

1. Pb isotope compositions of mineral species

The identification of minerals in this study was based on the Scanning Electron Microscopy (SEM) energy dispersive spectroscopy (EDS) mapping. The interstitial mesostasis and K-rich glass analyses provide a range of Pb isotope compositions, ranging from extremely radiogenic to compositions closer to the initial Pb values. The K-rich glass and mesostasis areas would be expected to yield radiogenic compositions as they are typically relatively U-rich compared to other phases. In cases where less radiogenic Pb isotope compositions were measured, it is possible that the SIMS analysis was sampling an adjacent K-Feldspar phase. In the one case (sample 12039) where K-Feldspar was unambiguously distinguished from K-rich glass (both phases are characterized in the element maps by concentrations of K, Al and Si – with higher Al and lower Si in K-feldspar), the SIMS analyses yielded some of the most convincing initial Pb compositions. The radiogenic compositions of sulfide analyses in 10044 and 12038 are also somewhat unexpected, as sulfides would typically be expected to concentrate Pb and with relatively little U, and therefore have Pb isotope compositions closer to the initial values. Cross-sampling of more radiogenic adjacent phases also seems like a likely explanation for this observation, particularly as the concentrations of initial Pb in lunar materials are generally very low, so even a relatively small amount of contamination from more radiogenic lunar material will significantly affect the Pb isotope compositions.

2. Construction of Pb isotope evolution models

2.1. Two-stage modelling calculations and assumptions

The two-stage source reservoir Pb evolution modelling in this study represents evolution in an initial primordial mantle with μ_1 (stage 1), followed by multiple differentiated silicate reservoirs with μ_2 -values (stage 2) that are the sources for the mare and KREEP-rich basalts. This modelling was first performed without compensating for the period of time between the formation of the Solar System (Connelly et al. 2012) and the Moon, which is assumed to take place at relatively low- μ (lower than that of terrestrial mantle, i.e. ~ 8) and, therefore, make an insignificant contribution to the radiogenic Pb of the lunar mantle and resulting lunar silicate reservoirs. However, additional runs of the model

were also performed, assuming more significant evolution of the Pb isotope compositions away from Canyon Diablo Troilite (CDT; $^{204}\text{Pb}/^{206}\text{Pb} = 0.107$; $^{207}\text{Pb}/^{206}\text{Pb} = 1.106$; Göpel et al. 1985) preceding the formation of the Moon (evolution in precursor material with μ -values of up to 200 was considered). This model and the relevant nomenclature used is summarised in Fig. 6a, which also indicates a final stage of Pb isotopic evolution for an individual basalt with μ_3 .

The two-stage Pb evolution model for the source reservoir of each sample analysed here can be expressed as:

$$\frac{^{206}\text{Pb}}{^{204}\text{Pb}_i} = \frac{^{206}\text{Pb}}{^{204}\text{Pb}_{\text{CDT}}} + \mu_1 * (e^{\lambda_{238} * t_0} - e^{\lambda_{238} * t_1}) + \mu_{2i} * (e^{\lambda_{238} * t_1} - e^{\lambda_{238} * t_i}) \quad [1a]$$

$$\frac{^{207}\text{Pb}}{^{204}\text{Pb}_i} = \frac{^{207}\text{Pb}}{^{204}\text{Pb}_{\text{CDT}}} + \mu_1 * \frac{(e^{\lambda_{235} * t_0} - e^{\lambda_{235} * t_1})}{137.88} + \mu_{2i} * \frac{(e^{\lambda_{235} * t_1} - e^{\lambda_{235} * t_i})}{137.88} \quad [1b]$$

where: $i=1 \dots 6$ – initial compositions and ages determined for the six analysed samples.

Unlike the single stage model, which implies that the source of each investigated sample evolved directly from CDT (and that the CDT composition did not evolve significantly between the start of the Solar System and lunar formation), the two-stage model assumes a period with an homogenous primordial lunar reservoir (with μ_i value for $^{238}\text{U}/^{204}\text{Pb}$) that eventually differentiated (at t_i) forming separate source regions with variable $^{238}\text{U}/^{204}\text{Pb}$ (μ_{2i}) that in time melted to produce the investigated basalts. The model also assumes that the main differentiation took place instantaneously, or at least in a period of time short enough not to produce any unaccounted Pb ingrowth in the different basalt sources. In light of the currently accepted views on the formation and early differentiation of the Moon, the strict two-stage model is valid if the sources of investigated rocks separated rather late in the sequence of crystallization of the Lunar Magma Ocean (LMO) that formed in the aftermath of the Moon's accretion. However, at the very least, and considering that residual urKREEP makes the main contribution to the increase of μ in the process of lunar differentiation, the time t_i defines an average age of urKREEP.

Bearing in mind that the first stage of Pb evolution under the model assumptions is similar for all investigated samples the equations [1a] and [1b] can be simplified thus:

$$\frac{^{206}\text{Pb}}{^{204}\text{Pb}_i} = \frac{^{206}\text{Pb}}{^{204}\text{Pb}_{t_1}} + \mu_{2i} * (e^{\lambda_{238} * t_1} - e^{\lambda_{238} * t_i}) \quad [2a]$$

$$\frac{^{207}\text{Pb}}{^{204}\text{Pb}_i} = \frac{^{207}\text{Pb}}{^{204}\text{Pb}_{t_1}} + \mu_{2i} * \frac{(e^{\lambda_{235} * t_1} - e^{\lambda_{235} * t_i})}{137.88} \quad [2b]$$

And eliminating μ_{2i} by dividing [2b] by [2a]

$$\frac{\frac{^{207}\text{Pb}}{^{204}\text{Pb}_i} - \frac{^{207}\text{Pb}}{^{204}\text{Pb}_{t_1}}}{\frac{^{206}\text{Pb}}{^{204}\text{Pb}_i} - \frac{^{206}\text{Pb}}{^{204}\text{Pb}_{t_1}}} = \frac{(e^{\lambda_{235} * t_1} - e^{\lambda_{235} * t_i})}{137.88 * (e^{\lambda_{238} * t_1} - e^{\lambda_{238} * t_i})} \quad [3]$$

This forms an equation with three unknown parameters; $\frac{^{207}\text{Pb}}{^{204}\text{Pb}_{t_1}}$, $\frac{^{206}\text{Pb}}{^{204}\text{Pb}_{t_1}}$ and t_1 , which are similar for all investigated rocks under the model conditions. As a result finding unknown parameters is reduced to the problem of minimization in a system of non-linear equations (Fig. A.4 attempts to diagrammatically describe this). In theory, having the three parameters above determined, the first stage can be treated as a single stage model in order to find μ_1 and t_0 . However, while minimising six equations corresponding to the six samples analysed in this study does converge on a single solution, the errors in the three parameters resulting from the currently available data set do not allow an explicit estimation of t_0 (i.e. age of the Moon). Nevertheless, they permit an estimate of the youngest possible limit for this age. The trial calculation of this limit was performed by expressing the first stage of the model in a form similar to equation [3] above:

$$\frac{\frac{^{207}\text{Pb}}{^{204}\text{Pb}_{t_1}} - \frac{^{207}\text{Pb}}{^{204}\text{Pb}_{CDT}}}{\frac{^{206}\text{Pb}}{^{204}\text{Pb}_{t_1}} - \frac{^{206}\text{Pb}}{^{204}\text{Pb}_{CDT}}} = \frac{(e^{\lambda_{235} * t_0} - e^{\lambda_{235} * t_1})}{137.88 * (e^{\lambda_{238} * t_0} - e^{\lambda_{238} * t_1})} \quad [4]$$

and including it in model calculations, adopting various t_0 ages, ranging from 4567 to 4425 Ma. The t_0 limit is provided by recognising that U and Pb partitioning between silicate minerals prohibits decrease of μ -values in a differentiation sequence involving silicates and, therefore, the μ_2 value cannot exceed the μ_1 value (Fig. 7). In addition, the model runs in this study were performed taking

into account that only three samples (10044, 12039 and 14072; Fig. A.4) have initial Pb compositions determined from multiple analyses and, therefore, provide the highest precision and degree of confidence. These three samples also provide the largest contrast in terms of the crystallization ages and initial Pb compositions. Samples 12038 and 12063 have initial Pb compositions determined from a single analysis in each sample and are likely to be slightly underestimating the true initial Pb values (this is apparent in Figs. 1b and 1d, where the second stage model line for each sample passes above the estimated initial Pb values). As discussed previously, the initial Pb composition of sample 15386 was not successfully measured directly, but inferred from the available data. Furthermore, the age of 15386 was determined with a relatively large uncertainty. Therefore, these three samples were excluded from the calculation of $\frac{^{207}\text{Pb}}{^{204}\text{Pb}}_{t_1}$, $\frac{^{206}\text{Pb}}{^{204}\text{Pb}}_{t_1}$ and t_1 and only added for the estimate of μ_{2i} -values of their respective sources (Extended Data Fig. A.4).

The known parameters (i.e. ages and initial Pb compositions of investigated samples) were randomly generated using normal distribution around the respective means with the observed analytical uncertainties, thus allowing for the propagation of these uncertainties into the model calculations. Ten thousand sets of random numbers generated in this manner were used then to estimate maximum likelihood (using the MatLab maximum likelihood function) and three unknown parameters. The mean and standard deviations of the resulting sets were used to assess the best estimates and variance of $\frac{^{207}\text{Pb}}{^{204}\text{Pb}}_{t_1}$, $\frac{^{206}\text{Pb}}{^{204}\text{Pb}}_{t_1}$, t_1 , μ_l and six μ_{2i} -values. The youngest limit for t_0 was determined at the point in time where μ_l starts to exceed values for μ_{2i} of mare basalts. A summary of the model results is presented in Table B.4.

2.2. Calculation of starting (t_0) Pb isotope compositions

The model runs performed with non-CDT starting compositions effectively assume that the Moon was formed entirely of material derived from the giant impactor that collided with the Earth (i.e. isotopically and chemically equivalent to a capture scenario for lunar formation). Contrary to this assumption, giant impact models predict varying proportions of terrestrial and impactor material being

incorporated into the Moon (Canup and Asphaug 2001). Mixing even small proportions of low- μ terrestrial material with high- μ impactor material can dramatically affect the resulting starting composition of the primordial lunar mixture. This is due to the low concentration of Pb in high- μ material compared to that of low- μ material, considering that a high- μ is the result of Pb loss rather than U gain, due to the volatile nature of Pb and refractory nature of U. The concentration of U, compared with Pb, is considered to be relatively constant throughout the Solar System.

If the concentration of ^{238}U is taken to be consistent (~ 1 , the exact value is not critical for models involving ratios) between the impactor and the Earth, then the effective μ -value that results from mixing different proportions of these materials can be calculated as:

$$\mu_{mix} = \frac{1}{f \frac{1}{\mu_E} + (1-f) \frac{1}{\mu_I}} \quad [5]$$

where μ_{mix} , μ_E and μ_I are the μ -values of the final mixture, Earth and the impactor, respectively, and f is the fraction of terrestrial material incorporated into the mix. The resulting Pb isotope composition of the mixture can then be calculated from CDT values using the μ_{mix} value.

This method does not take into account the effect of Pb-loss during the formation of the Moon. This may result in significant increases of the lunar μ -value at the time of formation. However, the Pb isotope composition of the mix will not be affected, provided Pb is lost uniformly from both the impactor and terrestrial fractions in the mixture.

3. Previous studies of Pb isotopes in lunar samples

As is briefly discussed in the main text, determining the Pb isotopic composition of lunar rocks and their source reservoirs has proved problematic ever since the first Apollo samples were returned (Tatsumoto 1970; Tera and Wasserburg 1972; 1974; Tatsumoto et al. 1987; Gaffney et al. 2007; Nemchin et al. 2011). This is due to both the low Pb concentration in most lunar samples and the very radiogenic nature of lunar Pb. Consequently, it has been extremely difficult to determine the isotopic composition of initial Pb in lunar samples. This has made the modelling of lunar Pb evolution troublesome and has resulted in a wide range of μ -values ($^{238}\text{U}/^{204}\text{Pb}$) being proposed for the source

reservoirs of different lunar rocks; from very high μ -values (>1000) predicted for the KREEP reservoir (Nemchin et al. 2011) and inferred on the basis of zircon U-Pb SIMS analyses (Compston et al. 1984), to lower values (~ 100 -600) for many mare basalts (e.g Tera and Wasserburg 1972; 1974; Gaffney et al. 2007; Nemchin et al. 2011; Tatsumoto et al. 1971), and even lower values (between 10-40) determined for Apollo 15 green glasses (Tatsumoto et al. 1987) and basaltic materials in several lunar meteorites (Tatsumoto et al. 1971; Misawa et al. 1993; Torigoye-Kita et al. 1995; Terada et al. 2007).

The very low μ -values determined in the Asuka 881757, Yamato 793169, Meteorite Hills (MET) 01210 and Dhofar 287A meteorites (Misawa et al. 1993; Torigoye-Kita et al. 1995; Terada et al. 2007; Terada et al. 2008) are of particular interest when compared with our results. Our two stage models indicate that the primordial lunar μ -value would have been more than 200 even if the Moon formed at the same time as the Solar System (i.e. 4567 Ma), but more likely would have been 462 ± 46 , assuming $t_0 = 4500$ Ma. It is clear that silicate differentiation alone would not be sufficient to lower this primordial μ -value sufficiently to reach the lower (by an order of magnitude) μ -values identified in the meteoritic basalts, and some other mechanism would be required such as, for example, the fractionation of sulfide phases (Gaffney et al. 2007; Nemchin et al. 2011).

Many of the $^{207}\text{Pb}/^{206}\text{Pb}$ ratios for the measurements are below 0.5, with the highest $^{207}\text{Pb}/^{206}\text{Pb}$ ratio of 1.0 being identified in Dhofar 287. Furthermore, it is notable that the SIMS analyses made by Terada *et al.* (Terada et al. 2007; Terada et al. 2008) and used to determine very low μ -values were made only in plagioclase and phosphate phases. From our own data (see complete datasets in Table B.1 and Fig. A.3) it is apparent how susceptible analyses of lunar samples are to the effects of terrestrial contamination, with many of the analyses having compositions that would plot away from the sample isochrons and towards the terrestrial contaminant in $^{207}\text{Pb}/^{206}\text{Pb}$ vs. $^{204}\text{Pb}/^{206}\text{Pb}$ coordinates. This is especially true of many analyses made in plagioclase, particularly in the mare basalts where the concentrations trace elements (including Pb) would be expected to be lower than those of the KREEP-rich samples. It is only in one KREEP-rich sample (14072) where analyses of plagioclase yielded Pb isotopic compositions that were used both to constrain the sample isochron, but were also non-

radiogenic enough to be used to calculate the initial Pb composition of the sample. Based on these observations, we would echo the sentiment of Terada *et al.* (2007), who advised that analysis of less radiogenic phases would be required to confirm the identification of any low- μ lunar reservoirs.

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