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Tungsten isotopic constraints on the origin and evolution of the Moon

T. S. Kruijer, T. Kleine

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Origin and evolution of the Moon, Tungsten isotopic constraints

Thomas S. Kruijer^{1,2} and Thorsten Kleine¹

¹University of Münster, Institut für Planetologie, Wilhelm-Klemm-Strasse 10, 48149 Münster, Germany.

²Lawrence Livermore National Laboratory, Nuclear and Chemical Sciences Division, 7000 East Avenue (L-231), Livermore CA, 94550, USA

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1 Introduction

The Moon most likely formed as the result of a collision between the proto-Earth and a differentiated body possibly the size of Mars (Cameron and Benz, 1991; Hartmann and Davis, 1975). The enormous amount of energy released by this giant impact caused widespread melting on the proto-Earth and the ejection of material into Earth's orbit from which the Moon subsequently accreted. Upon accretion of the Moon, the lunar mantle underwent global silicate differentiation most likely facilitated by a lunar magma ocean (e.g. Wood et al., 1970). Magma ocean crystallization likely produced the wide diversity of lunar source rocks and involved the successive crystallization of mafic cumulates consisting of olivine and pyroxene, followed by crystallization of plagioclase which floated to the lunar surface to form the lunar crust consisting of ferroan anorthosites (FAN). Finally, the residual liquid of the lunar magma ocean represents a separate component within the Moon termed KREEP (enriched in Potassium K, Rare Earth Elements, and Phosphorous). Re-melting of these magma ocean crystallization products of the low-Ti and high-Ti mare basalt source regions as well as the formation of Mg-suite lunar highland rocks.

Although a giant impact followed by magma ocean differentiation can account for most geochemical observations of lunar rocks, the origin and subsequent evolution of the Moon remain hotly debated. Nevertheless, our understanding of lunar evolution has been greatly enhanced by isotopic studies of lunar samples. In this chapter, we will review key insights about the evolution of the Moon as provided by isotope studies of lunar samples based on the element tungsten (W). Below we will first revisit the general principles of the short-lived ^{182}Hf - ^{182}W system and then present a brief historical overview of W isotope studies on lunar samples. Finally, we will present several key findings based on W isotopes regarding the timescales of lunar magma ocean differentiation, late accretion onto the Earth and Moon, and the origin of the Moon.

2 Key principles: Tungsten isotopes and the Hf-W chronometer

Tungsten ($Z=74$) is a refractory element with five stable isotopes (^{180}W , ^{182}W , ^{183}W , ^{184}W and ^{186}W). The radioactive decay of now extinct ^{182}Hf ($t_{1/2} \sim 8.9$ million years, Ma) to ^{182}W provides a chronometer for dating chemical processes that fractionate Hf and W during the first ~ 60 Ma of solar system history (see e.g. Kleine and Walker, 2017 and references therein). This time interval is particularly suited for studying the accretion and differentiation histories of planetary bodies in the inner solar system. Given that W, a moderately siderophile element, is largely partitioned in the metallic core of a planet, and Hf, a lithophile element, is retained in the silicate mantle, strong Hf/W fractionations occur during metal-silicate separation. Thus, following metal-silicate separation, the mantle and core of a planetary body develop markedly distinct ^{182}W signatures over time (Fig. 1). As such, the Hf-W system is ideally suited for examining the timescales of planetary core formation. Moreover, because of the different partitioning of Hf and W during silicate differentiation (Righter and Shearer, 2003), additional ^{182}W variations can be generated during early mantle differentiation processes such as magma ocean crystallization and crust formation (see e.g. Kleine and Walker, 2017). Finally, variations in ^{182}W may not only be used to study the timescales of core formation and silicate differentiation on planetary bodies, but, as will be shown below, can also provide key insights into the origin and evolution of the Moon.

3 Tungsten isotope studies of lunar samples

Over the past decades several studies have focused on determining the W isotope composition of lunar samples. The first of these found large and variable ^{182}W excesses in different lunar source lithologies (Lee et al., 1997). These ^{182}W variations were initially interpreted to result from radioactive decay of

^{182}Hf within the Moon, in which case the Moon would have formed and differentiated within the lifetime of ^{182}Hf , that is, within the first ~ 60 Ma of the solar system. However, subsequently it was recognized that ^{182}W variations among lunar samples at least to some degree are caused by superimposed secondary neutron capture effects resulting from the interaction of the lunar samples with galactic cosmic rays (Leya et al., 2000). As most lunar samples have been exposed to galactic cosmic rays for an extended time period, these effects can potentially be very large. The governing neutron capture reaction, $^{181}\text{Ta}(n,\gamma)^{182}\text{Ta}(\beta^-)^{182}\text{W}$, illustrates that such neutron capture effects not only depend on the neutron fluence of a sample but also on its Ta/W, leading to overall excesses in $^{182}\text{W}/^{184}\text{W}$. To account for these cosmogenic effects, subsequent W isotope studies of lunar samples employed different approaches to account for the effects of neutron capture (Kleine et al., 2005; Lee et al., 2002). One successful approach has been the analyses of lunar metal samples, which do not contain any Ta-derived cosmogenic ^{182}W (Kleine et al., 2005; Touboul et al., 2007). Using this approach applied to metal separates from mare basalts and KREEP-rich breccias, Touboul et al. (2007) found that there are no resolvable ^{182}W variations within the Moon, and that the ^{182}W composition of the Moon is indistinguishable from that of terrestrial rock standards (Fig. 2).

In recent years analytical improvements invoked another revival of W isotope studies in lunar samples. Tungsten isotope analyses utilizing multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) or thermal ionization mass spectrometry (TIMS) now routinely provide a measurement precision on W isotope ratios of ~ 5 parts-per-million (2σ); this is a five to ten-fold improvement in measurement precision compared to earlier studies. Accordingly, recent studies on lunar samples have employed high-precision W isotope measurements combined with novel ways to quantify the effects of secondary neutron capture. In particular, Kruijer et al. (2015) performed high-precision W isotope measurements on KREEP-rich samples by MC-ICPMS and used Hf isotopes as an empirical dosimeter to quantify the effects of secondary neutron capture. Touboul et al. (2015) performed high-precision W isotope measurements by NTIMS and analyzed large metal fractions of KREEP-rich samples to circumvent cosmogenic effects. Despite using different measurement techniques and approaches to quantify cosmogenic effects, both studies identified a small excess in $\mu^{182}\text{W}$ of *ca.* +26 ppm for KREEP-rich samples relative to the Earth's mantle (where $\mu^{182}\text{W}$ is the parts-per- 10^6 deviation in $^{182}\text{W}/^{184}\text{W}$ from terrestrial standard values) (Fig. 2). Note that these new $\mu^{182}\text{W}$ results are consistent with the earlier metal data from Touboul et al. (2007), but are significantly more precise, explaining why such ^{182}W excesses were not detected in the earlier study. In a subsequent study, Kruijer and Kleine (2017) found that low-Ti and high-Ti mare basalts, as well as Mg suite norite 77215 and lunar meteorite Kalahari 009 also exhibit similar excesses in $\mu^{182}\text{W}$ (Fig. 3). Taken together, these data therefore imply that (i) the bulk silicate Moon exhibits a uniform excess in $\mu^{182}\text{W}$ of *ca.* +26 ppm relative to the present-day bulk silicate Earth (Fig. 3), and (ii) that there is currently no evidence for resolvable ^{182}W variations within the lunar mantle, even at a very high level of precision.

4 Key research findings

4.1 Timescales of lunar differentiation

Crystallization of the lunar magma ocean led to distinct mantle reservoirs with markedly different Hf/W, where the source of high-Ti mare basalts is thought to be characterized by the highest (Hf/W of ~ 40 – 80) and KREEP by the lowest ratios (Hf/W ~ 10 – 20) (e.g., Kleine et al., 2005; Righter and Shearer, 2003; Touboul et al., 2007). Hence, if magma ocean crystallization occurred within the lifetime of ^{182}Hf , then these reservoirs should have evolved to distinct $\mu^{182}\text{W}$ over time. As such, the $\mu^{182}\text{W}$ compositions of different lunar source lithologies can be used to shed light on the timescales for the solidification of the magma ocean. However, all lunar samples for which cosmogenic ^{182}W effects have been quantified,

including low-Ti and high-Ti mare basalts, KREEP, Mg-suite norites and lunar meteorites, have indistinguishable pre-exposure $\mu^{182}\text{W}$ values (Fig. 3). The homogeneous $\mu^{182}\text{W}$ of lunar rocks despite the large range of source Hf/W ratios demonstrates that lunar differentiation occurred after the effective lifetime of ^{182}Hf , more than ~ 70 Ma after solar system formation, *i.e.* later than ~ 4.5 Ga (Kruijer and Kleine, 2017). This timescale is consistent with the 4.35–4.37 Ga ages derived for the major period of lunar differentiation using other dating methods. For instance, both the Sm–Nd isochron ages for lunar crustal rocks, the Sm–Nd and Lu–Hf model ages of KREEP, and the average Sm–Nd model age of the mare basalt sources, as well as a peak in Pb–Pb ages observed in lunar zircons all appear to converge at 4.35–4.37 Ga (see summary in Borg et al., 2015 and references therein). Collectively, these relatively young ages, combined with the lack of ^{182}W heterogeneity in the Moon, support the idea that the major period of differentiation on the Moon occurred relatively late. Note that such a late differentiation of the Moon only marginally overlaps the results of a recent Hf isotope study on lunar zircons which suggested that lunar differentiation may have occurred earlier, within *ca.* 60 Ma after CAIs (Barboni et al., 2017). The exact reason for this apparent discrepancy remains unclear, and resolving this issue will require a better understanding of the significance of the old inferred ages for individual lunar zircon grains versus the model ages inferred for large geochemical reservoirs on the Moon.

4.2 Origin of ^{182}W excess in the Moon

All lunar rock types investigated so far exhibit a uniform ^{182}W excess of *ca.* +26 ppm relative to the present-day bulk silicate Earth. This ^{182}W difference can in principle have three different origins. One option is that the ^{182}W excess is radiogenic in origin. This would require that the Earth and the Moon have different Hf/W and that the Moon formed within the lifetime of ^{182}Hf . However, the Hf/W of both the terrestrial and lunar mantles are not well defined, and as such it is currently unclear if these ratios are sufficiently different to produce a resolvable ^{182}W difference. Moreover, independent estimates for the age of the Moon strongly suggest that the Moon formed after the life-time of ^{182}Hf , making it quite unlikely that the ^{182}W excess of the Moon is radiogenic in origin. The second possibility is that the ^{182}W difference was generated during the giant impact and reflects a larger fraction of impactor material within the Moon. As discussed below (Section 4.3), such an ^{182}W excess is in fact predicted in the giant impact model for lunar origin. A corollary of this is that identifying any potential radiogenic ^{182}W excess in the Moon is merely impossible, because there is currently no way to distinguish such a signature from an ^{182}W difference generated during the giant impact.

The third possibility to explain the ^{182}W difference between the Moon and the present-day bulk silicate Earth is disproportional late accretion. Late accretion is defined as the ‘late’ addition of on average broadly chondritic material to the lunar and terrestrial mantles following the formation of the Moon and the end of core formation on Earth. Evidence for this ‘late veneer’ comes from the inferred abundances of highly siderophile elements (HSE) in the mantles of the Earth and the Moon. For both bodies, the HSE mantle abundances are higher than expected for metal-silicate equilibration during core formation. If the late veneer hypothesis is correct, then addition of such a late veneer would have led to a $\mu^{182}\text{W}$ difference between the Earth and the Moon, because (i) the late veneer material had a different $\mu^{182}\text{W}$ value to that of the bulk silicate Earth, and (ii) HSE evidence suggests that proportionally more late veneer material was added to the Earth than to the Moon (e.g. Day and Walker, 2015). The studies by Kruijer et al. (2015) and Touboul et al. (2015) both showed that the $\sim +26$ ppm ^{182}W excess in the Moon is remarkably consistent with the expected ^{182}W difference resulting from disproportional late accretion, with a total mass and composition inferred from HSE systematics (Fig. 4). Thus, the $\mu^{182}\text{W}$ anomaly in the Moon does not only provide strong support for the late veneer hypothesis, but also implies that the HSE budget of the bulk silicate Earth was set after the giant impact and core formation, implying that any previously accumulated HSE in the proto-Earth's mantle have been removed by metal

segregation during the giant impact. In detail, the magnitude of the effect of late accretion on $\mu^{182}\text{W}$ depends on the mass and composition assumed for the late veneer as well as on the W concentration of the pre-late veneer BSE. As such the calculated pre-late veneer $\mu^{182}\text{W}$ of the BSE may have been between *ca.* +10 and +50 ppm (Kleine and Walker, 2017). Thus, the $\sim +26$ ppm ^{182}W excess of the Moon is well within the range of expected compositions for the pre-late veneer BSE, meaning that no resolvable $\mu^{182}\text{W}$ difference between the pre-late veneer BSE and the Moon remains once the effects of late accretion are taken into account. As a result, there is currently neither strong evidence for a $\mu^{182}\text{W}$ signature from the impactor in the Moon nor for the existence of a radiogenic $\mu^{182}\text{W}$ difference between the Earth and the Moon.

4.3 Constraints on the origin of the Moon

The close agreement between the predicted late-veneer-induced $\mu^{182}\text{W}$ shift and that observed between the present-day BSE and the Moon implies that, prior to addition of the late veneer, the Earth's mantle and the Moon had indistinguishable $\mu^{182}\text{W}$ values. This $\mu^{182}\text{W}$ similarity between the Earth and the Moon is consistent with the isotopic homogeneity observed for other elements such as Ti, Si, and O (e.g., Wiechert et al., 2001; Zhang et al., 2012; Armytage et al., 2012). The latter might reflect that the proto-Earth and the impactor derive from an isotopically homogeneous reservoir (e.g., Dauphas et al., 2014) or that the Moon formed either from proto-Earth mantle material (e.g., Čuk and Stewart, 2012), or from equal portions of the mantles of two colliding half-Earths (Canup, 2012). However, such mechanisms cannot easily account for the similarity in $\mu^{182}\text{W}$. This is because unlike Ti, Si and O, $\mu^{182}\text{W}$ variations do not reflect a particular mix of presolar and solar nebula components in the precursor materials of the Earth and impactor, but instead reflect radiogenic ingrowth in the mantles of the proto-Earth and impactor following core formation in these bodies. As the accretion and core formation histories of the proto-Earth and impactor were likely different, the mantles of these two bodies should, therefore, have different ^{182}W compositions. In the context of the giant impact model the Moon can be considered a three-component mixture consisting of (i) impactor mantle, (ii) impactor core, and (iii) proto-Earth mantle. Given that these components likely each have distinct $\mu^{182}\text{W}$ and are mixed in random proportions during the giant impact, producing similar $\mu^{182}\text{W}$ between the Earth's mantle and the Moon seems very unlikely (Kruijer et al., 2015). Nevertheless, Dauphas et al. (2014) used an inversion model to illustrate that the lunar $\mu^{182}\text{W}$ composition can be reproduced for $\mu^{182}\text{W}$ and Hf/W values of the impactor mantle that are expected for planetary embryos that formed early in Solar System history. Similarly, Wade and Wood (2016) showed that, provided that the Moon predominantly derives from the proto-Earth's mantle, the lunar $\mu^{182}\text{W}$ composition can be explained by a giant impact of a strongly reduced impactor onto an oxidized proto-Earth. Nevertheless, while the above two studies demonstrate that the $\mu^{182}\text{W}$ similarity between the Earth and the Moon can in principle be produced in a giant impact, they have to resort to happenstance to account for the close similarity in $\mu^{182}\text{W}$ between the Earth and Moon.

To better assess the significance of the nearly identical ^{182}W compositions of Earth's mantle and the Moon immediately after the giant impact, Kruijer and Kleine (2017) calculated the expected ^{182}W composition of the Moon in various giant impact scenarios using a mixing model. This was done by randomly varying several key parameters, including the metal-silicate partition coefficients for W in the Earth and the impactor, the time of core formation in the impactor, the impactor-to-Earth mass ratio and the fraction of impactor core material in the Moon. The results of these calculations demonstrate that the Earth–Moon ^{182}W similarity is an unlikely outcome of any giant impact (Fig. 5), which regardless of the amount of impactor material incorporated into the Moon should have generated a significant ^{182}W excess in the Moon (most likely more than +100 ppm). Conversely, the probability of producing indistinguishable $\mu^{182}\text{W}$ is very small, only $\sim 5\%$ if the Moon predominantly consists of proto-

Earth material and ~1% if the Moon largely derives from the impactor (Fig. 5). As a result, regardless of which giant impact scenario is assumed, the $\mu^{182}\text{W}$ similarity is an unlikely outcome of the giant impact. Consequently, post-giant impact processes modifying the $\mu^{182}\text{W}$ value of the Moon seem to be required. This can be accomplished if the post giant impact state of the Earth–Moon system facilitated efficient isotopic homogenization, even for refractory elements like W (Pahlevan and Stevenson, 2007; Zhang et al. 2012), as may be the case for high-energy, high angular momentum giant impacts (e.g. Lock and Stewart, 2017). Alternatively, the lunar $\mu^{182}\text{W}$ value was modified by large, secondary impact(s) on the Moon after the giant impact.

5 Conclusions and outlook

Tungsten isotope studies on lunar samples demonstrate that there are no resolvable ^{182}W within the Moon, implying that lunar differentiation occurred later than ~70 Ma after Solar System formation. Nevertheless, the Moon is characterized by a uniform ^{182}W excess over the present-day BSE, which is most easily explained by disproportional late-accretion onto the Earth and Moon. After accounting for this effect, the ^{182}W signatures of the pre-late veneer BSE and Moon are indistinguishable, however. This ^{182}W similarity is an unlikely outcome of the giant impact, which should have generated a significant ^{182}W difference between the Earth and Moon. Thus, post giant impact processes appear required that modified the lunar ^{182}W composition.

To better understand the ^{182}W similarity between the Earth and the Moon future studies should focus on better constraining the composition of the late veneer as well as the relative masses of late accretion added to the Earth and Moon. For instance, it will be important to assess whether the low HSE abundances inferred for the lunar mantle truly reflect a low influx of late accreted material or instead internal processes on the Moon. Another research avenue that should be explored are secondary processes that may have modified the ^{182}W value of the Moon such as large secondary impacts. If the core of such an impactor directly merged with the lunar core, then such secondary impacts may have modified the ^{182}W of the lunar mantle without disturbing its HSE record. Finally, obtaining independent estimates for the pre-late veneer ^{182}W composition of the Moon would be desirable. Such estimates can potentially be derived by studying the ^{182}W systematics of terrestrial rocks with variable contributions of late veneer material.

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Figures:

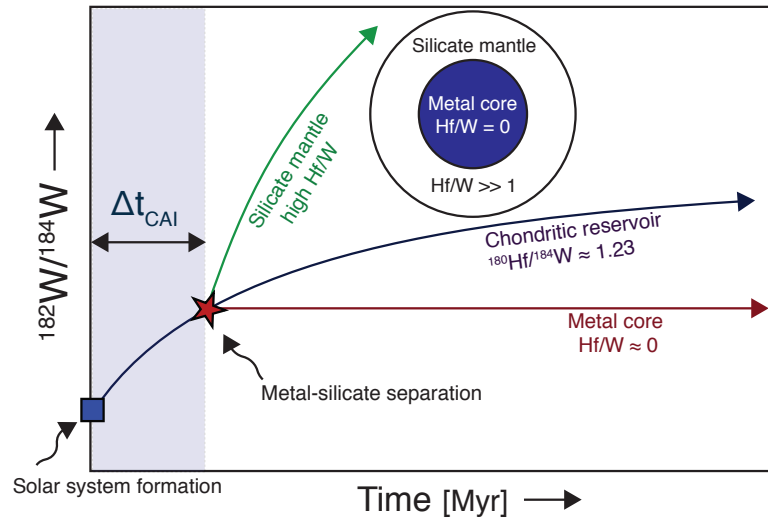


Fig. 1: Explanatory diagram showing $^{182}\text{W}/^{184}\text{W}$ vs. time with evolution lines for reservoirs with distinct $^{180}\text{Hf}/^{184}\text{W}$. Upon metal-silicate separation (red star) in a planetary body at a given time after Solar System formation (blue square), the silicate mantle (high Hf/W) follows a steeper trajectory than the chondritic reservoir, whereas the metal core ($\text{Hf}/\text{W} \approx 0$) retains the $^{182}\text{W}/^{184}\text{W}$ of the bulk body acquired at the time core formation. Shaded area denotes the time interval between a metal-silicate separation event and Solar System formation, as defined by the formation of Ca-Al-rich inclusions (CAIs).

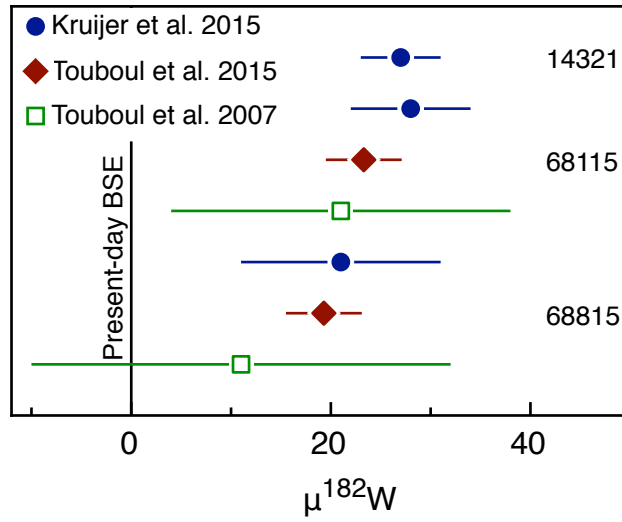
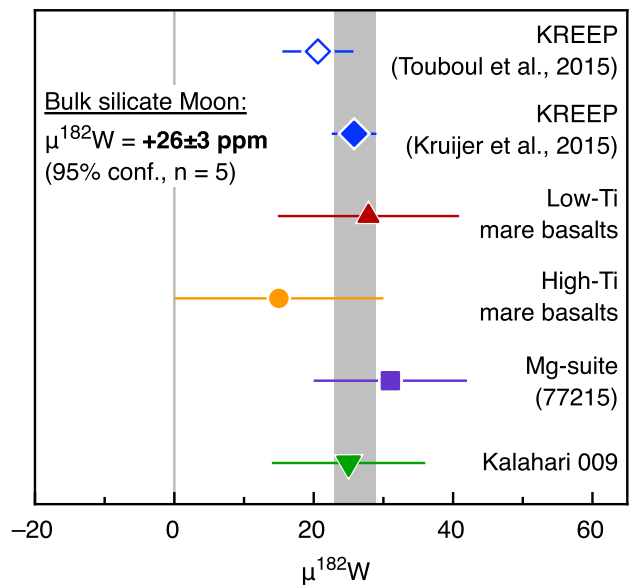


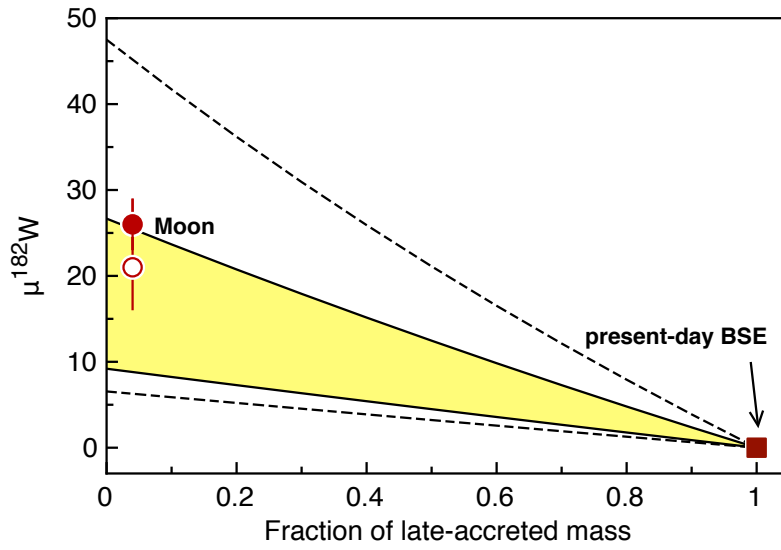
Fig 2: Comparison of $\mu^{182}\text{W}$ data for KREEP-rich samples 14321, 68115, and 68815 obtained in three different W isotope studies. These three samples are devoid of neutron capture effects as reflected by the absence of Hf isotope anomalies in these samples (Kruijer et al., 2015).

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Fig. 3. Pre-exposure $\mu^{182}\text{W}$ of different lunar rock types. Error bars denote external uncertainties (95% conf.) on pre-exposure $\mu^{182}\text{W}$. Hashed area shows the weighted mean $\mu^{182}\text{W}$ value and the associated 95% conf. limits. Data sources: Touboul et al. (2015), Kruijer et al. (2015), and Kruijer and Kleine (2017). Figure adopted from Kruijer and Kleine (2017).



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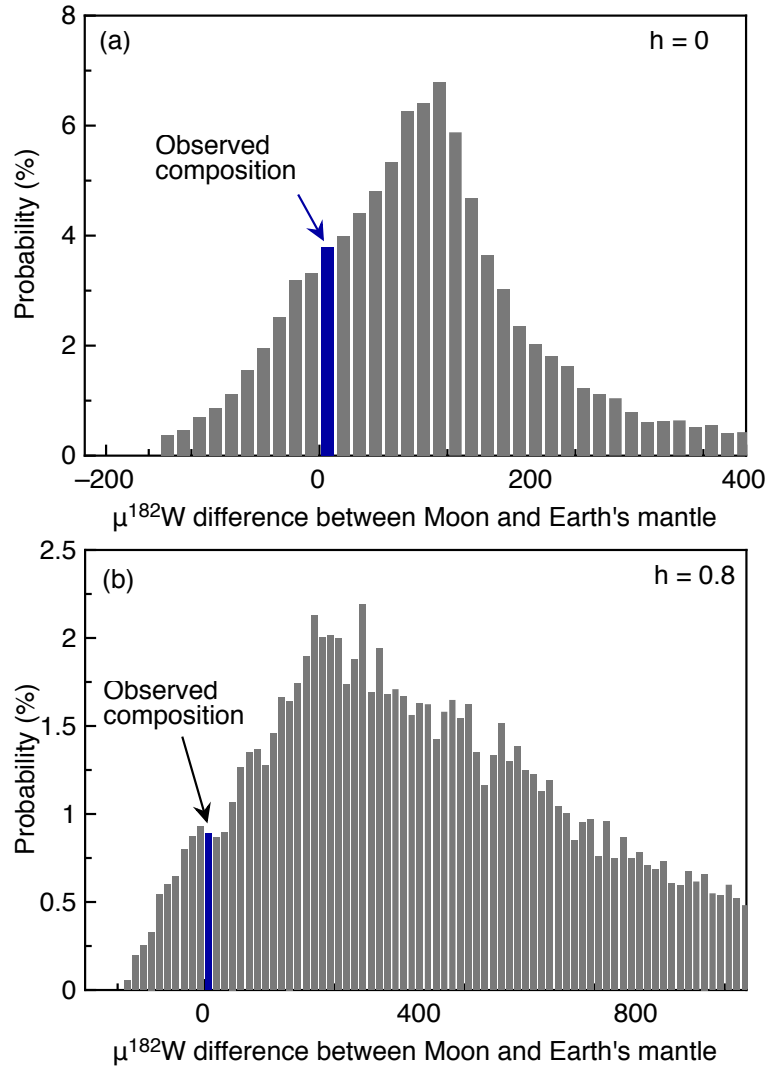
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Fig. 4: $\mu^{182}\text{W}$ versus the mass fraction of the late veneer on Earth. Mass balance calculations (yellow envelope) predict a positive $\mu^{182}\text{W}$ signature if the full complement of late accretion is subtracted from the present-day bulk silicate Earth (BSE; *right red square*) [assuming a W concentration of 200 ppb and $\mu^{182}\text{W} = -190$ for chondrites; and a late veneer complement in the present-day BSE between 3 and 8 wt%]. Dashed lines illustrate the additional uncertainty introduced when also considering the uncertainty on the W concentration of the BSE of 13 ± 5 ppb. The predicted $\mu^{182}\text{W}$ is consistent with the observed $\mu^{182}\text{W}$ value of the Moon [*solid red circle*, value for bulk silicate Moon from Kruijer and Kleine (2017) and Kruijer et al. (2015) and *open red circle*, value for KREEP from Touboul et al. (2015)]. Figure modified after Kruijer et al. (2015) and Kleine and Walker (2017).

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Fig. 5: Histograms showing the predicted $\mu^{182}\text{W}$ difference between the Moon and Earth's mantle. Shown are the result for two different giant impact scenarios (*a*, *b*), each involving a different mass fraction of impactor mantle (*h*) within the Moon. The observed ^{182}W composition of the Moon is shown for comparison. Figure modified after Kruijer and Kleine (2017).