TIMELINE OF LUNAR DIFFERENTIATION RECORDED IN CALCIUM AND MAGNESIUM STABLE ISOTOPES.
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Introduction: Traditional and new giant impact theories of the Earth-Moon system debate whether the giant impacts carried sufficiently high energy that vaporized the impactor and proto-Earth for chemical and isotopic homogenization within the Moon-forming disk [1]. As one of the most refractory major elements, calcium's isotopic compositions and variations of the bulk silicate Moon (BSM) carry crucial significance in clarifying the mechanisms for building the primordial Earth-Moon system. In addition, when used in conjunction with other isotopic systematics, Ca-isotope variations preserved in lunar rocks may serve as a powerful tool to study the magmatic differentiation of the lunar magma ocean (LMO). To date, reliable constraints of the BSM's Ca-isotope compositions remain lacking due to an underrepresented sample pool of analysis and the absence of stringent quantification approaches [2], hindering further applications.

To resolve the BSM Ca isotopic compositions and trace the lunar differentiation, we performed high-precision Ca-isotope measurements for 15 lunar rocks and minerals with TIMS, including the first Ca-isotope analyses for lunar olivine and ferroan anorthosite (FAN) samples (60015 and 60025) considered as primary floatation cumulates from the LMO.

Ca-isotope composition of the Moon: Our measurements for lunar basalts and highland samples show consistency with previously reported values (**Fig. 1A**) [2–4]. Combining our results and literature data yields distinct average $\delta^{44/40}$Ca values for low-Ti basalts [0.868 ± 0.007‰, two standard errors (2SE)], high-Ti basalts (0.824 ± 0.007‰), and feldspathic FANs and breccias (0.763 ± 0.012‰), suggesting significant mass-dependent fractionation during lunar igneous processes. The analyzed olivine mineral separate from 12012, a low-Ti basalt, is substantially heavier in Ca isotopes ($\delta^{44/40}$Ca = 1.09 ± 0.03‰). This result confirms the heavy Ca-isotope enrichment of lunar olivine, which, furthermore, infers that the lighter Ca isotopes of lunar basalts and highlands are likely balanced by the heavier Ca isotopes in the lunar mantle.

The FANs are thought to be the primary floatation cumulates crystallizing from the late-stage LMO (~70–100%) [5, 6]. We developed a Monte Carlo method that uses two representative LMO crystallization models of thermodynamic modeling [5] and experiments [6] to solve for the best-fit initial $\delta^{44/40}$Ca values of the LMO that reproduce the observed range of FANs and feldspathic breccias. The estimated BSM $\delta^{44/40}$Ca values have a mean of 0.929 ± 0.044‰ (95% confidence intervals) using the thermodynamic phase equilibrium LMO model [5] and 0.880 ± 0.048‰ using the exper-

imental LMO mineralogy sequence [6], both overlapping within error with the estimated Bulk Silicate Earth value of 0.94 ± 0.05‰ [7]. The indistinguishable BSM and BSE Ca isotopic compositions, along with the existing evidence from Mg and Fe isotopes [8, 9], support the hypotheses that (i) the moon-forming impactors and the proto-Earth shared the same isotopic composition and/or (ii) the impactors delivered high energies and angular momentum to form an Earth-Moon synestia that homogenized the isotopic compositions within the Moon-forming disk [1].
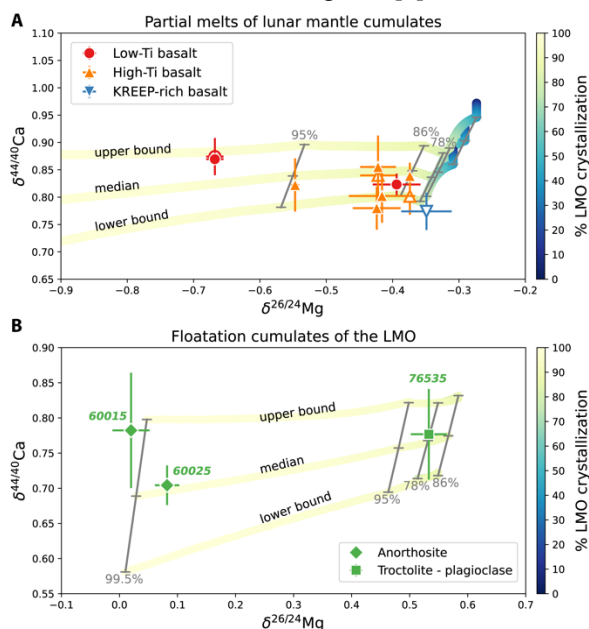

Fig. 1. Modeled Ca and Mg isotopic evolution of the LMO crystallization compared with lunar data. For the modeling curves, (A) plots the modeled LMO liquid line of descent, and (B) plots the modeled floatation cumulates.

Tracing the lunar differentiation with Ca and Mg isotopes: Mg-isotopes has also been tested as a sensitive tracer of lunar magmatic processes [8]. Combining Ca and Mg isotopic variations of the lunar samples now enables contextualizing their formation stages in the evolution of the LMO with greater confidence. We forward model the Ca and Mg isotopic fractionation throughout the LMO crystallization and compare the results with the available Ca (this study) and Mg [8] isotopic measurements. We present the $\delta^{44/40}$Ca vs. $\delta^{26/24}$Mg plots for the modeled LMO liquid (**Fig. 1A**) and flotation cumulate (anorthosite) (**Fig. 1B**) as a function of LMO crystallization calculated with the thermodynamic model [5]. Similar results were obtained with the experimental model and are not shown here due to limited space.

In **Fig. 1A**, the $\delta^{44/40}$Ca and $\delta^{26/24}$Mg data of the mare basalts fall closely along the modeled LMO liquid line of descent in evolved stages (from ~75 to 98% crystallization), supporting the mare basalts formation by partially melting lunar mantle cumulates and constrains these cumulates to have precipitated late in the LMO magmatic differentiation [4, 8].

In **Fig. 1B**, The Mg and Ca isotopic data of the two anorthosite samples, 60015 and 60025, agree well with the predicted values for primary flotation crusts and coherently indicate a formation near the end of LMO differentiation (>99% solidification). While the crystallization age of 60015 remains largely unclear, extensive geochronologic investigations have been performed for 60025. Traditionally, 60025 has been variably associated with the formation of early or late lunar crust. In circumventing the ambiguities led by traditional methodologies that compare debated absolute ages, our stable isotopic evidence provides an independent and critical resolution elucidating that 60025 marks the final solidification of the LMO. As a further profound implication, the formation age of 60025 should be used unambiguously to indicate the termination of the lunar differentiation.

Timeline of the Moon's formation and differentiation: We synthesized a database of representative chronologic evidence for various evolution stages throughout LMO solidification (**Fig. 2**). Given a relatively large uncertainty on the estimated timing of the Moon's formation (from ~30 to 152 Myr after the formation of the solar system) (**Fig. 2**) [10–13], the age of 60025 thus plays an essential role in gauging the timespan of the lunar differentiation.
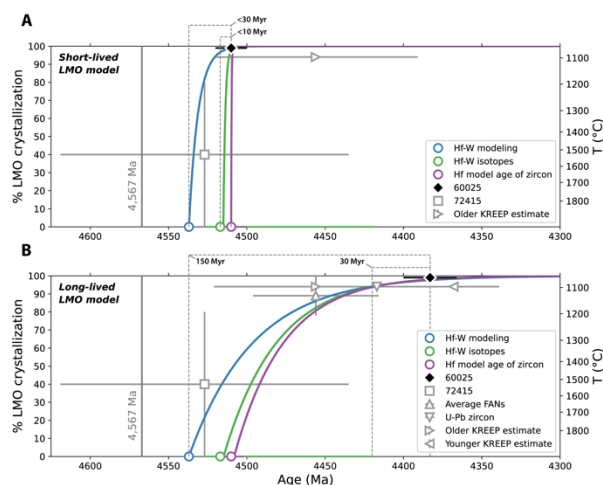

Fig. 2. Two lunar differentiation models permitted by chronologic evidence. (**A**) A short-lived LMO crystallization (<10–30 Myr) required by the old formation age of 60025 (4510 ± 10 Ma) [14]. (**B**) A long-lived LMO crystallization (~30–150 Myr) necessitated by the proposed young age of 60025 (4383 ± 17 Ma) [15].

If the old 4510 ± 10 Ma Pb-Pb age for plagioclases in 60025 [14] represents the sample's crystallization age, it requires an old Moon's formation predating ca. 4510 Ma and a rapid LMO solidification within the subsequent <10–30 Myr (short-lived LMO model, **Fig. 2A**), placing an upper bound on the completion of the lunar differentiation. Such a comparatively short duration has been explained by the LMO solidifying under a relatively high-conductivity anorthosite lid [15].

If the young Pb–Pb isochron age for pyroxene and Sm-Nd isochron ages for 60025 (4383 ± 17 Ma) [15] are valid, this would suggest a prolonged lunar differentiation that lasted ~30–150 Myr based on the variously estimated timing of the giant impact (long-lived LMO model) (**Fig. 2B**). This scenario puts a lower bound on the cessation of the lunar differentiation and sets the maximum duration of the LMO crystallization to be ~150 Myr. Such a longer timescale was inferred by [16] invoking mantle heat-piping and an insulating anorthosite lid with a lower thermal conductivity than that of [15]. A slushy LMO, lacking efficient crystal-liquid separation has also been used to argue for a long timescale [17].

Accounting for both proposed old and young dates as the true formation age of 60025, our new isotopic evidence requires the lunar magma ocean to have fully crystallized by either 4510 or 4387 Ma, with the total solidification timescales from <10–30 to ~30–150 Myr, respectively. A clearer distinction between a short-lived or long-lived LMO relies on scrutiny of absolute ages and stable isotopic signatures for more candidate samples of LMO primary records.

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