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Cosmogenic tungsten and the origin and earliest differentiation of the Moon

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Abstract

The decay of formerly live ^{182}Hf with a half-life of 9 Myr results in variations in the abundance of ^{182}W in early solar system objects. Here we demonstrate that major excesses in ^{182}W in some lunar samples are the results of cosmogenic additions. Apollo 17 high-Ti mare basalts yield high $^{182}W/^{184}W$ of up to $\varepsilon_w = +11 \pm 1$. Even more extreme variations of up to $\varepsilon_w = +22 \pm 1$ are found for mineral separates, although these lavas were erupted more than 500 Myr after the start of the solar system. The measured ^{182}W excess in the separated minerals is correlated with their Ta/W, confirming theoretical models that implicate the $^{181}Ta(n,\gamma)^{182}Ta(\beta^-)^{182}W$ reaction from cosmic irradiation as the most likely cause. In contrast, olivine–basalt 15555, which has a low cosmic ray exposure age, displays no internal ^{182}W variations and defines an ε_w of $+1.3 \pm 0.4$. This is consistent with earlier conclusions that the Moon formed about 50 Myr after the start of the solar system. The high-Ti mare basalt source, with very high Hf/W, has a W isotopic composition that is not grossly different, from which a time limit of $\sim$70 Myr after the start of the solar system can be inferred for the formation of ilmenite-rich layers in the final stages of the lunar magma ocean.

Keywords: tungsten; stable isotopes; Moon; magma oceans; cosmic rays; basalts

1. Introduction

Galactic cosmic rays comprise many different kinds of energetic particles that have been constantly bombarding our solar system ever since its formation. Consequently, a series of spallation reactions may occur if an object has been subjected to direct and prolonged contact with cosmic rays. Exactly which spallation reactions may occur and the magnitude of the resultant effects are generally governed by factors such as the cosmic ray fluence and the chemistry and geometry of the target. These have been widely studied both theoretically and experimentally [1–6]. In this paper we present the results of a search for such effects in the tungsten (W) isotopic compositions of lunar samples.

The ^{182}Hf–^{182}W system, $t_{1/2} \approx 9$ Myr, has been successfully applied to unravel the early accretion and differentiation histories of a wide variety of planetary bodies [7–10]. The high initial abundance and relatively long half-life of ^{182}Hf, together with the fact that both Hf and W are

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highly refractory with different behavior during core formation, render this short-lived chronometer very powerful [7–10]. Early efforts to quantify spallation reactions on W isotopes were focused exclusively on the $^{182}W(n,\gamma)^{183}W$ reaction [11], which was shown to be insufficient to explain the well-resolved ^{182}W deficiency in various iron meteorites [7–10]. Because of the limited effects of this ^{182}W burn out reaction, and the fact that it cannot explain the excess ^{182}W documented in a wide variety of meteorites and also on the Moon [12–16], no further attention was paid to the spallogenic modification of W until recently.

It has been shown recently that the $^{181}Ta(n,\gamma)^{182}Ta(\beta^-)^{182}W$ reaction can produce ^{182}W excesses in high Ta/W rocks with long exposure age and large neutron fluence [17]. The Ta/W ratio is critical because by capturing a neutron, ^{181}Ta is converted directly to ^{182}Ta, which subsequently decays to stable ^{182}W. The effect is negligible unless the Ta/W ratio in the target is significantly enriched ($\geq 10\times$) over the chondritic value (~ 0.15) and the exposure age is long (≥ 100 Myr) [17]. As a result, all of the meteorites studied thus far for the ^{182}Hf–^{182}W system should contain no resolvable cosmogenic ^{182}W.

Unlike the Earth, the Moon exhibits quite variable W isotopic compositions from $\varepsilon_W = 0$ (chondritic) to $\varepsilon_W > +6$, spanning a wide variety of lunar rock types [13]. This excess ^{182}W was thought to reflect in situ ^{182}Hf decay within a high Hf/W lunar mantle. This is the result of inheriting high Hf/W materials from the silicate Earth and the mantle of the putative impactor, followed by the extraction of a low Hf/W crust and a small lunar core [13,18–20]. This W isotopic effect has been used to constrain the age and the origin of the Moon, as well as the nature and early evolution of the lunar magma ocean [13,19]. However, some lunar samples are characterized by long exposure ages and high Ta/W [17]. Therefore, a significant portion of the observed ^{182}W excess in lunar rocks has been predicted to be the result of $^{181}Ta(n,\gamma)^{182}Ta(\beta^-)^{182}W$ reaction during exposure on the surface of the Moon [17]. Knowing precisely when and how the Moon formed is critical to the understanding of the accretion and differentiation history of larger planetary bodies such as the Earth. Therefore, an effort to better quantify the cosmogenic W on the Moon is urgently needed.

2. Methods

An accurate assessment of the cosmogenic W effects based on physical models of cosmogenic nuclide production [11,17] requires the knowledge of the relevant low-energy neutron fluences, which in turn requires analyses of the isotopic composition of elements such as Gd or Sm [21–23]. Because such data are often not available, and the model calculations are not yet very accurate, we have chosen to quantify the cosmogenic W effect by the relationship between Ta/W and W isotopic composition within individual lunar samples. While all the W isotopes are subjected to modifications through various spallation reactions, essentially all the effects are negligible except for that affecting ^{182}W [13,17]. Any cosmogenic ^{182}W should be essentially proportional to the amount of ^{181}Ta. Therefore, the $^{182}W/^{184}W$ of individual minerals within a sample should be proportional to Ta/W, because the neutron fluence will be the same for each mineral. Lunar mare basalts were erupted long after ^{182}Hf became extinct, therefore, a plot of $^{182}W/^{184}W$ against Ta/W for individual phases from a sample should define a positive slope that relates to the exposure history and neutron fluence. The W isotopic composition defined by the intercept of such a 'cosmochron' at the point at which Ta/W is equal to zero thus represents the initial W isotopic composition inherited directly from the magma source region within the Moon.

Bulk rocks and minerals from three Apollo 17 high-Ti mare basalts (70035, 75075 and 77516) and an Apollo 15 olivine–basalt (15555) have been analyzed, as well as a bulk rock norite (77215) to compare with previous results. All the samples were crushed with an aluminum oxide mortar under a laminar flow of HEPA-filtered air. The separation of all three major mineral phases (feldspar, ilmenite and pyroxenes) was achieved using a magnetic separator. Several passes through the magnetic separator were performed for each phases. Since this was already sufficient for our purpose, no further mineral picking was performed to avoid contamination. All the mineral fractions were digested sequentially with concentrated HF, 8 N HNO_3 and 6 N HCl. Roughly 10% of the solution was split and spiked with ^{180}Ta and ^{186}W, whereas the remaining solution was dried and re-dissolved in ~8 ml of 4 N HF. The chemical separation of W was the same as previously used [13]. The same column set up was also used for the spiked solutions [13], and W and Ta were collected sequentially with a mixture of 6 N HCl+1 N HF and 8 N HNO_3. Total procedural blank for W was ~0.5 ng. All isotopic measurements were performed using a Nu Plasma multiple collector inductively coupled-plasma mass spectrometer (MC-ICPMS) at ETH Zürich, Switzerland, with the exception of some samples which were measured at the University of Michigan using a VG Plasma 54 (see Table 1). The NIST-3163 W standard was run in between every sample to monitor the performance of the MC-ICPMS and to check for memory effects, which were negligible. All

Table 1
W isotopic compositions and Hf, W and Ta concentrations

Sample #	Hf (ppm)	Ta (ppm)	W (ppm)	^{180}Hf/^{184}W (atomic)	^{181}Ta/^{184}W (atomic)	^{182}W/^{184}W $\pm 2\sigma$ S.E.M.	ε_w^a $\pm 2\sigma$ S.E.M.
70035							
WR[b]	7.824	–	0.05385	171.4	–	0.865710 ± 88	8.2 ± 1.0
FS	–	0.07034	0.02332	–	10.0	0.865260 ± 82	3.0 ± 0.95
ILM	–	3.629	0.2282	–	52.74	0.865300 ± 40	3.5 ± 0.46
PX-1	–	1.473	0.04530	–	107.8	0.865686 ± 68	7.8 ± 0.79
PX-2	–	1.331	0.04493	–	98.22	0.865696 ± 78	8.0 ± 0.90
71566							
WR[b]	8.651	–	0.06336	161.1	–	0.865468 ± 76	5.4 ± 0.88
71596							
WR[b]	6.993	–	0.06058	136.2	–	0.865738 ± 100	8.5 ± 1.1
75075							
WR[b]	7.427	–	0.1356	64.63	–	0.865967 ± 81	11.2 ± 0.9
FS-1	–	0.1206	0.07404	–	5.399		
FS-2	–	–	0.02045			0.865545 ± 216	6.3 ± 2.5
ILM	–	–	0.09822	–	–	0.866877 ± 99	21.7 ± 1.15
PX-1	–	–	0.03400	–	–	0.866060 ± 62	12.3 ± 0.72
PX-2	–	–	0.03575	–	–	0.865843 ± 52	9.75 ± 0.60
PX-3	–	1.297	0.04870	–	88.26	0.866341 ± 130	15.5 ± 1.5
77516							
WR[b]	6.481	–	0.05763	132.7	–	0.865479 ± 102	5.5 ± 1.2
ILM	–	2.382	0.09596	–	65.59	0.865290 ± 39	3.35 ± 0.45
PX-1	–	1.315	0.07950	–	65.49	0.865369 ± 45	4.27 ± 0.57
PX-2	–	1.064	0.04962	–	77.47	0.865363 ± 49	4.20 ± 0.52
15555							
FS-1	–	0.02245	0.02980	–	2.497	0.865145 ± 132	1.68 ± 1.53
FS-2	–	0.02409	0.01602	–	4.987	0.865110 ± 63	1.27 ± 0.73
ILM	–	0.9296	0.2286	–	13.48	0.865108 ± 44	1.25 ± 0.51
PX-1	–	0.1306	0.05776	–	7.494	0.865106 ± 41	1.23 ± 0.47
PX-2	–	0.1244	0.04778	–	8.630	0.865116 ± 48	1.34 ± 0.56
WR	–	0.2761	0.06676	–	13.71	0.865098 ± 31	1.13 ± 0.36
77215							
WR	–	0.4371	0.2838	–	5.105	0.865030 ± 24	0.35 ± 0.28

[a] $\varepsilon_w = \{[(^{182}W/^{184}W)_{sample}/(^{182}W/^{184}W)_{standard}]-1\} \times 10^4$.

[b] Both the W isotopic composition and isotope dilution Hf/W ratio were measured using the Plasma 54 at the University of Michigan, whereas the other measurements were undertaken using the Nu Plasma at ETH (Fs = feldspar; Ilm = ilmenite; Px = pyroxenes; Wr = whole rock).

W isotopic measurements were normalized to $^{186}W/^{184}W = 0.927633$ [13]. The Nu Plasma gives a mean $^{182}W/^{184}W$ slightly lower than that of Plasma 54, probably reflecting differences in collector efficiencies between the two instruments. We have thus normalized all the data to the long-term mean of Plasma 54 ($^{182}W/^{184}W = 0.865$; [13]) for consistency. The quoted 2σ standard errors all refer to the least significant figures. Isotope dilution measurements for Ta and W were determined separately, and the uncertainty was typically 0.5% or better.

3. Results and discussion

The bulk rock W isotopic compositions of the high-Ti mare basalts extend the range of previously published lunar data to $\varepsilon_W \sim +11$ (Table 1). These rocks have extremely high Hf/W, reflecting ilmenite-rich sources produced in the lunar magma ocean [24]. Therefore, highly radiogenic W is not unexpected. However, the mineral separates for all three high-Ti mare basalts exhibit even more extreme variations of up to $\varepsilon_W \sim +22$. A positive linear correlation is found between the measured $^{182}W/^{184}W$ and the respective Ta/W ratio of each phase within an individual sample (Fig. 1), and this is consistent with cosmogenically produced ^{182}W additions [17]. All three high-Ti basalts show intercepts (at Ta/W = 0) of $\varepsilon_W \geq 0$ (Fig. 1). However, the uncertainty associated with the regression is quite significant in each case. Therefore, no conclusive evidence of a radiogenic W signature can be reliably deduced at this stage.

The magnitude of the cosmogenic ^{182}W is a function of the neutron fluence [17]. It is difficult to derive the neutron fluence quantitatively from the results of this study alone because other key information such as shielding depth is absent. Nevertheless, a first order calculation suggests that the neutron fluence was of the same magnitude as more direct assessments from other lunar samples based on Sm and Gd isotopes [21–23]. The data presented here are also agree to within 40% with the predictions from noble-gas-based exposure ages combined with model calculations [17].

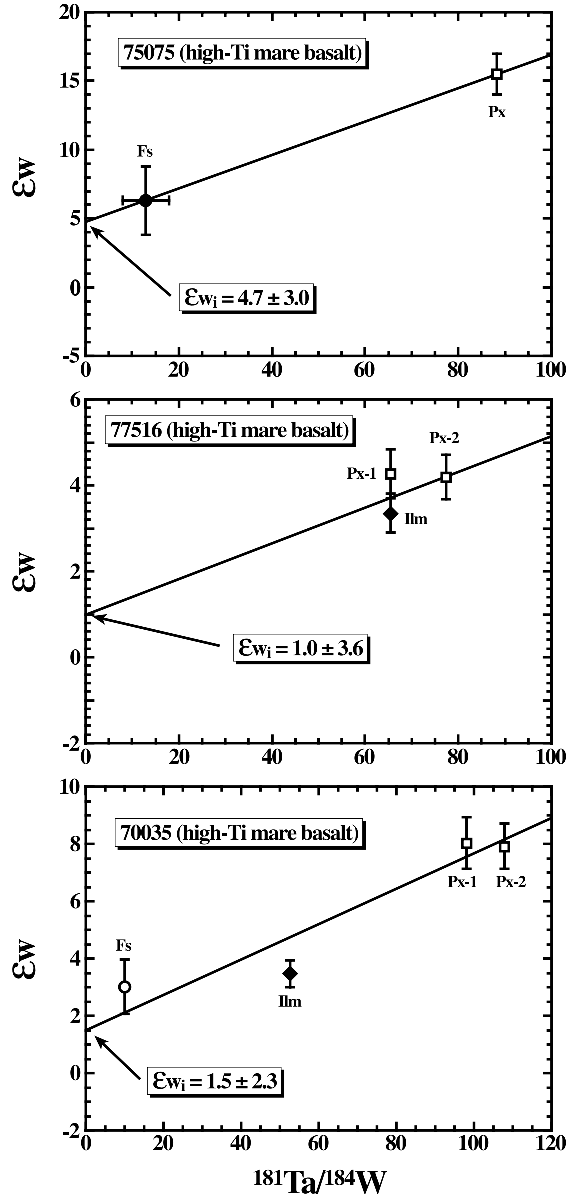

Fig. 1. Plots of ε_W versus $^{181}Ta/^{184}W$ for high-Ti mare basalts 75075, 77516 and 70035. The 'cosmochron' was calculated using the Isoplot/Ex Rev. 2.49 program from Dr. K.R. Ludwig. Fs = feldspar; Ilm = ilmenite; Px = pyroxenes.

In order to test that the same effects were not present in rocks with low exposure age we have performed the same experiment on separated minerals from olivine–basalt 15555 (Table 1; Fig. 2). This sample was previously shown to yield $^{182}W/$

^{184}W that is higher than chondritic [13], however, its Ta/W ratio and exposure age are far lower than those of the high-Ti mare basalts [17]. Despite variable Ta/W ratios, all of the mineral phases plus the whole rock of olivine–basalt 15555 exhibit identical W isotopic compositions, with a mean ε_W of $+1.3 \pm 0.39$ (Fig. 2). This is consistent with the prediction that there should be no detectable cosmogenic ^{182}W in 15555.

The mean ε_W of $+1.3 \pm 0.39$ is substantially lower than previously reported ($+6.7 \pm 0.4$) for 15555 [13], the reason for which is unclear. Because these two analyses were from different splits, we have re-analyzed the small remainder of our original sample split and found that the Ta/W ratio is consistent with the new data presented here. However, the ^{21}Ne exposure age ($\sim$11 Myr) from the original split is significantly younger than a previously published result of $\sim$80 Myr [17]. This raises the possibility of mislabeling for the original split because it was not in its original package when we received the sample. Nonetheless, the explanation for the discrepancy with the earlier data remains unclear, and an instrumental artifact on the first generation Plasma 54 used for the earlier measurements at Michigan also remains a possibility. To further check the integrity of the earlier data we have re-analyzed one of the most precisely determined samples from the earlier study. The bulk rock norite 77215 gives an $\varepsilon_W = +0.35 \pm 0.28$, which is identical within analytical uncertainty to the previous measurement of $+0.69 \pm 0.16$ [13]. This sample also has a low exposure age and Ta/W such that, as with 15555, the ^{182}W excess is best explained as a feature inherited from the lunar interior. Therefore, although some ^{182}W excesses found in lunar samples are indeed of cosmogenic origin, the Moon retains a resolvable radiogenic component, as previously suggested [13,19,20].

It is thought that the Moon formed as a result of a collision between the proto-Earth and a Mars-sized impactor. Most of the material ejected into orbit was made from the silicate portions of the two bodies, with the impactor dominating the material that formed the Moon [25–29]. The W isotopic composition of the lunar interior must reflect either incomplete mixing between the materials inherited from the proto-Earth and the impactor ('Theia'), or in situ radioactive decay of ^{182}Hf in the lunar mantle. It is difficult to envisage how any isotopic heterogeneities, radiogenic or stable, would have survived the incredibly energetic initial state of the giant impact, given that dynamic simulations estimate peak temperatures to be $\geq$10 000 K [25,26,29]. Furthermore, the subsequent formation of a lunar magma ocean should have erased any remaining isotopic heterogeneity. Uniform elemental and isotopic compositions on the Moon confirm that global-

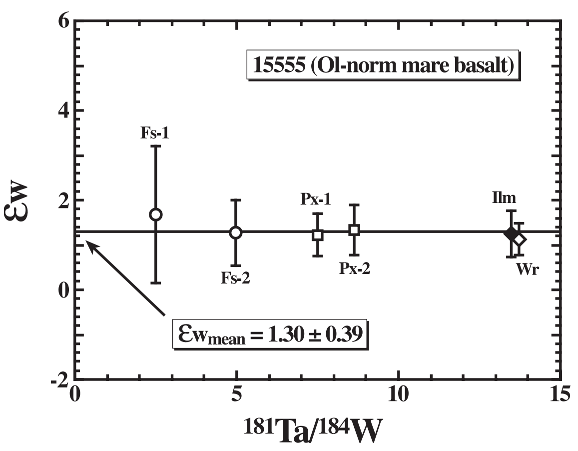

Fig. 2. Plot of ε_W versus ^{181}Ta/^{184}W for olivine–basalt 15555. The calculated mean ε_W was used to reflect the initial ε_W, and the quoted error reflects 2σ standard deviations. Fs = feldspar; Ilm = ilmenite; Px = pyroxenes; Wr = whole rock.

scale homogeneity was reached early in lunar history [30–32]. Given that the least radiogenic W found among lunar samples with low Ta/W and exposure age is chondritic, the radiogenic W is probably the result of decay of ^{182}Hf in the lunar mantle. The window of time in which the Moon could have formed with chondritic W while some differentiated high Hf/W reservoirs would still have been able to generate slightly radiogenic W is model dependent. However, it is most probably limited to 40–60 Myr after the start of the solar system [20], a conclusion also supported by the new W data. A less radiogenic W signature should correspond to result to a later formation time for the Moon. However, this is a small effect; the fact that any radiogenic ^{182}W is detected at all means that the Moon could not have formed much later than 60 Myr. Furthermore, some of the earliest lunar samples have been dated at around the same time [33–35].

The W data can also be used to place limits on the time-scales over which the high-Ti mare basalt source formed. Ilmenite is arguably the dominant phase on the Moon with exceedingly high Hf/W, and is also the last phase to have crystallized in the lunar magma ocean [24,36]. Because the Moon started with chondritic W, in principle, one can derive a single stage Hf–W model age [13] that marks the upper age limit for when the ilmenite layer formed, or the duration of the lunar magma ocean, if the Hf/W ratio in the high-Ti mare basalt source is known. Using the highest measured Hf/W ratio ($\sim$145; Table 1) one can define the maximum time that can have elapsed such that there was still sufficient ^{182}Hf in the high-Ti mare basalt to build up a radiogenic W signature of $\varepsilon_W = +4.7 \pm 3.0$ in the source of 75075 (Fig. 3). A Hf–W model age [13], the time at which the ilmenite layer differentiated from the chondritic Moon, of 62 ± 11 Myr, is obtained. Although model-dependent, this age indicates that differentiation and formation of high Hf/W ilmenite-rich layers occurred early. Therefore, the high-Ti mare basalt source formed within <30 Myr after the origin of the Moon. As ilmenite was the last phase to crystallize, this time window is short relative to conventional models of a lunar magma ocean [24]. Such an early formation age for the ilmenite layer is also in conflict with the Sm–Nd model age of KREEP dated at 4.32 ± 0.06 Ga (or $\sim 150 \pm 60$ Myr after the Moon formed [13,20]), which was also interpreted to mark the duration of the lunar magma ocean [37,38]. There is no clear resolution to the disagreement. However, the Nd model age of KREEP will overlap with that of the Hf–W model age if the lunar Nd evolved from a value that was slightly more radiogenic than chondritic, as hinted in the study of the ferroan anorthosite 60025 [34]. Before drawing these conclusions it must be emphasized that the Hf–W model age needs to be further refined with a more precise determination of the initial radiogenic W isotopic composition signature and the Hf/W ratio in the source of high-Ti mare basalts. Nevertheless, our estimate is in general agreement with several recent Nd and Hf isotopic studies that provide evidence indicating that a relatively short and localized lunar magma ocean was more likely than a protracted and long-lasted and global one [39,40].

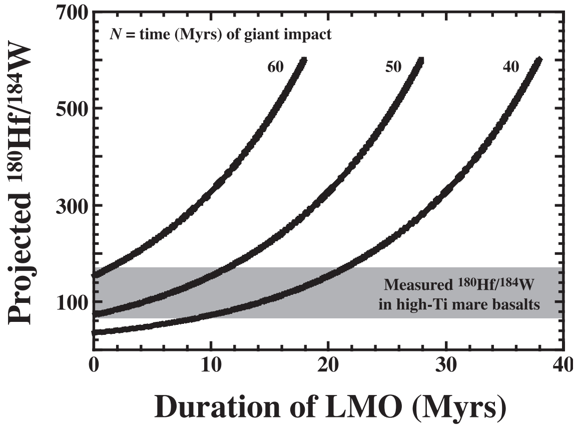

Fig. 3. Plot of projected ^{180}Hf/^{184}W in the high-Ti mare source regions versus the time (in Myr) required to built up a radiogenic W signature of $\varepsilon_W = +4.7$ observed in 75075 after the Moon formed. This timing is equivalent to the duration of the lunar magma ocean (LMO) since the lunar mantle will not acquire a sufficiently high Hf/W to develop the observed radiogenic W until the formation of ilmenite-rich layers at the end of the lunar magma ocean. Three calculations were made assuming the giant impact occurred at 40, 50 and 60 Myr after the solar system formed. The shaded area reflects the measured ^{180}Hf/^{184}W in the high-Ti mare basalts from this study, which should represent the minimum ^{180}Hf/^{184}W in their source regions.

4. Summary

All three Apollo-17 high-Ti mare basalts (70035, 75075 and 77516) display linear positive correlations between the measured W isotopic compositions and Ta/W ratio for different mineral phases within individual samples, confirming theoretical models that implicate the ^{181}Ta(n, γ)^{182}Ta(β^-)^{182}W reaction from cosmic irradiation as the most likely cause. All three high-Ti basalts show intercepts (at Ta/W = 0) of $\varepsilon_W \geq 0$, however, the uncertainty associated with the regression is quite significant in each case. Therefore, the exact radiogenic composition of the high-Ti mare basalt sources cannot be reliably deduced at this stage.

In contrast, all mineral phases and the whole rock of olivine–basalt 15555 show identical W isotopic compositions, despite variable Ta/W ratios, and the mean $\varepsilon_W = +1.3 \pm 0.39$ reflects a clearly resolvable radiogenic W signature on the Moon.

Due to its dynamic nature, it is inconceivable for any isotopic heterogeneities (radiogenic or stable) to have survived the Moon-forming giant impact and the subsequent lunar magma ocean [32]. Therefore, the radiogenic W signature on the Moon most likely reflects in situ decay of ^{182}Hf within the lunar mantle after its Hf/W was sufficiently enriched by the extraction of a low Hf/W crust and a small lunar core towards the cessation of lunar magma ocean. Using the measured W and Hf/W ratios in these mare basalts, the formation of the Moon is estimated at ca. 50 ± 10 Myr after the start of the solar system, identical to our previous estimates [13,19,20]. In addition, the duration of the lunar magma ocean is estimated to be no more than 30 Myr after the Moon formed.

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