

A Review of the Lunar ^{182}Hf - ^{182}W Isotope System Research

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Abstract: In recent years, the extinct nuclide ^{182}Hf - ^{182}W system has been developed as an essential tool to date and trace the lunar origin and evolution. Despite a series of achievements, controversies and problems exist. As a review, this paper details the application principles of the ^{182}Hf - ^{182}W isotope system and summarizes the research development on W isotopes of the Moon. A significant radiogenic $\epsilon^{182}\text{W}$ excess of 0.24 ± 0.01 was found in the lunar mantle, leading to heated debates. There are three main explanations for the origin of the excess, including (1) radioactive origin; (2) the mantle of the Moon-forming impactor; and (3) disproportional late accretion to the Earth and the Moon. Debates on these explanations have revealed different views on lunar age. The reported ages of the Moon are mainly divided into two views: an early Moon (30–70 Ma after the solar system formation); and a late Moon (>70 Ma after the solar system formation). This paper discusses the possible effects on lunar ^{182}W composition, including the Moon-forming impactor, late veneer, and Oceanus Procellarum-forming projectile. Finally, the unexpected isotopic similarities between the Earth and Moon are discussed.



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1. Introduction

A widely accepted hypothesis of lunar origin involves a “giant impact” between the proto-Earth (the Earth before the giant impact) and a Mars-sized impactor (generally named “Theia”) at about 4.5 Ga [1–3]. According to this hypothesis, an Earth-orbiting magma disk was formed by ejected materials from the proto-Earth’s mantle, the impactor’s mantle, and the impactor’s core. Subsequently, it accreted gravitationally to form the Moon [3–5]. Although the giant impact hypothesis has been developed over more than four decades [6–9], many controversial problems exist. Because of samples returned by the Apollo missions, a great deal of lunar research has been carried out since the 1990s. With the improvement of analytical technology, the ^{182}Hf - ^{182}W short-lived isotopic system has become an essential tool for lunar research. Hafnium (Hf) is a strongly lithophile, refractory, and incompatible element in silicate melt, while tungsten (W) is a moderately siderophile, refractory, and highly incompatible element. In particular, the extinct nuclide ^{182}Hf decays to ^{182}W with a half-life of 8.9 ± 0.09 Ma [10]. These unique geochemical properties of Hf and W make the ^{182}Hf - ^{182}W system a sensitive tracer for lunar origin [11–15] and a high-resolution chronometer for lunar formation and the subsequent differentiation [11,16–19]. In recent years, the ^{182}Hf - ^{182}W system has been used in solving problems related to lunar origin and evolution, combined with highly siderophile elements (HSEs, including Au, Re, Pd, Pt, Rh, Ru, Ir, and Os) and other stable elements (e.g., O, Si, Ti, Cr, V) [14,15,20–23]. Despite a series of achievements, the study of the ^{182}Hf - ^{182}W system is still in its infancy with many unsolved problems and disputes, concerning both its basic application principles and its

application on the Moon [1–5]. In this review article, we introduce the application principles of the ^{182}Hf - ^{182}W isotope system and present high-precision W-isotope measurements in lunar rocks. Moreover, we discuss the controversies in the studies of the giant impact hypothesis, late veneer hypothesis, and isotopic similarity between the Earth and Moon.

2. Application Principles of the ^{182}Hf - ^{182}W Isotope System

2.1. Basic Principles

There are five naturally occurring W isotopes (Table 1), of which ^{182}W can be formed by the β^- decay of radionuclide ^{182}Hf . In addition, ^{182}W can also be formed by an α decay of radionuclide ^{186}Os with an extremely long half-life (2×10^{15} years); therefore, the ^{182}W productivity should be ignored. Compared to other W stable isotopes, ^{182}W abundances in reservoirs depend on their initial Hf/W ratios and the time of Hf/W fractionation.

Table 1. The isotopic composition of tungsten in the Earth (modified after [24]).

	^{180}W	^{182}W	^{184}W	^{184}W	^{186}W
Abundance (%)	0.1194	26.498	14.313	30.641	28.428
$^{182}\text{W}/^{184}\text{W}$	0.00390 ± 2	0.86478 ± 4	0.467119	1	0.92776 ± 2

i: the mass number of W isotopes.

As Hf and W are highly refractory elements with 50% condensation temperatures (T_{50}) of 1684 °C and 1783 °C, respectively [25], Hf/W underwent little fractionation in the solar system, resulting in a uniform initial Hf/W ratio among various planetary bodies. This value is the same as that of the Chondritic Uniform Reservoir (CHUR), which is thought to represent the initial isotopic composition of the solar system. Hf was entirely retained in the silicate phases during core–mantle separation, while about 90% of W was partitioned into the metal phases [26], resulting in strong Hf/W fractionations. Enhanced Hf/W ratios and reduced Hf/W ratios were then generated in planetary silicate mantles and metallic cores, respectively. If the core formation took place in the lifetime of ^{182}Hf , a significant excess of radiogenic ^{182}W would develop in the mantle, while a deficit would develop in the core. The degree depends on the metal–silicate partition coefficient for W. In addition, during the crystal–liquid differentiation processes, W is more incompatible and, unlike Hf, prefers liquid phases, resulting in a further Hf/W fractionation. Discrepant Hf/W ratios are particularly evident in lunar rocks. For example, lunar mare basalts have the highest Hf/W of 25–50, while lunar rocks rich in potassium (K), rare-earth elements (REEs), and phosphorus (P) (KREEP-rich rocks) have the lowest Hf/W of 5–25 [18]. Moreover, if the crystal–liquid differentiation also occurred during the lifetime of ^{182}Hf , ^{182}W excess would be further raised in Hf-rich reservoirs. Variations of ^{182}W excesses have been found in the mantles of planetary bodies, such as the Bulk Silicate Earth (BSE) and the Bulk Silicate Moon (BSM) [15,17,27–29]. In contrast, significant ^{182}W deficits have been found in metallic cores and iron meteorites [6–8]. The degrees of excesses or deficits depend on the precise time of core formation and mantle differentiation. Therefore, the Hf/W ratios and ^{182}W abundances can be integrated to constrain the timescales of planetary formation and evolution.

2.2. Isochron Age of the ^{182}Hf - ^{182}W System

The ^{182}Hf - ^{182}W system isochron age can be used to obtain the initial $^{182}\text{Hf}/^{180}\text{Hf}$ and $^{182}\text{W}/^{184}\text{W}$ values of the CHUR, the BSE, the BSM, and other planetary reservoirs, as well as the ages of undifferentiated meteorites. Taking any primitive chondrite j as an example, we assume the isotopic evolution of $^{182}\text{W}/^{184}\text{W}$ in j evolved as a closed system after its formation. Similar to the standard geochronometry equation, the relationship of initial and present $^{182}\text{W}/^{184}\text{W}$ values can be expressed as the following:

$$(^{182}\text{W}/^{184}\text{W})_j^{t_p} = (^{182}\text{W}/^{184}\text{W})_j^{t_i} + (^{182}\text{Hf}/^{184}\text{W})_j^{t_p} \times (e^{\lambda(t_p - t_i)} - 1) \quad (1)$$

where t_j represents the time of formation of j and t_p represents the time since formation of the solar system, estimated to be 4.567 Ga [24]. The superscript of the isotopic ratios indicates the corresponding time, while the subscript indicates the related sample j . ^{184}W is the stable reference isotope. λ is the decay constant of ^{182}Hf , which is estimated to be $0.078 \pm 0.002 \text{ Ma}^{-1}$ [10]. By introducing a reference stable isotope ^{180}Hf , the immeasurable parameter $^{182}\text{Hf}/^{184}\text{W}$ can be replaced:

$$(^{182}\text{Hf}/^{184}\text{W})_j^{t_p} = (^{182}\text{Hf}/^{180}\text{Hf})_j^{t_p} \times (^{180}\text{Hf}/^{184}\text{W})_j^{t_p} \quad (2)$$

Besides, according to basic decay principles, we can obtain:

$$(^{182}\text{Hf}/^{180}\text{Hf})_j^{t_p} = (^{182}\text{Hf}/^{180}\text{Hf})_j^{t_j} \times e^{-\lambda(t_p - t_j)} \quad (3)$$

Combined with Equations (1)–(3), we can obtain:

$$(^{182}\text{W}/^{184}\text{W})_j^{t_p} = (^{182}\text{W}/^{184}\text{W})_j^{t_j} + (^{182}\text{Hf}/^{180}\text{Hf})_j^{t_j} \times (^{180}\text{Hf}/^{184}\text{W})_j^{t_p} \times (1 - e^{-\lambda(t_p - t_j)}) \quad (4)$$

Since t_p is much larger than t_j , $e^{-\lambda(t_p - t_j)}$ can be approximately equal to 0, so Equation (1) can then be written in terms of readily measurable parameters:

$$(^{182}\text{W}/^{184}\text{W})_j^{t_p} = (^{182}\text{W}/^{184}\text{W})_j^{t_j} + (^{182}\text{Hf}/^{180}\text{Hf})_j^{t_j} \times (^{180}\text{Hf}/^{184}\text{W})_j^{t_j} \quad (5)$$

In a plot of $^{182}\text{W}/^{184}\text{W}$ versus $^{180}\text{Hf}/^{184}\text{W}$, the intercept and slope yield the initial $^{182}\text{W}/^{184}\text{W}$ and $^{182}\text{Hf}/^{180}\text{Hf}$ values of j at t_j (Figure 1). Notably, the initial $^{182}\text{W}/^{184}\text{W}$ and $^{182}\text{Hf}/^{180}\text{Hf}$ values of the CHUR can be obtained by a set of primitive chondrites.

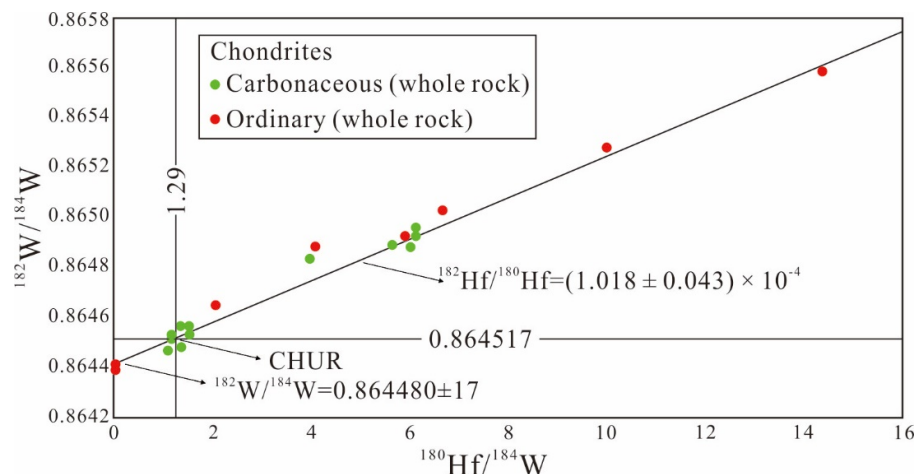


Figure 1. ^{182}Hf - ^{182}W system fossil isochron diagram of primitive chondrites. Data are taken from [30–32].

Then, t_j can be calculated by Equation (6):

$$t_j = -\frac{1}{\lambda} \times \ln \left[\frac{(^{182}\text{Hf}/^{180}\text{Hf})_j^{t_j}}{(^{182}\text{Hf}/^{180}\text{Hf})_{\text{CHUR}}^{t_0}} \right] \quad (6)$$

where t_0 represents the time of the solar system formation, $t_0 = 0 \text{ Ma}$. $(^{182}\text{Hf}/^{180}\text{Hf})_{\text{CHUR}}^{t_0}$ is the initial $^{182}\text{Hf}/^{180}\text{Hf}$ value of the CHUR, usually taken as $(1.018 \pm 0.043) \times 10^{-4}$ [29,32].

Analogously, the initial $^{182}\text{W}/^{184}\text{W}$ and $^{182}\text{Hf}/^{180}\text{Hf}$ values of the BSE, the BSM, and other planetary reservoirs can also be obtained from their fossil isochron diagrams.

2.3. Model Age of the ^{182}Hf - ^{182}W System

Planetary evolution processes are usually multistage. Taking the Earth as an example, the initial Earth formed with a CHUR-like W isotopes composition (Stage 1). After core formation, the BSE began with high Hf/W ratios and high $^{182}\text{W}/^{184}\text{W}$ values (Stage 2). Subsequently, the BSE underwent mantle differentiation, forming several early W-enriched reservoirs (EERs) and early W-depleted reservoirs (EDRs) (Stage 3). Assuming t_{cf} and t_{d} represent the time of core formation and mantle differentiation, respectively, the evolution of the ^{182}W composition in the Earth can be expressed as in Figure 2.

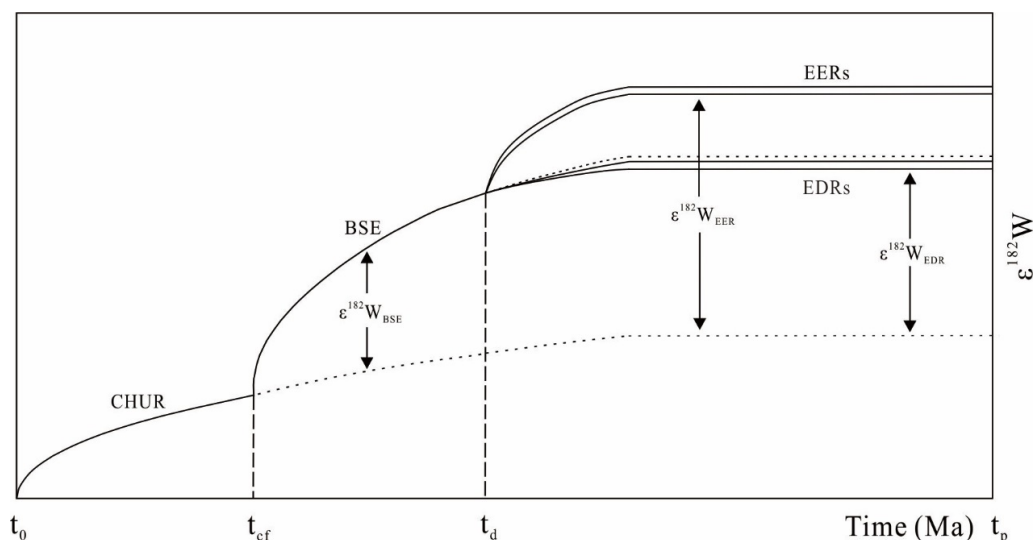


Figure 2. Three-stage evolution of ^{182}W composition in the Earth. W isotope data are generally reported with $\epsilon^{182}\text{W}$ values, expressed as $\epsilon^{182}\text{W} = [(^{182}\text{W}/^{184}\text{W})_{\text{sample}} / (^{182}\text{W}/^{184}\text{W})_{\text{BSE}} - 1] \times 10^4$, which means per 10,000 deviations of $^{182}\text{W}/^{184}\text{W}$ from the value of the BSE.

For the BSE, the initial $^{182}\text{W}/^{184}\text{W}$ and $^{182}\text{Hf}/^{180}\text{Hf}$ values can be obtained from its fossil isochron diagram, while its present $^{182}\text{W}/^{184}\text{W}$ and $^{180}\text{Hf}/^{184}\text{W}$ values can be measured in the laboratory. These values can be used to calculate the ^{182}Hf - ^{182}W system model ages, including t_{cf} and t_{d} . Assuming j represents any closed silicate reservoirs, t_{cf} can be expressed as:

$$t_{\text{cf}} = \frac{1}{\lambda} \times \ln \left[\frac{(^{182}\text{Hf}/^{180}\text{Hf})_{\text{CHUR}}^{t_0} \frac{(^{180}\text{Hf}/^{184}\text{W})_j^{t_p} - (^{180}\text{Hf}/^{184}\text{W})_{\text{CHUR}}^{t_p}}{(^{182}\text{W}/^{184}\text{W})_j^{t_p} - (^{182}\text{W}/^{184}\text{W})_{\text{CHUR}}^{t_p}} \right] \quad (7)$$

where the present $^{180}\text{Hf}/^{184}\text{W}$ and $^{182}\text{W}/^{184}\text{W}$ values of the CHUR are estimated to be 1.29 and 0.864517 [33]. Equation (7) is suitable for planets with a single and instantaneous core formation event, not for large bodies that most likely grew episodically in their long accretion, such as the Earth, Mars, and Venus. The exponential growth models are more suitable for these bodies (for details, see Jacobsen [24] and Kruijer and Kleine [15]). However, at least, Equation (7) gives a reliable lower limit for the time of their core formation.

Furthermore, the time of mantle differentiation (t_{d}) can be expressed as:

$$\epsilon^{182}\text{W}_{\text{MR}}^{t_p} = (^{182}\text{Hf}/^{180}\text{Hf})_{\text{CHUR}}^{t_0} \times Q_{182} \times \left\{ \left[e^{\lambda(t_{\text{cf}}-t_0)} - e^{\lambda(t_{\text{d}}-t_0)} \right] \times f_{\text{BSE}} + e^{\lambda(t_{\text{d}}-t_0)} \times f_{\text{M}} \right\} \quad (8)$$

where $Q_{182} = (^{180}\text{Hf}/^{182}\text{W})_{\text{CHUR}}^{\text{td}} \times 10^4$, $\epsilon^{182}\text{W}_{\text{MR}}^{\text{tp}} = \frac{(^{182}\text{W}/^{184}\text{W})_{\text{MR}}^{\text{td}} - (^{182}\text{W}/^{184}\text{W})_{\text{CHUR}}^{\text{td}}}{(^{182}\text{W}/^{184}\text{W})_{\text{CHUR}}^{\text{tp}}} \times 10^4$.

The notation f represents Hf/W fractionation relative to CHUR, and $f_{\text{BSE}} = \frac{(^{180}\text{Hf}/^{184}\text{W})_{\text{BSE}}^{\text{tp}}}{(^{180}\text{Hf}/^{184}\text{W})_{\text{CHUR}}^{\text{tp}}} - 1$, $f_{\text{M}} = \frac{(^{180}\text{Hf}/^{184}\text{W})_{\text{MR}}^{\text{tp}}}{(^{180}\text{Hf}/^{184}\text{W})_{\text{CHUR}}^{\text{tp}}} - 1$. The subscript MR denotes any EERs or EDRs.

2.4. Quantification of Cosmogenic ^{182}W

During the interaction with galactic cosmic rays (GCR), when lunar rocks were exposed to solar radiation, ^{181}Ta in rocks captured secondary neutrons, including thermal neutrons and epithermal neutrons. As a result, neutron capture reaction on ^{181}Ta ($^{181}\text{Ta} (n, \gamma) ^{182}\text{Ta} (\beta^-) ^{182}\text{W}$) took place, generating cosmogenic ^{182}W [34,35]. Similarly, ^{182}W captured secondary neutrons and then produced cosmogenic ^{183}W . Ta/W ratios in most lunar rocks are normally greater than 1 and reach ~25 in high-Ti mare basalts [18]. It is thus necessary to quantify the cosmogenic ^{182}W before accurate radiogenic ^{182}W can be obtained. Analyzing lunar metals is a direct way to obtain their radiogenic ^{182}W because metals are devoid of Ta [17,20,36]. However, metal content in lunar rocks is usually too low to meet the mass requirement for W isotope determination. Another simple and effective way is using empirical neutron dosimeters, such as ^{149}Sm , ^{157}Ga , ^{178}Hf , and ^{189}Os [14,15,35,37,38]. Taking ^{178}Hf as an example, ^{177}Hf captures secondary neutrons and produces ^{178}Hf , while ^{178}Hf captures secondary neutrons and produces ^{179}Hf . A similar sensitivity to Ta, W, and Hf's neutron energies makes ^{178}Hf a suitable empirical neutron dosimeter for ^{182}W [14]. For convenience in expression, ^{178}Hf is generally replaced by the stable isotope ^{180}Hf , resulting in a linear relationship between the $\epsilon^{182}\text{W}$ and $\epsilon^{180}\text{Hf} \times (\text{Ta}/\text{W})$ in lunar rocks [14]. For different types of lunar rocks, this relationship is extended to be:

$$\epsilon^{182}\text{W}_{\text{radiogenic}} = \epsilon^{182}\text{W} - \epsilon^{182}\text{Hf} \times (\text{Ta}/\text{W}) \times \text{slope} \quad (9)$$

where $\epsilon^{180}\text{Hf} = [(^{180}\text{Hf}/^{177}\text{Hf})_{\text{sample}} / (^{180}\text{Hf}/^{177}\text{Hf})_{\text{BSE}} - 1] \times 10^4$, means per 10,000 deviations of $^{180}\text{Hf}/^{177}\text{Hf}$ from the ratio of the BSE. The slope is yielded by the $\epsilon^{182}\text{W}$ vs. $\epsilon^{180}\text{Hf} \times (\text{Ta}/\text{W})$ diagram in Figure 3 [15].

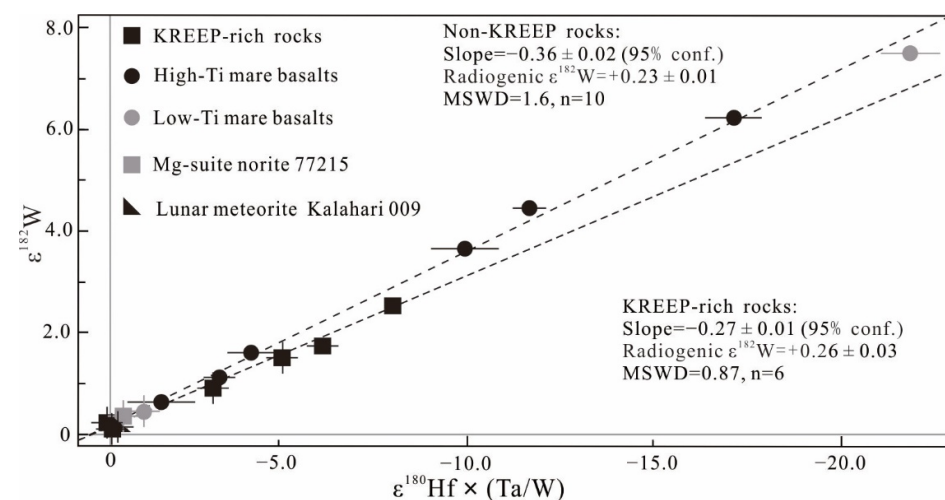


Figure 3. $\epsilon^{182}\text{W}$ vs. $\epsilon^{180}\text{Hf} \times (\text{Ta}/\text{W})$ diagram for lunar rocks (modified after [15]). The intercept of the dashed line represents the radiogenic $\epsilon^{182}\text{W}$ of the rocks. The slope was considered to reflect different neutron energy spectra of rocks with distinct chemistry compositions (-0.27 for KREEP-rich rocks and -0.36 for non-KREEP rocks).

2.5. Quantification of Nucleosynthetic ^{182}W

Variations in the abundances of ^{182}W also have nucleosynthetic origins. Among the W isotopes, ^{180}W is a pure p-process nuclide, while ^{182}W , ^{183}W , ^{184}W , and ^{186}W are produced by both s- and r-processes in supernovae and asymptotic giant branch (AGB) stars [15,39]. In different regions of the solar nebula, a heterogeneous distribution of p-, s-, and r-process nuclides will thus lead to nucleosynthetic anomalies of different W isotopes, including ^{182}W . Such nucleosynthetic ^{182}W anomalies have been found in different rocks, including pre-solar grains, Ca-Al-rich inclusions (CAIs), iron meteorites, and lunar rocks. For example, the nucleosynthetic ^{182}W anomaly in the Allende CAI was reported to be $\sim 0.23\epsilon$; it is thus necessary to distinguish these anomalies from those radioactive anomalies. Three ways have been put forward to quantify nucleosynthetic ^{182}W , including (1) W isotope measurements for pre-solar SiC grains; (2) theoretical models of stellar nucleosynthesis; and (3) measurement of ^{183}W . The nucleosynthetic ^{183}W has been proven to positively correlate with nucleosynthetic ^{182}W [28,39].

3. W Isotopic Composition in the Moon

Recognizing the difference of $\epsilon^{182}\text{W}$ between the Earth and Moon can provide critical information for constraining the earliest history of the Earth–Moon system. In the past two decades, with the technological improvement of thermal ionization mass spectrometry (TIMS) and multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS), the research on W isotopes has provided new insight into the lunar evolution. Lee et al. [28] reported the initial W isotope data for 22 lunar samples, including lunar mare basalts, lunar meteorites, picritic orange glass, ferroan anorthosite, and Mg-granulite. Significant $\epsilon^{182}\text{W}$ anomalies of $-0.50 \pm 0.60 \sim +6.75 \pm 0.42$ (2 SE) led to a conclusion that the Moon formed within 40–67 Ma after the solar system formation. However, in subsequent studies, part of this excess was recognized as cosmogenic ^{182}W accumulation [11,34]. After correction for some of these samples and several new lunar rocks, $\epsilon^{182}\text{W}$ anomalies of $-0.42 \pm 0.36 \sim +2.82 \pm 0.94$ (2 SE) remained, resulting in a lunar age of 30 to >100 Ma after the solar system formation [36]. On the other hand, Touboul et al. [17] reported identical $\epsilon^{182}\text{W}$ values in their investigated samples (metals separated from two KREEP-rich rocks, four low-Ti mare basalts, and five high-Ti mare basalts), averaging $+0.09 \pm 0.10$. It is consistent with the BSE within error range, indicating that the Moon formed beyond the lifetime of ^{182}Hf . However, this value was questioned because the precision of $^{182}\text{W}/^{184}\text{W}$ ratios is worse than 17 ppm (2 RSD), and the neutron capture burn-out effects on ^{182}W were not assessed.

Recently, with the developments of the W isotope analytical technique, the precision of $\epsilon^{182}\text{W}$ can be as good as 0.05ϵ [28,40–43]. Recently, several researchers have reported high-precision data on the $\epsilon^{182}\text{W}$ of lunar rocks [14,15,20]. The results are detailed in Table 2.

A uniform $\epsilon^{182}\text{W}$ value within the error range exists in different kinds of lunar rocks, including low-Ti basalts, high-Ti basalts, KREEP-rich rocks, Mg-suite norite, and lunar meteorites. The weighted mean $\epsilon^{182}\text{W}$ of 0.24 ± 0.01 in the BSM is much higher than that of the BSE. Three main explanations for this excess have been put forward by previous studies, which are summarized in the following:

- (1) Radiogenic origin [11,18,19,28,44]. The most straightforward explanation ascribes the lunar $\epsilon^{182}\text{W}$ excess to radiogenic ^{182}W accumulation. This explanation is possible if the BSM formed within the lifetime of ^{182}Hf and had a higher Hf/W ratio than the BSE. König et al. [45] estimated the Hf/W ratio of the BSE to be ~ 24.9 , and recently, Thiemens et al. [18] estimated the Hf/W ratio of the BSM to be 30.2–48.5, by analyzing the Hf and W mass fractions in 26 Apollo lunar rocks, including low-Ti basalts, high-Ti basalts, KREEP-rich rocks, and ferroan anorthosites (FANs). This high Hf/W ratio can be explained by a massive core (3% mass fraction of the total mass of the Moon) that formed with a $D_{\text{W}} = \sim 30$ (D_{W} means metal–silicate partition coefficient for W in the Moon) within 40–60 Ma after the solar system formation, as modeled by Thiemens et al. [18]. Therefore, radiogenic ^{182}W excess could have developed in

the BSM as the ^{182}Hf decayed. This explanation makes lunar core formation the only reason for the low Hf/W ratio and high $\epsilon^{182}\text{W}$ value in the BSM. However, this explanation has its drawbacks. It requires that the BSE and BSM have the same initial ^{182}W composition. It implies no $\epsilon^{182}\text{W}$ modification from other processes, which goes against the planetary accretion process [3]. In addition, the Hf/W ratio of the BSM was previously estimated to be the same as the BSE [9,10].

- (2) Disproportional late veneer on the Earth and Moon [14,15,20–22,46]. Since the “late veneer hypothesis” will be discussed at length later, it is necessary to introduce this hypothesis. The late veneer hypothesis is put forward to explain Earth’s chondrite-like HSEs abundances. HSEs were thought to be completely distributed into the core during planetary core–mantle separation because of their high $D_{\text{melt/silicate}}$ of 10^4 . However, Chou [11] found the chondritic relative and overestimated HSEs abundances ($1.0 \pm 0.4\%$ CI) in the BSE, and considered that the HSEs in the mantle were brought about by the accretion of chondrite materials. These materials might have evolved into a thin layer on the Earth’s surface before 3.8 Ga; that is, the late veneer stage [12]. The late veneer represents the Earth’s latest accretion stage and comprises the last 0.3–0.8% of the Earth’s mass [47,48]. The late veneer also occurred on the Moon because of its high HSEs abundances [13,14]. From the HSEs contents in chondritic meteorites, abundance estimations of the HSEs in the BSE, and the mass estimation of the BSE, the mass of the late veneer in the BSE was estimated to be 1.2×10^{22} – 3.2×10^{22} kg, ~0.3–0.8 wt% of the Earth’s total mass [49,50]. Because of the sub-nanogram HSEs abundances in the BSM, which are 40 times lower than in the BSE, the mass of late veneer in the BSM was estimated to be 1.5×10^{19} – 3.75×10^{19} kg, ~0.02–0.05% of the total lunar mass [51,52]. The added materials are enriched in W (150–200 ppb) but depleted in ^{182}W ($\epsilon^{182}\text{W} = -0.19$) [53]; therefore, the disproportional late veneer would have decreased the $\epsilon^{182}\text{W}$ values of the BSE and BSM by 0.20–0.30 and 0.01–0.04, respectively [49,52,54]. As a result, the BSM retained a higher $\epsilon^{182}\text{W}$ value of ~0.23 [55], coincidentally similar to its present-day estimated $\epsilon^{182}\text{W}$ excess (0.24 ± 0.01). This explanation considers $\epsilon^{182}\text{W}$ modification caused by the planetary accretion process. However, complex accretion models are required. The calculations reducing $\epsilon^{182}\text{W}$ are discrepant in different models, which may be caused by uncertainties in the calculation parameters (see Section 4.2).
- (3) Mantle of the impactor “Thia” [7,9]. In canonical giant impact models, 80 wt% mass of the Moon comprises materials from the impactor’s mantle, while the rest consists of materials from the impactor’s core and proto-Earth’s mantle [56]. The impactor’s mantle probably has a positive $\epsilon^{182}\text{W}$ value because of its earlier core formation, perhaps 10–20 Ma after the solar system formation [57]. Therefore, the reported lunar $\epsilon^{182}\text{W}$ excess could be explained by an appropriate mass combination of materials from the impactor’s mantle, impactor’s core, and proto-Earth’s mantle. Accretion models and the same initial ^{182}W composition between the BSE and BSM are not required in this explanation. However, the larger the proportion of Thia’s mantle in the Moon, the smaller the proportion of Thia’s core, which does not meet the core quality estimated by seismological detection results [15].

Each of the above explanations is likely reasonable and they might play a common role. It should be noted that determining the time of lunar origin and evolution is affected by which explanation is adopted.

Table 2. Ta, Hf, W abundances and $\epsilon^{182}\text{W}$ values of lunar rocks (modified after [15]).

Sample	Ta (ppb)	Hf (ppb)	W (ppb)	Ta/W $\times \epsilon^{180}\text{Hf}$	G- $\epsilon^{182}\text{W}$ (2 σ)	$\epsilon^{182}\text{W}$ (2 σ)
Low-Ti mare basalts						
12004	385	3220	106	-0.57 ± 0.22	0.47 ± 0.10	0.26 ± 0.09
15495	374	3030	67.8	-21.22 ± 1.10	7.44 ± 0.10	0.20 ± 0.10
High-Ti mare basalts						
10057	1805	16,600	401	-3.06 ± 0.32	1.23 ± 0.10	0.13 ± 0.10
70017	1499	84,800	63.1	-10.16 ± 1.56	3.97 ± 0.15	0.21 ± 0.15
70035	2058	12,500	101	-11.94 ± 0.73	4.80 ± 0.10	0.35 ± 0.10
70215	1405	65,600	58.5	-4.24 ± 0.82	1.79 ± 0.12	0.22 ± 0.12
79155	ND	ND	ND	-104.8 ± 5.70	37.9 ± 1.00	0.15 ± 0.90
75035	1861	11,300	86.5	-16.62 ± 1.29	6.13 ± 0.10	0.14 ± 0.10
Mg-suite norite						
77215	400	3480	212	-0.17 ± 0.09	0.37 ± 0.10	0.30 ± 0.13
Lunar meteorite						
Kalahari 009	31.5	422	16.5	-0.06 ± 0.17	0.25 ± 0.11	0.23 ± 0.20
KREEP-rich rocks ^a						
12034	2489	20,600	1328	-3.63 ± 0.19	1.26 ± 0.10	0.27 ± 0.09
14163	2782	22,900	1492	-7.47 ± 0.38	2.35 ± 0.04	0.33 ± 0.04
14130	2214	19,300	1101	-6.06 ± 0.33	1.87 ± 0.10	0.24 ± 0.09
14321	884	7510	351	-0.07 ± 0.02	0.27 ± 0.04	0.25 ± 0.02
68115	ND	ND	ND	-0.04 ± 0.10	0.29 ± 0.05	0.28 ± 0.05
62235	2012	19,600	959	-5.31 ± 0.30	1.63 ± 0.10	0.20 ± 0.09
Lunar metals separated from KREEP-rich rocks ^b						
68115, 114	ND	2230	3270	ND	ND	0.23 ± 0.04
68815, 394	ND	1410	2280	ND	ND	0.18 ± 0.03
68815, 396	ND	270	3630	ND	ND	0.20 ± 0.03
Average						
	1443	17,340	913	ND	ND	0.24 ± 0.01

a: data of seven whole-rock lunar samples reported by [14]; b: data of lunar metals separated from two Apollo 16 KREEP-rich impact-melt rocks reported by [20]; the rest are data of nine lunar rocks reported by [15]. Except for the lunar meteorite Kalahari 009, the rest are Apollo samples. G- $\epsilon^{182}\text{W}$ means measurement results without deduction of cosmogenic ^{182}W .

4. Controversy over the Age of the Moon

Determining the age of the Moon is fundamental to clarifying its formation and evolution processes. Dating the chemical differentiation events accompanying the crystallization of the lunar magma ocean (LMO) could be a direct way; however, it can only date the LMO solidification and requires all the minerals to crystallize synchronously. The other approach is dating the giant impact event through its effect on the Earth–Moon chemical evolution, including the ^{182}Hf – ^{182}W isotopic system and HSEs system. Ages of lunar core formation or the giant impact were estimated with the ^{182}Hf – ^{182}W system in previous studies, but it remains highly controversial. As shown in the following, the proposed ages of the Moon are inconsistent and mainly divided into two opposing categories:

- (1) The Moon formed early, around 30–70 Ma after the solar system formation [11,16–19]. This view attributes the lunar $\epsilon^{182}\text{W}$ excess to radiogenic ^{182}W and calculates the ages by the ^{182}Hf – ^{182}W system model age. With ^{182}W composition measurement, similar lunar ages were obtained from different lunar samples: an age of 50 ± 10 Ma was obtained by analyzing Apollo 17 high-Ti basalts [11]; an age of ~ 30 Ma was obtained by analyzing Apollo 15 lunar mare basalts [16]; and an age of ~ 60 Ma was obtained by analyzing metals separated from two lunar KREEP-rich rocks [17]. With a new estimation of lunar Hf/W ratios (30.2–48.5, much higher than 25.6 in previous studies), Thiemens et al. [18] reported an age of ~ 50 Ma that was obtained by analyzing 26 Apollo samples. On the other hand, the above age results are consistent with those obtained from other isotopic systems, such as the age measured by ^{176}Lu – ^{176}Hf for Apollo 14 zircon fractures (60 ± 10 Ma) [44] and U–Th–Pb evolution research for the BSE (69 ± 10 Ma) [58].

- (2) The Moon formed later than 70 Ma after the solar system formation; that is, after the extinction of ^{182}Hf [14,15,20–22,59]. This view attributes the lunar $\epsilon^{182}\text{W}$ excess to the disproportional late veneer on the Earth and Moon, meaning that there is no resolved radiogenic ^{182}W difference in the BSE and BSM. Because of the higher Hf/W in the BSM [17,18], the Moon is considered to have formed after the extinction of ^{182}Hf .

In conclusion, the first view neglects the effect of the late veneer on lunar $\epsilon^{182}\text{W}$, while the second view might overvalue the role of the late veneer. Furthermore, the effects of the impactor “Thia” and the addition of a large differentiated projectile that formed the Oceanus Procellarum were neglected. However, the totality of these effects has been understudied, as shown in the following.

4.1. Effect of the Impactor “Thia” on Lunar $\epsilon^{182}\text{W}$

Kruijer and Kleine [15] evaluated the possibilities of degrees of $\epsilon^{182}\text{W}$ values that formed during the giant impact, with an assumption that the Moon was formed by a simple physical mixing of different proportions of materials from the proto-Earth and impactor. The main parameters they used are shown in Table 3, and the results are shown in Figure 4.

Table 3. Calculation parameters used in the simulation for the lunar $\epsilon^{182}\text{W}$ value (modified after [15]).

Parameter	Description	Value
G	Mass ratio of the impactor to the Earth	0.04–0.15
Γ	Mass fraction of the mantle in the Earth and impactor	0.68
K	Mass fraction of the impactor core equilibrated with the Earth’s mantle	0–100%
H	Mass fraction of the Moon composed of the impactor’s mantle	0%, 20% or 80%
F	Mass fraction of the Moon composed of the impactor’s core	0–2.5%
$D_{\text{Earth}}^{\text{W}}$	Metal-silicate partition coefficient for W in the Earth after the giant impact	20–100
$D_{\text{Moon}}^{\text{W}}$	Metal-silicate partition coefficient for W in the Moon	1–100
$D_{\text{Impactor}}^{\text{W}}$	Metal-silicate partition coefficient for W in the impactor	5–100
t	Time of core formation in the impactor after solar system formation	5–20 Ma
$(\text{Hf}/\text{W})_{\text{CHUR}}$	Hf/W of chondrite meteorites	1.14
$(\text{Hf}/\text{W})_{\text{BSE}}$	Hf/W of the BSE	~23
$\epsilon^{182}\text{W}_{\text{CHUR}}$	Present-day $\epsilon^{182}\text{W}$ of chondrite meteorites	-1.9 ± 0.1
$\epsilon^{182}\text{W}_{\text{CAIs}}$	Initial $\epsilon^{182}\text{W}$ value of CAIs	-3.49 ± 0.07
$(^{182}\text{Hf}/^{180}\text{Hf})_{\text{CAIs}}$	Initial $^{182}\text{Hf}/^{180}\text{Hf}$ ratio of CAIs	1.018×10^{-4}

Ca-Al-rich inclusions (CAIs) are generally considered to be the first solid material formed within the solar nebula at about 4.567 Ga [39]. It represents the initial isotopic composition of the solar system.

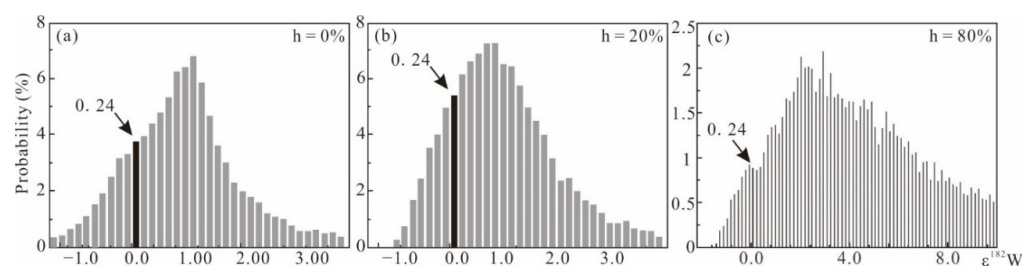


Figure 4. The lunar $\epsilon^{182}\text{W}$ values in three impact scenarios and their occurrence probabilities (modified after [15]).

As shown in Figure 4, the probability of calculated lunar $\epsilon^{182}\text{W}$ values being 0.24 is less than 6% in all scenarios in which the impactor’s mantle accounts for 0, 20, and 80% of

the total lunar mass. Instead, the probability of a significant $\epsilon^{182}\text{W}$ excess is much higher. Kruijer and Kleine [15] suggested that the initial lunar ^{182}W composition might be modified by post-giant-impact processes, such as the post-giant-impact equilibration and the synestia structure between the Earth and Moon (for details, see Section 5). However, the duration of these processes lacks constraints.

4.2. Effect of the Late Veneer on Lunar $\epsilon^{182}\text{W}$

With numerical modeling approaches, Kruijer et al. [14] summarized models for late veneer compositions, which give an average $\epsilon^{182}\text{W}$ decrease of 0.23 ± 0.15 in the BSE (Table 4). This value is almost the same as the lunar $\epsilon^{182}\text{W}$ excess, meaning no convincing radiogenic ^{182}W accumulation could be confirmed.

Table 4. Late veneer compositions and their effects on the $\epsilon^{182}\text{W}$ of the BSE (following from [14]).

Added Materials	[W] ^a	$[\epsilon^{182}\text{W}]$ ^b	Mass ^c	Pre-LV $\epsilon^{182}\text{W}$ ^d	$\epsilon^{182}\text{W}$ Decreases in the BSE
CI	113	−2.20	0.59	0.17	0.12–0.29
CM	127	−1.73	0.45	0.11	0.08–0.19
CO	169	−1.83	0.33	0.12	0.09–0.20
CK	199	−2.00	0.37	0.18	0.12–0.30
CV	171	−1.97	0.35	0.14	0.10–0.23
CR	165	−1.77	0.41	0.14	0.10–0.24
H	178	−2.25	0.32	0.16	0.12–0.28
L	129	−2.00	0.44	0.14	0.10–0.24
LL	95	−1.60	0.74	0.14	0.10–0.24
EH	128	−2.23	0.45	0.15	0.11–0.26
EL	135	−1.98	0.41	0.14	0.10–0.23
80% CC + 20% VIA	202	−2.60	0.34	0.22	0.16–0.38

^a: W concentration (ppb) of the added materials; ^b: $\epsilon^{182}\text{W}$ values of the added materials; ^c: mass fraction of late veneer relative to the Earth's mass; ^d: BSE's $\epsilon^{182}\text{W}$ values before late veneer (LV).

However, the calculated $\epsilon^{182}\text{W}$ has considerable uncertainty, which is passed from the calculation parameters that are used in numerical modeling approaches, including: (1) the HSEs and ^{182}W compositions of the BSE, the BSM, and the late veneer; and (2) mass fraction of late veneer materials on the Earth and Moon.

4.2.1. The HSEs and ^{182}W Compositions of the BSE

Protogenetic HSEs in the Earth are commonly considered to have been partitioned entirely into the Earth's core during the giant impact. Information about the HSEs composition of the BSE was mainly available from mantle xenoliths and tectonically exposed rocks derived from mid-ocean ridge basalt source mantle (DMM), subcontinental lithospheric mantle (SCLM), and oceanic crust [60]. As reported in previous studies, HSEs distribution patterns in the BSE are roughly chondritic ($\sim 0.008 \times \text{CI}$ chondrite) and are characterized as deficient in Pt, Ir, Os and rich in Pd, Ru (Figure 5) [61,62]. The $C_{\text{BSE/CI}}$ values of Re, Ir, Pt, Au, Os, Ru, Rh, and Pd are estimated to be 0.0094, 0.0083, 0.0088, 0.0224, 0.0087, 0.0111, 0.0092, and 0.0126, respectively [16]. Moreover, BSE has CI chondrite-like S/Se and Se/Te ratios, a CM chondrite-like chalcogen/HSE ratio, and an ordinary chondrite-like $^{187}\text{Os}/^{188}\text{Os}$ value [49,63]. In general, HSEs characteristics of the BSE are similar to those of the chondrites.

Although the $\epsilon^{182}\text{W}$ value of the present BSE is well defined, the $\epsilon^{182}\text{W}$ value of the primitive BSE (the BSE before late veneer) is needed. Information about the ^{182}W composition of the primitive BSE was mainly available from 4.3–2.4 Ga Archean komatiites, metamorphosed basalts, and magmatic cumulates, which represent partial melts of the ancient mantle [66]. $\epsilon^{182}\text{W}$ data were reported for these rocks, including rocks from the 3.8 Ga Greenland Isua Supracrustal Belt ($\epsilon^{182}\text{W} = 0.13 \pm 0.04$) [53], the 3.5 Ga Kostomuksha Greenstone Belt ($\epsilon^{182}\text{W} = 0.15 \pm 0.05$) [67], the 3.66 Ga Nuvvuagittuq Greenstone Belt ($\epsilon^{182}\text{W} = 0.13 \pm 0.06$) [68], the >3.71 Ga Saglek-Hebron complex ($\epsilon^{182}\text{W} = 0.11 \pm 0.03$) [69],

the 2.7 Ga Abitibi Greenstone Belt ($\epsilon^{182}\text{W} = 0.12 \pm 0.05$) [70], and the 3.45 Ga Pilbara Craton komatiites ($\epsilon^{182}\text{W} = 0.09 \pm 0.04$) [59]. These rocks of different ages, types, and locations have a nearly constant $\epsilon^{182}\text{W}$ excess (Figure 6) but no elevated HSEs abundances [60], revealing that they were probably produced by a common process, most likely the lack of late veneer. According to the HSEs-derived estimates, the amounts of the lack in the sources of these rocks range from 20 to 70%. Archer et al. [59] suggested that the true differences in the amounts of HSEs late veneer brought were overlapped by the inherent uncertainties of the HSEs estimates, which are associated with assumptions in calculation methods. Moreover, using a Monte Carlo approach, Archer et al. [59] reported the primitive BSE's $\epsilon^{182}\text{W}$ of 0.18 ± 0.08 (1 SD); they considered this value to overlap with the lunar $\epsilon^{182}\text{W}$ (0.24 ± 0.01 , 2 RSD). However, the error range seems unsatisfactory.

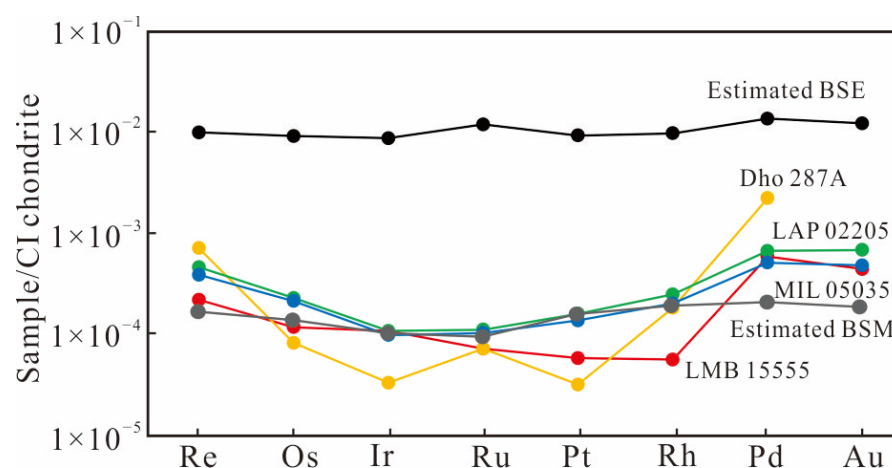


Figure 5. Estimated Os, Ir, Ru, Pt, Pd, Re abundances in the BSE and BSM. HSEs of both the BSE and BSM are roughly chondritic, $\sim 0.008 \times \text{CI chondrite}$ of the BSE and $\sim 0.0002 \times \text{CI chondrite}$ of the BSM. Data of the BSE and BSM were collected from [54,60]. Dho 287A, LAP 02205, MIL 05035, and LMB 15556 are lunar samples reported by [64]. Chondrite normalization follows [65].

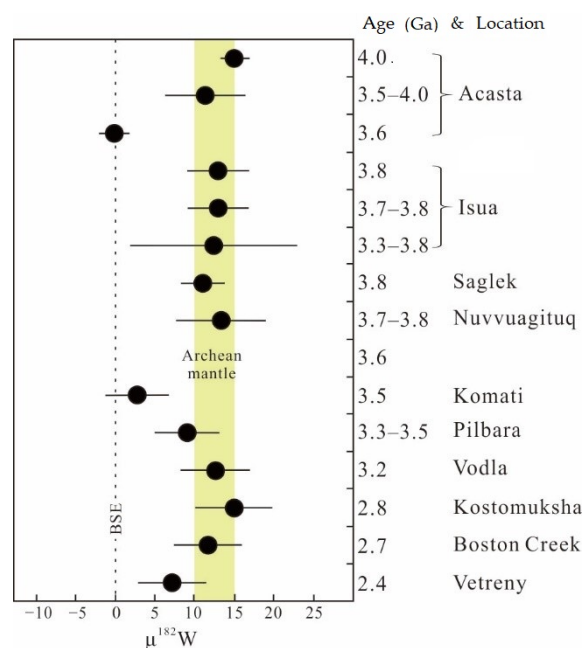


Figure 6. $\epsilon^{182}\text{W}$ values for Archean rocks (following from [59]). The yellow and gray shaded areas represent the $\epsilon^{182}\text{W}$ values of the Archean mantle and the BSM, respectively.

4.2.2. The HSEs Compositions of the BSM

Because of the lack of lunar deep mantle samples in existing collections, HSEs abundances in the BSM have traditionally been inferred from the HSEs abundances and $^{187}\text{Os}/^{188}\text{Os}$ values of 3–3.9 Ga lunar mare basalts and terrestrial counterparts [52,54]. Day et al. [54] used the chemical composition of Apollo 15 and 17 mare basalts to calculate the HSEs composition of the BSM. The result corresponded to $\sim 0.0002 \times$ the CI chondrite value, 20–40 times lower than the BSE (Figure 5). However, this conclusion has been challenged by the studies of (1) HSEs distribution during lunar core formation, (2) partition coefficient for HSEs in lunar mantle melting, and (3) meteorite contamination at the lunar surface.

In giant impact models, protogenetic HSEs in the BSM are considered to have been stripped by metals from the core of the Moon-forming impactor [34]. However, lacking experimental data on rates of metal–silicate equilibration of HSEs and degrees of lunar core–mantle equilibration, the efficiency of this process remains unknown. For example, a large amount of HSEs would be contained in the metals left behind in the mantle by inefficient core segregation [71]. In addition, the disproportionation of Fe^{2+} in the perovskite that produced Fe^{3+} would raise oxygen fugacity in the BSM [71]. Added metals from the impactor “Thia” would then be oxidized and mixed back into the BSM instead of the lunar core.

The behaviors of HSEs are mainly controlled by sulfide and metals during mare basalt crystallization [64,72]. Thus, knowledge of phase relations during partial melting of their mantle sources is required to assess the HSEs abundances in the BSM from lunar mare basalts. If the sources of lunar mare basalt had retained residual metal or sulfide, the estimates of the HSEs abundances in the BSM would be essentially unconstrained [64]. However, whether metals and sulfides are residual phases in the mantle sources or not has long been debated [52,60,64,72,73]. From the recent research on metals in Apollo 12 lunar mare basalts [52] and in situ determinations of the HSEs in lunar metals and sulfides [64], at least some sources of Apollo 12 lunar basalt were found to contain no metals and sulfides. In the end, this issue requires further investment. The dissimilar behavior of W and HSEs within the lunar mantle might cause uncertainties in estimates of the mass fraction of the late veneer. HSEs are more compatible than W during mantle melting, leading to their separation [59]. In addition, HSEs maintain chalcophile and partition into sulfides in the absence of metal, while W does not; the presence and transportation of sulfides in the mantle could potentially separate W and HSEs brought by late veneer [59].

Unexpected elevated HSEs abundances in the lunar surface are interpreted to reflect meteorite contamination, as the primordial lunar crust is typically devoid of HSEs [74,75]. An extensive 5–20 m thick surficial regolith is considered to have formed with elevated HSEs abundances 10^4 – 10^5 times higher than primary lunar basalt composition [64,72]. Brennan et al. [72] suggested that lunar mare basalts assimilated HSEs-rich materials from the contaminated regolith during their transit and eruption onto the lunar surface; thus, even <1% addition of the regolith would have a pronounced effect on their HSEs abundances. Therefore, the actual HSEs content of the BSM might be covered by meteorite contaminations.

4.2.3. The HSEs and ^{182}W Compositions of the Late Veneer

HSEs compositions of the late veneer are commonly obtained from the relative and absolute HSEs abundances and ratios of sulfur (S), selenium (Se), and tellurium (Te) in the BSE (usually ancient terrestrial samples) [63]. However, all the models of late veneer composition failed to completely meet the BSE’s HSEs characters mentioned above. For example, an ordinary chondrite-like composition failed to explain the BSE’s Ru/Ir, Pd/Ir, and Te/Se ratios; a carbonaceous chondrite-like composition failed to explain the BSE’s $^{187}\text{Os}/^{188}\text{Os}$ value. Similarly, the $\epsilon^{182}\text{W}$ value of the late veneer is not well constrained (Table 4).

4.2.4. Mass Fraction of Late Veneer on the Earth

The Earth is commonly assumed to retain the late veneer materials completely [23]. According to the abundance of HSEs in various types of terrestrial rocks and the estimated mass of the Earth, the mass of the late veneer was estimated to be 1.2×10^{22} – 3.2×10^{22} kg, ~0.3–0.8 wt% of the total mass of the Earth in some studies [49,50,52,54].

4.2.5. Mass Fraction of the Late Veneer on the Moon

The mass of the late veneer on the Moon is limited by the HSEs abundances of lunar mare basalts [52,54]. For example, Day et al. [54] conservatively estimated the mass of the late veneer on the Moon to be 1.50×10^{19} kg, ~0.02% of the total mass of the Moon. However, as shown in Section 4.2.2, HSEs in the lunar mare basalts might lose their reliability in constraining the mass of late veneer, as their actual content is veiled. In addition, if primordial HSEs had remained in the mantle during the giant impact, the mass of late veneer deduced from the current HSEs abundances would be overestimated. Independent of HSEs measurements, Kruijer et al. [22] limited the mass of the late veneer on the Moon to $<1.92 \times 10^{20}$ kg (0.256% of its total mass) by the Earth–Moon impact flux ratio. This value is much higher than that in previous studies.

Most importantly, the HSEs abundances in the BSM are not well constrained. The influence of late veneer and isotopic evolution on lunar HSEs and ^{182}W composition remains ambiguous. Additionally, the most propitious occurrence of the late veneer was within 150 Ma after the solar system formation because the thick permanent lunar crust could have prevented late veneer materials from reaching the lunar mantle [60]. On the other hand, new research was carried out on Eoarchean rocks regarding the late veneer hypothesis; for example, coupled depletions of ^{142}Nd and ^{182}W ($\epsilon^{142}\text{Nd} = -5.0 \pm 2.8$, $\epsilon^{182}\text{W} = -8.4 \pm 4.5$, 2SD) in 3.35 Ga South Africa Schapenburg komatiites [76]; $\epsilon^{182}\text{W}$ excess ($\epsilon^{182}\text{W} = -8.4 \pm 4.5$, 95% confidence interval) and normal W content in 3.5–3.26 Ga mafic-ultramafic assemblages, TTGs (trondjemite, tonalite, granodiorite), and Paleoarchean samples from the Isua region [77]. The $\epsilon^{182}\text{W}$ excesses in these terrestrial rocks are thought to have been produced by early mantle differentiation instead of the late veneer.

4.3. Effect of the Oceanus Procellarum-Forming Projectile on Lunar $\epsilon^{182}\text{W}$

After the late veneer, adding a large, differentiated projectile could significantly decrease the lunar $\epsilon^{182}\text{W}$, as the projectile's core would equilibrate with the lunar mantle. Recently, the Oceanus Procellarum was believed to have been formed by such a projectile, which might have impacted the Moon at about 1.963 ± 0.057 Ga [17]. The far side and near side of the Moon exhibit remarkable asymmetries in topography, crustal thickness, and chemical composition [78]. The far side of the Moon shows a layered structure composed of a primordial anorthositic crust and a more mafic-rich top layer [79]. At the same time, the near side lacks this structure and exhibits widespread low-Ca pyroxene, which was proposed to have an impact origin [80]. The Oceanus Procellarum (about 2900 km in diameter), which occupies most of the near-side area, was thought to be caused by the impact of a Ceres-sized asteroid [81]. As the asteroid dug down, the low-Ca pyroxene could have been formed by the mixture of molten crust and mantle materials. In contrast, a large amount of mantle material was scattered on the far side of the Moon to form the overlying mafic-rich layer [82]. A giant impact simulation made by Zhu et al. [83] proposed that the mass of the Ceres-sized asteroid (7.6×10^{20} kg) was ~25% of the mass of the Moon. The $\epsilon^{182}\text{W}$ value of the projectile's core was considered to be -3.0 to -5.0 ; thus, the lunar $\epsilon^{182}\text{W}$ would decrease by 0.10 – 0.15 [83]. Of note, most returned lunar samples were collected from the Oceanus Procellarum. This proposal needs to be confirmed with more samples from outside the Oceanus Procellarum.

Finally, while heated debates exist regarding the lunar age, there is much consensus about its mantle crystallization time. Although a significant difference in Hf/W ratios exists among the mantle reservoirs of different lunar rocks, radioactive ^{182}W ingrowth did not result in any difference in $\epsilon^{182}\text{W}$ values. For example, magma ocean crystallization

has given high-Ti mare basalts the highest Hf/W ratios of 40–80 and KREEP-rich rocks the lowest Hf/W ratios of 10–20 [12,16,17,84,85]; however, no difference in $\epsilon^{182}\text{W}$ values was found in these rocks. This indicates that the magma ocean crystallization happened later than 70 Ma. Similar ages of 150–240 Ma were given by other isotopic systems, such as ^{146}Sm – ^{142}Nd isochron ages for lunar FANs, Lu–Hf model ages of KREEP-rich rocks, and Pb–Pb ages for zircons separated from lunar mare basalts [86,87].

5. W Isotopic Constraints on the Lunar Origin

The Moon was traditionally thought to consist mainly of the impactor materials, suggesting that the BSM was chemically and isotopically different from the BSE [13]. However, with a mass of new high-resolution isotope data reported for terrestrial and lunar rocks, unexpected isotopic similarities of elements have been observed, including O [44,88], Si [89,90], K [91,92], Ti [93], Cr [94,95], and W [15]. The traditional giant impact scenario can possibly explain the similarities with an extremely particular combination of several parameters, including (1) a specific proportion of the impactor's core, impactor's mantle, and proto-Earth's mantle in the composition of the Moon; (2) a particular degree of equilibration of the impactor's core within the proto-Earth's mantle [14]. Kruijer and Kleine [15] estimated this possibility for W; as a result, the possibility of $\epsilon^{182}\text{W}$ similarity is less than 6% (Figure 4). In addition, by using 242 N-body simulations, Fischer et al. [23] came to a similar conclusion through detailed forward models of lunar and terrestrial accretion. As a result, possibilities of 1.6–4.7% for W and 5–8% for O were obtained.

The reconciliation of this contradiction can help us to understand the Earth–Moon system evolution. Three solutions have been proposed in recent studies, including (1) formation of the Earth and an impactor with identical initial isotopic compositions [96–98]; (2) alternative models in which the Moon predominantly derived from the mantle of the proto-Earth or a multiple impact scenario [7–9,90,93,97,99,100]; (3) post-giant-impact isotopic equilibration between the primitive Earth and primitive Moon [4,13,15,46]. With constraints provided by the ^{182}Hf – ^{182}W system and other elements, we will discuss the merits and demerits of these solutions in the following:

1. Formation of the Earth and impactor with identical initial isotopic compositions, most probably owing to the derivation of the proto-Earth and impactor from an isotopically homogeneous pre-solar disk reservoir. Nielsen et al. [101] suggested that the best chemical analogue to this reservoir is enstatite chondrites (and aubrite meteorites). This view concluded that the BSM should have the same isotopic composition as the BSE, as the Moon was composed of materials from the proto-Earth and the impactor. Similarities of stable isotopes, such as O, Cr, Ti, and V, were successfully explained because the isotopic composition of these elements in the proto-Earth and the impactor reflects their sources [97,98]. However, the ^{182}W composition of planetary mantles depends on their timescales and physical mechanisms (including temperature, pressure, metal–silicate equilibration, partition coefficients for W, and oxygen fugacity) of accretion, core formation, and mantle differentiation [33,56,102]. A positive $\epsilon^{182}\text{W}$ was considered to be generated in the mantle of the impactor because of its earlier core formation [103]. Therefore, the ^{182}W composition of the BSE and BSM should be disparate [55,104]. Moreover, the lunar debris disk probably contained metallic materials from the impactor's core, which are rich in W but defective in ^{182}W [14]. Finally, various degrees of metal–silicate equilibration without system-wide mixing might have led to ^{182}W heterogeneity in the Moon, even if the Earth and impactor had a uniform ^{182}W composition [46]. An inversion method was used to calculate the possibilities of similarity in W for the given unique Moon-forming impact scenarios; as a result, it was taken as a coincidence [14,97].
2. Alternative models in which the Moon predominantly derived from the proto-Earth mantle rather than the impactor [7–9,17,93]. Canup [7] proposed a scenario in which the Moon was formed primarily from materials that vaporized from the proto-Earth's mantle. This scenario successfully recreated the similarities of Si, O, and Cr [19,96].

Isotopic fractionation of Si depends on the core formation's temperature and pressure conditions. Light Si isotopes preferentially partition into metallic cores, resulting in isotopically-heavy mantles [89]. O isotopes had a mass-independent heterogeneity in the early solar system and were not fractionated by any petrologic process in the Earth or Moon [13]. Cr isotopes have sensitivity in tracing extra-terrestrial input. Therefore, the extreme similarities of Si, O, and Cr suggest that the Moon derived from the mantle of the proto-Earth after terrestrial core formation. As for W, $\epsilon^{182}\text{W}$ excesses of +0.10~+0.15 were reported in terrestrial Archean rocks (Figure 6), suggesting the ^{182}W compositions of the primitive BSE were generated by early mantle differentiation and then preserved to this day. This $\epsilon^{182}\text{W}$ excess is similar to that of the BSM, suggesting a derivation of the Moon from the primitive BSE. However, the formation of the isotopic heterogeneity in the BSE remains poorly investigated, and several views have been proposed, including metal–silicate equilibrium, late veneer, and core–mantle interaction. Cuk and Stewart [8] successfully explained the isotopic similarities between the Earth and Moon by using evection resonance to remove the Earth's angular momentum constraint. Although the Moon's excess of FeO content could not be met and a narrow range of initial conditions was needed in this model, it demonstrated the possibility of isotopic similarities in the case of loosening the angular momentum constraint. Similarly, Rufu et al. [99] proposed a multiple impact model in which the Moon was formed by various collisions between the Earth and smaller impactors. Compared to traditional Moon-forming impact scenarios, freedom in impact geometry and velocity allowed more lunar materials to be derived from the Earth, and the probability of the Earth–Moon similarity increased to tens of percentage points.

3. Post-giant-impact isotopic equilibration between the Earth and Moon via vaporized silicate. Pahlevan and Stevenson [13] devised a model of the Earth–Moon system as largely molten and partially vaporized after the giant impact. In this model, a deep terrestrial magma ocean and a proto-lunar magma disk were linked by a common silicate vapor atmosphere, which was vigorously convective to exchange materials. Under such conditions, the diffusive equilibrium of isotopic composition might result from mixing and equilibrating the Earth's mantle with the proto-lunar disk [13]. However, in the current high-temperature and high-pressure test, a shared silicate atmosphere only led to Earth–Moon equilibrium for Si and O [7–9], and not for refractory elements like Cr, Ti, and W [4,7,93]. Furthermore, based on a small V isotopic difference of $0.18 \pm 0.04\%$ between the BSE and BSM, Nielsen et al. [101] refuted the possibility of post-giant-impact equilibration between the Earth and Moon. Recently, a new giant impact model was proposed, in which the Moon was formed by high-energy, high-angular momentum giant impacts [92,105–107]. A new type of planetary structure named “synestia” was formed, in which the proto-lunar magma disk and terrestrial magma ocean combined to create a well-mixed reservoir. The Moon therefore had an identical isotopic composition to the Earth as it solidified from the reservoir (regardless of the possible mass-dependent isotope fractionations). However, the efficiency of this process for W homogeneity at $<0.1 \epsilon^{182}\text{W}$ level remains unknown [22].

6. Conclusions and Future Expectations

Reviewing the application of W isotopes in the Moon, the following insights were gained:

1. Relative to the BSE, the BSM has a significant $\epsilon^{182}\text{W}$ excess, which could be caused by radiogenic ^{182}W accumulation, disproportional late veneer on the Earth and Moon, and positive $\epsilon^{182}\text{W}$ in the mantle of the Moon-forming impactor.
2. Based on different explanations of the lunar $\epsilon^{182}\text{W}$ excess, the lunar ages are mainly divided into two categories: an early Moon that formed in 30–70 Ma after the solar system formation or a late Moon that formed later than 70 Ma after solar system formation.

3. Effects of the late veneer, meteorite contaminations on the lunar surface, and an Oceanus Procellarum-forming projectile could have profoundly influenced the lunar ^{182}W composition. However, these effects have yet to be proven, and significant uncertainties exist in the calculation parameters used in numerical modeling approaches.
4. The isotopic similarity between the Earth and Moon is a crucial constraint on the formation of the Moon. However, its origin is still unclear, and there are many hypotheses, such as (1) the formation of the Earth and the Moon from an isotopically homogeneous pre-solar disk reservoir; (2) the constitution of the Moon predominantly from the mantle of the proto-Earth; (3) post-giant-impact Earth–Moon equilibration. W isotopes could provide an essential constraint on these hypotheses.

Finally, these problems might be solved with the ultrahigh-precision W isotope measurement in lunar rocks and ancient terrestrial rocks lacking late veneer materials.

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