No ^{182}W evidence for early Moon formation

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The Moon-forming giant impact was probably the last major event in Earth's accretion, so dating this event is critical for determining the timeline of terrestrial planet formation. Recently, Thiemens et al.[1] used the short-lived ^{182}Hf-^{182}W system to argue that the Moon formed within the first 60 million years (Myr) of solar system history. Here we demonstrate, however, that mixing processes during and after the giant impact modified the ^{182}W compositions of the Earth and Moon, hampering the use of the Hf-W system to date the Moon. Our results show that the lunar ^{182}W record is fully consistent with a recently determined, younger age of the Moon of 142±25 Myr after solar system formation[2].

Thiemens et al.[1] argued that the +26 parts-per-million (ppm) ^{182}W excess of the Moon over the present-day bulk silicate Earth (BSE)[3-5] must reflect decay of short-lived ^{182}Hf (half-life = 8.9 Myr), because the lunar mantle has a higher Hf/W ratio than the BSE. However, two conditions must be met in order to reliably use the Hf-W system to date Moon formation: (1) the BSE and Moon must have had the same initial ^{182}W composition, and (2) the ^{182}W compositions of the lunar and terrestrial mantles were not modified by processes other than *in-situ* ^{182}Hf-decay. However, mixing processes during the giant impact and subsequent 'late accretion' to the lunar and terrestrial mantles very likely modified ^{182}W compositions[3,4]. Thus, only because the Hf/W ratios of the lunar and terrestrial mantles are different, there is no reason to assume that their present-day ^{182}W difference is purely radiogenic. Surprisingly though, Thiemens et al.[1] used the *present-day* μ^{182}W difference between the BSE and Moon to date the giant impact, and they did not evaluate whether the two aforementioned conditions are met.

Late accretion (the addition of broadly chondritic material to planetary mantles following core formation) can account for the highly siderophile element (HSE) budget of the BSE. Late accretion also occurred on other planetary bodies, and may be viewed as a natural stage of planetary formation, where leftover planetesimals continued to bombard planets[6]. The mass of late-accreted material is generally estimated from mantle HSE abundances and, in the case of Earth, corresponds to $(4.8\pm1.6)\times10^{-3}$ Earth masses ($M_{\oplus}$)[6]. Mass balance indicates that late accretion of this mass lowered the BSE's μ^{182}W (the ppm deviation from the terrestrial standard), where the exact effect depends on (1) the BSE's W concentration, (2) the chemical and ^{182}W composition of the late-accreted material, and (3) the late-accreted mass. All these parameters have inherent uncertainties, which propagate into the final uncertainty on the BSE's calculated pre-late accretion μ^{182}W. Taking these uncertainties into account reveals that this value is likely between ~10 and ~40 ppm (Fig. 1). The blue-shaded area in Figure 1 indicates the uncertainty introduced solely by the uncertainty on the BSE's W concentration (12±4 ng/g, ref. 7), demonstrating that even if the mass and composition of the late-accreted material were known exactly, significant uncertainty on the BSE's pre-late accretion μ^{182}W remains. For completeness we emphasize that this conclusion, and the inferred pre-late accretion μ^{182}W of BSE, is entirely independent of whether μ^{182}W anomalies in some terrestrial rocks reflect late accretion[8,9] or early Earth differentiation[10].

The HSE-derived late-accreted mass for the Moon is about three orders of magnitude lower than for Earth, and so the resulting effect on the lunar μ^{182}W was much smaller (~1 ppm)[3-5]. However, the Moon's late-accreted mass may have been ~10 times larger than the HSE-derived estimate, because some late accretion-derived HSE were removed to the lunar core[11]. It has also been argued that due to megaregolith contamination of lunar samples, HSEs provide no firm estimate on the amount of late-accreted material on the Moon[12]. Consequently, to better assess the effect of late accretion on the lunar μ^{182}W, it is useful to estimate the Moon's late-accreted mass *independent* of HSE measurements. A theoretical upper bound of the Moon's late-accreted mass may be obtained from the Earth/Moon impact flux ratio, which is ~20 (ref. 11). Using this ratio, and Earth's late-accreted mass of $\sim4.8\times10^{-3}$ $M_{\oplus}$, results in an expected impact flux to the Moon of $\sim2.4\times10^{-4}$ $M_{\oplus}$. However, for the Moon the impactor retention ratio (the fraction of impactor material remaining on the target) is only ~0.2, much lower than for Earth, which is commonly assumed to retain the impactor material completely[13]. Thus, of the putative $\sim2.4\times10^{-4}$ $M_{\oplus}$ impacting the Moon, only $\sim4.8\times10^{-5}$ $M_{\oplus}$ would be accreted. Moreover, the Earth/Moon impact flux ratio was likely larger than 20, because Earth samples the large-size end of the projectile distribution more efficiently than the Moon[11]. For instance, for an asteroid-like size distribution of the projectiles the Earth/Moon impact flux ratio would be ~100 (ref. 11), resulting in a lower estimated late-accreted mass for the Moon of $\sim1\times10^{-5}$ $M_{\oplus}$. We, therefore, conclude that while 4.8×10^{-5} $M_{\oplus}$ is a strict upper limit for the Moon's late-accreted mass, this mass was likely smaller.

Using these estimates, the calculated μ^{182}W difference between the pre-late accretion BSE and Moon overlap for the entire range of possible late-accreted masses on the Moon (Fig. 2). Consequently, the inherent uncertainties on the effect of late accretion on μ^{182}W make it impossible to confidently resolve a pre-late accretion μ^{182}W difference between the BSE and

Moon. As such, there is no resolved radiogenic $\mu^{182}W$ excess in the Moon and, therefore, no firm evidence for formation of the Moon during the lifetime of ^{182}Hf.

For the sake of argument, let us now assume that the Moon *has* a pre-late accretion $\mu^{182}W$ excess over the BSE. This putative $\mu^{182}W$ excess would then most likely be inherited from the giant impactor, because mixing of the giant impactor's mantle and core with proto-Earth's mantle is expected to have led to a $\mu^{182}W$ excess in the Moon for a wide range of impact parameters and compositions[3,14]. Note that the Earth-Moon isotopic similarity for elements such as O, Cr, and Ti by no means implies that the BSE and Moon also had the same initial ^{182}W composition[3,14]. The reason for this is that ^{182}W variations reflect the timing and mechanism of core formation, whereas O-Cr-Ti isotopes reflect the source region of an object. Thus, even if the Moon formed entirely from proto-Earth's mantle or if the impactor derives from the same nebula feeding zone as Earth—both of which would naturally account for the Earth-Moon isotopic similarity for elements such as O, Cr, and Ti—the Moon would still be expected to have a ^{182}W excess. This is because the Moon and BSE inevitably contain different proportions of impactor mantle, impactor core, and proto-Earth mantle, all of which had distinct ^{182}W compositions[3,14]. It may be possible that the Earth-Moon ^{182}W difference was erased during post-giant impact equilibration, but the efficiency of this process for W, and whether it would have homogenized ^{182}W at the <10 ppm level, is unknown[14,15].

We conclude that two crucial requirements for placing Moon formation within the ~60 Myr lifetime of ^{182}Hf are not fulfilled. First, the essential requirement of initial $\mu^{182}W$ homogeneity may not be a given, because mixing of proto-Earth and impactor material during the giant impact led to distinct initial ^{182}W compositions of the Moon and BSE. Second, the pre-late accretion ^{182}W compositions of the Moon and BSE overlap within uncertainty, and hence there is no resolved radiogenic ^{182}W difference between the BSE and the Moon. The Hf-W systematics are, therefore, consistent with the recently determined 'young' age of the Moon of 142±25 Myr age after solar system formation[2], well after the effective lifetime of ^{182}Hf.

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Figure captions:

Fig. 1: Effect of late accretion on the BSE's $\mu^{182}W$. Blue shaded area shows uncertainty on the BSE's pre-late accretion $\mu^{182}W$ that solely arises from the uncertainty on the BSE's W concentration (12±4 ppb); for the mass (4.8×10^{-3} $M_\oplus$) and composition of the late-accreted material (W = 150 ppb, $\mu^{182}W$ = –190) fixed average values were used. Yellow area shows additional uncertainty arising from uncertainties in the late-accreted mass [$(4.8\pm1.6)\times10^{-3}$ $M_\oplus$]. When also including the uncertainty on the composition of the late-accreted material (see Fig. 2), the BSE's pre-late accretion $\mu^{182}W$ may be as high as ~+50 ppm. The $\mu^{182}W$ of the Moon is shown at its HSE-derived late-accreted mass fraction, and plots well within the range of calculated pre-late veneer ^{182}W compositions of the BSE.

Fig. 2: Calculated $\mu^{182}W$ difference between the Moon and the BSE prior to late accretion as a function of the late-accreted mass added to the Moon. Pre-late accretion $\mu^{182}W$ values were calculated by mass balance using a Monte Carlo approach, and assume 12±4 ppb W in the BSE and the lunar mantle (varied independently), a late-accreted mass on Earth of $(4.8\pm1.6)\times10^{-3}$ $M_\oplus$, a maximum late-accreted mass of 4.8×10^{-5} $M_\oplus$ on the Moon (see text for details), a chondritic composition of the late-accreted material ($\mu^{182}W$ = –190±10; W = 150±50 ppb), and a present-day lunar $\mu^{182}W$ = 26+3. Blue dots represent individual trials in the Monte Carlo simulation, where the parameters were varied randomly within their respective bounds.