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Oxygen isotope constraints on the origin and differentiation of the Moon

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Abstract

We report new high-precision laser fluorination three-isotope oxygen data for lunar materials. Terrestrial silicates with a range of $\delta^{18}O$ values (−0.5 to 22.9‰) were analyzed to independently determine the slope of the terrestrial fractionation line (TFL; $\lambda=0.5259\pm0.0008$; 95% confidence level). This new TFL determination allows direct comparison of lunar oxygen isotope systematics with those of Earth. Values of $\Delta^{17}O$ for Apollo 12, 15, and 17 basalts and Luna 24 soil samples average 0.01‰ and are indistinguishable from the TFL. The $\delta^{18}O$ values of high- and low-Ti lunar basalts are distinct. Average whole-rock $\delta^{18}O$ values for low-Ti lunar basalts from the Apollo 12 (5.72±0.06‰) and Apollo 15 landing sites (5.65±0.12‰) are identical within error and are markedly higher than Apollo 17 high-Ti basalts (5.46±0.11‰). Evolved low-Ti LaPaz mare-basalt meteorite $\delta^{18}O$ values (5.67±0.05‰) are in close agreement with more primitive low-Ti Apollo 12 and 15 mare basalts. Modeling of lunar mare-basalt source composition indicates that the high- and low-Ti mare-basalt mantle reservoirs were in oxygen isotope equilibrium and that variations in $\delta^{18}O$ do not result from fractional crystallization. Instead, these differences are consistent with mineralogically heterogeneous mantle sources for mare basalts, and with lunar magma ocean differentiation models that result in a thick feldspathic crust, an olivine–pyroxene-rich mantle, and late-stage ilmenite-rich zones that were convectively mixed into deeper portions of the lunar mantle. Higher average $\delta^{18}O$ (WR) values of low-Ti basalts compared to terrestrial mid ocean ridge basalts ($\Delta=0.18‰$) suggest a possible oxygen isotopic difference between the terrestrial and lunar mantles. However, calculations of the $\delta^{18}O$ of lunar mantle olivine in this study are only 0.05‰ higher than terrestrial mantle olivine. These observations may have important implications for understanding the formation of the Earth–Moon system.
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Keywords: oxygen isotopes; laser fluorination; Moon; TFL; mare basalts; LaPaz; lunar magma ocean

1. Introduction

The oxygen isotope compositions of chondrite and achondrite meteorites place powerful constraints on the evolution of planetary materials, demonstrating heterogeneity with respect to the three stable isotopes of oxygen (^{16}O, ^{17}O, ^{18}O) in the solar system [1]. Observations of identical oxygen isotope systematics for lunar and terrestrial materials [2–4], and different oxygen isotope compositions for the Shergotty–Nakhla–Chassigny (SNC), Howardite–Eucrite–Diogenite (HED), and other achondrite groups [3,5–7] have provided both the forensic tools for identifying building blocks of

planets and planetesimals, as well as clues to the consequences of planetary accretion (e.g., [4,7]). Oxygen isotopes are a particularly useful tracer of petrogenetic processes in planetary materials, because $^{18}O/^{16}O$ and $^{17}O/^{16}O$ ratios are fractionated by most physical and chemical processes in a predictable, mass-dependent manner. The oxygen isotope variations in planetary materials are, therefore, dominantly controlled by interaction of isotopically distinct reservoirs and mass-dependant isotope fractionations. Increasingly, evidence suggests that both large (i.e., planet-sized) and moderately large (i.e., asteroids) bodies underwent extensive melting and homogenization prior to differentiation processes on the individual parent bodies; — i.e., they all adhere to simple mass-fractionation laws (e.g., [3,4,7]).

The Earth–Moon system is perhaps exceptional within the solar system because both bodies have identical oxygen isotope systematics (i.e., $\Delta^{17}O$ [4]) placing important constraints on their accretion histories. Identical $\Delta^{17}O$ for Earth and the Moon is consistent with the prevailing theory for their origin via a cataclysmic impact between the proto-Earth and a Mars-sized planet [8,9] only if the impactor has a $\Delta^{17}O$ close to that of the proto-Earth [4]. From the perspective of lunar differentiation, the observation of a plagioclase-rich crust for the Moon [10–12] has given rise to the concept of an early global-scale magma ocean (>4.4-Ga; [13]). Such models for the Moon can be tested using oxygen isotopes because a number of predictable consequences would be expected. First, oxygen isotopes should be in equilibrium for mantle and crustal reservoirs because of effective mixing of the magma ocean. Second, the crystallization sequence and floatation of low-density minerals (e.g., plagioclase) and settling of high-density minerals (e.g., olivine, pyroxene) would be expected to result in measurable differences in $\delta^{18}O$ for mantle and crustal reservoirs due to different mineral-melt fractionations. Unlike the Earth and possibly Mars [14], the Moon has been effectively devoid of volatiles and only high-temperature oxygen isotope fractionations are expected. If oxygen isotope ratios of mantle-derived melts from the Moon (e.g., mare basalts) are consistent with such predictions, it would strongly support the lunar magma ocean hypothesis.

In this contribution, we present our determination of the slope of the terrestrial fractionation line (TFL) with which to compare a new high-precision three-oxygen isotope dataset for lunar samples. We investigate oxygen isotope variability of high- and low-Ti lunar mare basalts to constrain mantle source compositions and the implications for planetary differentiation. Finally we consider the ramifications of differences between lunar and terrestrial basalt $\delta^{18}O$ values for the accretion of the Earth–Moon system.

2. Samples

We analyzed lunar meteorites and samples collected during the Apollo and Luna Missions. Samples include five Apollo 12, seven Apollo 15, and seven Apollo 17 mare basalts, as well as a Luna 24 soil and the basaltic lunar meteorites Dhofar 287A (basaltic portion of Dhofar 287 [15]) and LAP 02205, LAP 02224, LAP 02226, LAP 02436, and LAP 03632, a suite of paired Antarctic meteorites [16].

The Apollo and Luna missions focused upon the lunar maria, regions of extensive and variably aged (~4.0 to 2.8 Ga; e.g., [17]) igneous bodies, mainly thought to be basaltic lava flows [18]. Although basaltic in composition, there is a pronounced dichotomy in whole-rock compositions observed for the sample suites (Fig. 1), with some possessing TiO_2 contents akin to terrestrial basalts (generally less than 6 wt.%; Apollo 12, 14, 15, and Luna 16 and 24), whereas others contain TiO_2 in excess of 9 wt.% (Apollo 11 and 17; [19]). Remote sensing studies indicate that there is actually a continuum of compositions for mare basalts [18], thus samples from the Apollo collection represent end-members in the compositional spectrum. Other prominent features relating to mare volcanism include the absence of water and ferric iron, low abundances of alkali and other volatile elements, and the near-ubiquitous depletion of Eu [12,20]. Such variations in mare basalts have been considered the result of the melting of volatile-depleted
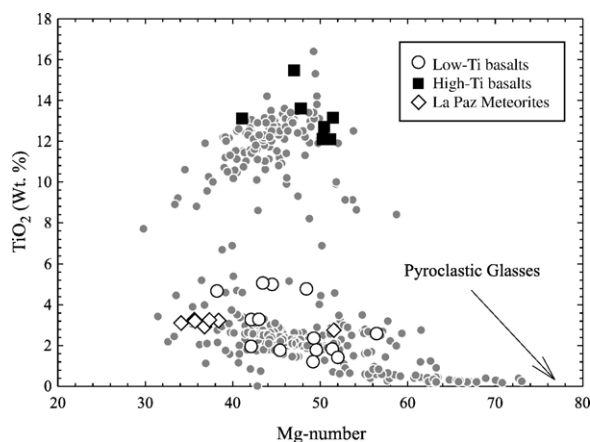

Fig. 1. Plot of Mg-number (molar Mg/Mg+Fe) versus TiO_2 (in wt.%) for lunar mare basalts and pyroclastic glasses illustrating the dichotomy in whole-rock compositions between low- and high-titanium variants. Samples analyzed in this study include low-Ti Apollo 12 and, Apollo 15 (open circles), LaPaz and Dhofar 287A (open diamonds) mare basalts and high-Ti Apollo 17 (filled squares) mare basalts. Shaded grey circles represent published compilations of mare basalts and pyroclastic glasses (data available from authors upon request).

Table 1
$\delta^{18}O$ and $\delta^{17}O$ analyses of lunar samples

Sample [a]	Rock type [b]	n	$\delta^{18}O\pm1\sigma$ [c]	$\delta^{17}O\pm1\sigma$ [c]	$\Delta^{17}O\pm1\sigma$ [c]
Low titanium mare basalt					
Apollo 12					
12018, 43	Olivine basalt	1	5.662	2.972	−0.002
12063, 321	Olivine basalt	1	5.694	2.986	−0.005
12052, 110	Olivine basalt	2	5.813±0.016	3.062±0.012	0.009±0.004
12051,48	Pigeonite basalt	1	5.722	3.014	0.009
12056, 18	Ilmenite basalt	2	5.715±0.090	3.021±0.053	0.019±0.004
	Apollo 12 average [d]		*5.721±0.056*	*3.011±0.035*	*0.005±0.010*
Apollo 15					
15016, 221	Olivine norm. basalt	2	5.616±0.016	2.970±0.006	0.020±0.003
15555, 950	Olivine norm. basalt	2	5.443±0.002	2.874±0.005	0.015±0.006
15555, 955	Olivine norm. basalt	2	5.631±0.212	2.961±0.115	0.004±0.003
15555, 958	Olivine norm. basalt	2	5.769±0.054	3.010±0.030	−0.020±0.003
15596, 24	Quartz norm. basalt	1	5.602	2.963	0.021
15475, 187	Quartz norm. basalt	1	5.682	2.998	0.014
15499, 154	Quartz norm. basalt	2	5.693±0.029	3.001±0.018	0.011±0.003
	Apollo 15 average [d]		*5.651±0.119*	*2.978±0.058*	*0.009±0.014*
LaPaz Antarctic meteorite					
LAP 02205, 21	Evolved mare basalt	1	5.763	3.027	0.000
LAP 02224, 17 (>25% FC [e])	Evolved mare basalt	1	5.653	3.021	0.052
LAP 02224, 17	Evolved mare basalt	1	5.632	2.959	0.000
LAP 02224, 18	Evolved mare basalt	1	5.640	3.005	0.043
LAP 02226, 13	Evolved mare basalt	1	5.629	2.973	0.017
LAP 02436, 8	Evolved mare basalt	1	5.701	3.029	0.035
LAP 03632, 8	Evolved mare basalt	1	5.687	3.002	0.015
	LaPaz average [d]		*5.672±0.049*	*3.003±0.027*	*0.023±0.020*
Dhofar 287	Low-Ti mare basalt	1	6.564	3.452	0.005
High titanium mare basalts					
Apollo 17					
70135, 98	A-type basalt	2	5.591±0.102	2.962±0.051	0.026±0.002
70215, 322	A-type basalt	1	5.529	2.900	−0.004
70017, 524	B-type basalt	2	5.578±0.010	2.939±0.006	0.009±0.011
70035, 180	B-type basalt	2	5.367±0.030	2.834±0.016	0.015±0.001
75075, 171	B1-type basalt	2	5.335±0.084	2.820±0.058	0.018±0.014
74255, 185	C-type basalt	2	5.407±0.087	2.848±0.052	0.008±0.009
74275, 240	C-type basalt	1	5.400	2.829	−0.007
	Apollo 17 average [d]		*5.458±0.105*	*2.876±0.057*	*0.009±0.012*
Lunar 'soil'					
Luna 24	Regolith	1	5.707	3.005	0.008

[a] Numerals after comma denote sub-sample ID of the main sample mass.

[b] Rock type nomenclature for Apollo mare basalts from [19] and references therein.

[c] $\delta^{18}O$ and $\delta^{17}O$ are the per mil (‰) deviation of $^{18}O/^{16}O$ and $^{17}O/^{16}O$ in the sample (s) from the international standard (std), V-SMOW, given by the relationship of $\delta^{18}O_s=1000\times((^{18}O/^{16}O_s/^{18}O/^{16}O_{std})-1)$ and $\delta^{17}O_s=1000\times((^{17}O/^{16}O_s/^{17}O/^{16}O_{std})-1)$, respectively. 1σ, 1 standard deviation of replicate analyses.

[d] Average values from this study.

[e] Fusion crust.

cumulate source regions generated during a magma–ocean event, early (∼4.4 Ga) in the evolution of the Moon.

Additional samples from the Moon are available as meteoritic falls. Because the Apollo and Luna missions collected samples from a small portion of the lunar

surface (∼6% foot-print; [21]), many lunar meteorites undoubtedly originated from areas not sampled by the Apollo or Luna missions. We analyzed the paired LaPaz low-Ti mare-basalt meteorites that fell in Antarctica and which are more evolved than the primitive low-Ti Apollo 12 and 15 lavas [16]; highly evolved magmas serve to demonstrate the potential effects of fractional crystallization on whole-rock $\delta^{18}O$ compositions of lunar lavas. We also analyzed a low-Ti olivine-rich mare-basalt clast, discovered in Oman, for which three-isotope oxygen data has previously been determined (Dhofar 287; [15]).

3. Analytical methods

In the following section, the analytical protocols employed and sampling strategy for this study are described, along with our determination of the terrestrial fractionation line (TFL).

3.1. System description and analytical procedures

In order to analyze $\delta^{17}O$, necessary modifications were made to an existing laser fluorination extraction line dedicated to the analysis of $\delta^{18}O$ [22]. Analytical protocols followed those of Wiechert et al. [4] except that all samples were run as chips and not as fused powders as discussed below. Standards and samples (1.5 to 3.0 mg) were prepared for analysis as described by Valley et al. [22].

Oxygen isotope measurements were performed on a Finnigan MAT 251 mass spectrometer using commercially available O_2 (Scott Specialty Gases) gas as the working standard. The $\delta^{17}O$ and $\delta^{18}O$ values for the standard gas were determined by analyzing UWG-2, a garnet standard with a recommended $\delta^{18}O$ value of 5.800‰ relative to V-SMOW [22], and a calculated $\delta^{17}O$ value of =3.046‰ based on our determination of the TFL (λ=0.5259). Deviations from the TFL ($\Delta^{17}O$), in this study reported in Table 1, were calculated where:

$$\Delta^{17}O = 1000\ln((\delta^{17}O/1000) + 1) \\ -0.5259 * 1000\ln((\delta^{18}O/1000) + 1)$$

The working standard O_2 gas used for the mass spectrometry is offset from the TFL ($\Delta^{17}O$=−0.31‰).

3.2. Determination of the slope of the terrestrial fractionation line

The TFL is widely used to describe the mass-dependant fractionation of oxygen isotopes of materials on Earth. Thus, the TFL serves as the baseline for oxygen

isotope studies of extraterrestrial materials and investigations of mass-independent processes. Despite evidence for mass-independent fractionation of oxygen in the primordial solar system [23] and in rare terrestrial planetary settings (e.g., [24,25]), mass-dependant processes control variations in the oxygen isotope systematics of homogenized planetary bodies.

The TFL was originally approximated by the relationship $\delta^{17}O \approx 0.52 \times \delta^{18}O$ [26] and deviations from the TFL reported as $\Delta^{17}O$, where $\Delta^{17}O = \delta^{17}O_{measured} - (0.52 \times \delta^{18}O_{measured})$ [27]. Miller [28] suggested a revision of the equation defining the TFL and the adoption of the term λ for the slope of the mass-dependent fractionation line where:

$$1000\ln[1 + (\delta^{17}O/1000)] = \lambda * 1000\ln[1 \\ + (\delta^{18}O/1000)] \\ + 1000\ln(1 + k)$$

In this equation, k is a measure of the deviation from the TFL and thus analogous to $\Delta^{17}O$. A principle advantage of this formulation for the TFL is that in contrast to previous formulations, it is truly linear, regardless of the magnitude of the δ values [28].

Four terrestrial samples that span a wide range in $\delta^{18}O$ values (from −0.5‰ to 22.9‰) were analyzed. These samples included UWG-2 (garnet, [22]), NBS-28 (quartz, [29]), 82-W-1 (garnet, [30]), and 95ADK-1 (diopside, [31]). The λ calculated for this data set is 0.5259±0.0008 (95% confidence level) with an R^2 of 0.99996 (63 total analyses). This value is in excellent agreement with the λ-values determined in other recent laser fluorination studies which measured silicates with a range in $\delta^{18}O$ values of >10‰ (e.g. [28,32]). Rumble et al. [32] report similar λ-values based on metamorphic garnets of 0.5255±0.0014 and 0.5263±0.0008. However, they also report slightly lower λ-values based upon hydrothermal quartz (0.5240 to 0.5245). The approximation of Wiechert et al. [4] of $\delta^{17}O=0.5245*\delta^{18}O$ yields nearly identical results for UWG-2 standard (0.004‰ lower than our value obtained using λ=0.5259). These discrepancies become important for evaluating small differences in $\Delta^{17}O$.

3.3. Daily standardization of $\delta^{18}O$ and $\delta^{17}O$

Each day, 3 to 4 aliquots of garnet standard (UWG-2) were analyzed to monitor and ensure accuracy and precision. All standard analyses were included in standardization. The average $\delta^{18}O$ value for all UWG-2 analyses on 12 different days is 5.82±0.05‰ (1 S.D., n=38, 1 S.E.<0.01‰). To account for small day-to-day

variations in the extraction system and mass spectrometry, we corrected the $\delta^{18}O$ and $\delta^{17}O$ of all samples based on the average values obtained for UWG-2 standards on the same day. Both $\delta^{18}O$ and $\delta^{17}O$ values were adjusted based on the values of 5.800‰ and 3.046‰ for UWG-2, respectively. Corrections were small (<0.04‰ on $\delta^{17}O$ and <0.06‰ on $\delta^{18}O$).

3.4. Memory effects and calibration versus the NBS-28 quartz standard

Memory effects were evaluated by analyzing UWG-2 garnet ($\delta^{18}O=5.80$‰) and 95ADK-1 diopside ($\delta^{18}O=22.9$‰; [31]). No memory effects were observed when consecutive analyses spanned a ∼17‰ range in $\delta^{18}O$. Values for 95ADK-1 analyzed directly after UWG-2 are within analytical error of previously reported values. The average corrected values of NBS-28 quartz yield $\delta^{18}O=9.51$ (±0.06‰ 1 S.D., $n=17$), in excellent agreement with previously reported values from the University of Wisconsin laboratory [22,33], and to a recent laser fluorination study by Kusakabe et al. [34].

3.5. Rock chips as whole-rock proxies; the mode effect

Laser fluorination typically requires the pretreatment of samples with a fluorinating agent to minimize blank contributions. Because they comprise minerals with differing reaction rates, pre-fluorination of whole-rock powders is problematic with results biased toward less reactive phases. Ultra-fine grain sizes exacerbate this problem, as the amount of material lost during pretreatment is a function of surface area. In a previous study of lunar materials, Wiechert et al. [4] fused whole-rock powders prior to analysis, effectively eliminating the concerns of preferential reaction during prefluorination. However, we refrained from this processing technique due to potential isotopic fractionation during the fusion process. Instead, we analyzed 2–3 mg chips split from larger sample masses (typically in excess of 2 g) minimizing preferential reaction by limiting surface area.

The use of rock chips for whole-rock proxies may also result in a mode-effect: where non-representative volumes of rock are chosen, resulting in greater variability in chemical measurements. This effect is only documented for one sample in this study, 15555, a particularly coarse grained lunar basalt, which we have analyzed multiple times from three separate 3 g subsamples. The results for 15555, summarized in Table 1, display a range in $\delta^{18}O$ of almost 0.4‰, nearly the entire oxygen isotope variability measured for low-Ti mare basalts ($\delta^{18}O=5.36–5.81$‰) using laser fluorina-

tion. Previous studies of 15555 determined the $\delta^{18}O$ values of the minerals present (feldspar, 6.2‰; pyroxene, 5.8‰; olivine, 5.2‰; and cristobalite, 7.6‰; [35]), and non-representative modal abundances readily explain the variability in whole-rock $\delta^{18}O$ values of mare basalt 15555 ($\delta^{18}O=5.36\pm0.06$‰, 1 S.D. $n=2$; [4], $\delta^{18}O=5.63\pm0.02$‰, 1 S.D., $n=2$; [35]). Six individual analyses of 15555 in our study yield a $\delta^{18}O$ value of 5.61 ± 0.20‰ (1 S.D., $n=6$). All other Apollo sample "duplicate" chips analyzed in this study differ by less than ±0.11‰. We also note a difference of 0.27‰ in previous $\delta^{18}O$ whole-rock determinations of 15555 [4,35], despite analyzing aliquots of powders generated from original samples weighing in excess of 1 g. This mode-effect has been noted numerous times for whole-rock major- and trace-element abundances in small (<0.5 g) Apollo sample allocations (e.g., [36,37]).

4. Results

4.1. Oxygen isotope ratios in Apollo and Luna samples

Results for five Apollo 12, seven Apollo 15, and seven Apollo 17 mare basalts, lunar meteorites and a Luna regolith sample are presented in Table 1. The average $\Delta^{17}O$ for the 19 Apollo mare basalts measured in this study is 0.008 ± 0.012‰ (1 S.D; Fig. 2), and all Apollo samples lie within 0.026‰ of the TFL (Fig. 3). In these data compilations, we averaged replicate
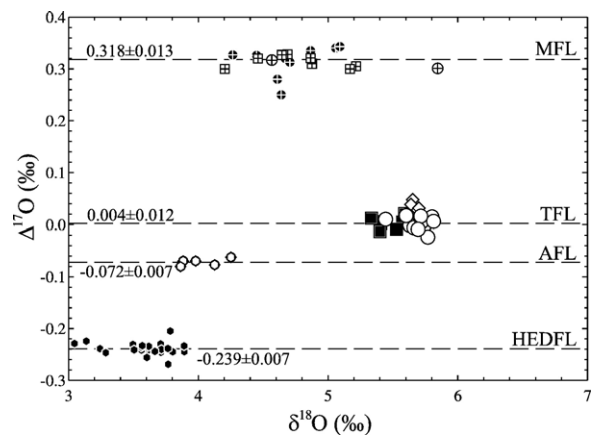

Fig. 2. Oxygen isotope mass fractionation lines for Mars, Earth, Moon, Vesta and the angrite parent body. MFL, Mars Fractionation Line; TFL, Terrestrial Fractionation Line; AFL, Angrite Fractionation line; HEDFL, Howardite–Eucrite–Diogenite Fractionation Line. HED (filled hexagons) and Angrite meteorite data (open hexagons) from [7]. Data for enriched (filled cross-hatched circles) and depleted shergottites (open cross-hatched circles) and nakhlites (open cross-hatched squares) from [5,6] and Spicuzza (unpublished data). Data for Apollo and LaPaz basalts (symbols as for Fig. 1), are from this study.
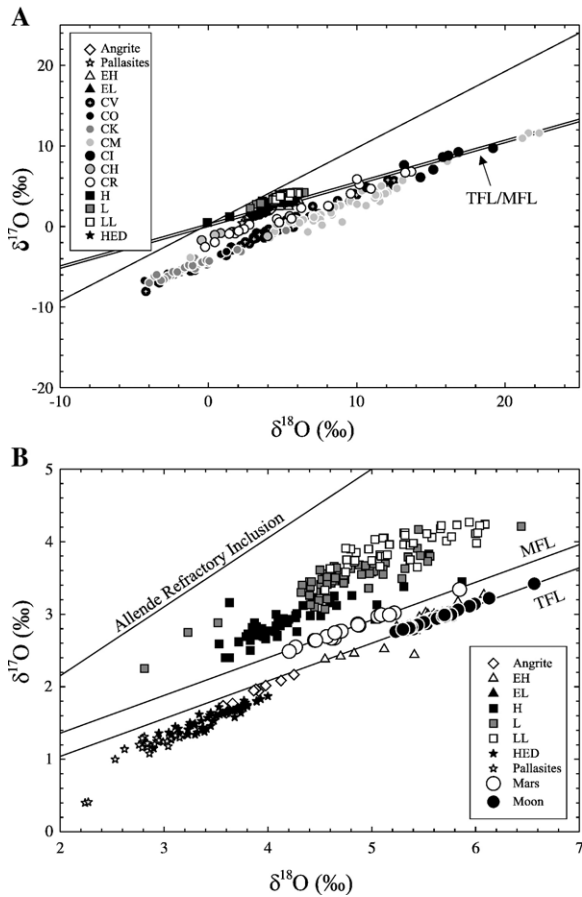
Fig. 3. (A) $\delta^{17}O$ versus $\delta^{18}O$ for chondrite groups versus HED, SNC (Mars), Pallasite, Angrite, and lunar materials (data sources as in Fig. 2). (B) Expanded scale illustrating the similar isotopic compositions of lunar, terrestrial, angrite, enstatite chondrite and HED/Pallasite inner solar system materials. Data for chondrite and achondrite groups from [1,3,39–41].

analyses of individual samples. The average $\delta^{18}O$ of Apollo 12 low-Ti basalts is $5.72\pm0.06‰$ ($\Delta^{17}O=0.005\pm0.010$; $n=5$; 1 S.D.) with a range of 5.66 to 5.81‰. Apollo 15 low-Ti basalts possess a similar range in $\delta^{18}O$ to Apollo 12 basalts, from 5.44 to 5.77‰ (Average $\delta^{18}O=5.65\pm0.12‰$; $\Delta^{17}O=0.009\pm0.014$, 1 S.D., $n=7$). Considering the isotopic variability among three sub-samples of basalt 15555, removal of this sample from the statistics does not change the average $\delta^{18}O$ but significantly reduces the variation (5.60–5.69‰, $\pm$ 0.05‰, 1 S.D., $n=4$).

High-Ti Apollo 17 mare basalts have $\delta^{18}O$ values that are lower than low-Ti Apollo 12 and Apollo 15 mare basalts (with one exception, 15555), and range from 5.34 to 5.59‰ (average $\delta^{18}O=5.46\pm0.11‰$; $\Delta^{17}O=0.009\pm0.012$, 1 S.D., $n=7$). This difference was less pronounced in previous analyses of low- and high-Ti mare

basalts [4]. Analysis of Luna 24 soil yielded a $\delta^{18}O$ of 5.71‰ and a $\Delta^{17}O=0.008$, which is similar to values given for 'breccias' and feldspathic regolith–breccia meteorite ALH 85001 [4]. Compared with terrestrial lavas, the average $\delta^{18}O$ values for low-Ti mare basalts are slightly higher (0.1–0.2‰) than the average fresh mid-oceanic ridge basalt lavas (MORB), which average $\sim5.5‰$ [42], and estimates of terrestrial mantle-derived melt $\delta^{18}O$ values based on mantle peridotites [38], and mantle zircons [43]. Fig. 4 combines our laser fluorination data with that of Wiechert et al. [4], displaying the differences in $\delta^{18}O$ among various lunar rock types.

4.2. Oxygen isotope ratios in lunar meteorites

Five paired LaPaz mare-basalts meteorites (LAP 02205, 02224, 02226, 02436, and 03632) and a subsample of Dhofar 287 (defined as Dhofar 287A; [15])
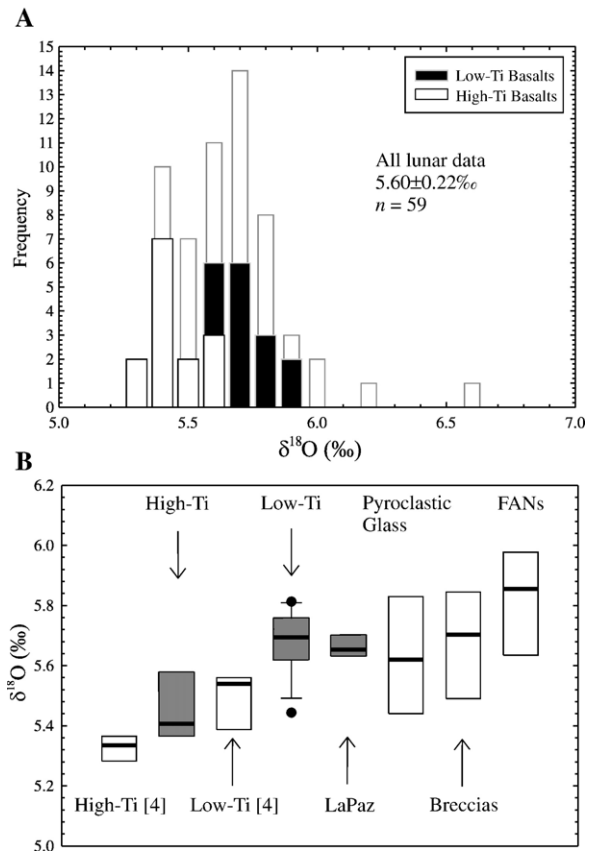

Fig. 4. Statistics for $\delta^{18}O$ in lunar whole-rocks (data from this study and [4]). (A) Histogram probability distributions of $\delta^{18}O$ for all lunar samples, low-Ti mare basalts (filled bars) and high-Ti mare basalts (open bars), indicating the difference in $\delta^{18}O$ for these basalt types (B) Box plot showing $\delta^{18}O$ distribution of lunar samples in this study (shaded grey), all others from [4]. FAN = Ferroan Anorthosite.

have been analyzed in this study and are presented in Table 1. The five LaPaz mare basalts have $\delta^{18}O$ values that are identical within analytical uncertainty (5.67 ± 0.05‰; $\Delta^{17}O = 0.023 ± 0.02$, 1 S.D., $n = 7$). To examine within-sample oxygen-isotope variability and the effect of fusion-crust material on oxygen isotope systematics, we analyzed three sub-samples of LAP 02224, one of which possessed a limited amount (∼25%) of fusion-crust and another from the interior portion of the meteorite (LAP 02224, 18). The $\delta^{18}O$ values indicate original homogeneity and a lack of significant post-fall terrestrial alteration of the LaPaz mare-basalt meteorites. The average $\Delta^{17}O$ for 7 analyses of LaPaz meteorites is slightly higher (0.01‰) and more variable than the Apollo sample set. The new oxygen isotope data for the LaPaz mare basalts confirm a lunar origin in agreement with independent confirmation methods for planetary heritage [16].

Dhofar 287A possesses the highest $\delta^{18}O$ (6.56‰, $\Delta^{17}O = 0.005$) of any lunar sample, in agreement with a previous analysis of this meteorite [15]. However, the anomalously high $\delta^{18}O$ value (6.56‰) determined for Dhofar 287A is most likely a result of low temperature desert alteration on Earth, prior to collection. Terrestrial alteration is suggested by the presence of calcite, gypsum, and celestite veins within this sample [15]. For this reason, we do not plot Dhofar 287A in comparison diagrams of lunar mantle-derived melts.

5. Discussion

5.1. Oxygen isotope constraints on the differentiation of the Moon

Mare volcanism produced a diverse suite of basalts and pyroclastic glasses that have a dichotomy in Ti contents, thought to be predominantly derived from different proportions of ilmenite in their mantle-source regions [19]. Mare basalts and pyroclastic glasses also exhibit pronounced negative Eu-anomalies indicating preferential removal of Eu from the mantle-source regions prior to mare-basalt melt extraction. Previously, the distinct chemical traits of mare basalts and other lunar rocks have given rise to the concept of a lunar magma ocean to account for the plagioclase Eu-enriched crust overlying a plagioclase Eu-depleted mare-basalt source region [10,11]. The lunar magma ocean hypothesis, serial-magmatism derivative models (e.g., [44–46]), and experimental and forward-modeling studies [47,48] predict mineralogical variations in lunar cumulate reservoirs and in the source regions of low- and high-Ti mare basalts. Such features can also explain the

significant Li–Sr–Nd–Hf isotope variations measured for lunar basalts (e.g., [16,49,50]). It would be expected, from existing knowledge of high-temperature mineral-melt partition coefficients for oxygen isotopes, that sources with variable modal mineralogies and/or mineral-source compositions would generate magmas with variable oxygen isotopic compositions.

Our data demonstrate a 0.20–0.25‰ offset in the average whole-rock $\delta^{18}O$ of high- and low-Ti basalts, consistent with a previous study by Wiechert et al. [4]. It has previously been established that none of the mare basalts discovered to date represent primary liquids; all have undergone some degree of fractional crystallization (e.g., [51–54]). Fractional crystallization can have a small, albeit significant, effect on the oxygen isotope composition of terrestrial mid-ocean ridge basalt (MORB) lavas, acting to increase $\delta^{18}O$ (whole-rock) with increasing degrees of fractionation (e.g., [42,55]). This effect may account for as much as a 0.1‰ difference between primary liquids and moderately fractionated by-products. Variations in mare-basalt $\delta^{18}O$ are subtle (range of 0.47‰) and may, in part, reflect the same style of shallow-level fractional crystallization observed in MORB. In contrast to studies of MORB glasses [42], however, we find no significant correlation between $\delta^{18}O$ and indices of fractional crystallization for low- and high-Ti basalts (Fig. 5). Nevertheless, it is important to understand the effects of fractionation on $\delta^{18}O$ and whether mare basalts are in oxygen isotopic equilibrium with their mantle sources.
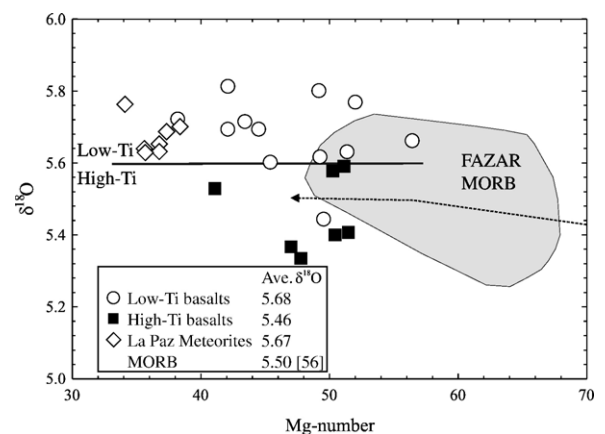

Fig. 5. Diagram of $\delta^{18}O$ versus Mg-number for lunar whole-rocks versus FAZAR Mid-Oceanic Ridge Basalts from the mid-Atlantic ridge (shown as a field; [55]). Also shown is the typical shallow-level fractionation for MORB samples (stippled line) and the approximate boundary of high-Ti mare basalts (thick line). Note the systematically lower Mg-numbers for mare basalts relative to MORB and the lack of correlation between $\delta^{18}O$ and Mg-number for low-Ti basalts.

We have quantitatively modeled the $\delta^{18}O$ of the basaltic magmas following the approach presented by Eiler [56]. This model assumes that oxygen isotope fractionation between silicate magmas and residual phases in the source regions can be determined by summing the calculated isotopic fractionations of the component phases represented by the normative mineralogy of the melt. We have calculated the $\delta^{18}O$ of olivine in high-temperature (1200 °C) equilibrium with a magma composition, represented by the major-element chemistry of the samples analyzed. There is excellent agreement between the predicted and measured values with all samples (excluding 15555) plotting within 0.16‰ (Fig. 6). Given the potential uncertainty of our measurements of the whole-rock $\delta^{18}O$, the positive correlation is striking and implies that the sources of the high- and low-Ti basalts were in high-temperature oxygen isotope equilibrium.

The lack of significant correlation (Fig. 5) between the large range in Mg# (molar Mg/Mg+Fe) for low-Ti mare-basalt samples analyzed (including the evolved LaPaz mare basalts) and measured $\delta^{18}O$ values suggests that whole-rock $\delta^{18}O$ values have been minimally affected by fractional crystallization. There is no difference in whole-rock $\delta^{18}O$ values, within error, between samples with Mg# <40 and those with Mg# >50. Similar arguments for the lack of large oxygen isotope fractionations during magma differentiation have been made for KREEP-related zircons ($\delta^{18}O = 4.9$ to 6.1‰) in lunar breccia 14321, where such effects would be expected to be most dramatic [57]. Therefore, we conclude
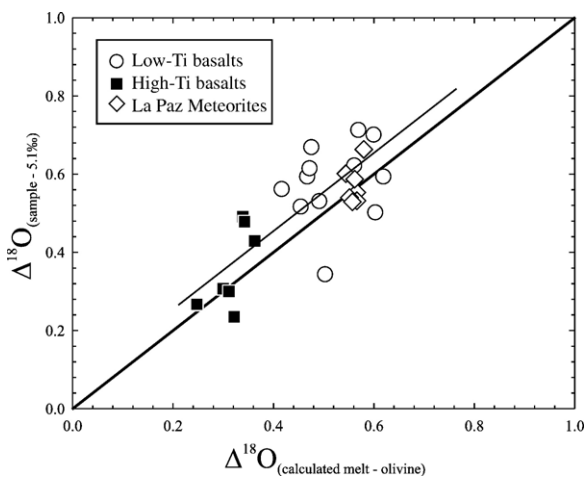

Fig. 6. Plot showing correlation between measured $\delta^{18}O$ whole-rock values for lunar basalts minus 5.1‰ (average olivine in equilibrium with MORB; [56]) and calculated $\delta^{18}O$ whole-rock values minus equilibrium olivine $\delta^{18}O$ using the methods and fractionation factors of [56]. Thick line=1:1. Thin line represents average values determined for lunar samples and is 0.05‰ higher than 1:1 line.

that variations in mare-basalt whole-rock $\delta^{18}O$ reflect variations in the melt-residue fractionation. Assuming olivine is ubiquitous in the residuum (e.g., [48]), and is in equilibrium with the melts produced, the $\delta^{18}O$ of the melt is primarily a function of the major-element chemistry of the magma. Thus, variations in melt compositions reflect source regions for high- and low-Ti mare basalts that were equilibrated with respect to oxygen isotopes but variable in terms of major-element chemistry (i.e., modal mineralogy).

A general consensus has been that the low- and high-Ti basalts differ simply because of the presence of ilmenite in the high-Ti basalt source (e.g., [17,19,47–49]). Ilmenite or armalcolite are the most logical choices for a high-Ti mineral in high-Ti basalt sources because of the low oxygen fugacity of the lunar interior and the physical presence of ilmenite and armalcolite in those basalts. If the proportions of ilmenite expected from theoretical calculations to be in the source of high-Ti basalts and the proportion of minerals in the sources of both low- and high-Ti basalt end-members are considered, the expected variation in $\delta^{18}O$ between these sources can be derived. Assuming source mineralogy equal to ~43% olivine, ~46% pigeonite, ~7–10% clinopyroxene, with ~3% ilmenite in the high-Ti basalt source [48] and the melting proportions of minerals equal to ilmenite>pyroxene>olivine during batch melting, we predict variations in excess of 0.2‰ for low- and high-Ti basalts. More complex models of melting, including polybaric melting models (e.g., [47,49]), are also consistent with the ranges in $\delta^{18}O$, if minerals with low fractionation factors, relative to olivine, are present in the source of high-Ti basalts.

The differentiation of the silicate portion of the Moon during a magma ocean event early in it's history would result in the formation of ilmenite only after 95% crystallization had already occurred [48], leaving the lowermost portions of the lunar mantle devoid of ilmenite with corresponding enrichment in the uppermost mantle regions. However, the similarity in estimates of initial melting depths [58], equilibration pressures, and Mg# for low- and high-Ti mare basalts require that; (1) dense ilmenite-rich differentiates sank into the deeper reaches of the lunar mantle [59], or (2), low-Ti derived magmas assimilated ilmenite prior to eruption [60]. Although theoretically plausible [61], it would require large amounts (~30%) of assimilation of an ilmenite and pyroxene cumulate, which ineffectively explains the range in Hf isotope compositions with Ti contents in Apollo 12 basalts [49], and the lack of KREEP-like signatures in high-Ti basalts (e.g., [17]). Such observations promote the conclusion that oxygen isotopes

reflect mineralogically distinct source regions for low- and high-Ti mare basalts.

The different $\delta^{18}O$ values of low- and high-Ti mare basalts and the identical $\Delta^{17}O$ for both basalt types, therefore, support the concept of effective mixing and homogenization of oxygen by whole-sale convection of a molten Moon prior to crystal differentiation of the lunar magma ocean. Magma oceans have been considered a necessary and inevitable consequence of planetary accretion (e.g., [62]), and whole-sale melting of planets and planetesimals appears increasingly more likely based upon geochemical observations [7,63]. In addition to the petrologic evidence for a feldspathic crust, the ubiquitous negative Eu-anomalies in lunar basalts, and the ancient ages for ferroan anorthosites [13], we consider the oxygen isotope dichotomy in mare basalts and the inferred oxygen isotope equilibrium of their mantle reservoirs as powerful evidence for lunar differentiation via a magma ocean event early (~4.53-Ga [64]) in the history of the Moon.

5.2. Planetary-scale oxygen isotope heterogeneity in the Earth–Moon system?

A number of competing processes are likely to have given rise to the present distribution of oxygen isotope variations in the solar system. It has been well demonstrated that the three isotopes of oxygen are heterogeneously distributed [1,3,23] indicating distinct solar system O isotopic source regions. However, the >10‰ variation in $\Delta^{17}O$ among chondrite groups is not matched by the differences between planetary and achondrite groups recognized so far. Therefore, the comparatively limited range in $\Delta^{17}O$ for these materials when compared with chondrites requires another set of processes, which may include homogenization by radial mixing of planetary feeding zones in the inner solar system (up to 4 AU) [4,65], temporal variations [66], or via planetary accretion processes such as vapor-exchange and diffusion reactions in hot accretionary disks [67]. In the most recent dynamical models for planetary accretion [62,68], the reduction of isotopic heterogeneity is a natural consequence of stochastic interaction and collision of increasingly larger planetary embryos, whereas smaller bodies may retain more of their initial isotopic variability.

The similarity of the oxygen isotope compositions of the Earth and Moon, both of which lie on the TFL ($\Delta^{17}O=0$), can be explained via the giant-impact hypothesis for the Earth–Moon system [4]. Similar isotopic homogeneity has been recognized in small planetesimal bodies, such as the Angrite or HED parent bodies [7], and is entirely consistent with massive melting of these bodies to form magma oceans; a process similar to lunar differentiation models (e.g., [10,11]), and for the variations in $\delta^{18}O$ values of mare-basalt source regions reported here. Numerical simulations of the hypothesized Moon-forming giant-impact indicate that the Moon inherited significantly higher proportions of its accretion material from the Mars-size impactor (70–90%) than from the proto-Earth (e.g., [8,9]). The identical $\Delta^{17}O$ for terrestrial and lunar samples is, therefore, somewhat surprising considering the known variability in $\Delta^{17}O$ for planetary materials. In order to overcome this dynamical problem, Wiechert et al. [4] suggested the progenitors of the Earth and Moon were at similar heliocentric distances, where oxygen isotopic compositions were the same. However, based on the fact that planetary accretion zones are small (0.01 AU; [68]), it may also be argued that there should have been at least small isotopic differences between the two colliding bodies; these would be expected to have left observable signatures due to the lack of apparent mixing between the impactor and the proto-Earth. Alternatively, it has been suggested that the coincidence of the oxygen isotope systematics of the Earth and Moon reflects extensive exchange of material between the impactor and the proto-Earth [69].

An important question remaining is whether there is a difference in the $\delta^{18}O$ of the Earth and Moon. In the absence of samples of the lunar mantle, we use melt products (e.g. mare basalts) to infer source characteristics. For oxygen isotopes, the most useful comparison might be between low-Ti mare basalts and the most ubiquitous magmas on Earth, MORB, which have been analyzed via laser fluorination as glasses [42,56]. We do not consider high-Ti basalts because of their unusual compositions and the obvious ilmenite control on oxygen isotope compositions noted above. It has long been argued that there are differences between major- and volatile-element compositions of the Earth and Moon, with the lunar mantle likely possessing a higher FeO content with respect to the terrestrial mantle [13,70]. In plots such as Mg# versus $\delta^{18}O$ (e.g., Fig. 5) there are differences between lunar low-Ti mare basalts and MORB lavas that cannot be accounted for by crystal fractionation or partial melting, despite identical $\Delta^{17}O$ values for the Earth and Moon. In contrast to a previous study using different sample preparation techniques [4], we find that the average $\delta^{18}O$ of low-Ti mare basalts (5.68‰) is 0.18‰ higher than the average determined for MORB.

Differences between lunar and terrestrial basalt $\delta^{18}O$ values could reflect differentiation processes causing fractionation of oxygen in the Earth and Moon, but the effects are limited to ~0.1‰ over the range of com-

positions considered here [56]. While the Moon has witnessed only high-temperature oxygen isotopic fractionations, observed $\delta^{18}O$ variations in both terrestrial (e.g., [42,55,71]) and martian [14] lavas indicate an important role for low-temperature oxygen isotope fractionations. The derivation of the high $\delta^{18}O$ terrestrial crust may have resulted in long-term but very small depletion of the terrestrial mantle of ^{18}O [72]. Differences in terrestrial and lunar mantle $\delta^{18}O$ values may also be complicated by uncertainty in whole-versus layered-mantle convection for the Earth [73]. For the Earth, mass balance constraints limit this effect to 0.07‰ if the crust is derived from the upper mantle and 0.02‰ if it is derived from the whole mantle.

If differences in $\delta^{18}O$ in the lunar and terrestrial mantles cannot be explained by mass-balance constraints that factor in high-$\delta^{18}O$ crust on Earth, then the variation could indicate initial isotopic differences between the proto-Earth and the impactor during the giant impact. In this scenario, differences in oxygen isotope compositions for the Earth–Moon system would be consistent with a significant portion of the Moon's mass being obtained from an impactor and not from a completely homogenized mixture of the proto-Earth and the impactor. Whereas the metallic portions of both the impactor and the proto-Earth pooled into the Earth, as indicated by HSE compositions of lunar and terrestrial rocks [74], the silicate portions of the two bodies were not fully homogenized. Assuming this scenario, the observed differences between low-Ti basalts and MORB (0.18‰) could indicate that the impactor had a higher $\delta^{18}O$ than the proto-Earth despite having identical or nearly identical $\Delta^{17}O$. However, the average calculated values for lunar mantle olivine are only elevated values by ~ 0.05‰ (Fig. 6) compared to terrestrial mantle olivine (5.1‰), and may more accurately reflect the bulk $\delta^{18}O$ of the Earth and Moon.

6. Summary

We have employed a high-precision three-oxygen isotope technique to investigate lunar mare basalts, to further constrain the $\Delta^{17}O$ of the Moon, and to critically evaluate the magma ocean hypothesis. We analyzed terrestrial silicates with a wide range of $\delta^{18}O$ values (~ 0–23‰) to independently determine the slope of the TFL ($\lambda = 0.5259$). The $\Delta^{17}O$ for Apollo 12, 15, and 17 basalts, and Luna 24 soil is within uncertainty of the TFL and averages 0.008 ± 0.010‰.

The oxygen isotope compositions of lunar mare basalts support the hypothesized early (~ 4.5 Ga) magma-ocean event that led to the differentiation of the Moon.

Average whole-rock $\delta^{18}O$ values for low-Ti lunar basalts from the Apollo 12 (5.72 ± 0.06‰) and Apollo 15 landing sites (5.65 ± 0.12‰), as well as the highly evolved low-Ti LaPaz mare-basalt meteorites (5.67 ± 0.05‰) are nearly identical and average 0.18‰ higher than average MORB. Whole-rock $\delta^{18}O$ values of Apollo 17 high-Ti basalts are lower than low-Ti basalts and average (5.46 ± 0.11‰). Both the high- and low-Ti mare-basalt mantle reservoirs appear to be in oxygen isotope equilibrium, a feature consistent with oxygen isotope homogenization in a global-scale magma ocean. The lack of variation of whole-rock $\delta^{18}O$ with Mg# suggests fractional crystallization effects on $\delta^{18}O$ are minimal, and a recent report of zircon $\delta^{18}O$ values from highly fractionated lunar rocks [57] also supports the idea that lunar mare-basalt $\delta^{18}O$ variations are primarily a function of lunar mantle-source mineralogy. Further constraints on the giant impact theory and the origin of the Earth–Moon system may be realized from additional efforts to constrain the bulk $\delta^{18}O$ of the Earth and Moon.

Acknowledgements

References

[1] R.N. Clayton, L. Grossman, T.K. Mayeda, A component of primitive nuclear composition in carbonaceous meteorites, Science 182 (1973) 485–488.

[2] R.N. Clayton, K. Mayeda, Genetic relations between the moon and meteorites, Proc. Lunar Planet. Sci. Conf. 6th, 1975, pp. 1761–1769.

[3] R.N. Clayton, K. Mayeda, Oxygen isotopic studies of achondrites, Geochim. Cosmochim. Acta 60 (1996) 1999–2017.

[4] U. Wiechert, A.N. Halliday, D.-C. Lee, G.A. Snyder, L.A. Taylor, D. Rumble, Oxygen isotopes and the Moon-forming giant impact, Science 294 (2001) 345–348.

[5] C.S. Romanek, E.C. Perry, A.H. Treiman, R.A. Socki, J.J. Jones, E.K. Gibson Jr., Oxygen isotopic record of silicate alteration in the Shergotty–Nakhla–Chassigny meteorite Lafayette, Meteorit. Planet. Sci. 33 (1998) 775–784.

[6] I.A. Franchi, I.P. Wright, A.S. Sexton, C.T. Pillinger, The oxygen isotopic composition of Earth and Mars, Meteorit. Planet. Sci. 34 (1999) 657–661.

[7] R.C. Greenwood, I.A. Franchi, A. Jambon, P.C. Buchanan, Widespread magma oceans on asteroidal bodies in the early Solar System, Nature 435 (2005) 916–918.

[8] A.G.W. Cameron, The origin of the Moon and the single impact hypothesis V, Icarus 126 (1997) 126–137.

[9] R.M. Canup, E. Asphaug, Origin of the Moon in a giant impact near the end of the Earth's formation, Nature 412 (2001) 708–712.

[10] J.A. Smith, A.T. Anderson, R.C. Newton, E.J. Olsen, P.J. Wyllie, A.V. Crewe, M.S. Isaacson, D. Johnson, Petrologic history of the Moon inferred from petrography, mineralogy, and petrogenesis of Apollo 11 rocks, Proc. Apollo 11 Lunar Sci. Conf. (1970) 1149–1162.

[11] J.A. Wood, J.S. Dickey, U.B. Marvin, B.N. Powell, Lunar anorthosites and a geophysical model of the Moon, Proc. Apollo 11 Lunar Sci. Conf. (1970) 965–988.

[12] S.R. Taylor, Planetary Science: A Lunar Perspective, Lunar Planetary Institute, Houston, 1982 512 pp.

[13] M.D. Norman, L.E. Borg, L.E. Nyquist, D.D. Bogard, Chronology, geochemistry, and petrology of a ferroan noritic anorthosite clast from Descartes breccia 67215: clues to the age, origin, structure, and impact history of the lunar crust, Meteorit. Planet. Sci. 38 (2003) 645–661.

[14] J.M.D. Day, L.A. Taylor, J.W. Valley, M.J. Spicuzza, Assimilation of high $^{18}O/^{16}O$ crust by Shergottite–Nakhlite–Chassigny (SNC) magmas on Mars, Eos, Trans. - Am. Geophys. Union 86 (52) (2005) (Fall Meet. Suppl. P51A-0902 [Abs.]).

[15] M.A. Anand, L.A. Taylor, K.C. Misra, S.I. Demidova, M.A. Nazarov, KREEPy lunar meteorite Dhofar 287A: a new lunar meteorite, Meteorit. Planet. Sci. 38 (2003) 485–499.

[16] J.M.D. Day, L.A. Taylor, C. Floss, A.D. Patchen, D.W. Schnare, D.G. Pearson, Comparative petrology, geochemistry, and petrogenesis of evolved, low-Ti lunar mare basalt meteorites from the LaPaz icefield, Antarctica, Geochim. Cosmochim. Acta 70 (2006) 1581–1600.

[17] G.A. Snyder, L.E. Borg, L.E. Nyquist, L.A. Taylor, Chronology and isotopic constraints on lunar evolution, in: R.M. Canup, K. Righter (Eds.), Origin of the Earth and Moon, University of Arizona Press, Tuscon, 2000, pp. 361–396.

[18] T.A. Giguere, G.J. Taylor, B.R. Hawke, P.G. Lucey, The titanium contents of lunar mare basalts, Meteorit. Planet. Sci. 35 (2000) 192–200.

[19] C.R. Neal, L.A. Taylor, Petrogenesis of mare basalts: a record of lunar volcanism, Geochim. Cosmochim. Acta 56 (1992) 2177–2211.

[20] BSVP, Basaltic Volcanism on the Terrestrial Planets, Pergamon, New York, 1981 1286 pp.

[21] P.H. Warren, The Moon, in: A. Davis (Ed.), Treatise on Geochemistry, vol. 1, Elsevier, Amsterdam, 2003, pp. 559–599.

[22] J.W. Valley, N. Kitchen, M.J. Kohn, C.R. Niendorf, M.J. Spicuzza, UWG-2, a garnet standard for oxygen isotope ratios: strategies for high precision and accuracy with laser heating, Geochim. Cosmochim. Acta 59 (1995) 5223–5231.

[23] R.N. Clayton, Self-shielding in the solar nebula, Nature 415 (2002) 860–861.

[24] J. Farquhar, M.H Thiemens, T. Jackson, Atmosphere–surface interactions on Mars: $\Delta^{17}O$ measurements of carbonate from ALH 84001, Science 280 (1998) 1580–1582.

[25] Y.-Q. Gao, R.A. Marcus, Strange and unconventional isotopic effects in ozone formation, Science 293 (2001) 259–263.

[26] R.N. Clayton, Oxygen isotopes in meteorites, Annu. Rev. Earth Planet. Sci. 21 (1993) 115–149.

[27] R.N. Clayton, T.K. Mayeda, Formation of ureilites by nebular processes, Geochim. Cosmochim. Acta 52 (1988) 1313–1318.

[28] M.F. Miller, Isotopic fractionation and the quantification of ^{17}O anomalies in the oxygen three-isotope system: an appraisal and geochemical significance, Geochim. Cosmochim. Acta 66 (2002) 1881–1889.

[29] G. Hut, Consultants' Group Meeting on Stable Isotope Reference Samples for Geochemical and Hydrological Investigations, International Atomic Energy Agency, Vienna, 1986 49 pp.

[30] J.W. Valley, J.R. O'Neil, Oxygen isotope evidence for shallow emplacement of Adirondack anorthosite, Nature 300 (1982) 497–500.

[31] K.J. Edwards, J.W. Valley, Oxygen isotope diffusion and zoning in diopside: the importance of water fugacity during cooling, Geochim. Cosmochim. Acta 62 (1998) 2265–2277.

[32] D. Rumble, M.F. Miller, I.A. Franchi, R.C. Greenwood, Variations in oxygen three-isotope terrestrial fractionation line revealed by an inter-laboratory comparison of silicate mineral analyses, Lunar Planet. Sci. XXXVII (2006) (CD-ROM #1416. [Abs.]).

[33] M.J. Spicuzza, J.W. Valley, M.J. Kohn, J.P. Girard, A.M. Fouillac, The rapid heating, defocused beam technique: a CO_2-laser based method for highly precise and accurate determination of $\delta^{18}O$ values of quartz, Chem. Geol. 144 (1998) 195–203.

[34] M. Kusakabe, S. Maruyama, T. Nakamura, T. Yada, CO_2 laser-BrF_5 fluorination technique for analysis of three oxygen isotopes of rocks and minerals, J. Mass Spectrom. Soc. Jpn. 52 (2004) 205–212.

[35] M. Javoy, S. Fourcade, $^{18}O/^{16}O$ ratios in lunar fines and rocks, Earth Planet. Sci. Lett. 21 (1974) 377–382.

[36] B. Mason, E. Jarosewich, W.G. Melson, G. Thompson, Mineralogy, petrology, and chemical composition of lunar samples 15085, 15256, 15271, 15471, 15475, 15476, 15535, 15555, and 15556, Proc. Lunar Planet. Sci. Conf. 3rd, 1972, pp. 785–796.

[37] G. Ryder, B.C. Schuraytz, Chemical variation of the Apollo 15 olivine-normative mare basalt rock samples, J. Geophys. Res. 106 (2001) 1435–1451.

[38] D.P. Mattey, D. Lowry, C. Macpherson, Oxygen isotope composition of mantle peridotite, Earth Planet. Sci. Lett. 128 (1994) 231–241.

[39] R.N. Clayton, T.K. Mayeda, Oxygen isotope studies of carbonaceous chondrites, Geochim. Cosmochim. Acta 63 (1999) 2089–2104.

[40] R.N. Clayton, T.K. Mayeda, A.E. Rubin, Oxygen isotopic compositions of enstatite chondrites and aubrites, J. Geophys. Res. 89 (1984) C245–C249.

[41] R.N Clayton, T.K. Mayeda, J.N. Goswami, E.J. Olsen, Oxygen isotope studies of ordinary chondrites, Geochim. Cosmochim. Acta 55 (1991) 2317–2337.

[42] J.M. Eiler, P. Schiano, N. Kitchen, E.M. Stolper, Oxygen-isotope evidence for recycled crust in the sources of mid-ocean-ridge basalts, Nature 403 (2000) 530–534.

[43] J.W. Valley, Oxygen isotopes in zircon, in: J.M. Hanchar, P.W.O. Hoskin (Eds.), Rev. Mineral. Geochem., vol. 53, 2003, pp. 343–385.

[44] D.N. Shirley, A partially molten magma ocean model, Proc. Lunar Planet. Sci. Conf. 13th, 1983, pp. A519–A527.

[45] D. Walker, Lunar and terrestrial crust formation, Proc. Lunar Planet. Sci. Conf. 14th, 1983, pp. B17–B25.

[46] J. Longhi, L.D. Ashwal, Two-stage models for lunar and terrestrial anorthosites: petrogenesis without a magma ocean, Proc. Lunar Planet. Sci. Conf. 15th, 1985, pp. C571–C584.

[47] J. Longhi, Experimental petrology and petrogenesis of mare volcanics, Geochim. Cosmochim. Acta 56 (1992) 2235–2251.

[48] G.A. Snyder, L.A. Taylor, C.R. Neal, A chemical model for generating the sources of mare basalts: combined equilibrium and fractional crystallization of the lunar magmasphere, Geochim. Cosmochim. Acta 56 (1992) 3809–3823.

[49] B.L. Beard, L.A. Taylor, E.E. Scherer, C.M. Johnson, G.A. Snyder, The source region and melting mineralogy of high-

titanium and low-titanium lunar basalts deduced from Lu–Hf isotope data, Geochim. Cosmochim. Acta 62 (1998) 525–544.

[50] T. Magna, U. Wiechert, A.N. Halliday, New constraints on the lithium isotope compositions of the Moon and terrestrial planets, Earth Planet. Sci. Lett. 243 (2006) 336–353.

[51] J.M. Rhodes, N.J. Hubbard, Chemistry, classification, and petrogenesis of Apollo 15 mare basalts, Proc. Lunar Planet. Sci. Conf. 4th, 1973, pp. 1127–1148.

[52] J.M. Rhodes, N.J. Hubbard, H. Weismann, K.V. Rodgers, J.C. Brannon, B.M. Bansal, Chemistry, classification and petrogenesis of Apollo 17 mare basalts, Proc. Lunar Planet. Sci. Conf. 7th, 1976, pp. 1467–1489.

[53] J.M. Rhodes, D.P. Blanchard, M.A. Dungan, J.C. Brannon, K.V. Rodgers, Chemistry of Apollo 12 mare basalts: magma types and fractionation processes, Proc. Lunar Planet. Sci. Conf. 8th, 1977, pp. 1305–1338.

[54] B.W. Chappell, D.H. Green, Chemical compositions and petrogenetic relationships in Apollo 15 mare basalts, Earth Planet. Sci. Lett. 18 (1973) 237–246.

[55] K.M. Cooper, J.M. Eiler, P.D. Asimov, C.H. Langmuir, Oxygen isotope evidence for the origin of enriched mantle beneath the mid-Atlantic ridge, Earth Planet. Sci. Lett. 220 (2004) 297–316.

[56] J.M. Eiler, Oxygen isotope variations of basaltic lavas and upper mantle rocks, in: J.W. Valley, D.R. Cole (Eds.), Stable Isotope Geochemistry, Rev. Mineral. Geochem., vol. 43, 2001, pp. 319–364.

[57] A.A. Nemchin, M.J. Whitehouse, R.T. Pidgeon, C. Meyer, Oxygen isotopic signature of 4.4–3.9 Ga zircons as a monitor of differentiation processes on the Moon, Geochim. Cosmochim. Acta 70 (2006) 1864–1872.

[58] D. Walker, J. Longhi, E.M. Stolper, T. Grove, J.F. Hays, Origin of titaniferous lunar basalts, Geochim. Cosmochim. Acta 39 (1975) 1219–1235.

[59] A.E. Ringwood, S.E. Kesson, A dynamic model for mare basalt petrogenesis, Proc. Lunar Sci. 7th, 1976, pp. 1697–1722.

[60] A.T. Anderson, Exotic armalcolite and the origin of Apollo 11 ilmenite basalts, Geochim. Cosmochim. Acta 35 (1971) 969–973.

[61] T.P. Wagner, T.L. Grove, Experimental constraints on the origin of lunar high-Ti ultramafic glasses, Geochim. Cosmochim. Acta 61 (1997) 1315–1327.

[62] F. Nimmo, C.B. Agnor, Isotopic outcomes of N-body accretion simulations: constraints on equilibration processes during large impacts from Hf/W observations, Earth Planet. Sci. Lett. 243 (2006) 26–43.

[63] M. Boyet, R.W. Carlson, ^{142}Nd evidence for early (>4.53 Ga) global differentiation of the silicate earth, Science 309 (2005) 576–581.

[64] T. Kleine, H. Palme, K. Mezger, A.N. Halliday, Hf–W chronometry of lunar metals and the age and early differentiation of the Moon, Science 310 (2005) 1671–1674.

[65] J.E. Chambers, Making more terrestrial planets, Icarus 152 (2001) 205–224.

[66] K. Ziegler, J.E. Chambers, E.D. Young, High-precision Δ^{17}O data: querying the meaning of Δ^{17}O in the inner solar system, Lunar Planet. Sci. XXXVII (2006) (CD-ROM #1894. [Abs.]).

[67] K. Pahlevan, D.J. Stevenson, The oxygen isotope similarity between the Earth and Moon — source region or formation process, Lunar Planet. Sci. XXXVI (2005) (CD-ROM #2382. [Abs.]).

[68] J.E. Chambers, Planetary accretion in the inner solar system, Earth Planet. Sci. Lett. 223 (2004) 241–252.

[69] R.N. Clayton, Meteorites and their parent asteroids, Science 313 (2006) 1743–1744.

[70] S.R. Taylor, G.J. Taylor, L.A. Taylor The Moon: A Taylor perspective. Geochimica et Cosmochimica Acta. (in press).

[71] C.G. Macpherson, D.R. Hilton, J.M.D. Day, D. Lowry, K. Grönvold, High-^{3}He/^{4}He depleted mantle and low-δ^{18}O recycled oceanic lithosphere in the source of central Iceland magmatism, Earth Planet. Sci. Lett. 233 (2005) 411–427.

[72] J.W. Valley, J.S. Lackey, A.J. Cavosie, C.C. Clechenko, M.J. Spicuzza, M.A.S. Basei, I.N. Bindeman, V.P. Ferreira, A.N. Sial, E.M. King, W.H. Peck, A.K. Sinha, C.S. Wei, 4.4 billion years of crustal maturation: oxygen isotope ratios of magmatic zircon, Contrib. Mineral. Petrol. 150 (2005) 561–580.

[73] R.K. O'Nions, N.M. Evensen, P.J. Hamilton, Geochemical models of mantle differentiation and crustal growth, J. Geophys. Res. 84 (1979) 6091–6101.

[74] J.M.D. Day, D.G. Pearson, L.A. Taylor, Accretion, differentiation and late bombardment history of the Moon deduced from Re–Os isotope systematics of mare basalts, Lunar Planet. Sci. Conf. XXXVII (2006) (CD-ROM #2235 [Abs.]).