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Tungsten Isotopes in Planets

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Abstract

The short-lived Hf-W isotope system has a wide range of important applications in cosmochemistry and geochemistry. The siderophile behavior of W, combined with the lithophile nature of Hf, makes the system uniquely useful as a chronometer of planetary accretion and differentiation. Tungsten isotopic data for meteorites show that the parent bodies of some differentiated meteorites accreted within 1 million years after Solar System formation. Melting and differentiation on these bodies took ~1–3 million years and was fueled by decay of ^{26}Al. The timescale for accretion and core formation increases with planetary mass and is ~10 million years for Mars and >34 million years for Earth. The nearly identical ^{182}W compositions for the mantles of the Moon and Earth are difficult to explain in current models for the formation of the Moon. Terrestrial samples with ages spanning ~4 billion years reveal small ^{182}W variations within the silicate Earth, demonstrating that traces of Earth's earliest formative period have been preserved throughout Earth's history.

Keywords

core formation; hafnium-tungsten isotopes; late accretion; model ages

1. INTRODUCTION

In the past two decades, the short-lived ^{182}Hf-^{182}W decay system has evolved to a well-established radiogenic isotope system that is widely applied for examining the timescales and processes of planetary accretion and differentiation. Norman & Schramm (1983) were the first to discuss the use of this system as a short-lived chronometer, and Harper et al. (1991) outlined how this system can be used to date core formation in planetary bodies. The latter study also reported the first ^{182}W data for a meteorite (the Toluca IAB iron), obtained by negative thermal ionization mass spectrometry. Through the advent of multicollector inductively coupled mass spectrometry, it became possible to analyze the W isotopic composition of a more comprehensive suite of extraterrestrial samples, and studies between

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1995 and 1998 demonstrated the presence of significant ^{182}W variation in early Solar System materials and showed that these variations are, at least in part, attributable to the decay of now-extinct ^{182}Hf (Harper & Jacobsen 1996; Horan et al. 1998; Lee & Halliday 1995, 1996, 1997; Lee et al. 1997).

Although the initial interest in the Hf-W system stemmed from its utility to constrain the timescales of planetary core formation, the system has evolved to become a versatile tool with a wide range of applications in geo- and cosmochemistry (Kleine et al. 2009). As such, the Hf-W system provides key constraints on such diverse topics as the formation of chondrules and the origin of the Moon. The past few years have seen a tremendous increase in the measurement precision of ^{182}W compositions (Kruijer et al. 2012, Touboul & Walker 2012, Willbold et al. 2011). This has opened up new research avenues, in particular with regard to the earliest history of the silicate Earth but also through the ability to resolve sub-million-year age differences in meteorites.

This review outlines the basic principles of the Hf-W system and discusses applications of this system to elucidate the origin, accretion, and differentiation history of meteorite parent bodies and Mars as well as the Earth and Moon.

2. THE HAFNIUM-TUNGSTEN CHRONOMETER

2.1. Basic Principles

The ^{182}Hf-^{182}W chronometer is based on the decay of short-lived ^{182}Hf to stable ^{182}W (half-life = 8.9 ± 0.1 Ma). Thus, compared to other stable W isotopes, the abundance of ^{182}W can vary depending on the Hf/W ratio and time of Hf/W fractionation in a sample. Both Hf and W are refractory elements but have very different geochemical properties. As a moderately siderophile element, W preferentially partitioned into the metallic cores of planetary bodies, whereas Hf, as a lithophile element, was entirely retained in their mantles. This strong Hf/W fractionation during metal-silicate separation makes the Hf-W system uniquely useful as a chronometer of planetary core formation (Harper et al. 1991). Following core formation, further Hf/W fractionation likely occurred in the mantles of planetary bodies because of the tendency of W to partition more favorably into the melt phase than Hf during silicate crystal-liquid differentiation (Righter & Shearer 2003). Thus, the timescales of early processes, such as magma ocean crystallization or partial melting of the mantle, can potentially also be dated using the Hf-W system. Finally, in addition to providing information on the timescales of planetary differentiation, the Hf-W system is a powerful tool to date individual, early-formed meteorites and meteorite components, because there is commonly sufficient spread in the Hf/W ratios of the constituent minerals in these samples.

Variations in the abundance of ^{182}W do not always result from ^{182}Hf decay but can also have nucleosynthetic or cosmogenic origins (Figure 1). These nonradiogenic W isotope variations must be quantified before accurate ages can be determined. Tungsten has five stable isotopes (^{180}W, ^{182}W, ^{183}W, ^{184}W, ^{186}W) with different nucleosynthetic origins: the rare ^{180}W is a pure *p*-process nuclide, whereas ^{182}W, ^{183}W, ^{184}W, and ^{186}W are synthesized during both the *s*- and *r*-processes. The heterogeneous distribution of *s*- and *r*-process W nuclides results in correlated variations of ^{182}W/^{184}W and ^{183}W/^{184}W (Figure 1), and so the magnitude of nucleosynthetic ^{182}W variations can be quantified via the measurement of ^{183}W/^{184}W (Burkhardt et al. 2012, Qin et al. 2008b). By contrast, W isotope variations induced by secondary neutron capture during the interaction with galactic cosmic rays (GCR) are more difficult to quantify because they predominantly affect ^{182}W (Leya et al. 2003). Correction of GCR effects, therefore, requires an independent proxy, such as Pt, Os, or Hf isotopes (Kruijer et al. 2013, 2015; Qin et al. 2015; Walker 2012; Wittig et al. 2013).

2.2. Data Notation

Tungsten isotopic data are commonly expressed in ε^{182}W values as the parts per 10,000 deviation of ^{182}W/^{184}W from the ratio of the terrestrial standards. Similarly, ε^{183}W represents variations in ^{183}W/^{184}W. In some modeling studies, which use Hf-W isotopic data to constrain the accretion history of Earth, ε^{182}W values are used differently and are defined as the deviation of ^{182}W/^{184}W from the chondritic composition (Jacobsen 2005, Nimmo & Agnor 2006). This notation can be useful; in this case, for example, bulk Earth, which is assumed to have the same W isotopic composition as chondrites, always has a ε^{182}W value of zero. We note, however, that W isotopic data are always reported as the relative deviation from terrestrial standard values, and we use this data notation throughout.

More recently, W isotope data have also been reported as μ^{182}W values (where $\mu^{182}\mathrm{W} = 100 \times \varepsilon^{182}$ W), reflecting the higher precision of the W isotopic measurements that can now be achieved by modern thermal ionization mass spectrometer (TIMS) and multicollector inductively coupled plasma mass spectrometer (MC-ICPMS) techniques (Kruijer et al. 2012, Touboul & Walker 2012, Willbold et al. 2011). To remain consistent with the data as they are reported in the literature, we use both notations.

2.3. Model Ages

To calculate a Hf-W age of core formation from the ^{182}W composition of the mantle or core of a planetary body, the ^{182}W composition and Hf-W isotopic evolution of the bulk planet must be known. Chondritic meteorites derive from small planetary bodies that did not undergo melting and chemical differentiation and therefore represent appropriate proxies for the ^{182}W composition of bulk planets. As both Hf and W are refractory elements, little Hf/W fractionation is expected among bulk planetary bodies, and so the assumption of uniform Hf/W ratios among bulk bodies is reasonable. Modest variations in Hf/W ratios do occur, however, as is evident from the different Hf/W ratios of ordinary chondrites. These variations are likely related to the different metal-to-silicate ratios of the different groups of ordinary chondrites (Kleine et al. 2008).

Model ages of core formation are calculated as the time of (instantaneous) Hf/W fractionation from a reservoir having chondritic Hf/W as follows:

$$t = \frac{1}{\lambda} ln\left(\frac{Q_W\, f^{\mathrm{Hf/W}}}{\varepsilon^{182}\mathrm{W}_{\mathrm{j}} - \varepsilon^{182}\mathrm{W}_{\mathrm{chondrites}}}\right), \quad (1)$$

where λ is the ^{182}Hf decay constant of 0.078 ± 0.002 Ma^{-1} (Vockenhuber et al. 2004), $\varepsilon^{182}\mathrm{W}_j$ is the ^{182}W composition of mantle or core, and $\varepsilon^{182}\mathrm{W}_{\mathrm{chondrites}}$ is the present-day ^{182}W composition of chondrites, taken to represent the bulk undifferentiated planet. Although initial attempts to determine the ^{182}W composition of chondrites did not find a resolvable difference between chondrites and the terrestrial standard (Lee & Halliday 1995, 1996), later studies firmly established a ε^{182}W value of −1.9 ± 0.1 for chondrites (Kleine et al. 2002, 2004a; Schoenberg et al. 2002; Yin et al. 2002). The other quantities in Equation 1 are

$$Q_W = \frac{\left(^{182}\mathrm{Hf}/^{180}\mathrm{Hf}\right)_{\mathrm{SSI}} \times \left(^{180}\mathrm{Hf}/^{184}\mathrm{W}\right)_{\mathrm{chondrites}}}{\left(^{182}\mathrm{W}/^{184}\mathrm{W}\right)_{\mathrm{standard}}} \times 10^4 = \varepsilon^{182}\mathrm{W}_{\mathrm{chondrites}} - \varepsilon^{182}\mathrm{W}_{\mathrm{SSI}} \quad (2)$$

and

$$f^{\mathrm{Hf/W}} = \frac{\left(^{180}\mathrm{Hf}/^{184}\mathrm{W}\right)_{\mathrm{j}}}{\left(^{180}\mathrm{Hf}/^{184}\mathrm{W}\right)_{\mathrm{chondrites}}} - 1\,. \quad (3)$$

The initial Hf and W isotopic compositions of the Solar System are $\varepsilon^{182}\mathrm{W}_{\mathrm{SSI}} = -3.49 \pm 0.07$ and $(^{182}\mathrm{Hf}/^{180}\mathrm{Hf})_{\mathrm{SSI}} = (1.018 \pm 0.043) \times 10^{-4}$, as defined by the Hf-W systematics of Ca-Al–rich inclusions (CAI) (Burkhardt et al. 2008, Kruijer et al. 2014a). These values yield a time-integrated $^{180}\mathrm{Hf}/^{184}\mathrm{W}_{\mathrm{chondrites}} = 1.35 \pm 0.11$, consistent with that directly measured for carbonaceous chondrites (Kleine et al. 2004a). Using these values and $(^{182}\mathrm{W}/^{184}\mathrm{W})_{\mathrm{standard}} = 0.864900$ yields $Q_{\mathrm{W}} = 1.59$, which by definition is the difference between $\varepsilon^{182}\mathrm{W}_{\mathrm{chondrites}}$ and $\varepsilon^{182}\mathrm{W}_{\mathrm{SSI}}$ (Equation 2).

Equation 1 is applicable only for a single, instantaneous core formation event. However, the cores of larger bodies, such as Earth and Mars, almost certainly grew episodically as accretion proceeded. Thus, for these bodies, a realistic age of core formation cannot be calculated using the two-stage model age equation. A better approach is to model core formation as a continuous process during protracted accretion (Halliday et al. 1996, Harper & Jacobsen 1996). To track the isotopic evolution of the mantle, it is often assumed that accretion occurred at an exponentially decreasing rate, such that $F = 1 - e^{-t/\tau}$. Here, F is the fractional mass of a body, and τ is the mean-life of accretion, defined as the time necessary to reach 63% of the body's mass (Harper & Jacobsen 1996). The exponential growth model is typically applied when utilizing ^{182}W data to determine timescales of core formation for Mars and Earth (see Sections 5 and 6).

3. TUNGSTEN ISOTOPES IN CHONDRITIC METEORITES

In addition to providing important information about the W isotope composition and Hf-W isotopic evolution of bulk planetary bodies, Hf-W studies of chondritic meteorites have been used to constrain the timescales and processes of chondrule formation and the thermal histories of chondrite parent bodies. Dating chondrites is possible because the formation of chondrite components was typically associated with some sort of metal-silicate separation and, hence, significant Hf/W fractionation. For instance, ordinary chondrites contain abundant metal and therefore can readily be dated via metal-silicate isochrons (Kleine et al. 2008). Similarly, metal-silicate fractionation during chondrule formation (Becker et al. 2015) led to distinct Hf/W ratios of chondrules and matrix such that chondrule formation can be dated.

To date, there is only one precise Hf-W age for a primitive chondrite. Budde et al. (2016b) reported a Hf-W isochron for chondrule and matrix separates from the Allende CV3 chondrite, corresponding to an age of 2.2 ± 0.8 Ma after CAI formation (Figure 2). This age is in good agreement with other chronological data indicating that the majority of chondrules formed ~2–3 Ma after CAI formation (e.g., Kita & Ushikubo 2012). Budde et al. (2016b) also found complementary nucleosynthetic W isotope anomalies in chondrules and matrix. Whereas the chondrule separates, each consisting of hundreds to thousands of chondrules, have positive ε^{183}W, the matrix samples exhibit negative ε^{183}W values (Figure 3). Budde et al. (2016a) subsequently demonstrated that the same samples also show complementary nucleosynthetic isotope anomalies for Mo but not for Ba. These observations are best explained by the preferential incorporation into the matrix of a presolar metal carrier enriched in *s*-process nuclides and the complementary depletion of this carrier in the chondrules. Budde et al. (2016a) argued that this process was likely associated with metal-silicate fractionation accompanying chondrule formation.

Nucleosynthetic W isotope anomalies are minor to absent in bulk meteorites, including Allende (Figure 3). This observation, combined with the presence of large ^{183}W variations in chondrules and matrix (from +2.4 to −1.5 ε^{183}W), indicates that these two components derive from a single reservoir of nebular dust; otherwise, there is no reason why they should show complementary isotope anomalies resulting from the uneven distribution of a single presolar carrier. These data, therefore, are inconsistent with an origin of chondrules by protoplanetary impacts (e.g., Johnson et al. 2015, Sanders & Scott 2012) and indicate that chondrules formed in the solar nebula. Moreover, after their formation, neither appreciable chondrules nor matrix could have been lost, because bulk Allende would otherwise show a significant ^{183}W anomaly. This implies that after their formation, chondrules and matrix accreted rapidly to their parent body and chondrules from a given chondrite group formed within a narrow time interval (Budde et al. 2016b). Taken together, these data suggest that chondrule formation was a critical step in the accumulation of dust into planetesimals.

Although the parent bodies of chondrites escaped large-scale melting and differentiation, they nevertheless underwent significant heating, resulting in aqueous alteration and thermal metamorphism. The latter process can be dated using the Hf-W system because the thermal metamorphism of ordinary chondrites resulted in the redistribution and enrichment of W into the metal phase of these chondrites (e.g., Humayun & Campbell 2002). Kleine et al. (2008) reported Hf-W isochrons for several H chondrites of petrologic types 4, 5, and 6. In general, these data show that the Hf-W ages become younger with increasing metamorphic grade (i.e., petrologic type), consistent with progressive thermal metamorphism in deeper layers of the parent body (Trieloff et al. 2003). Owing to the high closure temperature of the Hf-W system in ordinary chondrites, the Hf-W ages closely approximate the time of the thermal peak in these bodies, which occurred at ~10 Ma after CAI formation. This timescale of thermal metamorphism is consistent with decay of short-lived ^{26}Al as the major heat source determining the thermal history of ordinary chondrites (Kleine et al. 2008, Trieloff et al. 2003).

There will undoubtedly be more Hf-W studies on chondritic meteorites in the future. For instance, with the increased precision of ^{182}W data achievable with modern analytical techniques, it may be possible to determine the timing of solar nebula metal-silicate fractionation processes and to assess potential links of such processes to the formation of chondrules.

4. TUNGSTEN ISOTOPES IN DIFFERENTIATED METEORITES

Differentiation of meteorite parent bodies involves the physical separation of metal and silicate through the segregation of dense metal melts toward the center, forming a core, and the upward migration of silicate melts, forming a mantle and crust. The distinct classes of differentiated meteorites bear testimony to these processes, as they derive from the cores (iron meteorites) and the silicate portions (e.g., angrites, eucrites, ureilites) of several protoplanetary bodies. Application of the Hf-W isotope system to these meteorites can thus provide essential information on the timescales and processes of differentiation. Such information is critical for assessing the physical and chemical processes involved in the formation, separation, and segregation of metal and silicate melts during differentiation, for identifying the heat source(s) for melting, and for constraining the accretion timescales of small planetary bodies.

4.1. Iron Meteorites

Most iron meteorites are thought to derive from the metal cores of protoplanetary bodies. The term magmatic iron meteorites is often used for these samples because they formed predominantly by fractional crystallization of metallic magma (e.g., Scott & Wasson 1975). Based on their chemical composition, the magmatic irons are subdivided into several groups (e.g., IIAB, IIIAB, IVA, IVB), each of which represents metal from a distinct parent body (e.g., Scott & Wasson 1975).

As iron meteorites contain virtually no Hf, they preserve the ^{182}W composition at the time of metal-silicate fractionation on their parent bodies. Thus, an age of core formation on these bodies can be determined by measuring the ^{182}W composition of an iron meteorite (e.g., Horan et al. 1998, Lee & Halliday 1996), and Equation 1 simplifies to

$$t = \frac{1}{\lambda} ln\left(\frac{\varepsilon^{182}\mathrm{W}_{\mathrm{chondrites}} - \varepsilon^{182}\mathrm{W}_{\mathrm{SSI}}}{\varepsilon^{182}W_{\mathrm{iron}} - \varepsilon^{182}\mathrm{W}_{\mathrm{SSI}}}\right). \qquad (4)$$

There have been several extensive studies of ^{182}W systematics in iron meteorites (Horan et al. 1998, Kleine et al. 2005a, Markowski et al. 2006, Qin et al. 2008a, Scherstén et al. 2006), but only recently has it became it possible to quantify GCR-induced shifts on ε^{182}W in iron meteorites sufficiently well to calculate accurate and precise Hf-W ages (Kruijer et al. 2013, Kruijer et al. 2014b, Wittig et al. 2013). Kruijer et al. (2014b) reported combined W and Pt isotopic data for the major groups of magmatic irons (IIAB, IID, IIIAB, IVA, IVB). In that study empirical Pt-W isotope correlations and precise GCR-corrected (i.e., pre-exposure) ε^{182}W were obtained for each iron group (Figure 4). These data reveal resolved differences in ε^{182}W with values ranging from −3.40 ± 0.03 for the IIAB irons to −3.18 ± 0.05 for the IVB irons. The corresponding model ages for metal-silicate separation, calculated using Equation 4 from above, are 0.7 ± 0.6 Ma (IIAB irons) and 2.7 ± 0.8 Ma (IVB irons) after CAI formation (Kruijer et al. 2014b) (Figure 5). One major implication of these data is that decay of ^{26}Al was the major heat source for melting during core formation. This is because thermal modeling shows that only bodies accreted within <1.5 Ma after CAI formation will melt due to heating by ^{26}Al decay (e.g., Hevey & Sanders 2006), and that in these bodies core formation would occur within <3 Ma after CAI formation (Qin et al. 2008a), which is the timescale obtained from the ^{182}W data.

The ε^{182}W values (and hence core formation model ages) are inversely correlated with the degree of volatile element depletion and S content inferred for each core (Figure 5). As the S content exerts a strong control on the melting temperature of the core (e.g., Wasson & Huber 2006), these data indicate that the timing of metal segregation depended on the melting temperature of the core. To account for this observation, Kruijer et al. (2014b) argued that the different Hf-W ages reflect distinct stages of melting and melt segregation, because differentiation involved the consecutive formation of a eutectic Fe-FeS melt (at ~1,250 K), a silicate melt (~1,400 K), and, finally, a pure Fe metallic melt (~1,800 K). Thus, in S-rich bodies (e.g., IIAB), most of the metal melted early and segregated downward at approximately the same time as silicate melts migrated upward. By contrast, in S-poor bodies (e.g., IVA, IVB), most of the Fe metal could melt significantly only after silicate melt extraction, and so core formation in these bodies occurred later than in S-rich bodies (e.g., IIAB).

The slightly higher ε^{182}W of the IID and IVB irons could also reflect a later accretion time of their parent bodies, resulting in a later onset of melting and differentiation (Kruijer et al. 2014b). Of note, the IID and IVB irons not only have a higher ε^{182}W but also are the only irons that have nucleosynthetic W isotope anomalies (Kruijer et al. 2013, Qin et al. 2008a) (Figure 5). Budde et al. (2016a), using nucleosynthetic Mo isotope anomalies (Burkhardt et al. 2011), showed that the IID and IVB irons are genetically linked to carbonaceous chondrites, whereas the other irons (i.e., IIAB, IIIAB, IVA) belong to the non-carbonaceous group of meteorites. In light of this distinct genetic heritage, Budde et al. (2016a) argued that the IID and IVB irons formed in a different area of the solar nebula and their higher ε^{182}W therefore reflects a later accretion and differentiation of carbonaceous compared to non-carbonaceous iron meteorite parent bodies. This would be consistent with the idea that carbonaceous meteorites formed at a greater heliocentric distance than that of other meteorites, where accretion rates were slower. Using thermal modeling of asteroids internally heated by ^{26}Al decay shows that the parent bodies of non-carbonaceous irons probably accreted within ~0.4 Ma of CAI formation (Kruijer et al. 2014b), whereas the parent bodies of carbonaceous irons accreted later, ~1 Ma after CAI formation (Kruijer & Kleine 2016).

4.2. Eucrites, Angrites, and Ureilites

Eucrites and angrites are mafic igneous rocks from the crust of differentiated protoplanets (e.g., Mittlefehldt et al. 1998) and are characterized by some of the most radiogenic ε^{182}W observed in meteorites. As these samples likely underwent more than one stage of Hf-W fractionation, the Hf/W ratio and ε^{182}W of a given sample do not correspond to those of the bulk mantle of the parent body. Thus, for eucrites and angrites, an age of core formation cannot be calculated using Equation 1 but can instead be inferred using the Hf-W isotopic evolution of the mantle sources of these samples (Kleine et al. 2012, Touboul et al. 2015b).

Most eucrites investigated so far have Hf-W ages ranging from ~4 to ~22 Ma (Kleine et al. 2005b, Touboul et al. 2015b), although some eucrite zircons have younger Hf-W ages of up to ~35 Ma, post–CAI formation (Roszjar et al. 2016, Srinivasan et al. 2007). As such, these data provide evidence for a prolonged interval of magmatism and thermal metamorphism on the eucrite parent body. Touboul et al. (2015b) showed that eucrites seem to derive from a single source whose elevated Hf/W (i.e., ^{180}Hf/^{184}W ~19) was established <1 Ma after CAI formation. Angrites have Hf-W ages from ~5 to ~11 Ma after CAI formation and derive from at least two mantle sources characterized by different Hf/W ratios, resulting from distinct events of metal-silicate separation (Kleine et al. 2012, Markowski et al. 2007). As for the eucrites, the elevated Hf/W of the angrite sources was established early, well within ~2 Ma after CAI formation. The elevated Hf/W ratios of the eucrite and angrite sources most likely result from metal-silicate separation during silicate melt extraction, indicating that this event occurred within ~1–2 Ma of CAI formation.

Ureilites derive from an incompletely differentiated body and are mantle restites left behind after the extraction of both metal and silicate partial melts (e.g., Mittlefehldt et al. 1998). Lee et al. (2009) demonstrated that ureilites are characterized by strong ^{182}W deficits, and Budde et al. (2015), using higher-precision measurement techniques, subsequently showed that ureilites have an initial $\varepsilon^{182}\text{W} = -3.13 \pm 0.04$. This value is slightly more radiogenic than those of most magmatic irons (Figure 5). As the major Hf/W fractionation in ureilites results from the extraction of silicate partial melts, removing most of the Hf from the mantle, ureilites maintained the ^{182}W composition acquired at the time of silicate melt extraction. Consequently, as for iron meteorites, a model age for differentiation can be obtained from the mean ε^{182}W of ureilites (Equation 4), indicating that silicate melt extraction on the ureilite parent body occurred at 3.3 ± 0.7 Ma after CAI formation, ~2 Ma later than in the eucrite and angrite parent bodies and ~2 Ma later than core formation in most iron meteorite parent bodies (Figure 5).

This difference in differentiation timescales most likely reflects differences in the time of parent body accretion. Using thermal modeling, Budde et al. (2015) argued that the ureilite parent body accreted ~1.6 Ma after CAI formation and hence ~1 Ma later than the parent bodies of magmatic irons. Owing to this later accretion, the initial abundance of ^{26}Al in the ureilite parent body was too low to cause complete melting, leaving the parent body incompletely differentiated. By contrast, the parent bodies of iron meteorites, eucrites, and angrites accreted earlier and hence contained sufficient ^{26}Al to undergo complete differentiation. Conversely, the parent bodies of chondrites accreted later and thus contained too little ^{26}Al to melt and differentiate (Kunihiro et al. 2004). Taken together, these data reveal an inverse correlation between accretion time (and hence initial ^{26}Al content) and extent of melting and differentiation.

5. TUNGSTEN ISOTOPES IN MARS

Tungsten isotope analyses on Martian meteorites reveal large ^{182}W variations within the Martian mantle, with ε^{182}W ranging from approximately +0.2 to +3.0 (Foley et al. 2005, Kleine et al. 2004a, Lee & Halliday 1997). The ^{182}W variations are broadly correlated with variations in ^{142}Nd, the decay product of short-lived ^{146}Sm. As both Sm and Nd are lithophile, the ^{142}Nd variations bear testimony to early silicate differentiation on Mars, possibly related to the crystallization of a global magma ocean (e.g., Borg et al. 2016, Debaille et al. 2007). Thus, the correlation of ^{182}W with ^{142}Nd within the Martian meteorite suite indicates that at least some of the ^{182}W variations are also caused by silicate differentiation, and not core formation. As such, ^{182}W isotope studies of Martian meteorites have important applications with regard to constraining the timescales of accretion, core formation and early silicate differentiation.

The coupled ^{182}W-^{142}Nd systematics, combined with modeling parent-to-daughter fractionations during magma ocean crystallization, suggest large-scale differentiation of the Martian mantle ~20–40 Ma after CAI formation (Debaille et al. 2009, Foley et al. 2005, Kleine et al. 2004a). In particular, the elevated ε^{182}W of ~3 of the nakhlites, combined with their ε^{142}Nd of ~0.8, has been used to argue for an early differentiation of the Martian mantle, probably within ~25 Ma after CAI formation (Debaille et al. 2009, Foley et al. 2005). As the nakhlite source probably contained garnet, this source was characterized by high Hf/W, consistent with the radiogenic ^{182}W composition of the nakhlites. Regardless of the exact composition of the nakhlite source, its high ε^{182}W cannot be the result of core formation, because the Hf/W ratio estimated for the Martian mantle is too low (see below) to produce the ε^{182}W of ~3 observed for the nakhlites (Dauphas & Pourmand 2011, Nimmo & Kleine 2007).

To determine the timescale of core formation on Mars from the ^{182}W data, it is necessary to know the ε^{182}W of bulk silicate Mars. This value has been inferred from ^{182}W data for shergottites, the major group of Martian meteorites. The shergottites display less radiogenic ^{182}W compositions than the nakhlites and typically have ε^{182}W values ranging between ~0 and ~1 (Foley et al. 2005, Kleine et al. 2004a, Lee & Halliday 1997). More recent work, using higher-precision measurement techniques and a more diverse range of shergottites, reveals somewhat larger ^{182}W variations with ε^{182}W of up to ~2 for the most depleted shergottites (Kruijer et al. 2016). Nevertheless, most shergottites, including the enriched and intermediate subgroups, have very similar ^{182}W compositions (average ε^{182}W = 0.37 ± 0.04) and exhibit a limited range in ^{142}Nd compositions. Owing to nucleosynthetic Nd isotope heterogeneity among meteorites and planets, the precise ^{142}Nd/^{144}Nd of bulk Mars is difficult to quantify, but any reasonable composition is between the ^{142}Nd/^{144}Nd of the modern terrestrial mantle (ε^{142}Nd ~0) and those of ordinary chondrites (ε^{142}Nd ~−0.17) (Burkhardt et al. 2016). Because the average ε^{142}Nd value of enriched and intermediate shergottites is within this range (Borg et al. 2016, Caro & Bourdon 2010, Debaille et al. 2007) and because these samples all have indistinguishable ε^{182}W, their mean ε^{182}W = 0.37

± 0.04 may provide a good approximation of the ^{182}W composition of the bulk Martian mantle.

To utilize this ^{182}W composition for calculating an age of core formation also requires knowledge of the Hf/W ratio of bulk silicate Mars. Compared to Earth's mantle, the Martian mantle is characterized by a much lower Hf/W ratio, reflecting the more oxidized conditions of core formation on Mars as compared to Earth (Treiman et al. 1986). As for Earth's mantle (see below), the Hf/W ratio of bulk silicate Mars cannot be measured directly but must be inferred by comparing the abundance of W to that of a refractory lithophile element having an incompatibility similar to that of W. Studies on lunar and terrestrial basalts have shown that these conditions are met by U and Th (Arevalo & McDonough 2008; Newsom 1986, 1996; Palme & Rammensee 1981), and so the Hf/W ratio of bulk silicate Mars can be determined from the U/W (or Th/W) of Martian samples, multiplied by the chondritic Hf/U (or Hf/Th). This approach is based on the assumption that refractory elements such as U, Th, Hf, and W occur in chondritic relative proportions in bulk Mars (Nimmo & Kleine 2007). With this assumption, Dauphas & Pourmand (2011) obtained a precise Hf/W ratio for bulk silicate Mars, corresponding to ^{180}Hf/^{184}W = 4.0 ± 0.5. One important implication of this low Hf/W ratio is that the Martian mantle contains approximately four times more W than Earth's mantle, and so late accretion of chondritic material, which for Earth can produce significant ^{182}W variations within the mantle (see Section 6), is inconsequential for the ^{182}W composition of Martian samples.

The two-stage model age for core formation in Mars, calculated using Equation 1 and ε^{182}W = 0.37 ± 0.04 and ^{180}Hf/^{184}W = 4.0 ± 0.5 for bulk silicate Mars, is 4.1 ± 2.7 Ma after CAI formation. As noted above, the assumption of instantaneous core formation is likely not valid for larger bodies, and so the two-stage model age does not provide an appropriate estimate for the time of core formation. A more realistic age is obtained by assuming continuous core formation and an exponential growth model for Mars. Using this model, and the composition of the Martian mantle from above, gives a mean-life of accretion τ of ~2.4 Ma, with a range of ~0.7–~3.7 Ma. Thus, based on these data, Mars would have reached 63% of its mass by ~2.4 Ma and have been completely formed by ~10 Ma (Dauphas & Pourmand 2011) (Figure 6). These time constraints on Mars's growth history are dependent on the degree to which metal and silicates equilibrated during growth of the core. As discussed in more detail below (see Section 6.2), during giant collisions, the impactor core may not have fully equilibrated with the target mantle. If Mars formed in this manner, its accretion may have taken longer than the ~10 Ma calculated based on the assumption of full equilibration (Mezger et al. 2013, Morishima et al. 2013).

The comparatively small mass of Mars has been a challenge to standard accretion models for the terrestrial planets. Although these models are able to reproduce the mass and position of Venus and Earth, they consistently predicted a Mars that is too massive. One solution to this problem is to invoke a truncated disk at ~1 AU, in which case there simply was too little material for Mars to grow to a larger size (Hansen 2009). The truncation of the disk might be related to the inward-then-outward migration of Jupiter, as predicted in the Grand Tack model (Walsh et al. 2011). An alternative explanation for the small mass of Mars comes from a process called pebble accretion, in which terrestrial planets grow by the gradual accumulation of submeter-sized objects (Levison et al. 2015). The efficiency of this process decreases with heliocentric distance and, by its physical nature, would have led to a small mass for Mars. The ^{182}W data are consistent with these two scenarios for Mars's accretion in that they show growth of Mars halted much earlier than it did for Earth, resulting in the much smaller mass of Mars.

6. TUNGSTEN ISOTOPES IN THE EARTH

6.1. Hafnium and Tungsten in the Earth

To apply the Hf-W system to better understand the timing and nature of Earth differentiation processes, including core formation, it is necessary to determine the Hf/W of the bulk silicate Earth (BSE) as accurately as possible. As with the bulk silicate portion of Mars, the Hf/W of the BSE cannot be measured directly. This is true even for terrestrial mantle peridotites, because the incompatibilities of Hf and W differ considerably. Thus, one approach to obtain a Hf/W ratio for BSE is to estimate individual concentrations of Hf and W.

Concentration estimates of Hf in the BSE range narrowly from approximately 280 to 300 ppb with an uncertainty of ~10% (1σ) (McDonough & Sun 1995, Palme & O'Neill 2014). These estimates are based on the assumptions that Earth has a bulk chondritic Hf concentration (Blichert-Toft & Albarède 1997) and that Hf as a lithophile trace element is wholly concentrated in the silicate portion of the planet. Constraining the abundance of W in the BSE is much more challenging than for Hf because the majority of Earth's W resides in the inaccessible core. Further, as a highly incompatible trace element in the silicate Earth, W is also concentrated in the crust (Newsom et al. 1996). As ~40% of the W budget in the silicate Earth is in the continental crust, W abundances in specific mantle domains can be strongly modified by prior melt extraction (depletion) as well as incorporation of recycled, W-rich crust (enrichment). In addition, W can be fluid mobile, so the possibility of aqueous transport of W must also be factored into estimates based on W concentration measurements of rocks presumed to be representative of major silicate reservoirs (e.g., König et al. 2011, Touboul et al. 2014).

Most estimates for W concentrations in the BSE have been made by correlating W with other refractory, highly incompatible lithophile trace elements, such as U, Th, Ta, and Ba. The abundances of these elements in the BSE are much better constrained than that of W because they are presumed to have been excluded from the core (e.g., McDonough 2003). For example, Arevalo & McDonough (2008) estimated a W abundance of 13 ± 5 ppb (1σ) for the BSE based mainly on correlations between W and U for different major silicate reservoirs, for example, continental crust and depleted mantle, coupled with an assumed concentration of U in the BSE. König et al. (2011) estimated a similar abundance of 12 ppb based primarily on correlations between W and Ta; that study did not specify an uncertainty for the concentration. Assuming BSE concentrations for Hf and W of 280 ± 28 and 13 ± 5 ppb, respectively, the Hf/W of the BSE is 21.5 ± 8.7 (^{180}Hf/^{184}W = 25.4 ± 10.3).

Another approach to estimating the Hf/W ratio of the BSE is to determine the U/W (or Th/W) of the BSE and multiply it by the chondritic Hf/U (or Hf/Th). This approach is based on the assumption that the BSE contains refractory lithophile elements (such as Hf, U, Th) in chondritic relative proportions. Using W/U = 0.65 ± 0.05 for the BSE (Arevalo & McDonough 2008) and Hf/U = 12.5 ± 0.8 for chondrites (Dauphas & Pourmand 2011), the Hf/W of the BSE is 19.2 ± 1.9; using W/Th = 0.19 ± 0.05 (Newsom et al. 1996) for the BSE and Hf/Th = 3.57 ± 0.13 (Dauphas & Pourmand 2011), the Hf/W of the BSE is 18.8 ± 5.0. All three of these estimates are consistent with each other and, taken together, indicate that the Hf/W of the BSE is ~20 (^{180}Hf/^{184}W ~24) with an uncertainty of ~10–20%.

If Earth has a bulk chondritic W concentration of ~180 ppb, then mass balance requires that ~90% of Earth's W resides in the core, and that the core has a W concentration of ~500 ppb (McDonough 2003). These W concentration estimates for the core and BSE indicate an average metal/silicate D value (concentration ratio) of ~40 (e.g., Newsom et al. 1996, Wade & Wood 2005). This D value provides important information regarding the conditions of terrestrial core formation. Metal-silicate D values for W are highly variable depending on conditions of equilibration, such as f_{O2}, pressure, and temperature as well as the concentrations of the elements P, C, and S (Cottrell et al. 2009). Partitioning under low pressures and comparatively low temperatures results in metal/silicate D values >100 (e.g., Wade & Wood 2005). The comparatively high concentration of W in the silicate Earth therefore suggests that W equilibration occurred primarily under comparatively high pressure and temperature conditions, where D values are <50. The W abundance of the BSE can be well accounted for as a result of a series of metal-silicate equilibration events following major accretionary impacts, as the Earth grew (e.g., Rubie et al. 2011, Wade & Wood 2005).

6.2. Timescale for Terrestrial Core Formation

The ε^{182}W (or μ^{182}W) value of the mean mantle today by definition is 0, which is ~190 ppm more enriched in ^{182} W than bulk chondrites. This observation provides strong evidence that ^{182}Hf was extant while large parts of the Earth's core segregated. Using Equation 1 to calculate a two-stage model core formation age for the Earth, and taking the ^{180}Hf/^{184}W ratio of 24 ± 5 ($f^{Hf/W}$ = 17 ± 4) above, yields an age of 34 ± 3 Ma, post–CAI formation. As noted above, this calculation is applicable only for a single, instantaneous core formation event. However, even some iron meteorite groups that sample asteroid-sized bodies preserve evidence for multiple stages of core formation (e.g., Kruijer et al. 2014b), so the core of a large body such as the Earth almost certainly grew episodically as accretion proceeded. Given that it is difficult to envision any form of planetary growth resulting in a mantle with a Hf/W ratio that is less than chondritic, the two-stage model age records the earliest time the core formation process for Earth could have ceased (e.g., Halliday et al. 1996). Despite the somewhat loose constraint this places on the age of core formation, the ^{182}W of the mantle indicates that although most core formation likely occurred early in Solar System history, core growth in the Earth continued for several tens of Ma and was completed later than in meteorite parent bodies and Mars.

As it relates to deciphering the nature and timing of terrestrial core formation, more complex and probably more realistic models for the Hf-W system have been proposed (e.g., Halliday 2004, Harper & Jacobsen 1996, Jacobsen 2005, Kleine et al. 2004b, Nimmo & Agnor 2006), but there remain several unknowns that prevent significant tightening of constraints related to this. For instance, the exponential growth model suggests that ~63% of Earth's mass was reached by ~11 Ma, whereas ~95% was reached by ~30 Ma after CAI formation (Jacobsen 2005, Yin et al. 2002). However, in reality, Earth's core did not form by the continuous influx of metallic material, as assumed in the exponential growth model, but instead grew episodically by a few giant impacts that hit Earth (e.g., Nimmo & Agnor 2006). The stochastic nature of these giant impacts, combined with their strong effect on the ε^{182}W value of Earth's mantle (see below), prevents determining a unique age for the completion of Earth's accretion from the Hf-W data; these data are equally consistent with a last giant impact on Earth having occurred at ~30 Ma, as well as ~100–200 Ma, post–CAI formation (e.g., Nimmo & Kleine 2015, Rudge et al. 2010).

Another chief unknown in the interpretation of ^{182}W data in terms of core formation timescales is the degree to which metal and silicates equilibrated during giant impacts (Halliday 2004, Kleine et al. 2004b, Nimmo & Agnor 2006) and whether or not chemical and isotopic equilibration occurred at the same rate during accretionary events that led to growth of the core. Laboratory experiments as well as fluid dynamical modeling suggest that large impactor cores merged with Earth's core without prior equilibration with Earth's mantle (e.g., Dahl & Stevenson 2010; Deguen et al. 2011, 2014). As impactor core material is characterized by a lower ε^{182}W than the mantle, incomplete equilibration leads to a larger ^{182}W excess in Earth's mantle and ultimately to a later inferred core formation time compared to the full equilibration case (Figure 7). Unfortunately, precisely quantifying the degree to which impactor core material equilibrated with Earth's mantle has not yet been possible (Nimmo & Kleine 2015). For instance, Nimmo et al. (2010) incorporated isotopic evolution calculations in dynamical models of terrestrial planet formation and showed that the ^{182}W of Earth's mantle is reproduced if the degree of reequilibration was between ~30% and ~70%. Similarly, Rudge et al. (2010) showed that the Hf-W and Pb-Pb ages of Earth's core would be concordant at ~100–150 Ma, provided that on average only ~40–50% of the impactor core material equilibrated with Earth's mantle (see also Halliday 2004) (Figure 7). However, the Hf-W and Pb-Pb ages can also be brought into agreement by invoking full equilibration combined with a very rapid early accretion of Earth, followed by a long accretion hiatus and a late final giant impact at ~100–150 Ma after CAI formation (Rudge et al. 2010, Yu & Jacobsen 2011) (Figure 8).

These examples serve to highlight the fact that the stochastic nature of giant impacts and the unknown extent to which metal-silicate equilibration occurred during these events currently make it impossible to precisely determine the Hf-W age for core formation on Earth. Although the Hf-W data cannot be used to construct one simple accretion curve for Earth, they nevertheless provide bounds on accretion (Rudge et al. 2010). For instance, in the case of full metal-silicate equilibration, ~80% of Earth's mass must have accreted by ~35 Ma, whereas the last ~14% could have accreted any time after this (Figure 8). Rudge et al. (2010) argued that a reasonable lower limit for the degree of equilibration is ~40%, in which case the Hf-W systematics would indicate that ~50% of Earth's mass was accreted by ~60 Ma (Figure 8).

6.3. Tungsten Isotope Applications to Other Terrestrial Processes

Data published in the past several years have documented ^{182}W isotopic anomalies present among diverse materials from the silicate Earth (here, the term anomaly refers to ^{182}W/^{184}W ratios that vary outside of analytical uncertainties of the laboratory standards) (Figure 9). Thus, in addition to utilizing the average ^{182}W composition of the BSE to constrain the timing of terrestrial core formation, the Hf-W isotope system has important applications in the study of the past and present workings of the silicate portion of Earth.

Hadean to Eoarchean supracrustal rocks are characterized by μ^{182}W values that range from approximately −8 to +20 (in this subsection, because the variations in W isotopic composition are so small among terrestrial rocks, we use the μ^{182}W notation), although most of the data are dominated by values between +10 and +15 (Liu et al. 2016; Puchtel et al. 2016a,b; Rizo et al. 2016b; Touboul et al. 2012, 2014; Willbold et al. 2011, 2015) (Figure 9). Further, Rizo et al. (2016a) reported positive μ^{182}W values ranging from +12 to +48 for Phanerozoic flood basalts from the Ontong Java plateau (120 Ma) and the Baffin Bay locale (60 Ma) in Canada. Thus, isotopically anomalous portions of the mantle evidently have survived throughout most of Earth’s history. By contrast, no anomalies were found in the 3.3-Ga Komati komatiites of southern Africa (Touboul et al. 2012), nor for some samples of modern ocean island basalts and midocean ridge basalts (Liu et al. 2016, Rizo et al. 2016a, Touboul et al. 2012, Willbold et al. 2011).

The positive anomalies in many of the ancient supracrustal rocks and komatiites as well as the Phanerozoic flood basalts are of the opposite sign to the effects expected from core-mantle interactions, so they must be explained by one or more other processes. Several options have been considered. For example, Willbold et al. (2011) interpreted μ^{182}W values averaging ~+13 for Isua supracrustal rocks as having resulted from the derivation of precursor rocks from mantle that had not yet accumulated the major proportion of siderophile elements (and low μ^{182}W) added to the mantle by a process commonly termed late accretion. Late accretion, or late veneer, is normally defined as the late-stage addition of materials with bulk chondritic compositions to the mantle subsequent to core formation (Chou 1978).

^{182}W-enriched and -depleted domains within the mantle could also have been produced while ^{182}Hf was extant as a result of radioactive ingrowth. Ingrowth could follow either metal-silicate or silicate-silicate fractionation processes occurring within the first ~50 Ma of Solar System history (Touboul et al. 2012). For example, periodic passage of accreting metals through a chemically homogeneous mantle domain, such as a basal magma ocean, would lead to a reduction in the concentration of W (and highly siderophile elements, or HSEs) from this mantle domain compared to ambient mantle. This in turn would lead to an increase in Hf/W and eventual isotopic evolution of this mantle domain to a ^{182}W-rich composition.

Isotopic anomalies could also have been created wholly within the silicate portion of the Earth as a result of Hf and W partitioning in early-formed global or localized magma oceans/seas (Brown et al. 2014). Both elements behave as incompatible trace elements in silicate systems, but W is normally much more strongly partitioned into the melt compared to Hf (Arevalo & McDonough 2008, König et al. 2011). This means that any early geological process involving silicate crystal-liquid fractionation would lead to changes in Hf/W and, hence, eventually the μ^{182}W value of the reservoir.

The processes that can lead to ^{182}W heterogeneities in the mantle are not mutually exclusive. It is likely that more than one of these processes has been involved in the generation of the observed anomalies. Given these diverse models, it is therefore important to find ways to discriminate among the models for specific cases. One way is by identifying or excluding the collateral effects that would be expected for other short-lived isotopic tracer systems. For example, the short-lived ^{146}Sm-^{142}Nd system ($t_{1/2}$ = 103 Ma) is expected to broadly mimic the ^{182}Hf-^{182}W system, because Sm/Nd and Hf/W fractionations caused by crystal-liquid processes in silicate domains are generally similar. Processes that lead to increases in Sm/Nd, such as crystal accumulation, will also cause a corresponding increase in Hf/W, leading to eventual coupled increases in both ^{142}Nd/^{144}Nd and ^{182}W/^{184}W, if the fractionation occurs while ^{182}Hf is still alive. The converse is true for processes such as melting or liquid evolution. The magnitude in the variation of one isotopic ratio relative to the other will reflect the degree of fractionation (the process) and the timing. If the fractionation occurred during the first ~30 Ma of Solar System history, variations in ^{182}W/^{184}W could be much larger than variations in ^{142}Nd/^{144}Nd. Conversely, processes acting more than 50 Ma into Solar System history were likely to have generated larger variations in ^{142}Nd/^{144}Nd than ^{182}W/^{184}W (Brown et al. 2014, Rizo et al. 2016b).

Although ^{182}W and ^{142}Nd anomalies are present in most of the early-Earth supracrustal rocks noted above, no clear correlations between the two isotope systems are evident in any of the data sets yet published. Puchtel et al. (2016a), however, reported negative μ^{182}W (−8) and μ^{142}Nd (−5) values for 3.55 Ga komatiites from Schapenburg, South Africa (Figure 9). Although negative μ^{182}W in mantle-derived rocks is potentially an indication of core-mantle exchange (or any other metal-silicate equilibration process), such a process would have no effect on ^{142}Nd. Hence, the authors concluded that the negative anomalies for both systems were the result of a common process, which they attributed to crystal-liquid fractionation in an early silicate magma ocean.

There will undoubtedly be more discoveries of anomalous ^{182}W reported by future studies. Strong negative anomalies in modern, plume-derived rocks without evidence for anomalous ^{142}Nd will most likely be ascribed to some sort of exchange of W elemental or isotopic equilibration between the core and lowermost mantle. Mapping the extent of recent/modern anomalies might also allow identification of the locations of the primordial materials within the mantle.

7. TUNGSTEN ISOTOPES IN THE MOON

The Moon most likely formed as a result of a giant impact between the proto-Earth and a body that may have been as massive as Mars (e.g., Benz et al. 1986, Canup & Asphaug 2001, Hartmann & Davis 1975). The timing of this putative event and the genetic heritage of the materials that coalesced to form the Moon are still hotly debated. Dynamical models of the early Solar System indicate that the giant impact could have occurred during the lifetime of ^{182}Hf, so the Hf-W isotope system has important applications with respect to constraining the formation and differentiation ages of the Moon. Further, ^{182}W serves as an additional (radiogenic) isotopic tracer that complements other (nonradiogenic) genetic tracers, such as the isotopic compositions of O, Si, and Ti, with which to compare the make-up of the Earth and Moon, enabling the exploration of formational mechanisms. For example, the isotopic similarities between the Earth and Moon may indicate collisional processes involving a rapidly spinning proto-Earth (Cuk & Stewart 2012), collision between two similarly sized bodies (Canup 2012), or a very energetic hit-and-run collision (Reufer et al. 2012).

7.1. ^{182}W Composition of the Moon

The measurement history of W isotopes in lunar rocks and the conclusions resulting from the measurements have evolved considerably as our understanding of the processes involved and measurement techniques have advanced. It is useful to review the progression of these studies. Initial measurements of W isotopes in lunar rocks were reported by Lee et al. (1997). The study found significant ^{182}W heterogeneity within the Moon and concluded that the Moon formed and differentiated within the lifetime of ^{182}Hf, that is, within the first ~60 Ma of Solar System history. Subsequent studies (Lee et al. 2002, Leya et al. 2000) recognized that at least some of the isotopic variability was induced through the interaction of the lunar samples with GCR. Most important to this modification process is the $^{181}\mathrm{Ta}(n,\gamma)^{182}\mathrm{Ta}(\beta^-)^{182}\mathrm{W}$ reaction, which ultimately leads to apparent ^{182}W excess compared to the pre-GCR isotopic compositions (Leya et al. 2000). Initial attempts to correct for GCR effects significantly reduced the range of ^{182}W compositions observed among lunar samples, but some level of ^{182}W heterogeneity remained (Kleine et al. 2005c, Lee et al. 2002). As with previous studies, the isotopic heterogeneity was interpreted to mean that the Moon formed within the first 60 Ma of Solar System history, while ^{182}Hf was still extant, and variable Hf/W in the lunar mantle would lead to differences in isotopic composition.

Using refined chemical separation and mass spectrometric techniques, Touboul et al. (2007) reported ^{182}W data for metals separated from 13 chemically diverse basalts and impact melt rocks. Metals are desirable for the study of ^{182}W in lunar rocks because they are characterized by extremely low Ta/W, so Ta burnout effects are minimal. Touboul et al. (2007) found no statistically meaningful ^{182}W differences between the investigated samples and no difference between the average μ^{182}W value they obtained for the Moon (+9 ± 10) and Earth (0). They interpreted these results to indicate that the Moon formed, and its magma ocean crystallized, beyond the effective lifetime of ^{182}Hf. These conclusions were based on two assumptions. First, because of the different compatibilities of Hf and W during silicate crystal-liquid fractionation processes, it was assumed that the crystallization of the lunar magma ocean resulted in the formation of mantle domains (e.g., high and low Ti basalt sources; K + rare earth elements + P, or KREEP) with substantially different Hf/W ratios (Righter & Shearer 2003). Thus, the isotopic homogeneity among these lunar rocks argues that the lunar magma ocean crystallized after ^{182}Hf was no longer extant. Similarly, it was assumed that the mantles of the Earth and Moon have significantly disparate Hf/W ratios, so if the Moon originally formed with a ^{182}W composition identical to the proto-Earth, the isotopic uniformity of the two bodies today also argues that the Moon formed after ^{182}Hf was no longer extant.

Using recent developments in mass spectrometric techniques that now provide an analytical precision of ~± 5 ppm on ^{182}W, two recent studies showed that the Moon is characterized by a ~25 ppm excess in ^{182}W compared to the BSE (Figure 10). Touboul et al. (2015a) reported ^{182}W data for metal from two lunar samples, whereas Kruijer et al. (2015) reported data for seven whole-rock samples, combined with Hf isotope measurements to correct for GCR effects on ^{182}W. Both studies analyzed exclusively KREEP-rich impact melt rocks and reported uniform ^{182}W compositions within uncertainties with an average μ^{182}W of ~+25. This value is slightly higher than the mean composition of lunar metals reported by Touboul et al. (2007), most likely because the ^{182}W composition of some of the metal samples analyzed by Touboul et al. (2007) were modified by W burnout during GCR-interaction, similar to the effects observed for iron meteorites.

7.2. Origin of Excess ^{182}W in the Moon

As noted by Halliday (2008) and Walker (2014), even if the Moon formed with a ^{182}W composition that was identical to the BSE, it might not be expected that the silicate portions of the two bodies retained the same isotopic composition. Based on estimates for absolute and relative abundances of HSEs in the lunar and terrestrial mantles, it is likely that a final ~0.02 wt% and ~0.5 wt% of materials with chondritic bulk compositions were added to the mantles of the Moon and Earth, respectively, during the late accretionary stage of planetary growth (e.g., Day & Walker 2015, Day et al. 2007). As this probably happened primarily after formation of the Moon, the added materials would have increased the concentration of W in the BSE by as much as 10% but, more importantly, have decreased the μ^{182}W value of the BSE by 20 to 30 ppm (Figure 11). By contrast, the proportionally much less chondritic matter added to the lunar mantle would have led to a decrease in the μ^{182}W value of the lunar mantle by only ~1–4 ppm. If late accretion occurred in this manner, it is predicted that the lunar mantle should be enriched in ^{182}W by ~25 ppm, relative to the BSE (Walker 2014), which is exactly the ^{182}W composition measured for the Moon (Kruijer et al. 2015, Touboul et al. 2015a). One important implication of these data is that late accretion on the Earth and Moon started contemporaneously, such that the impactor core must have stripped the HSEs from the Earth's mantle on its way to merge with Earth's core (Touboul et al. 2015a).

The simplest interpretation of the data, therefore, is that the Moon formed with a μ^{182}W value identical to that of the BSE, and that radioactive ingrowth did not significantly modify the compositions of the mantle sources of the different rocks. Consequently, this means that the mantle source regions of the lunar rocks formed by magma ocean crystallization were generated after ^{182}Hf was no longer extant, more than 60 Ma into Solar System history. The projected common, immediate post–Moon formation μ^{182}W values for the Moon and Earth suggest the Moon also formed subsequent to the lifetime of ^{182}Hf, although this conclusion is based on the assumption that the mantles of the Moon and Earth have different Hf/W ratios. If this is not true, then the system provides no constraint on the lateness of formation of the Moon. As noted above, however, the Hf/W ratio estimate of the BSE is accompanied by large uncertainties, and this is also true for the lunar mantle. Hence, no strong conclusion can be reached at this time regarding the age of the Moon based on the Hf-W system, other than it likely formed comparatively late in Solar System history.

7.3. Origin of the Moon

A final important contribution of W isotopes to the story of the formation of the Moon comes from the projected identical $\mu^{182}W$ values for the Moon and Earth immediately following formation of the Moon. The isotopic similarity of the Moon and Earth with respect to genetically relevant isotopic tracers (e.g., O, Si, Ti) has been a major problem in the giant impact hypothesis for the formation of the Moon (e.g., Dauphas et al. 2014, Pahlevan & Stevenson 2007). This is because the canonical model of a giant impact between the proto-Earth and a Mars mass body would result in the formation of the Moon from materials largely derived from the impactor (e.g., Canup & Asphaug 2001). Given the seemingly low probability that the proto-Earth and impactor would have essentially the same genetic make-up (e.g., Pahlevan & Stevenson 2007), this has led to new impact models that may allow a higher proportion of the lunar mass to derive from the proto-Earth (Canup 2012, Cuk & Stewart 2012, Reufer et al. 2012). However, these models are dynamically far less probable than the canonical model and may be more likely than the canonical model to mix away ^{182}W isotopic heterogeneity in Earth's mantle (Nakajima & Stevenson 2015). It has also been argued that the impactor simply formed from materials genetically very similar to those of Earth, because both impactor and Earth derive from a homogeneous inner disk reservoir (Dauphas et al. 2014).

Tungsten isotopes add another dimension to the isotopic constraints for deciphering the origin of the Moon because, unlike other isotopic tracers, the ^{182}W composition of a planetary mantle does not reflect its genetic makeup but is ultimately dependent on the timing of core formation and the Hf/W ratio that results. It has been argued that the nearly identical ^{182}W isotopic compositions for the Earth and Moon are happenstance (Dauphas et al. 2014) and can be accounted for by an impact of a Mars-sized, strongly reduced impactor onto an oxidized proto-Earth, combined with only limited equilibration of the impactor core with Earth's mantle (Wade & Wood 2016). However, as the giant impact involved mixing of components with very different ^{182}W compositions, by far the most probable outcome is a significant ^{182}W anomaly in the Moon (Kruijer et al. 2015) (Figure 12), making the happenstance explanation unpalatable for W isotopes.

Taken together, the indistinguishable ^{182}W compositions of the pre-late veneer BSE and the Moon constitute a challenge to current models for the formation of the Moon. The similar ^{182}W signatures may be happenstance, reflecting a specific combination of impactor composition and giant impact condition. This scenario would imply a low degree of equilibration between the impactor core and Earth's mantle, because otherwise a strong downward shift in $\mu^{182}W$ of Earth's mantle would result, ultimately leading to a larger ^{182}W excess for the Moon. As noted above, however, interpreting the ~25 ppm ^{182}W excess of the Moon over the present-day BSE as being a result of disproportional late accretion to the Earth and Moon implies that the core of the Moon-forming impactor efficiently stripped the HSEs from Earth's mantle. This efficient HSE removal in turn implies a substantial (but poorly defined) degree of metal-silicate equilibration (Touboul et al. 2015a). Reconciling these disparate observations will require a more precise determination of the effects of late accretion on ^{182}W compositions, a better understanding of the fate of the impactor core during large collisions, and the accommodation of any post–giant impact processes that modified the ^{182}W compositions of lunar and terrestrial samples. In any event, if the Earth and Moon had identical W isotopic compositions immediately following formation of the Moon, any successful model of lunar origin must account for this.

8. CONCLUSIONS

Tungsten isotope measurements on extraterrestrial and terrestrial samples have led to several major discoveries:

- The parent bodies of differentiated meteorites accreted earlier than those of chondrites and underwent melting and differentiation due to internal heating by ^{26}Al decay.
- Complementary nucleosynthetic W isotope anomalies in chondrules and matrix indicate a solar nebular origin of chondrules and rule out that chondrules are the result of protoplanetary impacts.
- The timescales of accretion and core formation increase with increasing planetary mass: Meteorite parent bodies accreted within the first few Ma; accretion of Mars took ~10 Ma; and the earliest time growth of Earth and segregation of its core can have been completed is within ~34 Ma of Solar System formation.
- The Moon exhibits a small ^{182}W excess over the present-day silicate Earth, most likely resulting from the proportionally much lower mass of primitive material added to the Moon compared to Earth by late accretion.
- Immediately following the giant impact, the Moon's and Earth's mantles had indistinguishable ^{182}W compositions. This ^{182}W homogeneity is not predicted in current formation models of the Moon and presents a key constraint for any successful model of lunar origin.
- Terrestrial samples with ages spanning ~4 Ga reveal widespread ^{182}W variations within the silicate Earth. The ^{182}W anomalies either reflect derivation from mantle sources that lack some portion of the late veneer or are the product of very early differentiation processes in the mantle, predating the putative Moon-forming impact. Either way, the ^{182}W heterogeneities in the silicate Earth demonstrate that signatures of Earth's earliest formative period have been preserved throughout most of Earth's history.

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LITERATURE CITED

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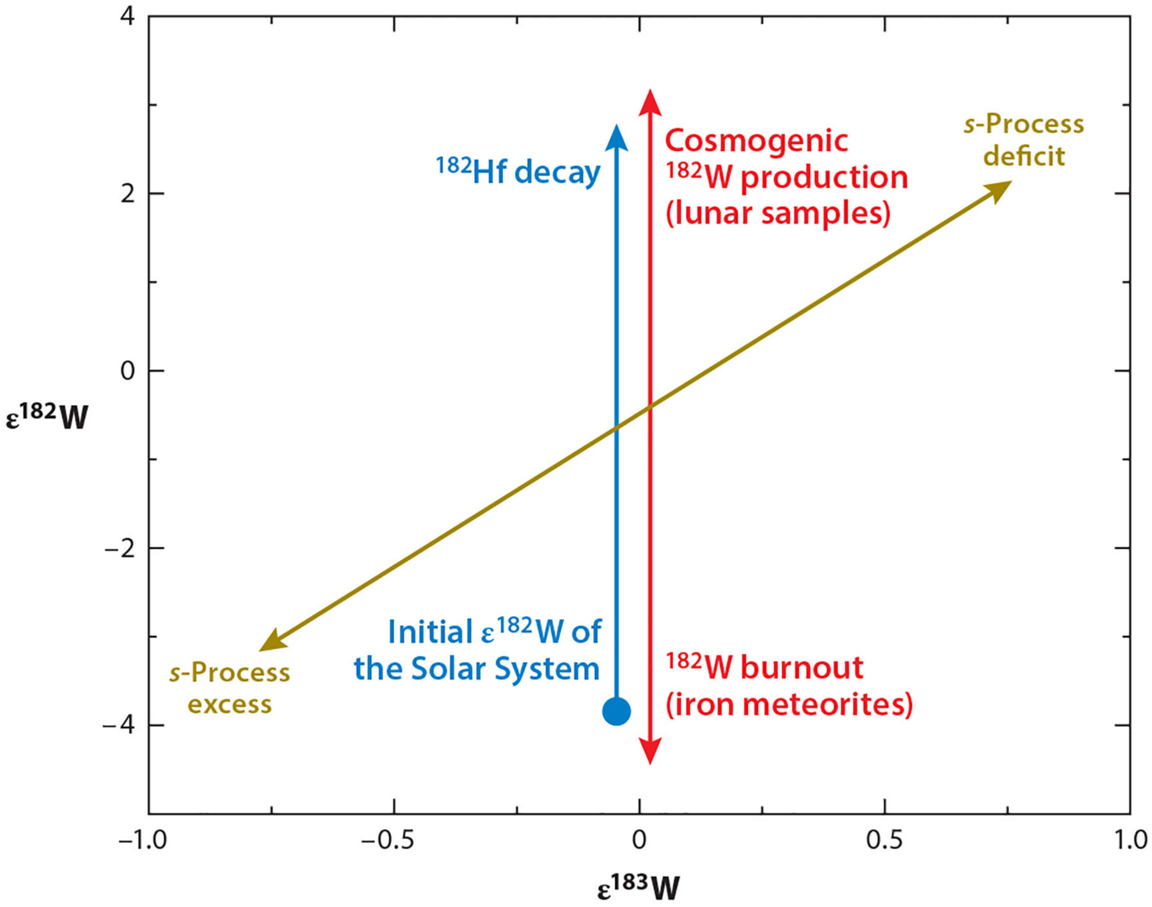

Figure 1.

Possible origin of W isotope variations, where ε^{182}W and ε^{183}W refer to the deviation in parts per 10,000 of ^{182}W/^{184}W and ^{183}W/^{184}W ratios from terrestrial standards. Note that cosmogenic effects do not result in resolvable ε^{183}W variations, because the neutron capture effects on ^{183}W, ^{184}W, and ^{186}W cancel out during fractionation correction of measured ^{183}W/^{184}W relative to ^{186}W/^{184}W (Kleine et al. 2005a). For nucleosynthetic isotope variations, ε^{182}W and ε^{183}W are correlated such that $\varepsilon^{182}\text{W} = 1.41 \times \varepsilon^{183}\text{W}$, as observed for acid leachates of primitive meteorites (Burkhardt & Schönbächler 2015, Burkhardt et al. 2012) and Ca-Al–rich inclusions (Burkhardt et al. 2008, Kruijer et al. 2014a). For chondrules and matrix from the Allende CV3 chondrite, a slightly shallower slope of approximately 1.25 has been observed (Budde et al. 2016b).

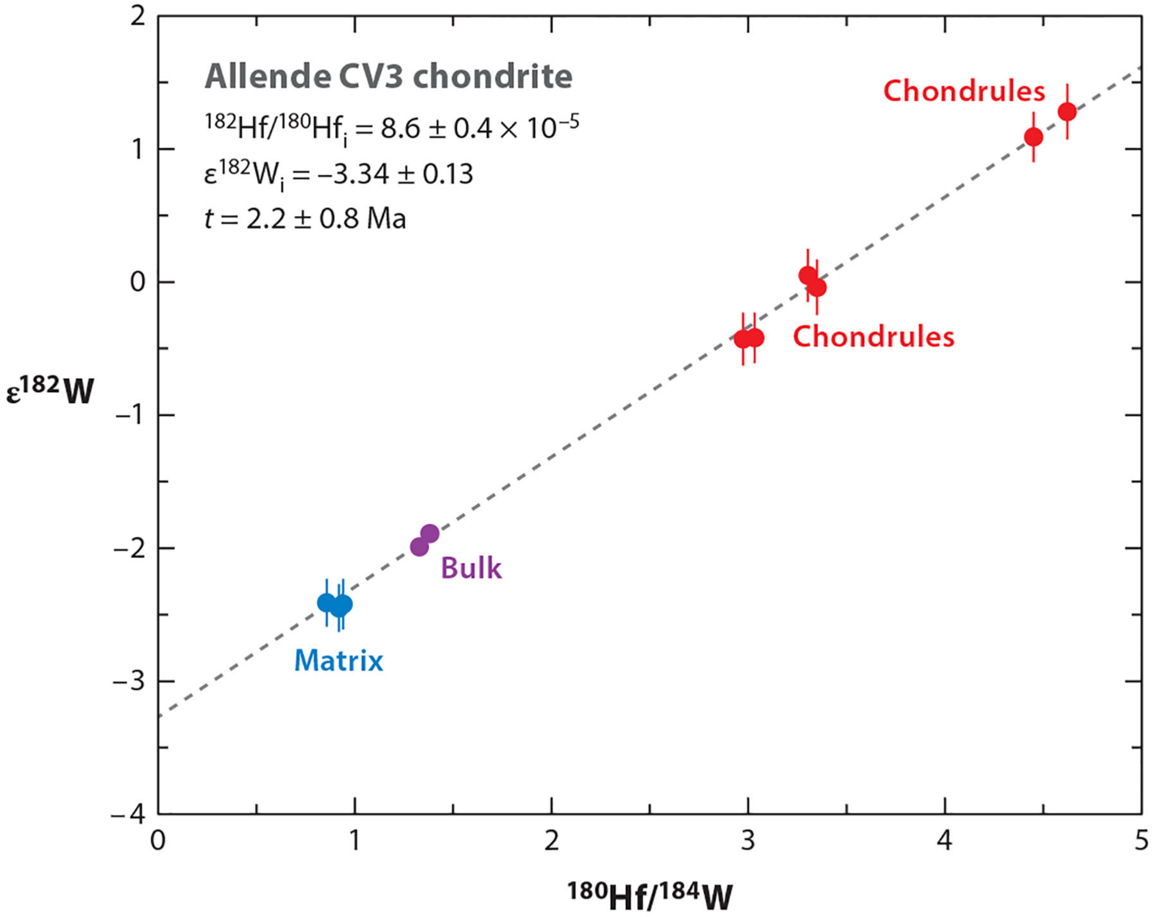

Figure 2.

Hf-W isochron for Allende chondrules and matrix. Linear regression (*gray dashed line*) of the data for matrix and chondrules yields an isochron with a slope of ^{182}Hf/^{180}Hf$_i$ = (8.6 ± 0.4) × 10^{-5}, corresponding to an age difference relative to CAI of 2.2 ± 0.8 Ma. Hf-W data from Budde et al. (2016b). Abbreviation: CAI, Ca-Al–rich inclusions.

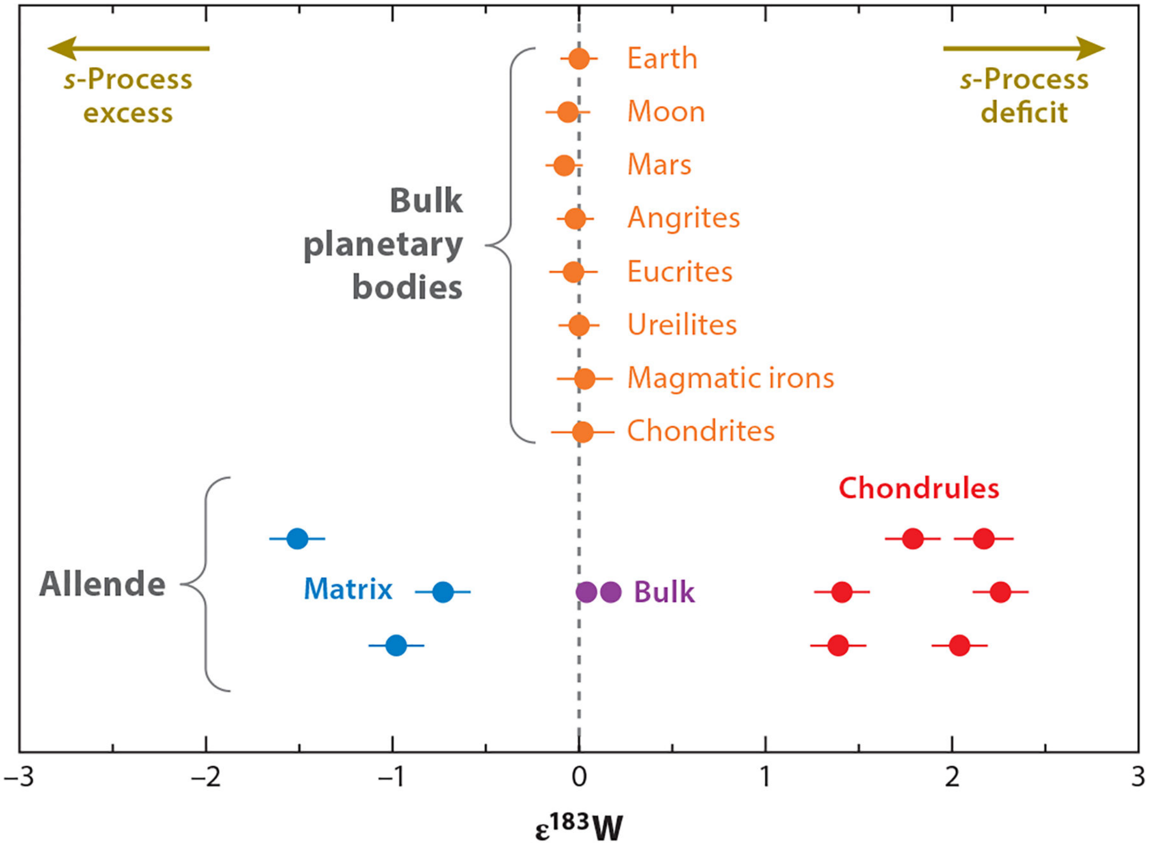

Figure 3.

Complementary nucleosynthetic W isotope variations in chondrules and matrix from the Allende CV3 chondrite. Data are from Budde et al. (2016b) and references therein.

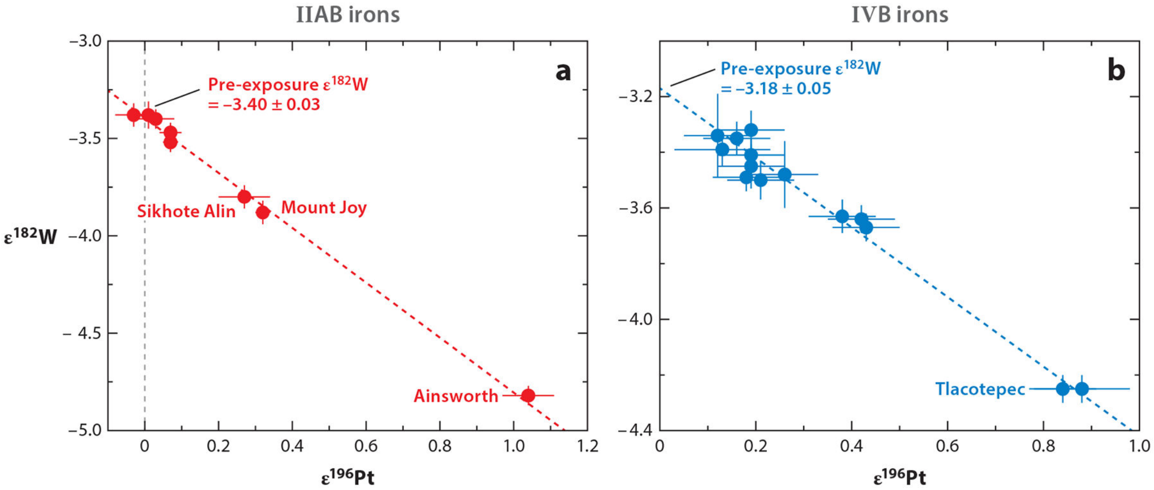

Figure 4.

Correlations of Pt and W isotope compositions measured for (*a*) IIAB and (*b*) IVB iron meteorites. Variations in ε^{196}Pt are caused solely by galactic cosmic ray (GCR)-induced neutron capture (predominantly on ^{195}Pt) and can thus be used to assess the magnitude of GCR-induced shifts in ε^{182}W. The pre-exposure ε^{182}W for each group is defined by the intercept of the Pt-W isotope correlation at $\varepsilon^{196}\text{Pt} = 0$. Similar correlations and precise pre-exposure ε^{182}W were also obtained for the IID, IIIAB, and IVA irons (Kruijer et al. 2014b). Figure adapted from Kruijer et al. (2014b).

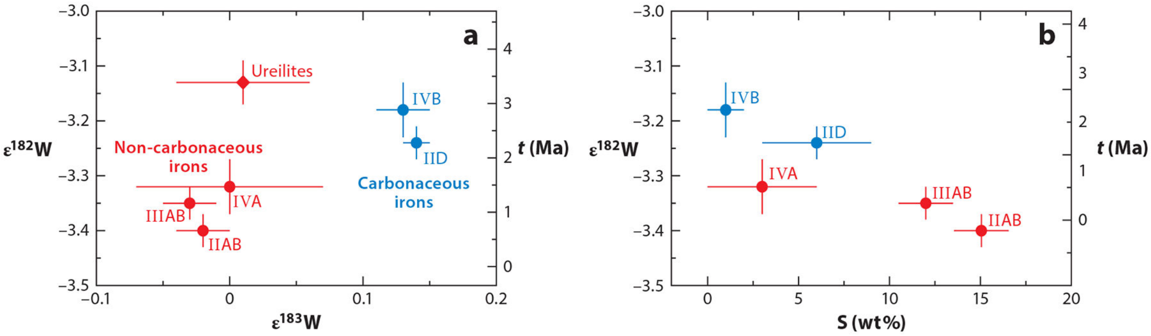

Figure 5.

(*a*) ε^{182}W versus ε^{183}W for magmatic iron meteorites and ureilites. Corresponding model ages are also shown. Note that only the IID and IVB irons have nucleosynthetic W isotope anomalies and these two irons display the highest ε^{182}W. These two irons belong to the carbonaceous group of meteorites, whereas the other irons and ureilites are non-carbonaceous meteorites (Budde et al. 2016a). Tungsten isotope data from Budde et al. (2015), Kruijer & Kleine (2016), and Kruijer et al. (2014b). (*b*) Correlation of ε^{182}W versus S content for parent bodies of magmatic iron meteorites. For the S content inferred for each core, see Goldstein et al. (2009).

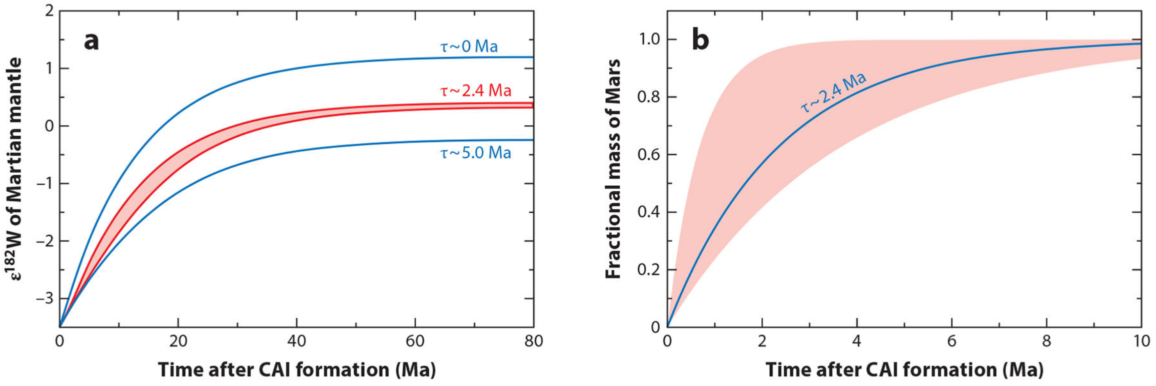

Figure 6.

ε^{182}W evolution of the Martian mantle during continuous core formation. (*a*) Evolution of ε^{182}W in the Martian mantle over time. (*b*) Mass versus time for the accretion of Mars, assuming an exponential growth model. The red-shaded areas in panels *a* and *b* indicate values of τ that are consistent with the ε^{182}W estimated for the bulk Martian mantle. Note that complete metal-silicate equilibration during core formation on Mars is assumed. Figure adapted from Dauphas & Chaussidon (2011), in which slightly different values for τ were obtained, because a different accretion model and bulk composition for Mars were assumed. Within uncertainty, the estimated accretion timescales are consistent, however. Abbreviation: CAI, Ca-Al–rich inclusions.

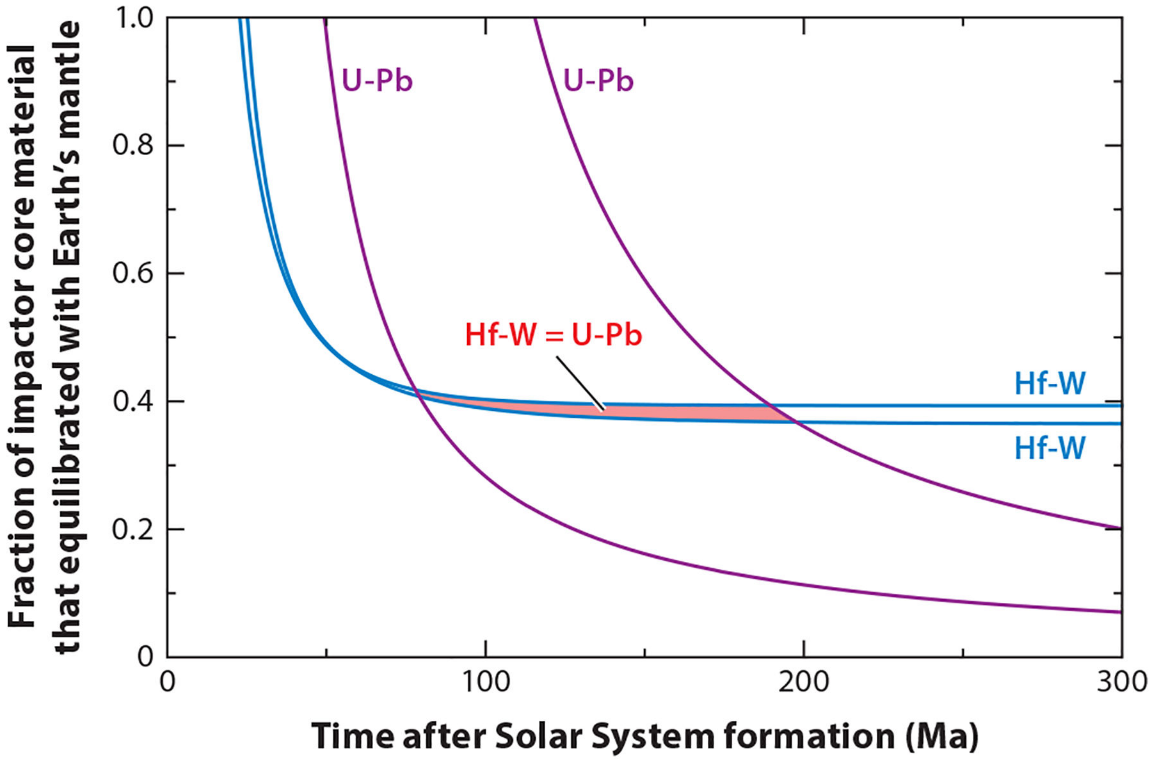

Figure 7.

Hf-W and U-Pb ages for the formation of Earth as a function of the degree of metal-silicate equilibration calculated assuming an exponential growth model for Earth. The ages shown correspond to the end of accretion, as defined by the time at which 90% of Earth's mass was reached. Figure adapted with permission from Kleine & Rudge (2011).

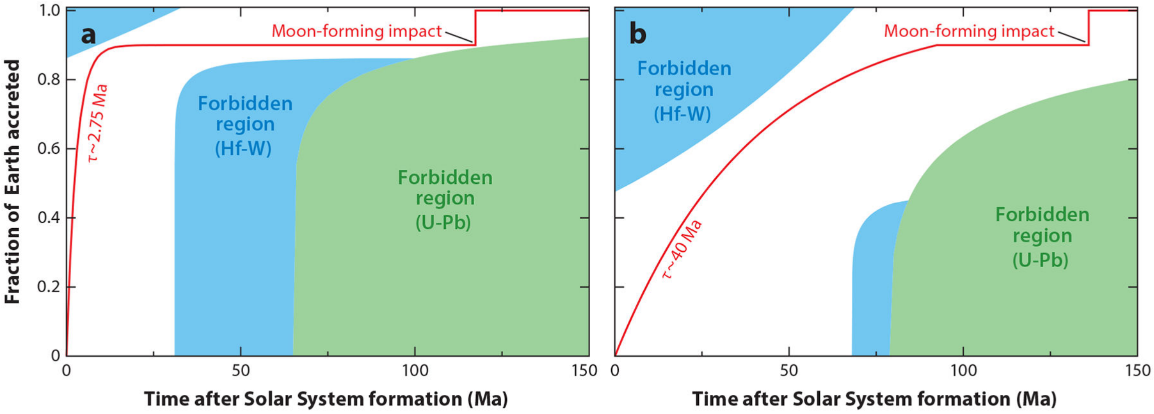

Figure 8.

Bounds on the accretion of Earth as inferred from Hf-W and U-Pb isotope systematics. The shaded regions are forbidden based on Hf-W (*blue*) and U-Pb (*green*) systematics. The red curve is an example of an accretion curve for Earth with a mean age of accretion indicated; the value of **τ** corresponds to the early stages of growth until approximately 90% of Earth's mass was accreted. The accretion curve for Earth must lie wholly in the unshaded region. The bounds on accretion depend on the degree of metal-silicate equilibration and cases for (*a*) full and (*b*) approximately 40% equilibration are shown. Figure adapted with permission from Kleine & Rudge (2011).

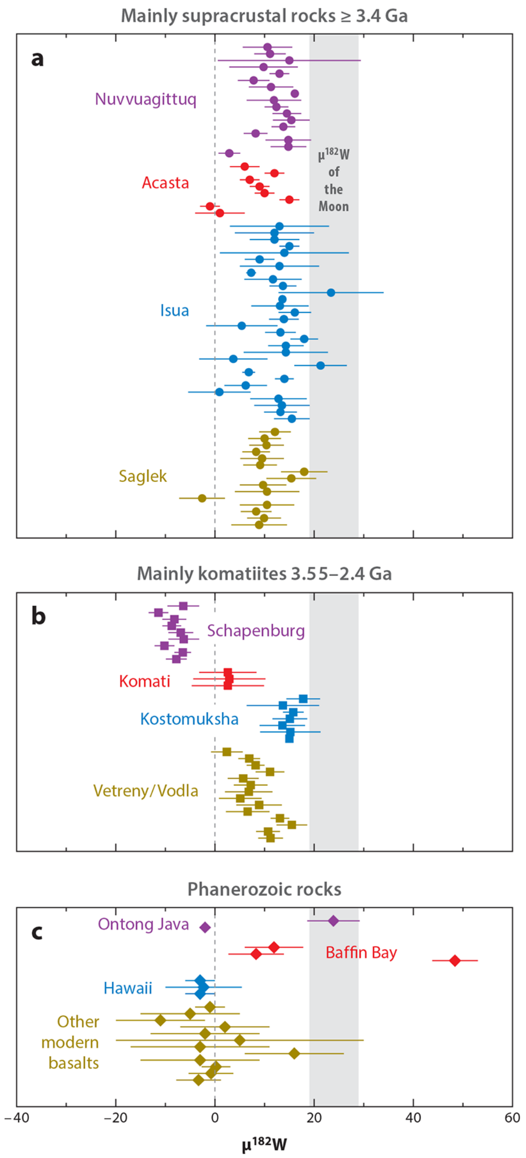

Figure 9.

$\mu^{182}W$ values for various ancient and modern terrestrial rocks. (*a*) Mainly supracrustal rocks ≥3.4 Ga. (*b*) Mainly komatiites ranging in age from 3.55 (Schapenburg) to 2.4 Ga (Vetreny/ Vodla). (*c*) Data for Phanerozoic rocks, including samples from Ontong Java (0.12 Ga), Baffin Bay (0.06 Ga), and modern oceanic and ocean island basalts. Note that in most instances, variability in isotopic composition relates to different rock types for a given location. Data are from Liu et al. (2016), Puchtel et al. (2016a,b), Rizo et al. (2016a,b), Touboul et al. (2012, 2014), and Willbold et al. (2011, 2015). The gray bar indicates the $\mu^{182}W$ of the Moon (see also Figure 10).

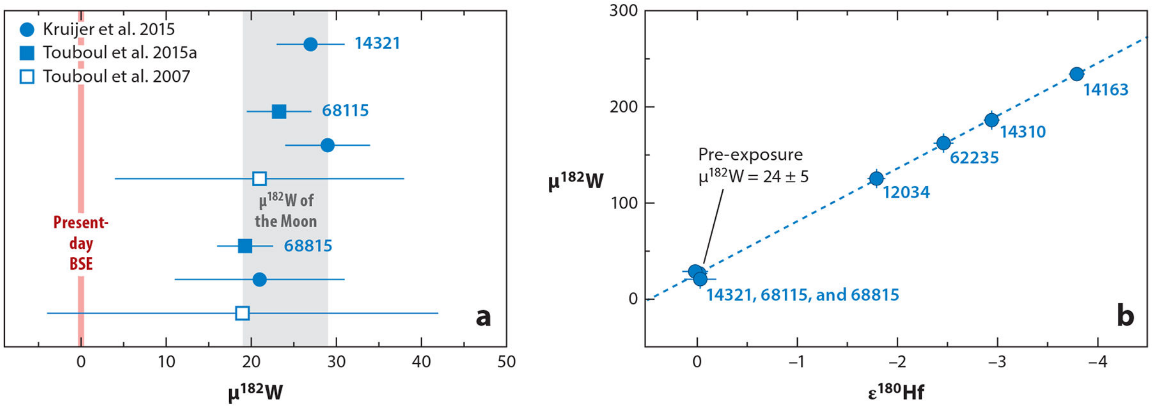

Figure 10.

^{182}W data for lunar samples. (*a*) Data for KREEP-rich samples 14321, 68115, and 68815 from three different studies. These three samples are devoid of GCR-induced effects on ^{182}W, as is evident from the absence of Hf isotope anomalies in these samples. Note the much higher precision of the two 2015 studies. (*b*) μ^{182}W versus ε^{180}Hf for KREEP-rich, whole-rock samples. ε^{180}Hf in lunar samples is modified only by secondary neutron capture during GCR exposure, not by radioactive decay. The well-defined correlation indicates that all samples had the same pre-exposure μ^{182}W. This value is defined directly by samples 14321, 68115, and 68815, which have no ε^{180}Hf anomaly (Kruijer et al. 2015; Touboul et al. 2007, 2015a). Abbreviations: BSE, bulk silicate Earth; GCR, galactic cosmic ray; KREEP, K + rare earth elements + P.

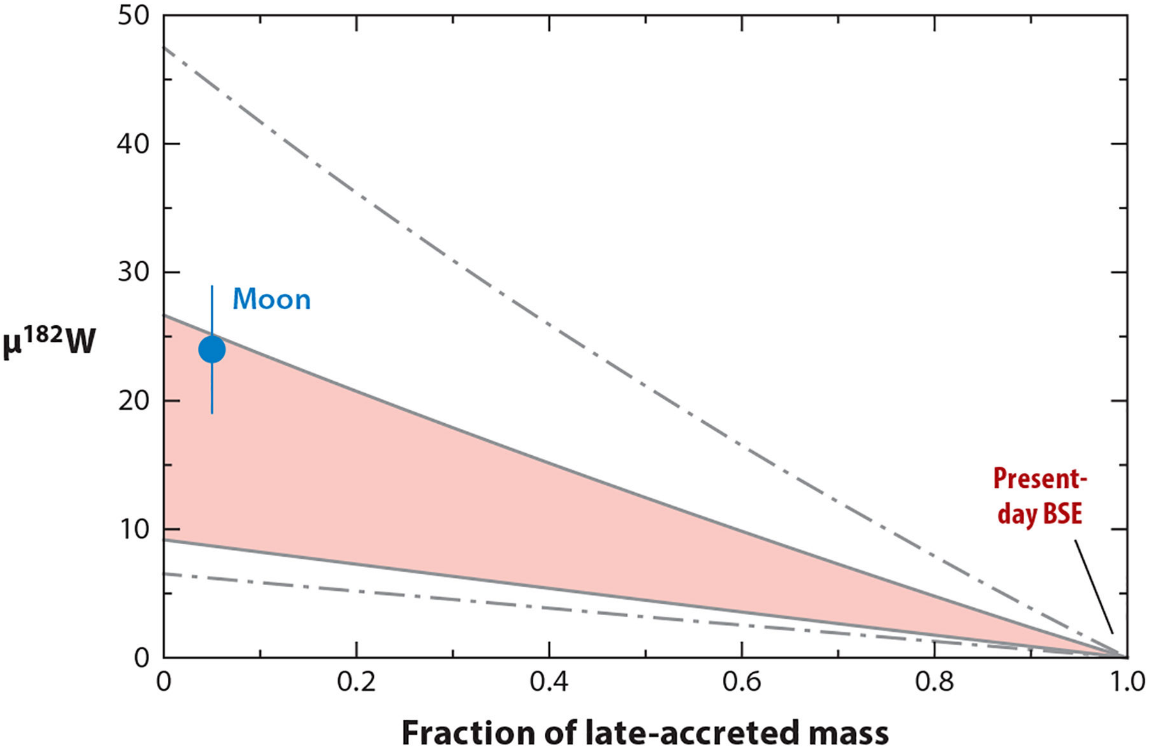

Figure 11.

Effect of late accretion on ^{182}W composition of Earth's mantle. Calculations assume 200 ppb W and $\mu^{182}W = -190$ for chondrites (late veneer) and 13 ppb W in the bulk silicate Earth (BSE). The red-shaded area shows the change in composition for a late veneer with a mass of highly siderophile element–bearing material retained in the mantle between 0.3% and 0.8% of Earth's mantle. The dashed-dotted lines indicate the uncertainties introduced by also considering the uncertainty in the W concentration of the BSE of 13 ± 5 ppb. The upper curve shows the effect for 8 ppb W in the BSE and 0.8% of late-accreted mass, whereas the lower curve shows the effects for 18 ppb in the BSE and 0.3% late-accreted mass.

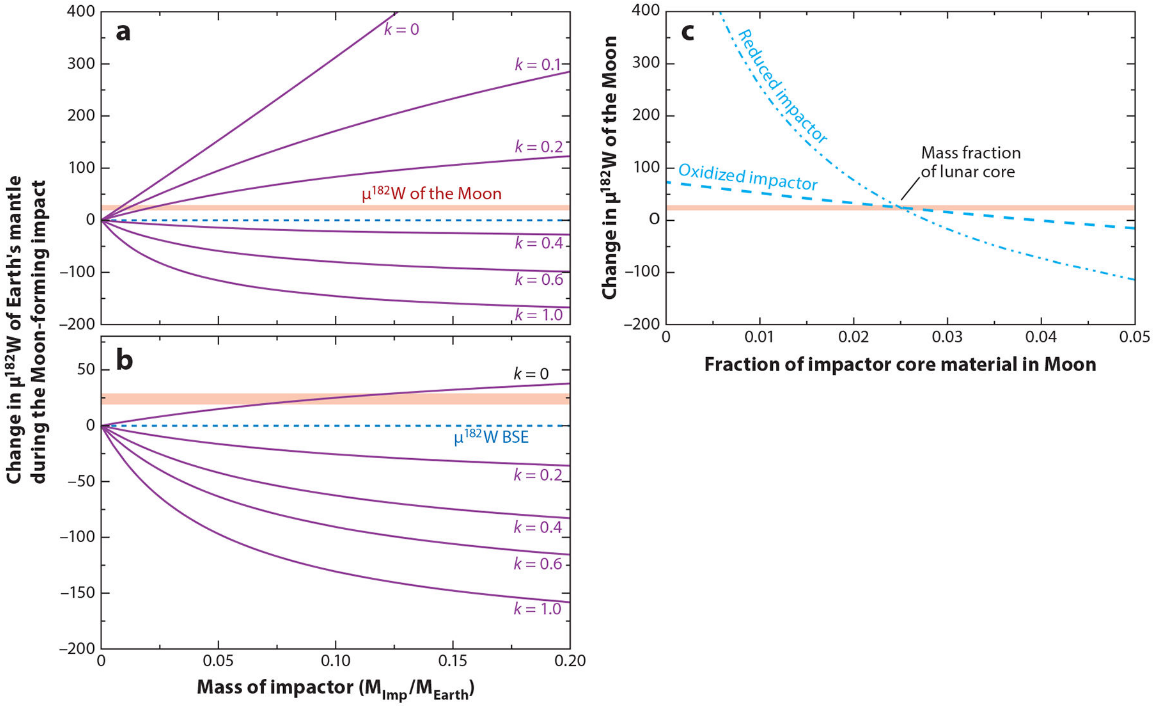

Figure 12.

Effect of the giant Moon-forming impact on the ^{182}W composition of Earth's mantle and the Moon. The red horizontal bars represent the μ^{182}W of the Moon, and the blue dashed lines are the present-day μ^{182}W of the bulk silicate Earth (BSE); note that immediately after formation of the Moon, the ^{182}W difference between the Moon and the BSE was likely smaller, because the present-day difference reflects, at least in part, the effects of late accretion on μ^{182}W in the BSE. The effects of the giant impact on the ^{182}W composition of the proto-Earth's mantle depend on the impactor composition and mass and the degree to which impactor core material equilibrates with Earth's mantle. The degree of re-equilibration is indicated by the value *k*, which is 1 for full equilibration and 0 for no equilibration. The effects are shown for two impactor compositions: (*a*) a reduced impactor with D = 100 for W, and (*b*) an oxidized impactor with D = 5. In both cases, a core formation time of 5 Ma was assumed for the impactor. Note that only specific combinations of impactor composition and degree of re-equilibration *k* leave the μ^{182}W of the Earth's mantle unchanged, whereas it is far more likely that a significant difference is produced. For instance, for a canonical impact (M_{Imp}/M_{Earth} = 0.1), the change of μ^{182}W of Earth's mantle could have been between +315 and −150 (for a reduced impactor) or between +25 and −130 (for an oxidized impactor). By contrast, the μ^{182}W difference between Earth's mantle and the Moon is +30 at most. Thus, the similar μ^{182}W values of Earth's mantle and the Moon are an unexpected outcome of the giant impact. (*c*) Mixing of impactor core material into the lunar accretion disk would have a strong effect on the μ^{182}W value of the Moon. For instance, an admixture of 2.5% core material, equivalent to the size of the lunar core, would have lowered the lunar μ^{182}W value by 50 to 700 ppm. The effects on μ^{182}W strongly depend on the composition of the impactor, and examples for adding core material from an “oxidized” impactor (μ^{182}W = −300; 385 ppb W) and a “reduced” impactor (μ^{182}W = −300; 800 ppb W) are shown.