

TOWARDS QUANTIFYING CALCIUM STABLE ISOTOPE FRACTIONATION AMONG LUNAR ROCK SUITES BY SIMS. M. C. Valdes^{1*}, V. Debaille¹, B. L. Jolliff², C. Jones², P. Carpenter², and D. Fike²,
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Introduction: The lunar magma ocean (LMO) hypothesis, which models how an initially extensively molten Moon differentiated to form a primary crust and chemically distinct mantle reservoirs, predicts stratigraphic age relationships in the rocks that crystallized [1]. Chronology for lunar rock suites has thus been used to constrain the timescales of lunar differentiation. In the model, the mafic cumulate sources of the mare basalts form first, followed shortly by ferroan anorthosites (FAN) that form the primary crust. This is followed by the crystallization of residual liquid enriched in potassium (K), rare earth elements (REE) and phosphorus (P) – “KREEP” [1-4]. Lastly, the magnesian (Mg-) suite likely forms as crustal intrusions of mantle partial melts [5]. According to the model, the mare basalt source and FAN ages should be similar and KREEP should post-date the two [1]. Mg-suite rocks should yield ages no older than those of the FANs [5].

However, this model is confounded by a lasting ambiguity concerning the rock suites’ relative ages. Some chronologic evidence implies an early FAN formation age (ranging from 4.536 Ga to 4.436 Ga, e.g. [6-8]), but there is also evidence pointing to FAN formation through late and rapid or prolonged crystallization of the LMO. For example, [7, 9] reported the younger crystallization ages of 4.29 Ga for FAN 62236 and 4.360 Ga for FAN 60025. Reported ages for lunar mare basalts range from 4.455 to 4.314 Ga (e.g. [10-13]) and perhaps points to protracted differentiation of the mare basalt source following early formation. [9] showed that the age range of Mg-suite rocks is large and partially overlaps with the age range reported for FANs. If the ages of FANs and Mg-suite rocks are indeed contemporaneous, the timing of LMO solidification and secondary magmatism are called into question.

To examine how the Mg-suite and mare basalt mantle source reservoirs are related to the timing of primordial lunar crust formation, we will measure the stable Calcium (Ca) isotopic composition of the minerals that compose lunar rock suites. Recent work has begun to both computationally and experimentally investigate inter-mineral Ca isotope fractionation in terrestrial magmatic systems (e.g. [14-16]). The data suggest that Ca isotopes fractionate among minerals in a differentiating magma and that the degree of fractionation changes as the composition of the residual magma evolves. Because crystals growing in a

differentiating silicate magma system are assumed to record changes in the isotope composition of the liquid from which they crystallize, quantification of inter-mineral Ca isotope fractionation can therefore be used to provide geological context for planetary isochrons.

Calcium is refractory and lithophile and has six stable isotopes: ⁴⁰Ca, ⁴²Ca, ⁴³Ca, ⁴⁴Ca, ⁴⁶Ca, and ⁴⁸Ca. We previously measured Ca stable isotope ratios in bulk lunar rock suites by MC-ICP-MS [17] and found a ~1‰ total range in $\delta^{44/40}\text{Ca}$. *In situ* analyses are important for documenting inter-mineral interactions, but measurement of Ca stable isotopes by SIMS is challenging, partially because of the high mass resolving power (MRP) necessary. Adequate mass resolution to measure the six stable isotopes of Ca has previously been achieved [18], but ion counting times were very long (>72 hours) and the internal error (>0.5‰) was too large for our purposes. In the present study we calibrate a method to measure relevant Ca isotope ratios by SIMS with high enough precision to give mineralogical context to bulk Ca isotope data obtained by MC-ICP-MS.

Sample preparation: We prepared 11 lunar samples, the ages of which have previously been determined: FANs 62255, 62236, 60025, 15415, Mg-suite norites 77215 and 78235 and troctolite 76535, and mare basalts 10017, 12005, 15555, 70017. Chips of 1-2 mm were mounted in epoxy in 1-inch graphite rounds and polished. For comparison, separated grains of plagioclase, olivine, opx, cpx, and amphibole (the Ca isotopic values of which have been previously estimated [16]) from the Guelb el Azib complex (GAC) were also mounted and polished. Polished rounds were carbon coated for imaging and chemical evaluation by electron probe micro-analysis (EPMA). After EPMA, the rounds were gold coated for *in situ* isotopic measurements by SIMS.

EPMA: Textural imaging and compositional point analyses were performed on the JEOL JXA-8200 at Washington University in St. Louis in BSE and SEI modes. Major and minor element chemistries of the grains and chips were obtained with 10-element scans (Na, Mg, Al, Si, K, Ca, Mn, Fe, Ti, and Cr). The operating conditions were 15 keV accelerating voltage and a current beam of 60 μA at a working distance of 20 mm.

SIMS Calibration for Ca Isotope Measurement: Experiments to calibrate the conditions for greatest

precision on Ca isotope measurement were performed on the ims 7f-geo SIMS at Washington University in St. Louis. To work out the measurement strategy, we began by analyzing a compositionally homogenous plagioclase from GAC anorthosite. Because Ca isotopic ratios measured with the ion microprobe would deviate systematically from the true isotopic ratios as a function of isotopic mass [18], the compositionally homogenous plagioclase, if also isotopically homogenous, could act as a robust standard for lunar samples.

Measurements were made using an O_2^- primary ion beam. The MRP required to isolate ^{40}Ca , ^{42}Ca , ^{43}Ca , ^{44}Ca , and ^{48}Ca was very high, so we had to use narrow slits to reduce the transmission. Then, in order to get high enough ion counts to provide good precision, we needed to use more primary current. This induced more ion charging and the counts became increasingly variable with time. Thus, initial experiments to measure Ca were performed with ^{40}Ca on a Faraday cup (FCp) detector and the minor isotopes ^{42}Ca , ^{43}Ca , ^{44}Ca , and ^{48}Ca on the electron multiplier (EM) detector. We also found that switching all the way from nominal mass 40 to 48 during a measurement meant that the time difference between successive measurements was too long to achieve good precision. For this reason, and for interference reasons detailed below, subsequent experiments only measured minor isotopes ^{42}Ca , ^{43}Ca , and ^{44}Ca .

Interferences. There is an interference by ^{48}Ti on ^{48}Ca , and a MRP of 10,500 (m/ Δ m) is required for separation. In the minerals we plan to analyze, Ti is either in very low concentration or at least subordinate to Ca. In mare basalts, Ca/Ti (atomic) ranges from ~5-10 in low-Ca pyroxene and ~5-30 in high-Ca pyroxene [19]. In FAN and Mg-suite rocks, Ca/Ti (atomic) is ~5-12 in low-Ca pyroxene and ~50-300 in high-Ca pyroxene [19]. Nonetheless, because ^{48}Ca has a natural abundance of only 0.187%, the correction at mass 48 is important for the pyroxenes. However, the internal error on $^{48/44}Ca$ was ~0.5–0.8‰—too large for our purposes—thus, we discontinued measurement of ^{48}Ca for the time being.

Doubly-charged strontium (Sr) poses a potential interference in plagioclase. The concentration of Sr is typically below 250 ppm in FAN suite rocks, where it is in the highest concentration of any of the minerals we will analyze [19]. We estimated the contribution of Sr^{2+} on the secondary ion signals of ^{42}Ca , ^{43}Ca , and ^{44}Ca by monitoring the $^{87}Sr^{2+}$ signal and comparing the inferred $^{84}Sr^{2+}$, $^{86}Sr^{2+}$, and $^{88}Sr^{2+}$ signals with measured signals of nominal masses 42, 43, and 44.

Beam Stability. We tried 1, 5, 10, and 15 nA primary ion currents and noted that 5 nA provided the stablest secondary ion signal. In order to remove sur-

face contamination, we presputtered the sample by focusing the primary beam on the sample surface for 60 seconds prior to data acquisition, and this greatly improved the stability of the secondary ion signal. Subsequently, Ca isotope intensities were measured in 150-400 magnet cycles. Experiments were conducted to determine the number of magnet cycles that yields lowest error. We tried 150, 200, and 350, and 400 cycles and it seemed that 350 was optimal; no improvement was observed with more cycles. Isotopic ratios ($^{42/44}Ca$ and $^{43/44}Ca$) were then calculated using raw ion intensities corrected for electron multiplier dead-time and drift-corrected mid-analysis values. We measured six points on the GAC plagioclase and calculated external errors.

Preliminary Remarks: The calibrations described result in an internal error on $\delta^{42/44}Ca$ of ~0.15%, similar to the error achieved on MC-ICP-MS measurements. We are certain now that we can make robust measurements, so we can begin to analyze minerals in the prepared FAN, Mg-suite, and mare basalt samples. Once we have obtained SIMS data for lunar samples, we will test various mass-fractionation laws.

We expect to see isotopic differences among lunar minerals. Both numerical models based on density functional theory (DFT) [14] and experiments on co-existing clinopyroxene and orthopyroxene in terrestrial peridotite xenoliths [15] indicate that inter-mineral isotopic fractionation can result from variation in the Mg and Fe contents of clinopyroxene and orthopyroxene. As the Mg content of LMO residue evolves over the course of differentiation, so we expect the Ca isotopic signature of crystallizing minerals.

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