

Calcium isotopic composition of the lunar crust, mantle, and bulk silicate Moon: A preliminary study

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Abstract

Calcium isotopes have the potential to explore genetic links between the Moon and Earth. Here, we constrain calcium isotopic composition of the bulk silicate Moon (BSM), using petrological, geochemical and calcium isotopic data obtained from five lunar meteorites (two basalts and three feldspathic breccia rocks), and on four anorthite crystals from two feldspathic breccia meteorites. The $\delta^{44/40}\text{Ca}$ of lunar feldspathic breccias are $0.76 \pm 0.06\text{‰}$ (2SD, $n = 3$), $0.78 \pm 0.10\text{‰}$ (2SD, $n = 6$) and $0.82 \pm 0.02\text{‰}$ (2SD, $n = 3$), respectively, consistent with previously determined calcium isotopic composition of feldspathic breccias. Four anorthite crystals yield a mean $\delta^{44/40}\text{Ca}$ value of $0.75 \pm 0.13\text{‰}$ (2SD, $n = 4$), inferred to represent the $\delta^{44/40}\text{Ca}$ value of the lunar crust. The $\delta^{44/40}\text{Ca}$ values of the two lunar basalts are $0.90 \pm 0.07\text{‰}$ (2SD, $n = 3$) and $0.96 \pm 0.11\text{‰}$ (2SD, $n = 4$), respectively, slightly heavier than the feldspathic breccias and anorthites. The $\delta^{44/40}\text{Ca}$ of the studied lunar basalts and literature data show negative correlations with CaO, Al_2O_3 , and anorthite mode, pointing to the effect of contamination by lunar crust rocks. Using the heaviest $\delta^{44/40}\text{Ca}$ found in the least contaminated lunar basalts and a 0.10–0.20‰ fractionation of calcium isotopes during partial melting, we estimate the $\delta^{44/40}\text{Ca}$ value of the lunar mantle to be 0.96–1.11‰. The $\delta^{44/40}\text{Ca}$ values of the BSM is estimated to be 0.89–0.95‰, using a two-end member mixing model. The Ca isotopic composition of the BSM is within error to that of the bulk silicate Earth ($0.94 \pm 0.05\text{‰}$), providing insights into the information of the comparison of the Earth-Moon system and the planets of inner Solar System.

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Keywords: Ca isotopes; Bulk silicate Moon; Lunar crust and mantle; KREEP-rich material; Lunar meteorites

1. INTRODUCTION

Calcium is a refractory, lithophile element whose isotopes are ideal for tracing the magmatic processes, condensation, and inheritance in the early Solar System (Simon et al., 2009, 2010, 2017; Huang et al., 2010a, 2011, 2012, 2017; Dauphas et al., 2014; Valdes et al., 2014; Kang et al., 2016, 2017; Feng et al., 2017; Amsellem et al., 2017; Schiller et al., 2018; Ionov et al., 2019). The Ca isotopic composition of meteorites can provide information

about planetary building blocks and the heterogeneity of the proto-planetary disk (Valdes et al., 2014; Schiller et al., 2016). Moreover, the Ca isotopic compositions of the Earth-Moon system can be studied to ascertain the building blocks of the Moon (Valdes et al., 2014; Kang et al., 2017).

Three sets of the calcium isotopic compositions (defined as $\delta^{44/40}\text{Ca} = ((^{44}\text{Ca}/^{40}\text{Ca})_{\text{sample}} / ((^{44}\text{Ca}/^{40}\text{Ca})_{\text{NIST-SRM-915a}} - 1) * 1000) \text{‰}$) have previously been calculated for the bulk silicate Earth (BSE) (Simon and DePaolo, 2010; Huang et al., 2010a, 2011; Kang et al., 2017). Simon and DePaolo (2010) calculated a $\delta^{44/40}\text{Ca}$ value of the $0.88 \pm 0.04\text{‰}$ for the BSE, using two clinopyroxene crystals from an ultramafic xenolith. On the basis of the calcium

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isotopic fractionation between clinopyroxene and orthopyroxene, and their proportions in the upper mantle (Amini et al., 2009; Feng et al., 2014), Huang et al. (2010a) estimated the BSE $\delta^{44/40}\text{Ca}$ value to be $1.05 \pm 0.04\%$. The $\delta^{44/40}\text{Ca}$ value for the BSE has also been estimated at $0.94 \pm 0.05\%$ through analysis of fertile spinel and garnet lherzolites from Vitim in Russia and Tariat in Mongolia (Kang et al., 2017). As discussed in Lu et al. (2019), Huang et al. (2010a)'s estimate is heavier than the other values, which likely results from the limited number of samples analyzed ($N = 2$) and/or a lab bias. Besides, Kang et al. (2017)'s estimate is in a good agreement with Simon and DePaolo (2010), He et al. (2017), and Chen et al. (2019). In considering these, we preferably select the value ($0.94 \pm 0.05\%$) as the value of BSE in this study.

Regarding the calcium isotopic composition of the bulk silicate Moon (BSM), the mean $\delta^{44/40}\text{Ca}$ value of five lunar basalts in Valdes et al. (2014) was $0.92 \pm 0.12\%$, the mean $\delta^{44/40}\text{Ca}$ value of seven lunar basalts' $\delta^{44/40}\text{Ca}$ in Simon et al. (2017) was $0.99 \pm 0.14\%$, and the mean $\delta^{44/40}\text{Ca}$ value of two feldspathic breccias and two basalts in Schiller et al. (2018) was $0.79 \pm 0.10\%$. The discrepancy between these values is likely due to the disparate, small, and partially representative nature of their sample sets. Unlike the scenario for the BSE, the Ca isotopic composition of the BSM cannot be estimated from direct measurements of the lunar mantle because of the difficulty in obtaining samples. Given that calcium did not volatilize or sink into the core during the evolution of the Moon (Rubin, 2011; Valdes et al., 2014), both the lunar crust and lunar mantle compositions are needed to bracket the Ca isotope composition of the BSM. The composition of the lunar mantle can be constrained by analyzing lunar basalts if the effects of differentiation, partial melting and assimilation processes are taken into account (Amini et al., 2009; Kang et al., 2016; Zhu et al., 2018). However, samples of the lunar crust (i.e., pure anorthite) are very rare (Neal, 2009; Taylor, 2009). This problem can be addressed by analyzing feldspathic breccias and the anorthite within it, and evaluating the influence of other minerals on the bulk composition of the anorthites.

In this study, we analyzed five lunar meteorites and four anorthite crystals collected from the feldspathic breccias. Using these results and published calcium isotopic data from the lunar samples (Simon and DePaolo 2010; Valdes et al., 2014; Schiller et al., 2018), we attempt to (1) constrain the calcium isotopic composition of the lunar mantle and crust; (2) discuss the early evolution of the calcium isotopic composition of the Moon, and (3) estimate the calcium isotopic composition of the BSM.

2. SAMPLES AND EXPERIMENTAL PROCEDURE

2.1. Samples

Five lunar meteorites and four anorthite crystals were analyzed. The five lunar meteorites were NWA 6950, NWA4734, Dhofar 1428, DaG 400 and NWA 5000. The anorthite crystals were drilled from Dhofar 1428 and DaG 400 using a NewWave MicroMill at the Geoevolution Laboratory of University of Science and Technology of

China, Hefei, and are referred to Dhofar 1428-A, Dhofar 1428-B, DaG 400-A, and DaG 400-B. We used a microscope to choose suitable areas to drill. The NewWave MicroMill used an 8 μm drill diameter, a variable drilling time of 2–5 min, and a rotational speed of 1200–3500 rpm depending on the size of the single crystal and the desired sample weight.

2.2. Scanning electron microscopy and electronic probe analysis

Backscattered electron images of the samples in thin-section were taken using a Carl Zeiss SUPRA55SAP-PHIRE field emission-scanning electron microscope (SEM) and electron probe micro-analysis (EMPA) on a JEOL JXA-8100 SuperProbe at the State Key Laboratory of Isotope Geochemistry (SKLaBIG), Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIGCAS). An accelerating voltage of 15 kV and a beam current of 20 nA were used. A variable dwell time of 20–60 s was used depending on the intensity of the characteristic X-ray line and desired precision. The working distance of the SEM was 6.9 mm and that of the EMPA was 11 mm. The resolution of the backscattered electron images is 2048 pixels * 1536 pixels.

2.3. Major and trace element analyses

Between 50 and 100 mg of each bulk-rock sample was powdered to 200 mesh in an agate mortar for elemental and isotopic analyses. The powder was digested using a 5:1 mixture of concentrated HF and HNO₃ in a 7 ml PFA beaker on a hot plate at 110 °C for about 3 weeks. After the digestions, the samples were dried down at 80 °C and re-dissolved in 6 N HCl several times to destroy fluoride complexes (e.g. CaF₂). The dried residue was finally dissolved in 4.000 ml of 2% HNO₃. The 4.000 ml solution was treated as the mother solution for Major-element, trace-element, and Ca isotope analyses. The detailed sample preparation followed the procedures described in Valdes et al. (2014). Major- and trace-element contents were measured using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, relative uncertainties ~5%) and ICP-Mass Spectrometry (ICP-MS, relative uncertainties ~2%) at SKLaBIG, GIGCAS, respectively (Liu et al., 1996; Wei et al., 2007; Tu et al., 2011). 0.100 ml mother solution was taken and diluted to 4.000 ml by adding 3.900 ml 2% HNO₃ for major element analyses. The wavelengths for Na, Al, Mg, K, Ca, Fe, Ti measurement are 589.59 nm, 308.21 nm, 202.58 nm, 766.49 nm, 318.12 nm, 259.94 nm, and 308.80 nm, respectively. 0.10 g mother solution was taken and diluted to 2.00 g by adding 1.90 g 2% HNO₃. After dilution, 2.00 g Rh-Re internal standard was added in the solution for trace element analyses. The experimental conditions can be seen in Liu et al. (1996).

2.4. Ca isotope analyses

An aliquot containing ~50 μg of Ca was mixed with ~0.3 g of ^{42}Ca – ^{43}Ca double-spike solution. The spiked

samples were expected to have a $^{40}\text{Ca}/^{42}\text{Ca}$ ratio of around 7. The samples were then dried down and re-dissolved in 50 μl of 1.6 N HCl for the column chemistry. Calcium was purified using 1 ml of Bio-Rad AG MP-50 (100–200 mesh) resin with 1.6 N HCl (Zhu et al., 2016). The recovery for each column separation was >99%, collected from the pre-cut and after-cut solutions. The recovery was measured using ICP-AES. About 5 μg of purified Ca was loaded as calcium nitrate onto a 99.995% Ta filament and was measured using thermal ionization mass spectrometry (Thermo Triton) following the procedures described by Zhu et al. (2016). The measurement of calcium began when the intensity of the ^{40}Ca signal reached 15 V, and each run consisted of 8 blocks and 26 cycles. Instrumental fractionation was corrected using the ^{42}Ca – ^{43}Ca double spike technique using an offline iterative routine with an exponential law, similar to the method of Heuser et al. (2002). Details of the chemical purification process and TIMS determination are given by Liu et al. (2015), Zhu et al. (2016), Liu et al. (2017), and Kang et al. (2017). Blanks from the digestion and chemical procedures were <100 ng, which are insignificant relative to the amount of Ca processed. The mean measured $\delta^{44/40}\text{Ca}$ values, relative to SRM 915a of NIST SRM 915a, IAPSO seawater, BHVO-2, and BCR-2, are $0.02 \pm 0.08\text{‰}$ (2SD, $n = 26$), $1.82 \pm 0.11\text{‰}$ (2SD, $n = 17$), $0.76 \pm 0.09\text{‰}$ (2SD, $n = 19$) and $0.80 \pm 0.08\text{‰}$ (2SD, $n = 18$), respectively, which are in good agreement with those of previous studies (e.g. Amini et al., 2009; Huang et al., 2010a; Valdes et al., 2014).

3. RESULTS

NWA 4734 has a typical sub-ophitic texture and consists of mainly of pyroxene (~30%), olivine (~20%), anorthite (~30%), and accessory minerals (e.g. pyrrhotite, ilmenite, and chromite) (Fig. 1a, b). The feldspathic breccias are composed of various types of clast cemented by a matrix (Fig. 1c, e, f), and their main component is anorthite. The diameters of the largest anorthite in Dhofar 1428 and DaG 400 are ~2 mm and ~3 mm, respectively. Of particular note is that NWA 5000 contains K-rich minerals (Fig. 1d), which are rare in the feldspathic breccia (Jolliff et al., 2006). NWA 6950 has been previously described by Ruzicka et al. (2014), and it is dominated by olivine, low-Ca pyroxene, pigeonite, and subcalcic augite, with interstitial anorthite. Detailed petrographic descriptions of these samples can be found in previous studies (Bunch et al., 2006; Fernandes et al., 2009; Zhang et al., 2009; Hidaka et al., 2010; Wang et al., 2012; Elardo et al., 2014; Nagurny et al., 2016; Grange et al., 2016).

The major- and trace-element composition of the lunar meteorites and the terrestrial rock standards are listed in Table 1. As shown in Fig. 2, NWA 6950 and NWA 4734 are lunar mare basalts, Dhofar 1428 and DaG 400 are feldspathic lunar meteorites, and NWA 5000 plots in the area of the KREEP basalt field (rich in potassium, rare-earth elements, phosphorus) owing to the presence of KREEP-bearing materials in this sample (Humayun and Irving, 2008). NWA 5000 is further distinguished by its unusually high REE contents and negative Eu anomaly (Fig. 3).

Given their TiO_2 contents, NWA 6950 (0.51 wt%) and NWA 4734 (3.21 wt%) are classified as very-low Ti basalts and low Ti basalts, respectively.

Calcium isotopic composition of the five lunar meteoritic samples, four anorthite crystals, and other lunar samples from the literature are given in Table 2. The mean $\delta^{44/40}\text{Ca}$ values of the two lunar basalt samples are $0.90 \pm 0.07\text{‰}$ (2SD, $n = 3$, n is the number of replicate analyses) and $0.96 \pm 0.11\text{‰}$ (2SD, $n = 4$), relative to SRM 915a, in agreement with previous measurements (Simon and DePaolo, 2010; Valdes et al., 2014; Schiller et al., 2018). The lunar feldspathic breccias have a narrow range of $\delta^{44/40}\text{Ca}$ values, from $0.76 \pm 0.06\text{‰}$ (2SD, $n = 3$) to $0.82 \pm 0.02\text{‰}$ (2SD, $n = 3$), which are lower than those of the lunar basalts. The lowest $\delta^{44/40}\text{Ca}$ value was obtained from the anorthite crystals drilled from the lunar feldspathic breccias, ranging from 0.65‰ to 0.80‰, with a mean value of $0.75 \pm 0.13\text{‰}$ (2SD, $N = 4$, N is the number of samples).

4. DISCUSSION

4.1. Calcium isotopic composition of the lunar crust and KREEP-rich material

A direct approach to constrain the $\delta^{44/40}\text{Ca}$ value of the lunar crust is to study pure lunar feldspar rocks or anorthites, which are considered to be the main components of the lunar crust (Warren, 2005; Jolliff et al., 2006). However, the pure lunar feldspar rocks are rare. Only one norite's and two lunar feldspathic breccias have been analyzed for Ca isotope (77215, 1.06‰; Dhofar 026, 0.76‰; Dhofar 287, 0.80‰; Bermingham et al., 2011; Schiller et al., 2018), but no calcium isotopic compositions have been reported so far for pure feldspar rocks or anorthites. Therefore, the study on the lunar feldspathic breccias and anorthites can be a fundamental complement.

To ascertain the calcium isotopic composition of the lunar crust, we analyzed three lunar feldspathic breccias and four anorthite crystals within them. The high-precision analyses of the feldspathic breccias yield $\delta^{44/40}\text{Ca}$ values ranging between 0.76‰ and 0.82‰ (Fig. 4), consistent with the previous work (Schiller et al., 2018). Of note is that pristine anorthosite 60025 and norite 77215 appear to have heavier calcium isotopic compositions than the other anorthosites (Farkaš et al., 2010; Bermingham et al., 2011). This may be due to larger proportion of isotopically heavy olivine in 60025 and of orthopyroxene in 77215 (Bermingham et al., 2011). Therefore, the calcium isotopic compositions of the feldspathic breccias, as well as of 60025 and 77215, cannot be used directly to constrain the composition of the lunar crust, because other minerals (e.g. pyroxene and olivine) and clasts within the breccias may also contribute to the $\delta^{44/40}\text{Ca}$ of the breccias. According to the lunar magma ocean (LMO) model, remote sensing data, and sample return missions (e.g. Taylor et al., 1974, 2009), anorthite is the main component of the lunar crust. The mean $\delta^{44/40}\text{Ca}$ value of the four anorthite crystals analyzed is $0.75 \pm 0.13\text{‰}$ (2SD, $N = 4$), representing the best estimated $\delta^{44/40}\text{Ca}$ value of the lunar crust.

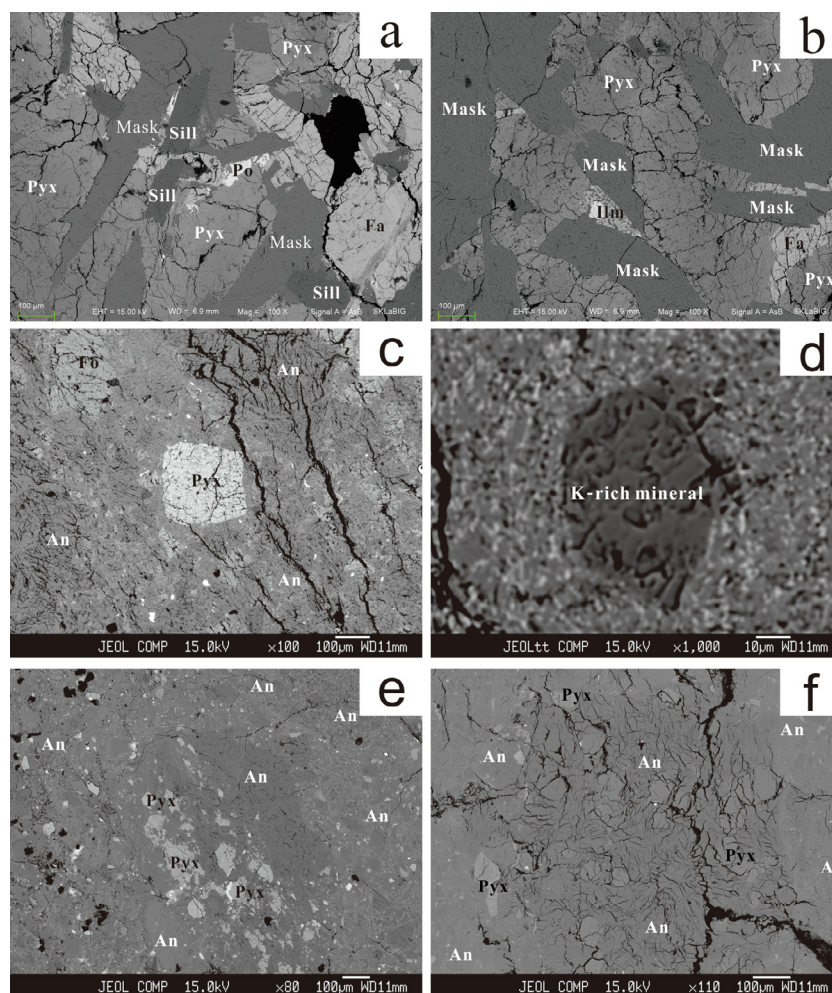


Fig. 1. Backscattered electron images of studied lunar meteorites. Panels a and b shows images of the basalt NWA 4734; NWA 4734 is a medium-coarse-grained, subophitic-textured mare basalt. The anorthite content in NWA 4734 is $\sim 30\%$. Anorthite was converted to maskelynite. Panels c and d, demonstrates the images of the feldspathic breccia NWA 5000, which contains K-rich minerals; Panel e show the images of the feldspathic breccia Dhofar 1428; Panel f is the image of feldspathic breccia DaG 400. All of the feldspathic breccias are composed primarily of anorthite. The dark phases are silica, K-feldspar and Si, K-rich glasses, and the bright phases are mostly ilmenite (elongated), spinel, and fayalite. Pyx: pyroxene, Fa: fayalite, An: anorthite, Msk: maskelynite, Ilm: ilmenite, Po: pyrrhotite, and Tro: troilite.

KREEP-rich material, as the product of the last stage of the LMO, is an important record of the magmatic activity on the Moon (e.g. Taylor et al., 1974; Jolliff et al., 2006). However, the calcium isotopic composition of KREEP-rich material is currently poorly constrained. We found that NWA 5000, which contains KREEP-rich material, has a similar $\delta^{44/40}\text{Ca}$ value ($0.78 \pm 0.10\text{‰}$, 2SD, $n = 6$) to that of the feldspathic breccia. This implies that KREEP-rich material may also have the same calcium isotopic composition as feldspathic breccia. Alternatively, the proportion of KREEP-rich material in NWA 5000 may not be large enough to have an effect on the bulk rock composition. Using the mean contents of Th (0.37 ppm) and K_2O (0.027 wt%) in the lunar crust (Korotev et al., 2003) and in KREEP-rich material (Th, 12.4 ppm; K_2O , 0.5 wt%; Neal and Taylor, 1992; Hess and Parmentier, 2001), as well as the bulk composition of NWA 5000, we estimate that NWA 5000 contains approximately 30–50% KREEP-rich material. Thus, the CaO content of KREEP-rich material

(7–12%) can be calculated using the CaO content of the lunar crust and NWA 5000. Given that NWA 5000 is composed of KREEP-rich material and feldspathic breccia (Humayun and Irving, 2008), the $\delta^{44/40}\text{Ca}$ value of the KREEP-rich material is calculated to be 0.82–0.86‰. This indicates that the $\delta^{44/40}\text{Ca}$ value of the KREEP-rich material is indistinguishable from that of the lunar crust ($0.75 \pm 0.13\text{‰}$). Therefore, we consider that the KREEP material, as well as the lunar crust, is the low- $\delta^{44/40}\text{Ca}$ end-member in the Moon.

4.2. Calcium isotopic composition of the lunar mantle

4.2.1. Origin of $\delta^{44/40}\text{Ca}$ variation in lunar basalts

Lunar basalts, which were derived from high degree partial melting of olivine and pyroxene cumulates (e.g. Taylor et al., 1974, 2009; Beard et al., 1998), are ideal material for constraining the calcium isotopic composition of the lunar mantle. Unlike the estimation of the magnesium isotopic

Table 1
Major (wt%) and trace element ($\times 10^{-6}$) compositions of the lunar meteorites.

Sample	NWA 5000	Dhofar 1428	DaG 400	NWA 6950	NWA 4734	BCR-2	BHVO-2	BHVO-2*
SiO ₂	44.91	42.46	47.24	44.30	43.76	54.20	48.91	49.60
TiO ₂	0.82	0.19	0.18	0.51	3.21	2.25	2.73	2.73
Al ₂ O ₃	24.41	28.37	25.35	6.01	10.95	13.63	13.62	13.44
FeO	6.46	4.10	3.56	21.41	23.94	13.37	11.78	11.51
MnO	0.08	0.06	0.06	0.25	0.30	0.20	0.17	0.17
MgO	5.83	5.08	4.71	24.56	7.79	3.75	7.66	7.26
CaO	16.38	19.20	17.77	5.28	12.52	7.48	12.09	11.4
Na ₂ O	1.08	0.64	0.65	0.44	0.65	2.94	2.13	2.22
K ₂ O	0.30	0.04	0.07	0.05	0.09	1.64	0.47	0.51
P ₂ O ₅	0.31	0.06	0.53	0.11	0.13	0.39	0.28	0.27
Sc	11.7	7.7	6.7	22.9	58.1	31.8	31.9	31.8
V	20	18	17	74	113	399	317	318
Cr	482	529	620	2179	2233	14	278	287
Co	17	13	15	87	36	36	44	45
Ni	177	122	159	203	29	11	118	119
Ga	6.0	3.7	3.0	2.8	4.6	23.0	21.7	21.4
Rb	6.57	0.90	1.33	1.92	1.88	48.00	9.80	9.26
Sr	212	619	232	107	136	321	387	394
Y	72.5	7.9	8.7	34.9	58.2	35.7	26.7	25.9
Zr	270	26	29	183	182	187	174	171
Nb	23.72	2.61	2.87	13.93	14.81	16.11	24.77	18.1
Ba	414.9	75.7	233.4	121.1	121.5	248.0	3.9	130.9
La	23.99	2.07	2.49	10.71	11.43	24.23	15.37	15.2
Ce	63.18	4.77	5.65	26.74	24.63	51.39	37.96	37.53
Pr	8.83	0.73	0.86	3.81	4.08	6.91	5.57	5.40
Nd	38.2	3.3	3.8	16.7	19.1	28.4	24.8	24.3
Sm	10.61	0.95	1.10	4.63	6.22	6.49	6.18	6.20
Eu	1.79	0.7	0.74	0.32	1.10	1.89	2.07	2.04
Gd	11.62	1.07	1.25	5.2	7.82	6.67	6.23	6.21
Tb	1.98	0.20	0.22	0.90	1.46	1.02	0.93	0.93
Dy	12.13	1.30	1.42	5.65	9.56	5.99	5.21	5.28
Ho	2.69	0.29	0.32	1.27	2.16	1.33	1.03	0.99
Er	6.96	0.80	0.88	3.36	5.85	3.45	2.46	2.51
Tm	1	0.12	0.13	0.5	0.87	0.52	0.34	0.33
Yb	6.39	0.79	0.86	3.21	5.71	3.33	2.08	2.00
Lu	0.86	0.11	0.12	0.46	0.82	0.5	0.29	0.28
Hf	6.18	0.64	0.71	3.81	4.51	4.46	4.21	4.47
Ta	1.01	0.11	0.12	0.56	0.63	0.91	1.38	1.15
Th	4.32	0.35	0.41	1.71	1.93	6.06	1.29	1.22
U	1.10	0.17	0.36	0.46	0.47	1.69	0.43	0.41

SiO₂ was calculated, by subtracting the wt% of the other oxides, including trace elements, from 100 wt%.

* Represents the suggested values for BHVO-2 (The values were taken from the GeoReM database (<http://georem.mpch-mainz.gwdg.de>)).

composition of the lunar mantle (Sedaghatpour et al., 2013), the $\delta^{44/40}\text{Ca}$ value of the lunar mantle cannot be estimated from the average of that of lunar basalt, because Ca isotopes fractionate during high degree partial melting and crystals fractionation process while the Mg isotopes do not (Teng et al., 2007; Kang et al., 2017; Zhu et al., 2018; Zhang et al., 2018; Valdes et al., 2019; Kang et al., 2019). Data from Kang et al. (2017), Zhu et al. (2018), and Zhang et al. (2018) suggest that $<0.10\text{--}0.20\%$ fractionation is expected between residue and partial melt when the partial melt fraction is less than 25%, with the heavier Ca isotopes being concentrated in the residue.

Compared with the feldspathic breccias, the lunar basalts are rich in heavy Ca isotopes in general (Table 2; Fig. 4). The $\delta^{44/40}\text{Ca}$ value of the basalts in the present study varies from 0.90‰ to 0.96‰, falling within the published range of lunar basalt (0.78–1.08‰) (Simon et al.,

2010; Valdes et al., 2014; Schiller et al., 2018). The relatively wide variation in the $\delta^{44/40}\text{Ca}$ values ($\sim 0.30\%$) of the lunar basalts cannot be caused by partial melting, but can be attributed to (1) the fractional crystallization process; (2) contamination by lunar crust rocks; and (3) the heterogeneity of the lunar mantle.

The Ca isotopic fractionation may be as a result of fractional crystallization as suggested by Valdes et al. (2019). Here, the fractional crystallization of anorthite (An), clinopyroxene (Cpx), orthopyroxene (Opx), and olivine (Ol) are considered as they are the phenocrysts in the basalts. In the case of crystallization of An, the calcium isotopic composition of the lunar basalts should negatively correlate with MgO, because An has lower $\delta^{44/40}\text{Ca}$ values than other minerals and its fractionation would raise the $\delta^{44/40}\text{Ca}$ values in evolved basalts. The negative correlation between $\delta^{44/40}\text{Ca}$ and CaO (Fig. 5a) is apparently consistent

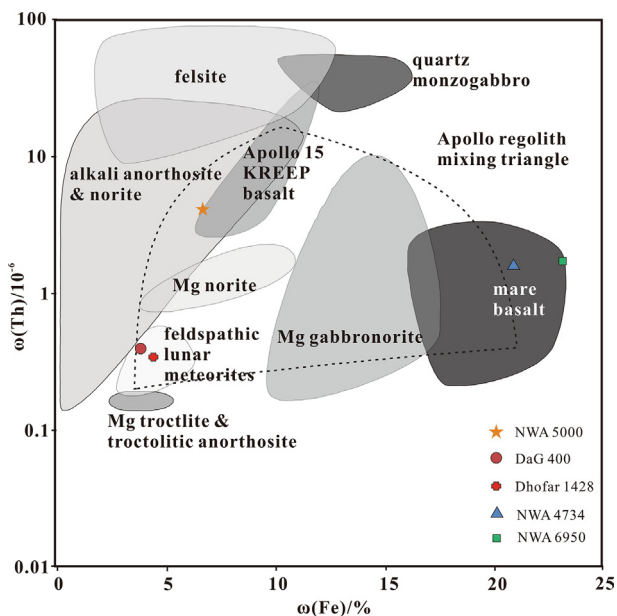


Fig. 2. Lunar samples in FeO–Th space (Jolliff et al., 2006). DaG 400 and Dhofar 1428 fall in the feldspathic lunar meteorites field, NWA 5000 falls in the hybrid origin field, and NWA 4734 and NWA 6950 fall in the mare basalt field.

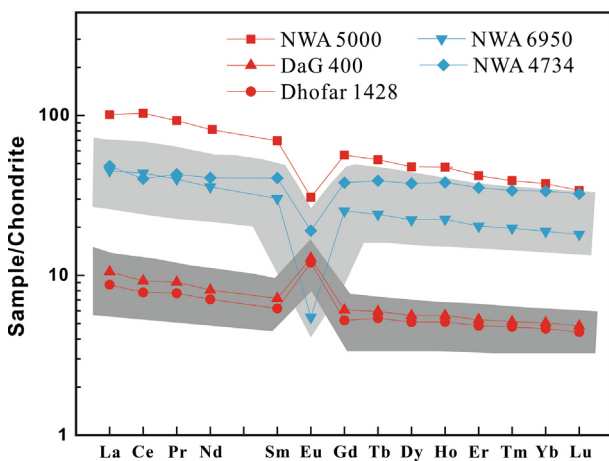


Fig. 3. Primitive-mantle-normalized (McDonough and Sun, 1995) REE patterns of lunar meteorites. The gray and dark-gray areas depict the compositions of mare basalts and lunar feldspathic breccia, respectively. NWA 5000 has high REE contents and a negative Eu anomaly owing to the presence of KREEP-bearing materials in this sample (Humayun and Irving, 2008).

with fractionation of An. In the fractionation of An scenario, the higher $\delta^{44/40}\text{Ca}$ are expected for the more fractionated basalts. However, among the lunar basalts analyzed so far, the most fractionated samples have lowest $\delta^{44/40}\text{Ca}$ values (Fig. 5b); thereby arguing against the role of the fractional crystallization of An.

The Ca isotopic fractionation factors between Cpx and basaltic melt ($\alpha_{\text{Cpx-melt}}$) at magmatic temperatures are close

to 1 inferred by Zhang et al. (2018). That is to say, negligible $\delta^{44/40}\text{Ca}$ variations is associated with the fractional crystallization of Cpx from the basaltic melt (Chen et al., 2019; Kang et al., 2019). In addition, there is no measurable $\delta^{44/40}\text{Ca}$ variation in basalts which have undergone significant fractionation of Ca-rich minerals (Zhang et al., 2018). To further elucidate the effect of crystallization of An and Cpx on Ca isotopic fractionation, we use a Rayleigh distillation equation:

$$\delta\text{Ca}_{\text{melt}} = (\delta\text{Ca}_{\text{initial melt}} + 1000) * f^{(\alpha-1)} - 1000$$

where f represents the fraction of Ca remaining in the melt and α represents the isotopic fractionation factor between the crystals and the melt. Here we use the value of NWA 6950 (0.96‰) as the $\delta\text{Ca}_{\text{initial melt}}$. 0.10‰ represents the analytical precision of Ca isotope at present. The $\alpha_{\text{Cpx-melt}}$ (1.00009) and $\alpha_{\text{An-melt}}$ (0.99985) are suggested by Zhang et al. (2018). The calculation results (Fig. 6) show that, the measurable effect on the $\delta\text{Ca}_{\text{melt}}$ can only be seen when (1) An fractional crystallization process caused a 50% of the Ca loss, or (2) Cpx fractional crystallization process caused a 70% of the Ca loss, which is almost impossible in natural process. The fractional crystallization of Opx and Ol would only cause a $\delta^{44/40}\text{Ca}$ variation of <0.05‰ due to the low Ca content in these minerals (Chen et al., 2019; Huang et al., 2019). All these suggest that the observed $\delta^{44/40}\text{Ca}$ variation in the lunar basalts cannot be attributed to the fractional crystallization process.

Therefore, we prefer that the negative correlation between $\delta^{44/40}\text{Ca}$ and CaO is indicate of accumulation of An. In other words, the Ca isotope variation in lunar basalts may result from contamination by lunar crust rock, which is predominated by anorthosite. This explanation gains further support from the negative correlation between $\delta^{44/40}\text{Ca}$ and Al_2O_3 content (Fig. 5c) and the mode of the An in the basalts (Fig. 5d). All these features indicate that anorthites (rich in Al and Ca) may affect the calcium isotopic composition of the lunar basalts. We discussed the heterogeneity of the lunar mantle in the Section 4.2.2.

4.2.2. Calcium isotopic composition of the lunar mantle

If the lunar basalts were contaminated by the lunar crust via assimilation of anorthosite during their eruption, only the least contaminated sample (i.e., with the lowest mode of anorthite) can be used to infer the calcium isotopic composition of the lunar mantle. NWA 6950 meets the criterion, as it contains only minor interstitial anorthites (Ruzicka et al., 2014). It is no means to say that NWA 6950 is representative of the lunar mantle, but as far as calcium isotopic composition of the lunar mantle is concerned, NWA 6950 best represents the lunar mantle.

As a result of preferential incorporation of the lighter Ca isotopes into magma melt (Kang et al., 2017; Zhu et al., 2018), the calcium isotopic composition of the lunar mantle can be best represented by the heaviest $\delta^{44/40}\text{Ca}$ found in lunar basalts. Among the lunar basalts analyzed, 12,012 shows the heaviest $\delta^{44/40}\text{Ca}$ ($1.08 \pm 0.05\text{‰}$, 2SE, $n = 2$). However, this value cannot be used to calculate the minimum $\delta^{44/40}\text{Ca}$ value of the lunar mantle because 12,012 contains 21.6% olivine (Neal et al., 1994,

Table 2

Ca isotopic compositions of lunar meteorites, USGS standards and lunar samples in literature.

Sample	Material	$\delta^{44/40}\text{Ca}^a$ (‰)	n ^b	2SD ^c	2SE ^d	Reference
<i>Lunar sample</i>						
NWA 6950	basalt	0.96	4	0.11	0.05	This study
NWA 4734	basalt	0.90	3	0.07	0.04	This study
NWA 4734 Replicate	basalt	0.87	3	0.06	0.04	This study
Dhofar 1428	feldspar breccia	0.82	3	0.02	0.01	This study
DaG 400	feldspar breccia	0.76	3	0.06	0.04	This study
NWA 5000	feldspar breccia	0.78	6	0.10	0.04	This study
10057	basalt	0.81	4		0.09	Valdes et al., 2014
12012	basalt	1.08	7		0.05	Valdes et al., 2014
14053	basalt	0.76	4		0.04	Valdes et al., 2014
15016	basalt	0.91	8		0.05	Valdes et al., 2014
10017	basalt	0.87	4		0.04	Simon et al., 2010
NWA 4734	basalt	0.82	7		0.04	Schiller et al., 2018
Dhofar 026	feldspar breccia	0.76	2		0.00	Schiller et al., 2018
NWA 8632	basalt	0.78	2		0.13	Schiller et al., 2018
Dhofar 287	feldspar breccia	0.80			0.03	Schiller et al., 2018
77,215	norite	1.06				Birmingham et al., 2011
<i>Single mineral</i>						
Dhofar 1428-A	anorthite	0.80	4	0.06	0.03	This study
Dhofar 1428-B	anorthite	0.76	3	0.00	0.00	This study
DaG 400-A	anorthite	0.65	3	0.04	0.02	This study
DaG 400-B	anorthite	0.77	3	0.10	0.05	This study
<i>Standard</i>						
BCR-2		0.80	18	0.08	0.02	This study
BHVO-2		0.76	19	0.08	0.02	This study
Seawater		1.82	17	0.12	0.03	This study
NIST 915a		0.02	26	0.10	0.02	This study

^a $\delta^{44/40}\text{Ca}$ is relative to NIST SRM 915a.^b The number for replicate analyses.^c 2SD: two standard deviations.^d 2SE: two standard deviation of the mean. $2SE = 2SD/\text{Sqrt}(N)$.

rator.jsc.nasa.gov/lunar/lsc/), which implies that the sample was likely derived from melting of a residue (Pearce, 1968; Kang et al., 2017; Zhang et al., 2018; Zhu et al., 2018). In

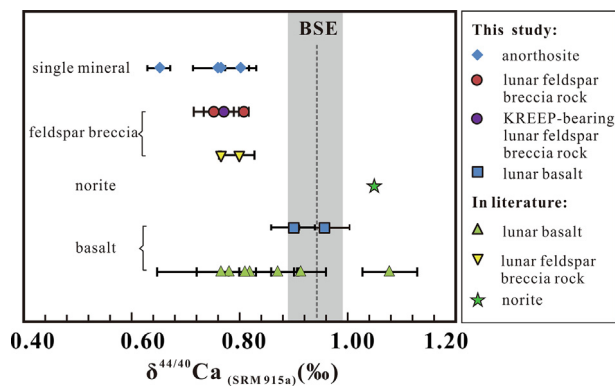


Fig. 4. Calcium isotopic data of lunar samples relative to NIST SRM 915a. The gray bar represents the values of the BSE estimated by Kang et al. (2017). Literature Ca isotopic data are from Simon and DePaolo (2010), Birmingham et al. (2011), Valdes et al. (2014), and Schiller et al. (2018). $\delta^{44/40}\text{Ca}$ was calculated from $\delta^{44/42}\text{Ca}$ by multiplying by 2.099 (Fantle and Tipper, 2014). The results are normalized to reference NIST 915a. Error bars represent two times the standard error of the mean.

addition, the Apollo 12 olivine basalt suite is considered to derive from the bottom of the lunar mantle (e.g. Walker et al., 1976). For these reasons, we consider the highest $\delta^{44/40}\text{Ca}$ value of the remaining basalts, that of NWA 6950 ($0.96 \pm 0.11\text{‰}$, 2SD, $n = 4$), to be the minimum $\delta^{44/40}\text{Ca}$ estimate of the lunar mantle with a corresponding CaO content of 5.28 wt%. Taking into account the calcium isotopic fractionation that occurs during partial melting (0.10–0.20‰, we used 0.15‰ in our calculation), the maximum $\delta^{44/40}\text{Ca}$ value of the lunar mantle is 1.11‰ with a corresponding CaO content of 3.06 wt% based on the model of Warren (2005).

Recently, Huang et al. (2019) investigated equilibrium calcium isotopic fractionation of Ca-bearing minerals using first-principles calculations based on the density functional theory. Those authors also simulated the solidification of the LMO and predicted that the $\delta^{44/40}\text{Ca}$ value of the lunar mantle is 0.26–0.33‰ higher than that of the lunar crust. Our experimental data and calculations show a good agreement with their model. Our analyses of lunar samples suggest that the $\delta^{44/40}\text{Ca}$ values of the lunar mantle and crust are 0.96–1.11‰ and $\sim 0.75\text{‰}$, respectively. Furthermore, Huang et al. (2019) estimated that the mean $\delta^{44/40}\text{Ca}$ of the lunar anorthositic crust is by 0.1‰ lower than that of the BSM, whereas the lunar mantle could have a $\delta^{44/40}\text{Ca}$ value 0.17–0.26‰ higher than that of the BSM if the mantle was

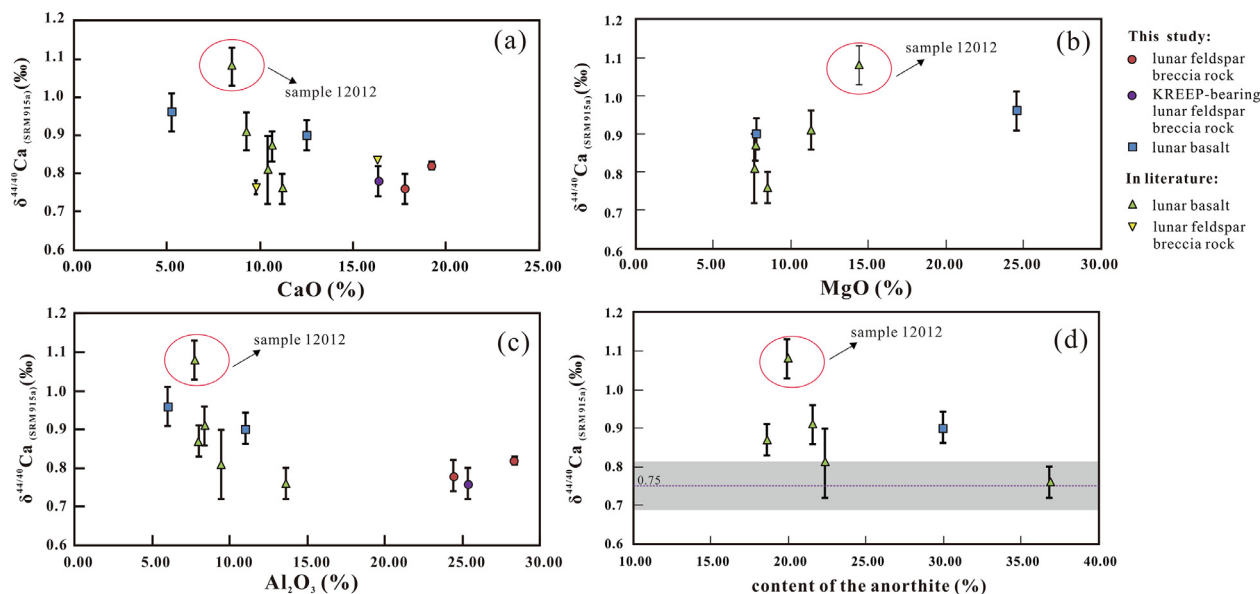


Fig. 5. Plots of $\delta^{44/40}\text{Ca}_{\text{SRM915a}}$ against (a) CaO, (b) MgO, (c) Al_2O_3 , and (d) anorthite content. NWA 6950 is not plotted in (d) due to the lack of petrographic data. Error bars represent two times the standard error of the mean. Sample 12012 is considered unrepresentative of the lunar mantle as it contains olivine cumulates (Pearce, 1968; <https://curator.jsc.nasa.gov/lunar/lsc/>).

fully overturned, or only by 0.06–0.08‰ for the case of fully mixing. Since the Ca budget of the lunar mantle is larger than that of the lunar crust (e.g. Taylor and Jake, 1974; Warren, 2005; Bermingham et al., 2011), the $\delta^{44/40}\text{Ca}$ value of the BSM is close to the $\delta^{44/40}\text{Ca}$ value of the lunar mantle. Our results support the second case in Huang et al. (2019) (by 0.06–0.08‰), meaning that the lunar mantle is fully mixed and isotopically homogeneous in Ca isotope. Nevertheless, further studies are desirable to confirm this assessment because the currently analyzed lunar samples are rather limited.

4.3. Constraining the calcium isotopic composition of the BSM

As calcium does not sink into the core during the early accretion and differentiation of a planet (Rubin et al., 2011), the calcium isotopic composition of the BSM can

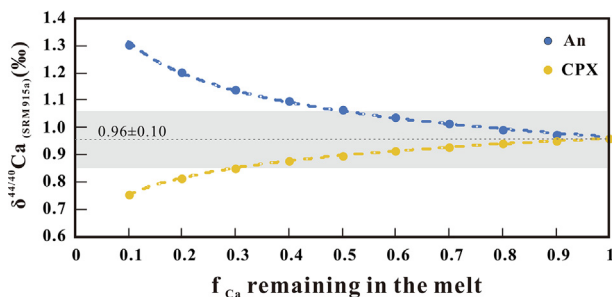


Fig. 6. Calculated $\delta^{44/40}\text{Ca}$ variation by a Rayleigh distillation model in the residual basaltic liquid during the fractional crystallization of An and Cpx. The blue and orange curves represent the fractional crystallization of An and Cpx, respectively. The gray bar represents analytical uncertainty of Ca isotopes.

be viewed as a mixture of the lunar mantle and crust. Typical lunar crust has ~20 wt% CaO (i.e., the CaO content of anorthite), whereas the lunar mantle contains 3.06–5.28 wt % CaO (Warren, 2005; Simon et al., 2010; Valdes et al., 2014). Fig. 7 shows the results of mixing different propor-

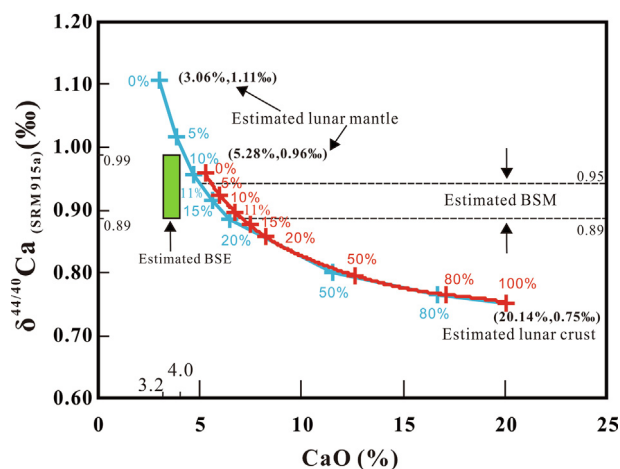


Fig. 7. A two-member mixing model between lunar mantle and crust, on a plot of $\delta^{44/40}\text{Ca}_{\text{SRM915a}}$ versus CaO. Lunar crust: CaO = 20.14 wt%, $\delta^{44/40}\text{Ca}_{\text{SRM915a}} = 0.75\text{‰}$. Two estimated lunar mantle compositions (CaO and $\delta^{44/40}\text{Ca}_{\text{SRM915a}}$) are used in the calculation: CaO = 3.06 wt% and $\delta^{44/40}\text{Ca}_{\text{SRM915a}} = 1.11\text{‰}$, and CaO = 5.28 wt% and $\delta^{44/40}\text{Ca}_{\text{SRM915a}} = 0.95\text{‰}$. The percentages in red and blue mark the proportion of lunar crust added to the mantle. The green rectangle is the estimate of the composition of the BSE (CaO: 3.20–4.00 wt%; $\delta^{44/40}\text{Ca}$: 0.89–0.99‰; Kang et al., 2017). The area between the two dotted lines is the estimated $\delta^{44/40}\text{Ca}$ value of the BSM (0.89–0.95‰). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

tions of the lunar mantle and crust, with two possible end-members for the lunar mantle (Table 3). Assuming that ~11% of the total lunar Ca is in the lunar crust, as suggested by Bermingham et al. (2011), we estimate the $\delta^{44/40}\text{Ca}$ value of the BSM to be 0.89–0.95‰, which is similar to that of the BSE ($0.94 \pm 0.05\text{‰}$; Kang et al., 2017). The indistinguishable Ca isotopic compositions of the Moon and the Earth support the hypothesis that the majority of the material that formed the Moon came from the proto-Earth rather than Theia (e.g. Zhang et al., 2012). Alternatively, Theia may also have the same calcium iso-

topic composition as the proto-Earth. The calcium isotopic composition of the BSM is also identical within error to the estimates of the Martian mantle ($1.04 \pm 0.09\text{‰}$), which can be taken as an approximation of Bulk Silicate Mars (Magna et al., 2015). This supports the hypothesis that the inner Solar System planets are homogeneous with respect to their calcium isotopes (Huang et al., 2010b; Magna et al., 2015). Owing to the limited number of samples analyzed with the comparable precision and accuracy reported here, we by no means regard our BSM $\delta^{44/40}\text{Ca}$ estimate as final. Rather, because the calcium isotopic com-

Table 3

Input and output model parameters for Fig. 6.

	CaO	$\delta^{44/40}\text{Ca}$		CaO	$\delta^{44/40}\text{Ca}$
Lunar mantle	3.06	1.11		5.28	0.96
Lunar crust	20.14	0.76		20.14	0.76
Lunar crust added into the Lunar mantle (%)			Ca budget from the lunar crust (%)		Ca budget from the lunar crust (%)
0	3.06	1.11	0.00	5.28	0.96
5	3.91	1.02	25.73	6.02	0.92
7	4.26	0.99	33.13	6.32	0.91
10	4.77	0.96	42.24	6.77	0.90
11	4.94	0.95	44.86	6.91	0.89
15	5.62	0.92	53.74	7.51	0.88
20	6.48	0.89	62.20	8.25	0.86
50	11.60	0.80	86.81	12.71	0.79
80	16.72	0.76	96.34	17.17	0.76
100	20.14	0.75	100.00	20.14	0.75

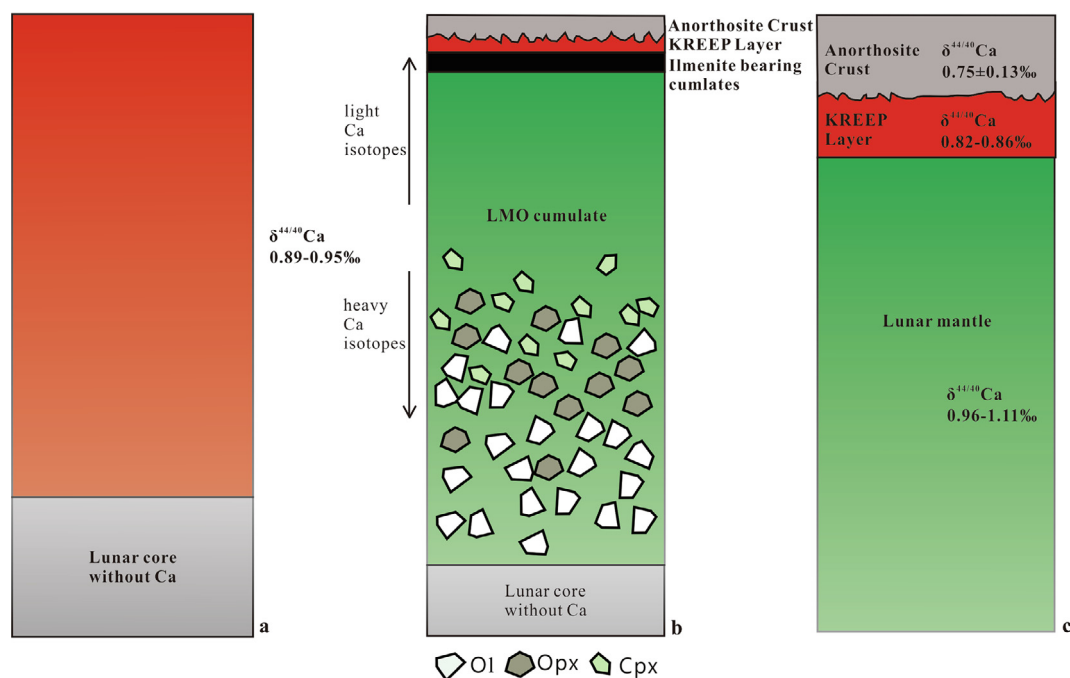


Fig. 8. A preliminary model of the behavior of Ca isotopes in the LMO (after Elardo et al., 2011). (a) Calcium isotopic composition of the BSM estimated by Fig. 7 and Table 3. The lunar core has no Ca as calcium does not volatilize or sink into the core during the evolution of the Moon (Rubin, 2011; Valdes et al., 2014). (b) Early-crystallizing minerals are enriched in heavy calcium isotopes, whereas late-stage anorthite contains more lighter calcium isotopes than olivine (Ol), orthopyroxene (Opx), and clinopyroxene (Cpx) (Huang et al., 2019; Valdes et al., 2019). (c) The estimated calcium isotopic compositions of the lunar crust, KREEP-rich material, and lunar mantle.

positions of many types of lunar sample have not been studied (e.g. the Mg, alkali, and ferroan-anorthositic suits), our study provides a preliminary constraint on the calcium isotopic composition of the BSM.

In Fig. 8, we present a preliminary model for the behavior of Ca isotopes in the LMO. In the first stage of this model (Fig. 8a), the lunar core forms contemporaneously with the LMO. As Ca is incompatible in the core, the core lacks Ca. The $\delta^{44/40}\text{Ca}$ value of the LMO is estimated to be 0.89–0.95‰. In the second stage (Fig. 8b), during the cooling of the LMO, mafic minerals, such as olivine and pyroxene, crystallized before anorthite. The early-crystallizing minerals tend to have heavier calcium isotopes than the late-crystallizing minerals. The KREEP-rich materials, which are commonly considered to be the products of the last stage of crystallization, may have low $\delta^{44/40}\text{Ca}$ values, similar to that of the anorthites. Fig. 8c shows that the estimated $\delta^{44/40}\text{Ca}$ values of the lunar crust, KREEP-rich material, and lunar mantle are $0.75 \pm 0.13\text{‰}$, 0.82–0.86‰, and 0.96–1.11‰, respectively.

Alternatively, if we assume that the $\delta^{44/40}\text{Ca}$ value of the BSM is $0.94 \pm 0.05\text{‰}$, the same as that of the BSE, we can estimate the CaO content of Moon. The calculated curves in Fig. 7 show mixing between various lunar mantle and crust end-members. The estimated CaO content of 4.26–6.48 wt% for the Moon is higher than that for the bulk Earth (3.20–4.00 wt%; Hofmann, 2014; Kang et al., 2017) and estimate agrees with those of previous studies (e.g. Taylor and Bence, 1975; Taylor, 1982). Bulk Moon compositions with the high refractory element (e.g. Ca) contents imply that the deep mantle contains garnet and trace-spinel with low-Ca pyroxene and olivine, whereas bulk Moon compositions without refractory element contents suggest that the deep mantle contains low-Ca pyroxene but no aluminous phase (Elardo et al., 2011). This difference is vital to understanding the LMO, as an LMO with enriched refractory elements will likely produce anorthite earlier, and in greater quantities, leading to a thicker primary crust. Therefore, the enrichment of Ca in the bulk Moon, compared with the bulk Earth, may provide important information on the formation and evolution of the Moon.

5. CONCLUSIONS

We report Ca isotopic data for five lunar meteorites and four anorthite crystals to constrain Ca isotopic compositions of the lunar crust, mantle, KREEP-rich material, and BSM.

- (1) The $\delta^{44/40}\text{Ca}$ value of the lunar crust, estimated from the anorthite, is approximately $\sim 0.75\text{‰}$. KREEP-rich material might have a similar calcium isotopic composition with the anorthite.
- (2) The observed variation in Ca isotopic compositions of the basalts is likely due to contamination by the lunar crust. Using the $\delta^{44/40}\text{Ca}$ value of the least contaminated basalts, and assuming Ca isotopic fractionation caused by partial melting, we estimate a $\delta^{44/40}\text{Ca}$ value of 0.96–1.11‰ for the lunar mantle.

- (3) Estimated $\delta^{44/40}\text{Ca}$ of the BSM (0.89–0.95‰) is similar to that of the BSE, suggesting a genetic relationship between the Earth and the Moon, which means that the Earth and Moon likely have developed from the same source.

Declaration of Competing Interest

We declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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APPENDIX A. SUPPLEMENTARY MATERIAL

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.gca.2019.12.001>.

REFERENCES

- Amini M., Eisenhauer A., Böhm F., Holmden C., Kreissig K., Hauff F. and Jochum K. P. (2009) Calcium isotopes ($\delta^{44/40}\text{Ca}$) in MPI-DING reference glasses, USGS rock powders and various rocks: evidence for Ca isotope fractionation in terrestrial silicates. *Geostand. Geoanal. Res.* **33**, 231–247.
- Amsellem E., Amsellem E., Moynier F., Pringle E. A., Bouvier A., Chen H. and Day J. M. D. (2017) Testing the chondrule-rich accretion model for planetary embryos using calcium isotopes. *Earth Planet. Sci. Lett.* **469**, 75–83.
- Bermingham K., Gussone N., Magna T. and Mezger K. (2011) Calcium isotopes in lunar crust. *Mineral. Mag.* **75**, A519.
- Beard B. L., Taylor L. A., Scherer E. E., Johnson C. M. and Snyder G. A. (1998) The source region and melting mineralogy of high-titanium and low-titanium lunar basalts deduced from Lu-Hf isotope data. *Geochim. Cosmochim. Acta* **62**(3), 525–544.
- Bunch T. E., Wittke J. H. and Korotev R. L. (2006) Petrology and composition of lunar feldspathic breccias nwa 2995, dhofar 1180 and dhofar 1428. *Meteoritics Planet. Sci.* **41**(8), 5254.
- Chen C., Dai W., Wang Z., Liu Y., Li M., Becker H. and Foley S. F. (2019) Calcium isotope fractionation during magmatic processes in the upper mantle. *Geochim. Cosmochim. Acta* **249**, 121–137.
- Dauphas N., Chen J. H., Zhang J., Papanastasiou D. A., Davis A. M. and Travaglio C. (2014) Calcium-48 isotopic anomalies in bulk chondrites and achondrites: Evidence for a uniform isotopic reservoir in the inner protoplanetary disk. *Earth Planet. Sci. Lett.* **407**, 96–108.
- Elardo S. M., Draper D. S. and Shearer C. K. (2011) Lunar magma ocean crystallization 423 revisited: bulk composition, early cumulate mineralogy, and the source regions of the 424 highlands Mg-suite. *Geochim. Cosmochim. Acta* **75**, 3024–3045.

- Elardo S. M., Shearer C. K., Fagan A. L., Borg L. E., Gaffney A. M., Burger P. V., Neal C. R., Fernandes V. A. and McCubbin F. M. (2014) The origin of young mare basalts inferred from lunar meteorites northwest africa 4734, 032, and lapaz icefield 02205. *Meteorit. Planet. Sci.* **49**(2), 261–291.
- Farkaš J. and Huang S. (2010) Mass-dependent calcium isotope composition of solar system objects. lunar and planetary Science Conference, 2266 (abstr.).
- Fantle M. S. and Tipper E. T. (2014) Calcium isotopes in the global biogeochemical Ca cycle: implications for development of a Ca isotope proxy. *Earth-Sci. Rev.* **129**, 148–177.
- Fernandes V. A., Korotev R. L. and Renne P. R. (2009) 40Ar-39Ar Ages and Chemical Composition for Lunar Mare Basalts: NWA 4734 and NWA 4898. Lunar and Planetary Science Conference, Vol.40 (abstr.).
- Feng C., Qin T., Huang S., Wu Z. and Huang F. (2014) First-principles investigations of equilibrium calcium isotope fractionation between clinopyroxene and Ca-doped orthopyroxene. *Geochim. Cosmochim. Acta* **143**, 132–142.
- Feng L. P., Zhou L., Yang L., DePaolo D. J., Tong S.-Y., Liu Y. S., Owens T. L. and Gao S. (2017) Calcium isotopic compositions of sixteen USGS reference materials. *Geostand. Geoanal. Res.* **41**, 93–106.
- Grange M. L., Norman M. D. and Assis Fernandes V. (2016) Clues to the Origin of Gabbroic Lunar Meteorite Northwest Africa 5000. Lunar and Planetary Science Conference, Vol.47 (abstr.).
- Hidaka Y., Yamaguchi A. and Ebihara M. (2010) Trace element characteristics of a lunar meteorite dhofar 1428. *Meteorit. Planet. Sci. Suppl.* **45**, 7.
- Hess P. C. and Parmentier E. M. (2001) Thermal evolution of a thicker KREEP liquid layer. *J. Geophys. Res.: Planets* **106**, E11.
- Heuser A., Eisenhauer A., Gussone N., Bock B., Hansen B. T. and Nögler Th. F. (2002) Measurement of calcium isotopes ($\delta^{44}\text{Ca}$) using a multicollector TIMS technique. *Int. J. Mass Spectrom.* **220**, 385–397.
- He Y., Wang Y., Zhu C., Huang S. and Li S. (2017) Mass-independent and mass-dependent Ca isotopic compositions of thirteen geological reference materials measured by thermal ionisation mass spectrometry. *Geostandards Geoanal. Res.* **41**, 283–302.
- Hofmann A. W. (2014) Sampling Mantle Heterogeneity through Oceanic Basalts: Isotopes and Trace Elements. In *Treatise on Geochemistry*, 2nd edition. Elsevier, Oxford, pp. 67–101.
- Huang S., Farkaš J. and Jacobsen S. B. (2010a) Calcium isotopic fractionation between clinopyroxene and orthopyroxene from mantle peridotites. *Earth Planet. Sci. Lett.* **292**, 337–344.
- Huang S., Farkaš J. and Jacobsen S. B. (2010b) Non-mass dependent Ca isotopic composition in the inner Solar System objects. Lunar and Planetary Science Conference, 1379 (abstr.).
- Huang S., Farkaš J. and Jacobsen S. B. (2011) Stable calcium isotopic compositions of Hawaiian shield lavas: evidence for recycling of ancient marine carbonates into the mantle. *Geochim. Cosmochim. Acta* **75**, 4987–4997.
- Huang S., Farkaš J. Y. G., Petaev M. I. and Jacobsen S. B. (2012) Calcium isotopic ratios and rare earth element abundances in refractory inclusions from the Allende CV3 chondrite. *Geochim. Cosmochim. Acta* **77**, 252–265.
- Huang F., Zhou C., Wang W. Z., Kang J. T. and Wu Z. Q. (2019) First-principles calculations of equilibrium Ca isotope fractionation: implications for oldhamite formation and evolution of lunar magma ocean. *Earth Planet. Sci. Lett.* **510**, 153–160.
- Huang S. and Jacobsen S. B. (2017) Calcium isotopic compositions of chondrites. *Geochim. Cosmochim. Acta* **201**, 364–376.
- Humayun, M., and Irving, A. J. (2008) Impactor metal in gabbroic lunar meteorite Northwest Africa 5000. In Goldschmidt Conference abstracts, A402.
- Ionov D. A., Qi Y. H., Kang J. K., Golovin A. V., Oleinikov O. B., Zheng W., Anbar A. D., Zhang Z. F. and Huang F. (2019) Calcium isotopic signature of carbonate and silicate metasomatism, melt percolation and crustal recycling in the lithospheric mantle. *Geochim. Cosmochim. Acta* **248**, 1–13.
- Jolliff, B. L., Wieczorek, M. A., Shearer, C. K. and Neal, C. R. (2006) New Views of the Moon. Mineralogical Society of America.
- Kang J. T., Zhu H. L., Liu Y. F., Liu F., Fei W., Hao Y. T., Zhi X. C., Zhang Z. F. and Huang F. (2016) Calcium isotopic composition of mantle xenoliths and the minerals from Eastern China. *Geochim. Cosmochim. Acta* **174**, 335–344.
- Kang J. T., Inoov D. A., Liu F., Zhang C. L., Golovin A. V., Qin L. P., Zhang Z. F. and Huang F. (2017) Calcium isotopic fractionation in mantle peridotites by melting and metasomatism and Ca isotope composition of the Bulk Silicate Earth. *Earth Planet. Sci. Lett.* **474**, 128–137.
- Kang J. T., Inoov D. A., Zhu H. L., Liu F., Zhang Z. F., Liu Z. and Huang F. (2019) Calcium isotope sources and fractionation during melt-rock interaction in the lithospheric mantle: Evidence from pyroxenites, wehrlites, and eclogites. *Chem. Geol.* **524**, 272–282.
- Korotev R. L., Jolliff B. L., Zeigler R. A., Gillis J. J. and Haskin L. A. (2003) Feldspar lunar meteorites and their implications for compositional remote sensing of the lunar surface and the composition of the lunar crust. *Geochim. Cosmochim. Acta* **67**, 4895–4923.
- Liu Y., Liu H. C. and Li X. H. (1996) Simultaneous and precise determination of 40 trace elements in rock samples using ICP-MS. *Geochimica* **25**, 552–558.
- Liu Y. F., Zhu H. L., Liu F., Wang G. Q., Xu J. F. and Zhang Z. F. (2015) Methodological study of chemical separation of calcium for TIMS measurements. *Geochemical.* **44**, 469–476.
- Liu F., Zhu H. L., Li X., Wang G. Q. and Zhang Z. F. (2017) Calcium isotopic fractionation and compositions of geochemical reference materials. *Geostand. Geoanal. Res.* **41**, 675–688.
- Lu W. N., He Y., Wang Y. and Ke S. (2019) Behavior of calcium isotopes during continental subduction recorded in metabasaltic rocks. *Geochim. Cosmochim. Acta* **1**, 1–5. <https://doi.org/10.1016/j.gca.2019.09.027>.
- Magna T., Gussone N. and Mezger K. (2015) The calcium isotope systematics of Mars. *Earth Planet. Sci. Lett.* **430**, 86–94.
- McDonough W. F. and Sun S.-S. (1995) The composition of the Earth. *Chem. Geol.* **120**, 223–253.
- Nagurney, A. B., Treiman, A. H. and Spudis, P. D. (2016) Petrology, Bulk Composition, and Provenance of Meteorite Northwest Africa 5000. Lunar and Planetary Science Conference Vol.47 (abstr.).
- Neal C. R. and Taylor L. A. (1992) Petrogenesis of mare basalts - A record of lunar volcanism. *Geochim. Cosmochim. Acta* **56**, 2177–2211.
- Neal C. R., Hacker M. D., Snyder G. A., Liu Y. G. and Schmitt R. A. (1994) Basalt generation are the Apollo 12 site, Part 1: New data, classification and re-evaluation. *Meteoritics* **29**, 334–348.
- Neal C. R. (2009) The Moon 35years after Apollo: What's left to learn?. *Chem Erde.* **69**(1), 3–43.
- Pearce T. H. (1968) A contribution to the theory of variation diagrams. *Contribut. Mineral. Petrol.* **19**(2), 142–157.
- Rubin A. E. (2011) Origin of the differences in refractory-lithophile-element abundances among chondrite groups. *Icarus* **213**, 547–558.
- Ruzicka A., Grossman J. and Garvie L. (2014) The Meteoritical Bulletin, No. 100, 2014 June. *Meteorit. Planet. Sci.* **49**, E1–E101 <http://www.lpi.usra.edu/meteor/>.

- Schiller M., Gussone N. and Wombacher F. (2016) High temperature geochemistry and cosmochemistry. In *Calcium Stable Isotope Geochemistry*. Springer, Berlin, Heidelberg, pp. 223–245.
- Schiller M., Bizzarro M. and Fernandes V. A. (2018) Isotopic evolution of the protoplanetary disk and the building blocks of Earth and the Moon. *Nature* **555**, 507–510.
- Sedaghatpour F., Teng F. Z., Liu Y., Sears D. W. G. and Taylor L. A. (2013) Magnesium isotopic composition of the Moon. *Geochim. Cosmochim. Acta* **120**, 1–16.
- Simon J. I., DePaolo D. J. and Moynier F. (2009) Calcium isotope composition of meteorites, Earth, and Mars. *Astrophys. J.* **702**, 707–715.
- Simon J. I. and DePaolo D. J. (2010) Stable calcium isotopic composition of meteorites and rocky planets. *Earth Planet. Sci. Lett.* **289**, 457–466.
- Simon J. I., Jordan M. K., Tappa M. J., Schauble E. A., Kohl I. E. and Young E. D. (2017) Calcium and titanium isotope fractionation in refractory inclusions: Tracers of condensation and inheritance in the early solar protoplanetary disk. *Earth Planet. Sci. Lett.* **472**, 277–288.
- Taylor, S. R., Jakes, P. (1974) The geochemical evolution of the Moon. *Proc Lunar Sci Conf* 5, 1287–1305.
- Taylor, S. R. (1982) *Planetary Science: A Lunar Perspective*. Lunar and Planetary Institute, Houston, p. 502.
- Taylor, S. R. and Bence, A. E. (1975) Evolution of the lunar highland crust. *Proc. Lunar Sci. Conf.* 6, 1121–1141.
- Taylor G. J. (2009) Ancient lunar crust: origin, composition, and implications. *Elements* **5**(1), 17–22.
- Teng F. Z., Wadhwa M. and Helz R. T. (2007) Investigation of magnesium isotope fractionation during basalt differentiation: Implications for a chondritic composition of the terrestrial mantle. *Earth Planet. Sci. Lett.* **261**, 84–92.
- Tu X. L., Zhang H., Deng W. F., Ling M. X., Liang H. Y., Liu Y. and Sun W. D. (2011) Application of RESOLUTION in-situ laser ablation ICP-MS in trace element analyses [in Chinese with English abstract]. *Geochimica* **40**, 83–89.
- Valdes M. C., Moreira M., Foriel J. and Moynier F. (2014) The nature of Earth's building blocks as revealed by calcium isotopes. *Earth Planet. Sci. Lett.* **394**, 135–145.
- Valdes M. C., Debaille V., Berger J. and Armytage R. M. G. (2019) The effect of high-temperature fractional crystallization on calcium isotopic composition. *Chem. Geol.* **509**, 77–97.
- Walker D., Longhi J., Stolper E.M., Grove T.L. and Hays J.F. (1976) Differentiation of an Apollo 12 pictite magma. *Proc Lunar Sci conf* 7, pp. 1365–1389.
- Wang Y., Hsu W. B., Guan Y. B., Li X. H., Li Q. L., Liu Y. and Tang G. Q. (2012) Petrogenesis of the Northwest Africa 4734 basaltic lunar meteorite. *Geochim. Cosmochim. Acta* **92**, 329–344.
- Warren P. H. (2005) “New” lunar meteorites: Implication for composition of the global lunar surface, lunar crust and the bulk Moon. *Meteorit. Planet. Sci.* **40**, 477–506.
- Wei G. J., Deng W. F., Liu Y. and Li X. H. (2007) High-resolution sea surface temperature records derived from foraminiferal Mg/Ca ratios during the last 260 ka in the northern South China Sea. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **250**, 126–138.
- Zhang A. and Hsu W. (2009) Petrography, mineralogy, and trace element geochemistry of lunar meteorite Dhofar 1180. *Meteorit. Planet. Sci.* **44**(9), 1265–1286.
- Zhang H. M., Wang Y., He Y. S., Teng F. Z., Jacobsen S. B., Helz R. T., Marsh B. M. and Huang S. C. (2018) No measurable calcium isotopic fractionation during crystallization of Kilauea Iki lave lake. *Geochem., Geophys., Geosyst.* <https://doi.org/10.1029/2018GC007506>.
- Zhang J., Dauphas N., Davis A. M., Leya I. and Fedkin A. (2012) The proto-Earth as a significant source of lunar material. *Nat. Geosci.* **5**, 251–255.
- Zhu H.L., Zhang Z.F. and Sun W.D. (2016) Calcium isotopic fractionation during partial melting: constraints from mid-ocean ridge basalts. *Goldschmidt Conf.* 1365(abstr.).
- Zhu H. L., Liu F., Li X., Wang G. Q., Zhang Z. F. and Sun W. D. (2018) Calcium isotopic compositions of normal Mid-Ocean Ridge Basalts from the southern Juan de Fuca Ridge. *J. Geophys. Res.: Solid Earth* **123**, 1303–1313. <https://doi.org/10.1002/2017JB014699>.

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