn value of the urKREEP endmember. This is done using a mass balance calculation that assumes that the MGS parent magmas are derived from a mixture of primitive mafic magmas, anorthositic cumulates, and urKREEP (Elardo et al., 2011; 2020). The first constraint is an estimate for the Zn concentration in the bulk silicate Moon. Based on current data and previously published studies by O'Neil (1991) and Albarede et al., (2015), we estimate that the BSM had a Zn/Fe ratio of ~5×10^{-6}. If the Moon contained an FeO concentration between 7.7 and 13 Wt% (Taylor et al., 2006) then we estimate a Zn concentration between 0.3-0.5 ppm in the BSM, which is similar to concentrations in low-Ti mare basalts (0.6 to 1.5 ppm, Table 1). Because Zn has a partition coefficient of ~1 in olivine and pyroxene (Le Roux et al., 2010) we can assume that partial melts of primitive LMO cumulates had similar Zn concentrations to their source regions. Thus, we assume primitive Mg-rich magmas had Zn concentrations ~ 0.5 ppm. Although Zn is relatively incompatible in plagioclase (Bedard et al., 2006), redistribution of volatiles in the lunar crust has resulted in highly variable Zn concentrations in FAS rocks that are unlikely to reflect concentrations in the primary minerals (Kato et al., 2015). For this reason, the lowest measured Zn concentration in any FAS, 0.6 ppm in 15415 (Kato et al., 2015), is likely to be the most representative of Zn concentrations in pristine anorthosites. Estimating the Zn concentration of the urKREEP endmember relies on previous analyses of KREEP rich basalts such as 15386. Based on compiled data in Warren (1989), we assume that urKREEP contained ~5ppm Zn, an order of magnitude higher than Zn in mafic magmas or anorthositic rocks. Using these endmember concentrations, if the MGS parent magma comprised 25-50% KREEP and the remainder was a 50-50 mixture of primitive mafic magma and anorthosite, then 77-91% of Zn present in the MGS is required to have derived from KREEP. Based on this mass balance, we estimate that the δ^{66}Zn value of the urKREEP endmember is between 4.0-4.6‰, assuming the δ^{66}Zn values of the mafic magma and ferroan anorthosite were similar to mare basalts (~1.25‰).

4.3. Mechanism of Zn fractionation in urKREEP

The relative enrichment in isotopically heavy Zn in urKREEP is consistent with Cl and K isotope systematics (e.g. Boyce et al., 2015; Barnes et al., 2019; Tian et al., 2019) and a well-defined correlation exists between δ^{66}Zn and δ^{37}Cl values that extend from mare basalts to KREEP-rich rocks and the MGS (Fig. 7). Because the degree of Zn, Cl and K isotopic fractionation between KREEP-rich rocks and the BSE scales with element volatility, it is likely that degassing drove the urKREEP reservoir to such heavy isotopic compositions.

A simple mechanism to explain isotopic fractionation of MVEs in urKREEP is if the LMO underwent progressive degassing of volatiles during its solidification. The Zn isotopic fractionation factor (α) during evaporative loss is controlled by the speciation of degassed Zn, the vapor saturation and the chemical composition of the gas species into which degassing takes place (Richter et al., 2011). The degree of isotopic fractionation is maximized under a vacuum (α = 0.984) and becomes negligible in thick vapor atmospheres ($\alpha \sim 1$). Previous modelling of Zn isotopic fractionation during LMO degassing indicated that isotopic fractionation of 3-5‰ could be generated with α values up to 0.994 (Dhaliwal et al., 2018). For context, pressures associated with transient atmospheres generated by mare basalt magmatism on the Moon are up to ~0.01 atm (Needham & Kring 2017), under which the α value for K is estimated at ~0.992 (Yu et al., 2003; Wang & Jacobsen 2016). If the α for Zn is similar to K during magmatic outgassing, then this first order modelling suggests that ‰-level fractionation of Zn in the LMO is a plausible consequence of degassing during LMO solidification. An advantage of the magmatic degassing scenario is that urKREEP would remain at the base of the anorthositic crust, enabling its interaction with mafic magmas and anorthositic melts to generate the MGS parent magmas (Elardo et al., 2011). Furthermore, the isotopically fractionated composition of the mare basalts would be inherent to their source regions, meaning secondary processes such as mantle overturn or assimilation during magmatic ascent are not required.

The major problem with invoking LMO degassing as a driver of isotopic fractionation in mare basalts and urKREEP is that the crystallization of plagioclase and formation of an anorthositic cumulate floatation crust insulated the magma ocean after ~80 PCS (Snyder et al., 1992; Elkins-Tanton et al., 2011). Depending on the permeability of this crust to gas species, it is likely that this would have inhibited the continued degassing of volatiles (Boyce et al., 2018; Barnes et al., 2016).

However, the insulating properties of the early anorthositic crust are largely theoretical, and the permeability of the crust to magmas and gas species imparted by fracturing and impact excavation are not well constrained. In theory, capilliary fracturing and veining in the lunar crust may have allowed partial degassing from shallow crustal depths, as shown for the Earth (e.g. Parmigiani et al., 2017). Furthermore, recent impact simulations of the Giant Impact event suggest that debris remaining from the Moon forming Giant Impact could have re-impacted the Earth and Moon for 10-100Ma after the initial Moon forming event (Jackson & Wyatt 2012; Perera et al., 2018), potentially exposing liquid magma to vacuum. Thus, continuous magmatic degassing cannot be excluded as a driver of MVE isotopic fractionation in mare basalts and KREEP without further evidence. If degassing of the LMO did occur throughout its solidification history then the implications for the isotopic composition of Zn, Cl and K in the lunar mantle are clear; isotopic compositions in mare basalts likely record the isotopic composition of source cumulates after ~86PCS, rather than the isotopic composition of the Moon when it accreted. If this is true, the initial MVE isotopic composition of the Moon would have been closer to compositions of chondritic meteorites and the Earth.

An alternative mechanism to continuous degassing of the LMO that could explain isotopically heavy MVE compositions in urKREEP is degassing generated by impact events that penetrated the lower crust after LMO solidification (Barnes et al., 2016; Boyce et al., 2018; Tian et al., 2020). For this mechanism to be correct, degassed urKREEP would have remained at the top of mantle to explain isotopically heavy Zn in the intrusive MGS rocks. If degassed KREEP-melts were in the lowermost crust, then their potential interaction with dense, gravitationally unstable IBCs could have resulted in transport of material with an isotopically heavy MVE composition to the mare basalt source cumulates. Alternatively, ascent of basaltic magmas through KREEP rich regions of the lower crust could have resulted in KREEP assimilation into the mare basalt parent magmas (Munker 2010; Dygert et al., 2013). Both mechanisms could, in theory, have enabled interaction of urKREEP with basaltic magmas or their source regions. However, petrogenetic modelling of mare basalts has indicated that the percentage of urKREEP incorporated into their parent magmas was relatively small (1-2%, Snyder et al., 1992; Hallis et al., 2014). At such low levels, could KREEP addition have perturbed the Zn isotope systematics of mare basalts?

To address this question, simple mass balance calculations were performed to test whether the removal of 2% urKREEP from a low-Ti mare basalt would decrease the Zn isotopic composition to Earth-like values. Here, the chemical and isotopic composition of low-Ti mare basalts are used as proxies for the basaltic parent magmas after KREEP addition, and isotopic compositions of KREEP-rich basalts and MGS rocks are used for the urKREEP endmember. If the current chemical and isotopic composition of low-Ti mare basalts were affected by addition of KREEP rich material, simple subtraction of 2% KREEP should generate a 'KREEP-free' composition that is more representative of the bulk Moon when it accreted. This simple calculation produces a basaltic reservoir with δ^{66}Zn value of +0.52‰, within the range of Zn isotopic compositions measured for carbonaceous chondrites (Luck et al., 2005) and indicating that small proportions of KREEP addition could have imparted ‰-level isotopic fractionation of Zn in mare basalts.

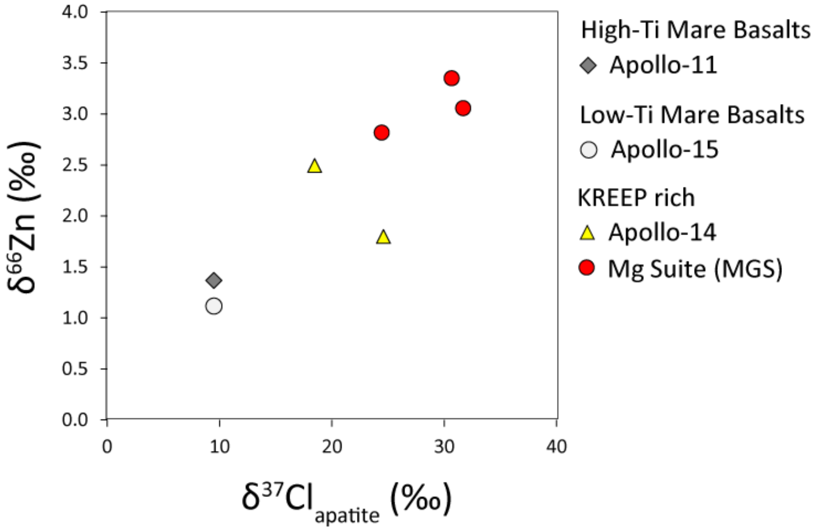

Fig. 7 – Relationship between the δ^{66}Zn value of whole rock samples and the δ^{37}Cl value of apatites from the same rock samples. Apatite data from Sharp et al., (2010), Barnes et al., (2016), Potts et al., (2018), Barnes et al., (2019) and Stephant et al., (2019).

A potential problem with the crust breaching impactor hypothesis is whether it is feasible for KREEP that was exposed at the surface to then be redistributed into the upper mantle to generate the MGS. The downwelling of relatively dense IBCs and associated KREEPy liquids prior to LMO solidification is a viable mechanism to get KREEP from the upper mantle into the lower mantle (Hess & Parmentier 1995), but it seems very unlikely that such a process could have operated on a KREEP-rich reservoir that was exposed at the surface. Recent modelling of mass transfer associated with the South Pole Aiken (SPA) impactor suggests that KREEP and late stage LMO cumulates may have been pushed down into the mantle by the impact event and redistributed to the lunar nearside (i.e., PKT) after initiation of hemispheric convection (Zhang et al., 2022). However, to be a viable mechanism to produce urKREEP with heavy Zn isotopic composition such a process must also result in degassing of the redistributed KREEP and/or allow this material to subsequently be involved in petrogenesis of the MGS and other KREEP-rich lithologies. This, so far, has not been demonstrated. An alternative hypothesis is that the purported impactor into the PKT region partially excavated some of the lunar crust but did not penetrate into the mantle. In this case, shallowing of the crust together with fracturing could have promoted enhanced degassing of urKREEP while allowing it to remain at the base of the crust. Currently, however, there is no unambiguous evidence that the surface expression of the PKT reflected a Procellarum impactor. Recent gravity analyses by GRAIL indicate that the PKT may have been a region of thin, hot crust that underwent cooling and contraction, evidenced by a series of linear dykes (Andrews-Hanna et al., 2014). Perhaps the impact occurred early enough (~4.36 Ga) that viscoelastic rebound of the early hot crust obscured physical evidence of the impact site (Barnes et al., 2016). Ultimately, there are still questions associated with the crust breaching impactor hypothesis as a driver of urKREEP degassing. That being said, given the ubiquity of KREEP in and around the Apollo sampling locations (Wieczorek & Phillips 2000), the redistribution of degassed KREEPy material into major lunar reservoirs remains a viable mechanism to have caused increases in MVE isotopic compositions. Similar to our conclusions from the magmatic degassing mechanism, if true, this would mean that current isotopic compositions of MVEs in mare basalts are unlikely to be representative of the initial MVE isotopic composition of the Moon.

5. Implications for constraining the isotopic composition of MVE's in the Moon

Previous estimates for the bulk isotopic composition of Zn and Ga in the Moon were derived from the average composition of mare basalts (Paniello et al., 2012; Kato et al., 2015; van Kooten et al., 2020). However, we clearly show that magmatic differentiation processes and volatile redistribution at the lunar surface have introduced heterogeneities to basaltic Zn and Ga isotopic compositions. Furthermore, highly fractionated Zn isotope ratios in KREEP rich rocks indicate that urKREEP underwent significant degassing, either during LMO solidification or following a crust breaching impactor, which would have had consequences for the isotopic composition of Zn in LMO cumulates and derived melt products. Thus, prior assertions that isotopic differences between the MVE isotopic composition of mare basalts and terrestrial rocks reflect compositional differences inherent to planetary accretion are unlikely to be correct. Instead, we show that the isotopic composition of Zn and Ga in lunar rocks reflect secondary processes that occurred on the Moon after it had accreted.

If the Moon and Earth initially formed with similar Zn and Ga isotopic compositions, it suggests that the proto-Earth and Theia were also isotopically similar prior to the Giant Impact. This would remove the requirement for considerable loss of volatile species from lunar building blocks prior to, or during, accretion. Instead, it is likely that both planetary bodies were already depleted in volatiles prior to the impact event, consistent with recent interpretations of lunar Rb-Sr data by Borg et al., (2022).

Current disparities in volatile content between the Earth and Moon can most plausibly be explained by a late addition of volatile elements from chondritic meteorites, or late veneer (Kruijer et al., 2015), from which a smaller mass of material would have been added onto the Moon (Day et al., 2007). Recent mass-independent analyses of Zn in terrestrial rocks and chondritic meteorites from the inner and outer Solar System (NC and CC) agree that ~30% of the Earth's Zn, and other MVEs, derived from CC materials that may have accreted late (Savage et al., 2022; Steller et al., 2022), consistent with the late veneer hypothesis. Given that CC meteorites are typically highly enriched in volatiles compared to terrestrial and lunar rocks, the mass of CC material required in a late accretion scenario is minor, at ~5% (Savage et al., 2019; Dauphas 2017). This means that the late accretion of CC material can have caused the current disparity in volatiles between the Earth and Moon, while preserving mass independent isotopic homogeneities.

6. Future work: refractory stable isotope systems (Mg, Fe, Li and Ni)

During this award period, new Mg, Fe, Ni and Li isotope data were obtained for a subset of the samples previously analysed for Zn and Ga. The rationale here was clear; if Zn and Ga isotopes were controlled by magmatic differentiation processes, we might expect to see correlations between their isotopic composition and those of refractory stable isotope systems that also have variable isotopic compositions in lunar rocks. In general, the results are consistent with previously published studies (e.g. Sedaghatpour & Jacobsen 2019; Poitrasson et al., 2019; Magna et al., 2006). However, correlations are shown to exist between isotopic data and trace element abundances that have not previously been observed and may help to elucidate the isotopic composition of these elements in the initial LMO. For example, the Fe isotope ratios of mare basalts covary with abundances of compatible trace elements such as Co (Fig. 8). Similar correlations are seen between Li isotopes and compatible trace elements. In these cases, rocks with lower compatible element abundances have Fe and Li isotope ratios that are more fractionated from chondritic compositions. It follows that more primitive samples, such as green picritic glass from 15426, should have the highest compatible element abundances and lowest δ^{56}Fe and δ^{7}Li compositions. Preliminary investigation of Fe isotope ratios in green glass beads appears to confirm this (Fig. 8). If these isotope systems were not affected by degassing processes, the most likely cause of isotopic fractionation is magmatic differentiation. Interestingly, we observe correlations between Fe, Mg and Zn isotope data for high-Ti mare basalts (Fig. 8a, c), which appears to confirm that the formation of Ti-bearing oxide phases late in the LMO crystallization sequence was an important source of isotopic variability in the lunar mantle and derived melt products for a range of isotope systems. Conversely, there is no clear correlation between refractory stable isotope systems and δ^{71}Ga, indicating that plagioclase crystallization did not drive extensive isotopic fractionation for other stable elements.

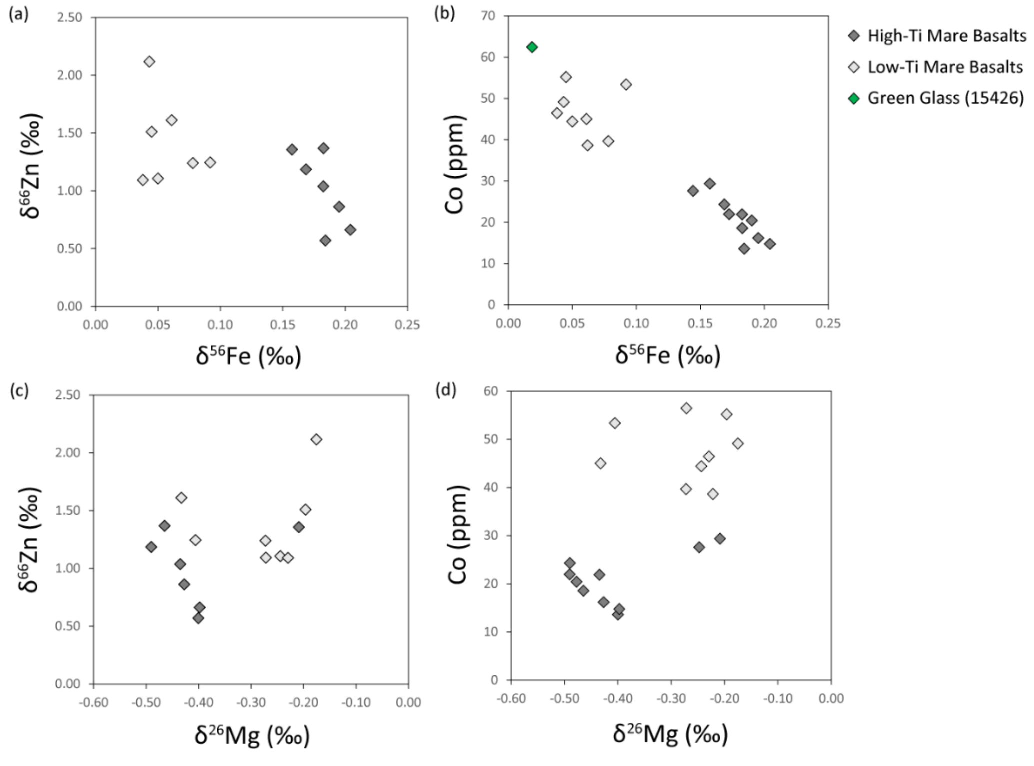

Fig. 8 – Relationship between Fe, Mg and Zn isotopes in mare basalts and picritic green glass.

Ultimately, this preliminary data is consistent with findings from detailed investigation of the behavior of Zn and Ga in lunar rocks; that the isotopic compositions of elements such as Fe and Mg are more heterogeneous than expected from igneous rocks on Earth and that simply averaging the isotopic composition of a single lithology (e.g. low-Ti mare basalts) may not yield an isotopic composition that is representative of major lunar reservoirs. As shown here, it is critical to understand the fractionating processes for any stable isotope system before one can make robust estimates of their isotopic compositions in a large-scale magmatic reservoir or planetary body such as the Moon. To understand the behavior of these isotopic systems in lunar magmatic systems requires robust understanding about whether equilibrium conditions were established or whether isotopic fractionation was driven by kinetic processes. If the former case, it is critical to gain more robust assessment of equilibrium fractionation factors between minerals and silicate melts, both through detailed analysis of mineral separates from lunar rocks, and through experimentation. Assessment of equilibrium or kinetic fractionation will require detailed in situ analyses of mineral grains by laser ablation or SIMS, to identify the presence/absence of diffusion profiles that could reflect a non-steady state environment.

7. Conclusions

The main conclusions from this study are as follows:

- Gallium isotope ratios in lunar rocks are significantly more isotopically heterogeneous and relatively heavy compared to most terrestrial rocks. Evidence from mare basalts indicate that the crystallization and extraction of plagioclase from the LMO drove the residual magma to increasingly isotopically heavy δ^{71}Ga values. This is supported by isotopic analysis of rocks from the ferroan anorthosite suite and handpicked samples of picritic green glass. We estimate that the pre-plagioclase δ^{71}Ga value of the Moon was ~0.12‰.
- Zinc isotope ratios in lunar rocks were fractionated by a range of processes including volatile redistribution at the surface of the Moon (due to impacts), heating and evaporative loss and fractional crystallization of Ti-bearing oxide minerals. Although the isotopic composition of Zn in mare basalts is significantly heavier than terrestrial rocks, a combination of LMO degassing and extraction of late-stage ilmenite bearing cumulates would have driven the LMO to heavier δ^{66}Zn values, culminating in a highly fractionated urKREEP reservoir. Either LMO degassing or addition of KREEP rich material to the mare basalts can explain their shift to heavier δ^{66}Zn values. Thus, it is plausible that the Moon and Earth initially had similar δ^{66}Zn values.
- Although the behavior of other MVE's, such as K, Cu and Rb, were not studied here, we hypothesize that their isotopic compositions could also be sensitive to magmatic differentiation processes, with implications for current estimates of the initial composition of the BSM.
- Preliminary analyses of refractory stable isotope systems in mare basalts confirm that magmatic differentiation processes play an important role in controlling the isotopic composition of rocks from the Moon for elements including Fe, Mg, Li and Ni. The fact that similar behaviors are exhibited for both volatile and refractory elements indicate that these processes can potentially play an important role in controlling the behavior of MVEs.
- If the Moon and Earth initially formed with similar Zn and Ga isotopic compositions, it suggests that the proto-Earth and Theia were also isotopically similar prior to the Giant Impact. This is consistent with their precursors being highly depleted in volatiles prior to the purported giant impact, and would support the assertion that they accreted from similar regions of the inner disk.

Published manuscripts:

Wimpenny J., Sio C., Borg L., (2022) The Gallium Isotopic Composition of the Moon. *Earth and Planetary Science Letters, 578*, 117318.

Render J., Wimpenny J., Borg L., (2023) Gallium isotopic constraints for the origin of the Earth-Moon system. In revision, *Earth and Planetary Science Letters, 611*, 118146

Manuscripts in preparation:

Wimpenny J., Sio C., Render, J., Borg L., Sanborn M., Huyskens M., Yin Q.-Z., Fractionation of Zn Isotopes by Post Accretion Volatile Loss from the Moon. For submission to Earth and Planetary Science Letters.

Sio C., Wimpenny J., Borg L., Iron isotopic composition of the Moon. For submission to Geochemical Perspectives Letters.

Conference Abstracts:

Render J., Wimpenny J., Borg L., Sio C., (2023) The nickel isotopic composition of the Moon. 2023 Goldschmidt Conference

Render J., Wimpenny J., Borg L., (2023) Implications for the Origin of the Earth-Moon System from Gallium Isotopes. LPI Contributions 2806, 2457

Render J., Wimpenny J., Borg L., (2022) Ga Isotopic Heterogeneity in Lunar Highland Rocks. 2022 Goldschmidt Conference.

Render J., Wimpenny J., Borg L., (2022) Gallium Isotope Heterogeneity in Lunar Highland Rocks. LPI Contributions 2695, 6502

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