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Calibrating volatile loss from the Moon using the U-Pb system

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Abstract

Previous isotope studies of lunar samples have demonstrated that volatile loss was an important part of the early history of the Moon. The radiogenic U-Pb system, where Pb has a significantly lower T_{50\%} condensation temperature than U, has the capacity to both recognize and calibrate the extent of volatile loss but this approach has been hindered by terrestrial Pb contamination of samples. We employ a novel method that integrates analyses of individual samples by Ion Microprobe and Thermal Ionization mass spectrometry to correct for ubiquitous common Pb contamination, a method that results in significantly higher estimates for $\mu$-values ($^{238}\text{U}/^{204}\text{Pb}$) than previously reported. Using this method, six of seven samples of low-Ti basaltic meteorites return $\mu$-values between 1900 and 9600, values that are consistent with a re-evaluation of published results that return $\mu$-values of 510–2900 for both low- and high-Ti basalts. While some degree of fractionation during partial melting may increase $\mu$-values, we infer that the source region(s) for the basalts must also have had elevated $\mu$-values by the time the lunar magma ocean solidified. Models to account for the available initial Pb isotopic compositions of lunar basalts in light of timing constraints from thermal modelling imply that their source regions had a $\mu$-value of at least 280, consistent with the elevated $\mu$-values of lunar basalts and that inferred for their sources. Such high $\mu$-values are attributed to the preferential loss of more than 99% of the Pb over U relative to a precursor with a Mars-like composition in the aftermath of the giant impact. Such an extensive loss of Pb is consistent with previously reported losses of other elements with comparable volatility, namely Zn, Rb, Ga and CrO$_2$. Finally, our modelling of highly-radiogenic lunar Pb isotopes assuming crystallization of the lunar magma ocean over 10$^8$ of millions of years shows that the elevated $\mu$-values allows for, but does not require, a young Moon formation age.

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Keywords: Earth-Moon formation; U-Pb isotope system; $\mu$-value; Volatiles; Giant impact

1. INTRODUCTION

Knowledge of the source and inventory of volatile elements, including water, in the terrestrial planets is fundamental to our understanding of planet formation and habitability as well as evaluating the likelihood of life in exoplanetary systems. The volatile content of the Moon is important in this context in that it offers insights into processes that control the abundances of volatile elements during a formation history that includes primary accretion, a giant impact, secondary accretion, crystallization of a magma ocean and, finally, widespread volcanic activity,
but lacks plate tectonics (see reviews by Halliday, 2008; Day and Moynier, 2014).

Exploiting the U-Pb and Rb-Sr isotope decay systems, the volatile depleted nature of the Moon was quickly established upon return of the Apollo samples (e.g. Tatsumoto et al., 1971; Nyquist et al., 1973 and summarized in Premo et al., 1999). In more recent studies, the volatile inventory of the Moon has been commonly addressed by analyzing lunar samples to characterize either elemental abundances and/or the isotopic compositions of volatile elements to look for evidence of evaporative loss (e.g. Paniello et al., 2012; Kato et al., 2015; Wang and Jacobsen, 2016; Pringle and Moynier, 2017; Kato and Moynier, 2017; Sossi et al., 2018; Day et al., 2020). These methods characterize individual samples that may be tied to their immediate precursor reservoirs but are not related easily to the bulk composition of the Moon. As these methods of assessing volatile inventories in the lunar interior depend on different assumptions, the concordancy of results would improve confidence in the various models.

The relative abundances of the refractory element U relative to the moderately volatile element Pb in the Moon’s interior can be assessed by two different approaches. First, since the rate of ingrowth of radiogenic Pb is directly related to the U/Pb ratio, the initial Pb isotope compositions of lunar basalts of different ages provides a means to model the U/Pb ratios of their source reservoirs with assumptions about ingrowth times (e.g. Snape et al., 2016). Assuming no U loss, this provides a direct measure of the amount of Pb and, therefore by inference, volatile elements present within the lunar interior. Second, the U/Pb ratios of individual lunar samples can be measured and then related through fractionation models to their source reservoirs. This second method of directly measuring the U/Pb ratio of individual lunar samples is made difficult by the ubiquitous presence of terrestrial Pb contamination (Pb t) that typically results in an underestimation of this ratio.

In this paper, we use both methods to understand the U-Pb evolution of the Moon. We employ a novel approach using new whole rock Pb isotope data to determine accurate U/Pb ratios of individual samples that we use to evaluate the U/Pb ratio of their source regions. These results are considered in the context of previously published initial Pb isotopic compositions of a wider range of ages of individual samples that provide complementary insights into the diversity of U/Pb ratios of their respective reservoirs. Integrating the new and existing data allows us to model the U-Pb evolution of the Moon, confirm that the source regions for lunar basalts are highly depleted in moderately volatile elements relative to the bulk Solar System and provide estimates for the degree of volatile loss. Finally, the U-Pb isotopic evolution of the identified lunar reservoirs are evaluated in light of the hypothesis that the Moon-forming giant impact occurred substantially later than the formation of the Solar System (e.g. Tera and Wasserburg, 1974; Carlson and Lugmair, 1988; Borg et al., 2011; Gaffney and Borg, 2014; Connelly and Bizzarro, 2016; Borg et al., 2019).

2. BACKGROUND INFORMATION

2.1. The U-Pb decay system

Lead has four naturally occurring isotopes, 204Pb, 206Pb, 207Pb and 208Pb, that were inherited from the Solar System’s molecular cloud in relative abundances estimated using troilitite from the Type IAB Canyon Diablo iron meteorite (Tatsumoto et al., 1975). All Pb isotopes except 204Pb have increased their abundances through the radioactive decay of 238U to 206Pb, 235U to 207Pb and 232Th to 208Pb. As 204Pb preserves its primordial abundances, the radiogenic ingrowth of Pb isotopes is most conveniently expressed as 206Pb/204Pb, 207Pb/204Pb and 208Pb/204Pb ratios that evolved according to the general equation:

\[
\frac{207}{204}Pb_{\text{today}} = \left( \frac{207}{204}Pb_{\text{today}} \right)_{\text{Pb}} + \left( \frac{235}{238}U \cdot \frac{232}{238}Th \right)_{\text{today}} (e^{\lambda t} - 1),
\]

where \( t \) represents the time before present and \( \lambda \) represents the decay constant of the parent isotope. In objects with only initial Pb (Pb i) and radiogenic Pb (Pb r) present, three independent ages based on the \( \frac{235}{238}U, \frac{207}{206}Pb, \frac{232}{238}Th, \frac{206}{208}Pb \) decay systems may be calculated. However, only the two U isotopes have decay constants large enough to provide ages with errors of less than 1 Myr. To calculate an age based only on Pb isotopic ratios, combining the two U-Pb decay equations of:

\[
\frac{207}{204}Pb_{\text{today}} = \left( \frac{207}{204}Pb_{\text{today}} \right)_{\text{Pb}} + \left( \frac{235}{238}U \right)_{\text{today}} (e^{\lambda t} - 1),
\]

and

\[
\frac{206}{204}Pb_{\text{today}} = \left( \frac{206}{204}Pb_{\text{today}} \right)_{\text{Pb}} + \left( \frac{235}{238}U \right)_{\text{today}} (e^{\lambda t} - 1),
\]

derives the combined equation:

\[
\frac{207}{206}Pb_{\text{today}} = \left( \frac{207}{206}Pb_{\text{today}} \right)_{\text{Pb}} + \left( \frac{235}{238}U \right)_{\text{today}} (e^{\lambda t} - 1),
\]

where the left side of the equation equals the radiogenic \( \frac{207}{206}Pb_{\text{today}} \) ratio \([\frac{207}{206}Pb_{\text{today}}]_r\) so that Eq. (4) can be reduced to:

\[
\frac{207}{206}Pb_{\text{today}} = \frac{\left( \frac{235}{238}U \right)_{\text{today}} (e^{\lambda t} - 1)}{\left( \frac{238}{235}U \right)_{\text{today}} (e^{\lambda t} - 1)}.
\]

Eq. (5) forms the basis for determining ages based on radiogenic \( \frac{207}{206}Pb_{\text{today}} \) ratios (Geiss, 1954), including those based on the “inverse Pb-Pb diagram” that plots \( \frac{204}{206}Pb_{\text{today}} \) versus \( \frac{207}{206}Pb_{\text{today}} \) ratios (Fig. 1a). In this construct, the y-intercept of the array corresponds to the Pb isotope composition that lacks \( 204Pb \) and must, therefore, equal the radiogenic \( \frac{207}{206}Pb_{\text{today}} \) ratio.

2.2. A new method to define the U/Pb of lunar samples

Ion microprobe Pb isotope data from five samples from the Northwest Africa (NWA) 773 clan (NWA 3170, NWA
3333, NWA 2727, NWA 2977 and NWA 4734 were used to define their initial and radiogenic Pb compositions (Merle et al., 2020a where this suite of samples is described). Plotted in $^{204}\text{Pb}/^{206}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$ space, the isochron for each sample represents the left hand edge of the triangular space defined by three component mixtures of initial Pb, radiogenic Pb and modern terrestrial Pb. The y-intercept of the isochron representing the radiogenic $^{207}\text{Pb}/^{206}\text{Pb}$ ratio is used in Eq. (5) to calculate the age of the sample. The upper end of the isochron is interpreted to represent the initial Pb composition although it is acknowledged that this may represent a minimum value and that some U and, therefore, radiogenic Pb may be present in the phases used to define this end point.

Data plotting within the triangular space defined by the three end-member components (Pb$_i$, Pb$_r$ and Pb$_c$) in $^{204}\text{Pb}/^{206}\text{Pb}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$ space attests to the ubiquitous presence of modern terrestrial Pb present in each sample. Determining the bulk rock U/Pb ratio, more commonly expressed as the $^{238}\text{U}/^{204}\text{Pb}$ ratio or $\mu$-value, of individual samples requires removal or subtraction of the modern terrestrial Pb. Given that attempts to physically remove the modern terrestrial Pb in the laboratory may fractionate U and Pb from the sample, we have developed a method to arithmetically subtract modern terrestrial Pb to determine the amount of $^{204}\text{Pb}$ in each sample and, in turn, their corrected $\mu$-values.

Our approach to estimating the $\mu$-value of a sample is illustrated using one of the samples (NWA 3170) investigated in this study (Fig. 1). It takes into account that many lunar samples are contaminated to various degrees by terrestrial Pb, a fact established by the early Thermal Ionization Mass Spectrometer (TIMS) work (e.g. Tatsumoto et al., 1971; Nyquist et al., 1973 and summarized by Premo et al., 1999) and confirmed by more recent Secondary Ion Mass Spectrometry (SIMS) studies (Snape et al., 2016; Merle et al., 2020a). In the case of Apollo samples, contamination must come from sample processing (such as cutting and mineral separation) in various laboratories (see Day et al., 2018), whereas meteorite samples can also acquire terrestrial Pb during their residence on the surface of the Earth prior to their discovery. SIMS analyses of the interior parts of minerals permit filtering data to obtain true Pb-Pb isochrons formed by binary mixtures of initial and in-situ accumulated radiogenic Pb, a method that is described briefly below and in more detail elsewhere (Snape et al., 2016). However, it is not possible to produce a reliable whole rock $\mu$-value of a sample by SIMS analyses given that only small domains of individual mineral are analyzed, the lowest U/Pb phases in lunar samples tend to have the lowest Pb concentrations and the determination

![Fig. 1. Inverse Pb-Pb diagrams (A and B) and U-Pb diagram (C) for sample NWA3170 to illustrate the method employed to calculate a $\mu$-value corrected for terrestrial Pb contamination. (A) The intersection of the mineral isochron defined by SIMS data from Merle et al. (2020a) with a line defined by the bulk rock TIMS data and the isotope composition of modern terrestrial Pb (see text) represents the corrected bulk Pb isotope composition of NWA 3170. Note that over 50% of the Pb in this analysis represents modern terrestrial contamination. B) Enlarged section of Figure A to show the initial Pb composition of NWA 3170, the intersection described in (A) with its uncertainties. C) The intersection between a line defined by modern terrestrial Pb and the measured $^{238}\text{U}/^{204}\text{Pb}$ bulk composition of NWA 3170 and a horizontal line (blue) defining the corrected $^{207}\text{Pb}/^{206}\text{Pb}$ composition determines the corrected $^{238}\text{U}/^{206}\text{Pb}$ ratio and uncertainty of this sample.](image-url)
of U/Pb ratios requires mineral standards with a similar structure and chemistry that are not readily available. Consequently, only TIMS studies involving complete digestion and homogenisation of representative amounts of a sample can provide accurate and precise information about the µ-value of lunar rocks. However, due to the ubiquitous presence of terrestrial Pb in TIMS analyses, a combination of SIMS and TIMS data for a single sample is required to calculate a µ-value that is corrected for terrestrial contamination.

As a first step, a contamination corrected Pb isotope composition of a bulk rock analysis is determined by the intersection of the SIMS isochron and a line drawn through the bulk rock TIMS analysis and terrestrial Pb composition in 

\[
\frac{^{207}Pb}{^{206}Pb} \text{ versus } \frac{^{204}Pb}{^{206}Pb}
\]

coordinates (Fig. 1a,b where the terrestrial Pb composition is derived from a literature compilation of global environmental Pb isotope studies (Monna et al., 1994; Flament et al., 2002; Freydier and Viers, 2003; Kaste et al., 2003; Graham et al., 2006; Notten et al., 2008; Evans et al., 2017; Nakata et al., 2017; Peng et al., 2020; see Supplementary Materials Table S1). We find average values of 0.85466 ± 4.1% and 0.05470 ± 4.4% for the terrestrial Pb 

\[
\frac{^{207}Pb}{^{206}Pb} \text{ and } \frac{^{204}Pb}{^{206}Pb}
\]

ratios, respectively, where the uncertainties represent 2SD%. These values, which are highly correlated, overlap the estimates for modern terrestrial Pb by Stacey and Kramers (1975).

The uncertainties on the terrestrial Pb composition are propagated onto the uncertainty on the SIMS-TIMS intersection Pb isotope composition using a Monte Carlo approach that varies the composition of the terrestrial Pb within the stated uncertainties. Following the determination of the corrected bulk Pb isotopic composition, the µ-value of the sample can be determined by two independent methods.

The first method (herein Method A) takes advantage of estimates of the initial Pb composition and age provided by the SIMS data (Snape et al., 2016; Merle et al., 2020a). Assuming that the estimate of initial Pb composition by SIMS is correct, the radiogenic ingrowth from this initial composition to the SIMS-TIMS intersect composition reflects the µ-value and age of the sample. Using the SIMS determined age, the µ-value can be calculated by the following formula:

\[
\mu = \frac{1}{1 - e^{t \lambda}} - 1
\]

where \( \lambda \) is the decay constant of 238U and \( t \) is the determined age. The robustness of any µ-value calculated by this method is strongly dependent on the accuracy of the SIMS-derived initial Pb composition, which, in turn, depends on the number of individual analyses of the least radiogenic component that defines an isochron in 

\[
\frac{^{207}Pb}{^{206}Pb} \text{ versus } \frac{^{204}Pb}{^{206}Pb}
\]

coordinates. Confidence will be increased with the number of analyses defining an overlapping Pb composition within their respective uncertainties. Since the initial Pb composition could be less radiogenic (but not more), any estimate of the µ-value based on this method should be viewed as a minimum µ-value.

A second approach to calculate µ-value of a sample relies on a calculated U-Pb ratio of the sample plus terrestrial contamination as determined by the TIMS-isotope dilution method (herein Method B). Correction for the terrestrial contamination is accomplished by utilising a 

\[
\frac{^{207}Pb}{^{206}Pb}\text{ versus } 238U/206Pb
\]

plot (Fig. 1c). In these coordinates, a line can be drawn through the uncorrected TIMS

\[
\frac{^{207}U}{^{206}Pb}
\]

and an estimate of the terrestrial Pb composition corresponding to a 

\[
\frac{^{207}U}{^{206}Pb}
\]

value on the x-axis provides the terrestrial contamination corrected 

\[
\frac{^{207}U}{^{206}Pb}
\]

ratio of the sample. The µ-value of the sample can be calculated using the corrected 

\[
\frac{^{207}Pb}{^{206}Pb}
\]

ratio (from the intersection of the SIMS and TIMS lines) of the sample and the formula:

\[
\mu = \frac{\left(\frac{^{207}U}{^{206}Pb}\text{ corrected}\right)}{\left(\frac{^{207}Pb}{^{206}Pb}\text{ corrected}\right)}
\]

The uncertainties on the terrestrial contamination Pb composition and the SIMS-TIMS intersection composition are propagated through to the uncertainties on the corresponding µ-value. Higher amounts of terrestrial contamination Pb will have the effect of a larger uncertainty on the intersections on both the 

\[
\frac{^{204}Pb}{^{206}Pb} \text{ versus } \frac{^{207}Pb}{^{206}Pb}
\]

and the 

\[
238U/206Pb\text{ versus } \frac{^{207}Pb}{^{206}Pb}
\]

diagrams and, consequently, the µ-value calculated by both methods.

The TIMS-isotope dilution method (Method B) is susceptible to fractionation of U and Pb during sample processing leading to either an underestimation or overestimation of the µ-value. Some of the lunar basalts are known to contain resilient accessory phases enriched in U (such as baddeleyite, zirconolite, tranquillityite and zircon; Connolly et al., 2008) that require dissolution in high temperature and pressure bombs. Lack of complete digestion of these U-rich phases would result in an underestimation of the calculated µ-value. Samples prepared for full digestion and U-Pb analyses by TIMS are commonly pre-cleaned using weak acids to remove more labile contamination Pb. However, even weak acids have the potential to remove more soluble phases such as sulphides and U-rich phosphates or leach Pb from major minerals (e.g. Connelly and Bizzarro, 2009; Merle et al., 2020b). As such, any precleaning that involves weak acids has the potential to create both artificially high and low estimates of a µ-value. Finally, adding the mixed U-Pb tracer used to calculate the U-Pb ratio after an evaporation step when the sample is not fully in solution will result in either a µ-value that is too high or too low if either U or Pb has been incorporated in a precipitate (Connelly et al., 2017).

In this study, we took the following precautions to ensure that the calculated µ-values are robust: 1) samples were wetted and rinsed only in distilled water to remove fine particulate material that formed during the light crushing of the sample, 2) we have used high temperature–pressure Parr Instruments® dissolution bombs at 210 °C to facilitate the full dissolution of the most insoluble phases, and 3) the samples were spiked as soon as possible after their removal from the oven and a 5% aliquot was transferred into a clean 3 ml Savillex vial. As such, we are confident that our pre-
ferred \(\mu\)-values calculated by Method B are not biased by any of the potential issues raised above.

Finally, we note that the two approaches have distinct, unrelated pitfalls so that the concordance of \(\mu\)-values determined by these two approaches increases our confidence that the calculated values are accurate.

3. SAMPLE DESCRIPTIONS

For the purpose of this study, we targeted meteorite samples for which petrography and chemistry were available and, most importantly, their ages and initial Pb ratios were well constrained by SIMS. We have selected seven lunar gabbros and basalts all belonging to the low-Ti chemical group that represents the dominant type of lunar mafic rocks (e.g. Neal and Taylor, 1992). All samples are enriched in incompatible elements that has been interpreted for some of them as reflecting a contribution of a component of KREEP (high K, REE and P) (Anand et al., 2003; Jolliff et al., 2003; Elardo et al., 2014 and summarized in Merle et al., 2020a). Within the set analysed, four (NWA 773, NWA 2977, NWA 3170 and NWA 3333) are coarser grained and commonly described as gabbros. Two samples, NWA 2727 and Dhofar 287, are finer grained and generally described as basalts. The last sample, NWA 4734, has been described by Connolly et al. (2008) as an unbrecciated basalt displaying a coarse-grained texture containing mm-sized crystals of pyroxene and plagioclase. All the meteorites used in this study were found in hot, arid deserts.

Lead-lead ages and Pb initial ratios for these samples were recently constrained by in situ Pb-Pb dating using SIMS (Merle et al., 2020a) and following the Pb-Pb isochron methodology outlined in Snape et al. (2016; 2019). Dhofar 287 is the oldest sample with a crystallization age of 3209 ± 22 Ma (Merle et al., 2020a). Four of the NWA 773 clan meteorites (NWA 773, NWA 2727, NWA 2977, NWA 3170) return SIMS crystallization ages indistinguishable within uncertainties, ranging from 3081 to 3089 Ma whereas sample NWA 3333 has a distinctly younger crystallization age of 3041 ± 20 Ma. Sample NWA 4734 has the youngest crystallization age of 2979 ± 20 Ma (Merle et al., 2020a). A comprehensive comparison of these SIMS data and all other available age estimates can be seen in Figure 9 of Merle et al. (2020a).

4. ANALYTICAL METHODS

Samples used in this study were selected from the collections at the Natural History of Denmark. A fragment of each sample weighing 56–100 mg (Table 1) was placed in a 3 ml Savillex® teflon screw-top vial in distilled water and ultrasonicated for 5 minutes. The water and any fine particulate matter in suspension were removed using a clean Eppendorf® pipette after which the sample was rinsed several times in distilled water. With as much water removed as possible after the final rinse step, a 3:1 mixture of concentrated HF and 7 M HNO₃ was added to the sample for dissolution by placing the Savillex® vial in a Parr Instruments® dissolution bomb in an oven at 210 °C for 4 days. The vials were then placed open on a hotplate to evaporate the acid mixture after which the vials were placed closed on a hotplate with 6 M HCl for 24 hours. Vials with solid residues after this step had 7 M HNO₃ added and returned to the hotplate for another 24 hours. After verification using a reflecting-light microscope that all samples were fully in solution, approximately 5% of the solution was removed for U and Pb isotopic analyses. A mixed 205Pb,235U tracer was added to each 5% aliquot before it was fluxed closed on a hotplate for 3 hours and then evaporated to dryness. The sample was then converted to 1 M HBr in preparation for the first stage chemical purification of U and Pb. Lead was purified first using the mixed HBr/HNO₃ procedures outlined in Connelly and Bizzarro (2009). The washes from the Pb purification were dried down and dissolved in 3 M HNO₃ in preparation for the U purification using Eichrom Industries® U-TEVA resin. The samples were loaded onto a pre-cleaned 200 µl resin bed, washed with 3 M HNO₃ and the U finally eluted in 0.05 M HCl. The purified Pb and U were analysed separately on a ThermoFisher Triton® TIMS located at the Centre for Star and Planet Formation in the GLOBE Institute, (University of Copenhagen) using silica gel (Gerstenberger and Haase, 1997) and zone-refined Re filaments. Most samples were large enough for 206Pb, 203Pb and 208Pb to be analyzed using faraday detectors with 204Pb and 203Pb analyzed using an axial secondary electron ion-counting (SEM-IC) system and a single peak jump. To avoid bias related to SEM-IC versus faraday measurements, the 204Pb/206Pb and 203Pb/208Pb ratios were also determined using the same filament in a separate analyses via a triple peak jump with the filament current reduced enough to allow 206Pb to be analyzed by the SEM-IC. Uranium was measured as an oxide using the SEM-IC and a peak jumping routine between 235U16O2 and 238U16O2. The absolute amount of each isotope of Pb and U were calculated based on the known concentrations of 205Pb and 235U in the tracer, and assuming a 238U/235U ratio of 137.786 (Connelly et al., 2012). The reported isotopic abundances and ratios (Table 1) were corrected for the tracer composition and 0.2 pg of Pb and U blank.

5. RESULTS

The seven bulk rock samples exhibit a wide range of 204Pb/206Pb ratios and plot at various distances from their respective SIMS-defined isochrons on the inverse Pb-Pb diagram (Fig. 2). The raw \(\mu\)-values calculated from the measured ratios (uncorrected for terrestrial contamination) for the seven samples range from 22 to 2003 (Table 1), with these values reflecting the total amount of 206Pb in each sample minus tracer and laboratory blank contributions. The terrestrial contamination corrected \(\mu\)-values using the two different methods outlined above are similar in four gabbric samples (NWA 773, NWA 2977, NWA 3170 and NWA 3333) and two basaltic samples (NWA 2727 and NWA 4734) with the difference between the results of the two methods being less than 17%, increasing our confidence in these estimates (Supplementary Materials Table S2). The \(\mu\)-values are also similar within the uncertainties for the two replicate TIMS analyses of NWA 3170 and NWA 4734.
further increasing our confidence in the method. The $\mu$-value estimated based on the SIMS initial compositions in sample Dhofar 287 is significantly smaller than that corrected using the U-Pb TIMS approach (but see discussion below). We infer that the SIMS initial composition of this sample may be significantly underestimated, a conclusion supported by the lower $^{207}\text{Pb}/^{206}\text{Pb}$ ratio of this sample relative to the main cluster of ratios of 1.1 to 1.3 for the other samples. The $\mu$-values corrected using Method B are taken as the best estimates of the true $\mu$-values of the samples in the discussion that follows (Table 2).

Three gabbroic samples from NWA 773 clan show high $\mu$-values ranging from 5400 ± 400 (NWA 2977) to 9600 ± 2500 (NWA 3170). The fourth gabbro sample from this group, NWA 3333, has significantly lower $\mu$ of 1900 ± 200, but this sample is also distinguished by a younger age. The single basaltic sample from NWA 773 clan analyzed here (NWA 2727) also has a relatively low $\mu$ of 1900 ± 300. Two samples that do not belong to the NWA 773 clan show diverse $\mu$-values (Table 2). The two analyses of NWA 4734 are identical at 2200 ± 100 and are similar to the low-$\mu$ group. The $\mu$-value for Dhofar 287 represents the highest calculated value at 18800 ± 6000 with the large uncertainty reflecting the longest extrapolation from the TIMS analyses to the SIMS isochron. This value is, therefore, more susceptible to the terrestrial Pb composition and is considered the least reliable of the meteorites studied. Nonetheless, it is clear that it possesses a high $\mu$-value, consistent with the other samples studied here. Despite the relatively large uncertainties on the $\mu$-value of some of these samples, they are consistently very elevated so that the conclusions drawn from these values are sound.

The new $\mu$-values presented here are for a limited number of younger low-Ti gabbro and basalt samples, all from a hot, arid desert. These $\mu$-values indicate significant depletions of Pb in the samples relative to U. To assess whether these very high values are restricted to this suite of younger mafic rocks or a more general feature of 3.9–3.0 Ga lunar basalts of various compositions, we re-assess below a subset of published U-Pb data for selected samples from the Apollo missions for which SIMS and TIMS data are available.

### 6. RECALCULATED -VALUES FOR LUNAR SAMPLES FROM LITERATURE DATA

We have reprocessed the published U-Pb data of 15 Apollo samples for which SIMS isochron Pb-Pb data and TIMS Pb data allows for the calculation of corrected $\mu$-values by our new method (see Supplementary Materials Table S2). Four high-Ti Apollo 11 samples, 10,017 (type-A), 10,003 (type-B2) as well as 10,020 and 10,045 (both type-B3) have been investigated using both SIMS (Snape et al., 2019) and TIMS (Tatsumoto, 1970; Silver, 1970; Gaffney et al., 2007a). The low-Ti Apollo 12 samples 12,021 (pigeonite), 12,038 (feldspathic) and 12,063 (ilmenite) were studied both by SIMS (Snape et al., 2019) and TIMS (Tatsumoto et al., 1971). Within low-Ti Apollo 15 samples, olivine normative basalt 15,555 and the quartz...
normative samples 15,085 and 15,065 have been investigated by SIMS (Snape et al., 2019) and TIMS (Tatsumoto et al., 1972; Tera and Wasserburg, 1974; Unruh and Tatsumoto, 1977). Finally, SIMS (Snape et al., 2019) and TIMS (Nunes et al., 1974; Tera and Wasserburg, 1974; Mattinson et al., 1977; Chen et al., 1978; Tilton and Chen, 1979) data have been published for high-Ti type-A samples 75,035 and 70,055, type-B samples 70,017 and 75,075 and type-C sample 74,275 from the Apollo 17 landing site. A number of samples have been analysed by different authors using separate splits of the rocks allowing for an additional level of comparison of calculated $\mu$-values.

Despite the range of potential mechanisms described above to fractionate U from Pb during the sample preparation for TIMS analysis, the majority of investigated Apollo samples show remarkable similarity (within uncertainties) between $\mu$-values based on the SIMS initial Pb compositions (Method A) and the ID-TIMS intersection approach (Method B). This similarity suggests that $\mu$-values for most of the samples within their stated uncertainties overlap the true values. This further implies that the initial Pb compositions determined by SIMS are also, within their uncertainties, representative of true compositions (at least for $^{204}$Pb/$^{206}$Pb used in the $\mu$ calculations). One sample, 10045, shows a SIMS $\mu$-value defined by Method A that is slightly lower than that defined by Method B, suggesting that the SIMS initial composition for this sample could be less radiogenic than measured. Two Apollo 12 samples (12038 and 12063) analyzed by Tatsumoto et al. (1971) show reversed relationships by as much as 8%. Recognizing that the early work of Tatsumoto et al. (1971) avoided acid washing of the samples prior to dissolution, the most likely explanation of the observed differences is incomplete digestion of the samples. This seems to be further supported by the difference in the $\mu$-value estimates obtained here for two splits of sample 12,063 and analysed by Tatsumoto et al. (1971). The TIMS-derived $\mu$-value for one split does not overlap that derived by the SIMS-based method whereas they do overlap for the second split.

Five other Apollo samples have been analysed at least twice, in one case (10017) by different groups. Four of those
m-values within their respective errors. The fifth sample 10,017 was analysed by Silver (1970), Tatsumoto (1970) and more recently by Gaffney et al. (2007a). The first two studies did not use sample acid washing, whereas the latter applied 10 min washing in cold 2 N HCl. The m-values estimated using data from the two earlier studies agree well within the errors (average value: 2150 ± 200, 2SD abs). However, data from the later analyses using an acid washing step gives a significantly larger estimate for the m-value (2900 ± 100). It is important to note that calculations using two different approaches utilised here give results internally consistent for each split of the sample, even though the same SIMS initial composition is used for all calculations. This is most readily explained by a real difference of m-values in different splits, suggesting that they are not fully representative of the bulk sample.

In general, the highest m-values determined for Apollo samples overlap with the lowest m-values estimated for meteorites in our study. High-Ti Apollo 11 basalts show the largest values ranging from about 1300 ± 500 to about 2200 ± 300 (or even 2900 ± 100, if Gaffney et al. (2007a) data for 10,017 are included). These values are significantly higher than those obtained for high-Ti Apollo 17 basalts that range between 510 ± 10 and 1390 ± 20. A similar, but less pronounced pattern is visible in low-Ti basalts where Apollo 12 samples appear to show slightly larger m-values between about 1300 ± 20 and about 1900 ± 30, whereas Apollo 15 rocks have a range between 760 ± 70 and 1280 ± 30. Internal variability for each landing site is impossible to assess due to relatively small number of samples investigated.

7. DISCUSSION

7.1. Bulk m-value of the Moon

The corrected m-values of a diverse sampling of 3.9 to 3.0 Ga lunar mafic rocks analysed in this study display a wide range from 1900 ± 300 to 9600 ± 2500, values that are systematically higher than the few available estimates for the same samples or rock types. This discrepancy is attributed to the widespread inclusion of terrestrial contaminant Pb in previous reports that effectively lowers the m.
value. As an example, sample NWA 2977 was recently reported as having a bulk $\mu$-value of 25 (Moromoto et al., 2019) but we define a corrected $\mu$-value of $5400 \pm 400$. For this example, we calculate that removal of 63% of the total $^{204}$Pb is necessary to obtain an accurate $\mu$-value that reflects the true bulk composition of this meteorite. In all, we estimate the need to remove between 63.0 and 99.4% of the terrestrial contaminant $^{204}$Pb present in the samples to obtain accurate estimates of the $\mu$-values from these seven samples. This highlights the necessity of

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{204}$Pb/$^{206}$Pb</th>
<th>err 2s abs</th>
<th>$^{207}$Pb/$^{206}$Pb</th>
<th>err 2s abs</th>
<th>$^{238}$U/$^{204}$Pb</th>
<th>err 2s abs</th>
</tr>
</thead>
<tbody>
<tr>
<td>DHO 287</td>
<td>0.000240</td>
<td>0.000081</td>
<td>0.32221</td>
<td>0.02288</td>
<td>18,800</td>
<td>6000</td>
</tr>
<tr>
<td>NWA 773</td>
<td>0.000201</td>
<td>0.000018</td>
<td>0.29085</td>
<td>0.00169</td>
<td>7100</td>
<td>600</td>
</tr>
<tr>
<td>NWA 2727</td>
<td>0.000727</td>
<td>0.000115</td>
<td>0.26368</td>
<td>0.00138</td>
<td>1900</td>
<td>300</td>
</tr>
<tr>
<td>NWA 2977</td>
<td>0.000261</td>
<td>0.000115</td>
<td>0.31100</td>
<td>0.00025</td>
<td>5400</td>
<td>400</td>
</tr>
<tr>
<td>NWA 3170#1</td>
<td>0.000184</td>
<td>0.000052</td>
<td>0.30509</td>
<td>0.01877</td>
<td>9600</td>
<td>2500</td>
</tr>
<tr>
<td>NWA 3170#2</td>
<td>0.000189</td>
<td>0.000052</td>
<td>0.30713</td>
<td>0.01854</td>
<td>9200</td>
<td>2300</td>
</tr>
<tr>
<td>NWA 3333</td>
<td>0.000644</td>
<td>0.000053</td>
<td>0.38573</td>
<td>0.00087</td>
<td>1900</td>
<td>200</td>
</tr>
<tr>
<td>NWA 4734#1</td>
<td>0.000633</td>
<td>0.000015</td>
<td>0.41254</td>
<td>0.00040</td>
<td>2200</td>
<td>100</td>
</tr>
<tr>
<td>NWA 4734#2</td>
<td>0.000633</td>
<td>0.000016</td>
<td>0.41269</td>
<td>0.00042</td>
<td>2200</td>
<td>100</td>
</tr>
</tbody>
</table>

Notes:
1. Corrected for terrestrial Pb contamination using Method B (see text).
2. $\mu$-values rounded to appropriate significant figures from Supplementary Materials Table S2.
employing a method that accurately accounts for contaminant Pb in lunar samples.

While contaminant terrestrial Pb may be expected in meteorites that have been exposed to the terrestrial elements and typically experienced undocumented curation, the careful handling and storage of the Apollo samples was expected to minimize Pb contamination. However, our re-evaluation of the existing U-Pb data in the literature shows that these samples also contain a significant amount of terrestrial Pb that must have been added to the samples during their preparation for distribution at NASA or in the isotope laboratories where they were analyzed (see discussion of curation in Day et al., 2018; McCubbin et al., 2019). In any case, we find that the corrected μ-values are also highly elevated for all of the Apollo samples we examined (Supplementary Data Table S2).

In the context of understanding the formation and evolution of the Moon, our interest in the μ-values of individual samples lies in their implications about their source regions and, in turn, about the U-Pb composition of the bulk Moon. There are two possible scenarios to explore in accounting for the very high μ-values of 3.9–3.0 Ga lunar basalts: 1) the source regions have significantly lower μ-values but partial melting and fractional crystallization reactions have effectively resulted in the retention of Pb in the residues, or 2) the source reservoirs have comparably high μ-values and U-Pb has not been significantly fractionated in the melting reactions that produced these rocks.

Given that U and Pb are comparably incompatible elements in the context of partial melting of silicate reservoirs (e.g. Blundy and Wood, 2003), we are not aware of any mechanism that would dramatically change the μ-value of the resulting melts relative to the source reservoir. That U/Pb ratios are not substantially changed by fractionation during partial melting in the mantle is supported by the observation that the Pb isotope composition of terrestrial continents (as measured from river sediments; Asmerom and Jacobsen, 1993) fall within the terrestrial Pb isotope mantle array (Stracke et al., 2005). An alternative suggestion that sulphides may serve as a reservoir for Pb in the lunar mantle (Gaffney et al., 2007a) is not supported by any direct evidence (Steenstra et al., 2020). To the contrary, several recent studies have concluded that the lunar mantle is highly depleted in S such that sulphides cannot be responsible for retaining Pb (Ding et al., 2018; Day, 2018). Even if the lunar mantle has a higher sulphide content than these authors suggest, analyses of sulphide phases in lunar rocks to date show that they are very low in Pb (Snape et al., 2019). As such, we conclude that the lunar mantle is characterized by highly-elevated μ values in the range of 1900–9600 based on our work. It is important to note that this large range corresponds to only a 0.1% difference in 206Pb and, therefore, should not be taken to reflect significant heterogeneity of the mantle.

That the source regions for the basalts and gabbros analysed here have high μ-values is fully supported by the radiogenic signatures of the initial Pb of the samples considered in this study and in previous reports (see summary in Premo et al., 1999). Regardless of whether the age of differentiation of the Moon is 4.5 Ga or 4.4 Ga (see discussion below), the μ-values of the source regions must be highly elevated relative to CI chondrites or the mantles of Earth and Mars. Snape et al. (2016) estimated a minimum μ-value of 462 for the bulk Moon by assuming differentiation at 4.5 Ga. A younger differentiation age would require a higher μ-value.

Accepting that the lunar mantle source regions have high μ-values, we now explore reasons for such values in the lunar mantle. For the sake of this discussion, we assume that U, as a refractory lithophile element, has been not been significantly gained or lost. The absolute concentration of U in the lunar mantle may be higher than CI chondrites given the loss of Fe and Ni to the core and the loss of volatile elements to space, but the ratio of U to other refractory elements are considered to be comparable to CI chondrites. Therefore, we attribute the high μ-values to the strong depletion of Pb in the lunar mantle relative to U. Below we discuss previously identified mechanisms to explain this depletion, namely: A) Pb was already lost from the precursor material prior to the giant impact that accreted to form the proto-Earth-Moon system (pre-impact depletion), B) Pb as a siderophile element may have been effectively sequestered to the Moon’s Fe-Ni core (differentiation-related depletion), and/or C) Pb as a moderately volatile element was lost by evaporation either during the immediate aftermath of the giant impact (e.g. post-impact but pre-reaccretion), or from the lunar magma ocean stage of the Moon’s history and/or via volcanic venting.

A) Strongly Pb-depleted precursor material. Recent models for terrestrial planet growth suggest that chondrules and matrix efficiently and rapidly accrete to form the precursors to terrestrial planets in the first 5 Myr of the Solar System’s existence (Schiller et al., 2018; 2020; Johansen et al., 2021). Although there is a temporal evolution in the nucleosynthetic make up of this material accreting to make the terrestrial planets (Schiller et al., 2018; 2020), this model predicts that Mars and the precursor material to the Earth-Moon system will have had comparable elemental abundances. As such, we infer that the μ-value of Mars of between 2–4 (Gaffney et al., 2007b) represents our best estimate for the pre-collisional precursor material to the Earth-Moon system and that a strongly-depleted precursor material does not account for the observed high μ-values.

B) Sequestration of Pb into the Fe-Ni Core. There are a number of studies that have evaluated the removal of Pb from a planetary mantle (Earth or Moon) via high-pressure–temperature experiments. The conclusions have varied from Pb being effectively removed by core formation (e.g. Wood and Halliday, 2010) to core formation having little effect on the Pb budget of the mantle except to increase its relative concentration (e.g. Lagos et al., 2008). The varying conclusions reflect the complexity of quantifying the tendency of Pb removal by core formation and the number of parameters that may affect this process (e.g. temperature, pressure, redox conditions, and the concentrations of elements such as Si, S, C). Given that we cannot fully quantify these parameters for the core formation of the Moon, whether or not Pb loss to the core represents a viable mechanism to explain elevated μ-values of the lunar mantle may remain unknown. However, we note that the data available
for the content of Pb in iron meteorites and their sulphidic inclusions, albeit limited, suggests that Pb is not effectively sequestered to the cores of planetary embryos or planetesimals (e.g. Tatsumoto et al., 1973; Connelly et al., 2008; Blichert-Toft et al., 2010). On the basis of these observations, we consider it more likely that Pb was not predominantly lost from the lunar mantle during core formation after the Moon-forming impact.

(C) Pb loss by evaporation. The loss of volatile elements from the lunar mantle has been evaluated using the isotopic composition of other volatile and moderately volatile elements, including Zn, Rb, K, Ga and Cr as Cr-oxide (Pаниело et al., 2012; Kato et al. (2015); Day et al. (2020); Pringle and Moynier, 2017; Wang and Jacobsen, 2016; Kato and Moynier, 2017; Sossi et al., 2018). These studies have hypothesized that substantial evaporative loss of these moderately heavy elements by any mechanism would result in easily measurable mass dependant fractionation typically leaving the Moon isotopically heavy relative to the Earth or Mars. This again assumes that the precursor materials for Mars and the precursor material to the Earth-Moon system was homogeneous so that at least Mars can be used for comparison.

For Zn, Pаниело et al. (2012), Kato et al. (2015) and Day et al. (2020) found that the Earth and Mars have fixed, overlapping Zn isotopic compositions that indicate a well-mixed mantle with minimal evaporative losses. In contrast, the lunar samples show a range of Zn isotopic compositions that span the Earth-Mars composition, indicating the loss of Zn from the Moon. Given the widespread evidence of significant Zn mass-dependant fractionation, these authors favoured global process of evaporative loss, likely linked to lunar accretion and the post-accretion lunar magma ocean phase to explain the preserved variability.

As a moderately volatile element, Rb would also be susceptible to mass dependant fractionation if evaporative loss was an important process in the Moon’s evolution. As with Zn, Pringle and Moynier (2017) found a range of Rb isotopic compositions in different Apollo lunar samples in contrast to the more fixed composition of a wide variety of samples from Earth. The fixed isotopic composition of Rb on Earth establishes that magmatic processes do not effectively fractionate Rb such that the range of lunar compositions are most readily explained by evaporative processes. They discount local losses by volcanic venting citing the lack of any complementary compositions to mass balance the Rb budget. However, these authors did not distinguish between evaporative loss in the immediate aftermath of the giant impact or during the subsequent lunar magma ocean phase.

Potassium is a moderately volatile, lithophile element that is strongly depleted in absolute abundances in lunar rocks and shown to be in low abundances in remote surveys of the lunar surface. Long assumed to have been lost by evaporative processes, Wang and Jacobsen (2016) documented an enrichment in the heavy K isotope $^{41}$K that they inferred was due to high temperature evaporative loss from the post-impact debris disk from which the Moon accreted.

Gallium is a moderately volatile element that is depleted by a factor of approximately 10 relative to Earth (Kato and Moynier, 2017). The Moon is mainly enriched in heavier isotopes of Ga, consistent with a model of global scale evaporative loss of volatile elements during high temperatures associated with the lunar magma ocean (Kato and Moynier, 2017). A range of Ga isotopic compositions of early-formed anorthosite crust is attributed an interplay between evaporation and condensation at the lunar surface combined with impact-related reworking of anorthosites to incorporate this isotopically diverse mix.

Chromium metal is a refractory element with a high $T_{50\%}$ condensation temperature but becomes more volatile in oxidizing environments with CrO$_2$ more volatile than CrO. With heavier isotopes preferentially complexing with the more oxidized and more volatile CrO$_2$ form, evaporative loss would leave the Moon with a lighter Cr isotope signature. Sossi et al. (2018) document overall isotopically lighter signatures in a range of lunar samples when compared to the more consistent composition of terrestrial samples. They infer that the Cr isotope results are most consistent with evaporative loss at temperatures lower than those expected for either the post-impact re-accretion or the lunar magma ocean stage. As such, they infer that CrO$_2$ was lost by evaporation related to localized, lower temperature volcanic activity. Chromium is the only element whose isotope system is interpreted to reflect such relatively late stage evaporative loss.

Taking this collection of studies at face value implies that evaporative loss of volatile and moderately volatile elements was an important mechanism in the formation of the Moon but that no single process is responsible. Accepting that the precursor material for the terrestrial planets was elementally approximately homogeneous, Zn and K isotopes suggest that the first significant loss of volatiles would have occurred in the immediate aftermath of the giant impact and the formation of a hot debris disk around the proto-Earth. The post-re-accretion lunar magma ocean is also identified as an important phase of volatile element loss to explain Rb and Zn isotopes. Finally, Cr isotopes are reportedly best explained by volatile loss at lower temperatures likely related to more localized volcanic activity.

Given that Pb has a comparable or lower $T_{50\%}$ condensation temperature than Zn, Rb and K, it seems unavoidable that Pb was also lost by devolatilization during these stages of lunar evolution. Assuming a starting CI chondrite µ-value of 0.2, at least 99.96% of Pb is missing to explain a whole rock µ-value of 510, the lowest value estimated here. Assuming that the precursor material to the Earth-Moon system would have been similar to Mars with a µ-value upper estimate of 4, we calculate that at least 99.2% of the Pb is missing from the samples reported here relative to the lunar precursor material. Accepting our assertion that U and Pb were not significantly fractionated in the production of the parental melts to these samples, this requires that over 99% of Pb was lost from those parts of the lunar mantle that were sampled by the diverse array of mafic rocks reported here. This result is consistent with the conclusion of Day et al. (2020) based on Zn isotopes that the Moon experienced 96% volatile loss compared to a starting composition of Earth, an amount that would correspond to a lunar µ value of 240.
7.2. Evaluating the efficiency of Pb loss by devolatization

If Pb loss by devolatization was an important process in the high-temperature events following the giant impact, then there should be abundant evidence of similar behaviour in other examples from the meteoritic record where high temperatures were attained. Indeed, we see indications of efficient Pb loss at various scales, from mm-sized chondrules formed in the protoplanetary disk to differentiated planetesimals. More specifically, chondrules commonly have low Pb contents and exhibit a wide range of Pb isotopic compositions. Lead loss on the angrite parent body was apparently so extensive that several of the basaltic meteorites also contain no measurable initial Pb. Isochrons to define their ages back project to a modern terrestrial Pb composition (Amelin, 2008; Connelly et al., 2008). This observation is consistent with the general depletion of volatile elements in the angrite meteorites (e.g. Pringle et al., 2014). Similarly, recent Pb-Pb data from the iron-silicate Steinbach meteorite presumed to come from the parent body of Group IVA meteorites shows that this sample essentially lacks any initial Pb with the isochron projecting back to a composition of modern terrestrial Pb. Blichert-Toft et al. (2010) also defined isochrons for Group IVA meteorites that projected to a modern terrestrial composition with no measurements of less radiogenic compositions. Collectively, these examples show that the loss of Pb and other volatile elements by devolatilization occurred at all scales and was an important process in the high-temperature formative stages of different Solar System objects.

7.3. Implications of post-impact Pb and volatile element loss from the Moon

Assuming that the volatile inventory in the precursor material to the Earth-Moon system was akin to Mars and that volatiles were lost in the aftermath of the Moon-forming impact, we now consider the implications for volatile elements in the inner Solar System materials. Recent models for planetary growth infer two important constraints for terrestrial planet growth. First, the planets are thought to represent a mixture of predominantly chondrules with a smaller component of fine-grained dust. As discussed above, chondrules are known to be variably depleted in volatile elements whereas the fine-grained dust is most likely to contain CI-chondrite abundances of volatile elements. Such a model adequately explains the volatile element inventory of Mars and its μ-values of 2–4 (Gaffney et al., 2007b). The second important recent discovery is that the protoplanets precursor material likely comprised a continuum of outer Solar System material that would have been devolatilized by elevated inner Solar System temperatures early in their accretionary history but became more volatile rich as temperatures dropped (Schiller et al., 2018; Schiller et al., 2020). Such a model predicts that the terrestrial planets will have a sub-CI-chondrite inventory of volatile elements governed by the duration of accretion. Longer accretion times resulting in larger bodies accreting more volatile rich than those that accreted early and were subsequently isolated. As such, the accretion model of Schiller et al. (2018) suggests that the precursor embryos for the Earth-Moon system may have been more rich in volatile and moderately-volatile elements than Mars.

Accepting that the Moon has lost a large fraction of its volatile elements after the giant impact, the question arises as to the extent to which Pb in Earth was affected by similar events. Assuming a range of μ-values of Mars between 2–4 and a value of less than 10 for the present-day Earth’s mantle, we calculate that the Earth’s silicate mantle lost at least between 60–80% of the 204Pb that was present in its Mars-like precursor material.

7.4. Implications for the timing of the Earth-Moon system forming giant impact

There is now abundant evidence from decades of research that the initial Pb isotope compositions of lunar basalts formed between 3.9 and 3.0 Ga are commonly highly radiogenic (e.g. Tatsumoto et al., 1971; Nyquist et al., 1973 and summarized in Premo et al., 1999), a condition that requires a history of appropriate combinations of ingrowth times and μ-values. As discussed above, we assume that the elevated μ-values of the bulk Moon in general and that of the basaltic source regions specifically reflect a history of Pb loss in the aftermath of the giant impact. Recent suggestions of a young age for the Moon combined with previously reported moderate μ-values (e.g. Gaffney et al., 2007a) would leave insufficient time for Pb isotopic compositions to evolve in the source regions of basalts by the time they were extracted. However, a young age can be reconciled with the highly-radiogenic Pb signatures if the μ-values of the source regions are higher than previously assumed and consistent with the results here. In the following section, we explore permissible time spans between the giant impact and the formation of the source regions for the basalts and the implications for lunar μ-values.

A realistic model to explain the range of variable, highly-radiogenic initial Pb compositions of basalts at least requires at least a three-stage evolution, namely: Stage 1 from Solar System initial Pb compositions to the time of the giant impact (t0 to t1 with a μ-value of μ0). Stage 2 from the giant impact to the cooling, differentiation and solidification of the Moon to form a mantle (t1 to t2 with a bulk Moon μ-value of μ1), and Stage 3 from solidification of the different basaltic source regions to the time of basaltic melt extraction between 3.9 to 3.0 Ga (t2 to tcrystallization with end-member low and high μ-values of μlow-Ti cumulate and μKREEP, respectively.

For the purposes of this modelling, we accept the conclusions from thermal modelling (e.g. Elkins-Tanton et al., 2011) that the LMO would cool, differentiate and solidify within 10s of millions of years. We assume that
the first differentiates of the LMO, the low-Ti cumulates, would start to crystallize within 10 Myr of the giant impact and that urKREEP would have crystallized within 30 Myr.

Since the aim of this modelling is only to evaluate the magnitudes of the $\mu$-values, the exact durations of these processes within 10s of Myr are not critical to the conclusions. We consider a giant impact at 4.50 Ga and 4.37 Ga as the oldest and youngest likely ages for the Moon forming event. Assuming that the 3.9 to 3.0 Ga basalts represent various mixtures of cumulate and urKREEP sources at their respective ages, the $\mu$-values of the cumulate and urKREEP sources are selected so that the Stage 3 growth curves bracket the Pb initial compositions of the 3.9 to 3.0 Ga basalts (Fig. 3). Since none of the basalts are considered to be pure urKREEP products, the $\mu$-values estimated for this reservoir must be minimum values.

For the oldest giant impact age of 4.50 Ga, the required $\mu_{\text{low-Ti cumulate}}$ and $\mu_{\text{urKREEP}}$ are estimated to be 255 and 2650, respectively whereas for the youngest giant impact age of 4.37 Ga, the required $\mu_{\text{low-Ti cumulate}}$ and $\mu_{\text{urKREEP}}$ are estimated to be 340 and 4600, respectively (Fig. 3a and b). Since the stage 2 evolution is short, only 10 Myr for low-Ti cumulate material and 30 Myr for urKREEP material, the model is not very sensitive to the bulk Moon value ($\mu_1$) selected. We have assigned a value of 1000 as being intermediate to the high $\mu$ and low $\mu$ source regions, but changing this by a factor of two either way does not significantly change the estimated $\mu$-values for the stage 3 growth curves. A $\mu$-value for the bulk Moon of 1000 would require fractionation factors of 2.5 to 5.0 to create both the lower $\mu$-value low-Ti cumulate source and the higher $\mu$-value urKREEP. This range of $\mu$-values seems consistent with the high $\mu$-values determined in this and previous studies for 3.9–3.0 Ga basalts, requiring only modest fractionation of U and Pb during the lunar magma ocean crystallization.

In more detail, the Pb initial compositions of the basalts should lie on appropriate-aged mixing tie lines between the low-$\mu$ and high-$\mu$ source regions assuming the basalts represent various mixtures of these end-member reservoirs. In fact, neither the 4.50 Ga or 4.37 Ga giant impact ages result in stage 3 growth curves with mixing tie lines that fit well with the Pb initial compositions of the basalts. The 3.4–3.0 Ga basalts fall too low on the mixing array that reflects a 4.5 Ga impact age (Fig. 3a). In contrast, the initial Pb compositions of the youngest basalts fall too high on the mixing array that reflects a 4.37 Ga giant impact (Fig. 3b). By adjusting the values for $t_1$ (and maintaining the same age offsets for the crystallization of the low-Ti and urKREEP source regions) and the $\mu$-values $\mu_{\text{low-Ti cumulates}}$ and $\mu_{\text{urKREEP}}$, we find that the best fit for the Pb initials is achieved for a $t_1$ of 4430 Ma and $\mu$-values of 280 and 3500 for $\mu_{\text{low-Ti cumulates}}$ and $\mu_{\text{urKREEP}}$, respectively. This combination generates mixing tie lines between the bracketing growth curves with ages closest to the basalt Pb initial values for their crystallization ages of 3.9–3.0 Ga (Fig. 3c).

Given the relatively large uncertainties on the Pb initial compositions and the degrees of freedom in choosing $t_1$, $t_2$ and the corresponding $\mu$-values, it should be stressed that none of the ages calculated here are definitive. Instead, the exercise is intended to show the range of ages that are possible to explain the diverse, highly-radiogenic Pb iso-
topic compositions of the lunar mantle. In particular, it is important to note that the modelling shows that Pb isotopes can be explained by a young Moon forming event in the context of recent suggestions of an isotopically homogeneous mantle at 4.34 Ga that infers a Moon-forming impact not significantly older than 4.38 Ga (e.g. Borg et al., 2019).

8. CONCLUSIONS

By integrating SIMS and TIMS analyses of single samples, we have devised an approach to strip terrestrial contaminant Pb and calculate an accurate μ-value of lunar basalts and gabbros. The results show significantly elevated μ-values between 1900 ± 200 and 9600 ± 2500 for the samples we analysed (excluding Dhofar 287). Applying the same method to previously published results for Apollo samples where both SIMS and TIMS data are available for both low- and high-Ti basalts also derives elevated μ-values of between 510 ± 10 and 2900 ± 100. Accepting that fractionation of U and Pb is likely to be limited during partial melting and fractional crystallization, we conclude that the elevated μ-values for these basalts are an inherent feature of the contributing source regions and, in turn, that the precursor lunar magma ocean must also have had a highly-elevated μ-value of at least 510. We attribute this to reduced amounts of Pb in the lunar magma ocean as part of volatile loss in the aftermath of the giant impact, consistent with previous documentation of reduced amounts of other elements with comparable or higher T50% condensation temperatures such as Zn, Rb and Ga.

In the modelling of Pb isotope evolution to explain the highly-radiogenic initial Pb isotopic compositions of lunar basalts in light of these elevated μ-values, we construct a three stage evolution model punctuated by the: 1) giant impact, 2) differentiation and solidification of the lunar magma ocean, and 3) the extraction of melts to form basalt samples between 3.9 and 3.0 Ga. We assume that a low-μ reservoir solidified first approximately 10 Myr after the giant impact and that the high-μ urKREEP representing the final stage of solidification occurred 20 Myr later. We evaluate end-member ages of 4.50 and 4.37 Ga for the giant impact and calculate growth curves to bracket initial Pb isotope compositions of 3.9 to 3.0 Ga basalts. This approach is motivated by the assumption that the initial Pb isotope composition of basalts reflect varying mixtures of low- and high-μ-value reservoirs at the time of basaltic melt generation. An old age for the giant impact requires low- and high-μ-values of 255 and 2650, respectively, whereas the younger age for the giant impact requires low- and high-μ-values of 340 and 4600, respectively. These elevated μ-values are consistent with our finding that the μ-values for the 3.9–3.0 Ga basalts measured in this study and calculated from published literature data are significantly higher than previous estimates. In more detail, the mixing lines of appropriate ages between low- and high-μ-value reservoirs to explain basalt initial Pb compositions are matched better with the ages of basalts with an intermediate impact age of 4.43 Ga. This scenario predicts low- and high-μ reservoirs with values of 280 and 3500, respectively. While these models cannot uniquely define an age for the giant impact, they demonstrate that the radiogenic Pb isotope compositions of 3.9–3.0 Ga basalts can be explained by a young impact age with high μ-values for the source regions that are consistent with our new results.

Declaration of Competing Interest

The authors 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 DATA

Supplementary data to this article can be found online at https://doi.org/10.1016/j.gca.2022.02.026.

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