Hf–W chronology of the accretion and early evolution of asteroids and terrestrial planets

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Abstract

The 182Hf–182W systematics of meteoritic and planetary samples provide firm constraints on the chronology of the accretion and earliest evolution of asteroids and terrestrial planets and lead to the following succession and duration of events in the earliest solar system. Formation of Ca,Al-rich inclusions (CAIs) at 4568.3 ± 0.7 Ma was followed by the accretion and differentiation of the parent bodies of some magmatic iron meteorites within less than / C24 1 Myr. Chondrules from H chondrites formed 1.7 ± 0.7 Myr after CAIs, about contemporaneously with chondrules from L and LL chondrites as shown by their 26Al–26Mg ages. Some magmatism on the parent bodies of angrites, eucrites, and mesosiderites started as soon as / C24 3 Myr after CAI formation and may have continued until / C24 10 Myr. A similar timescale is obtained for the high-temperature metamorphic evolution of the H chondrite parent body. Thermal modeling combined with these age constraints reveals that the different thermal histories of meteorite parent bodies primarily reflect their initial abundance of 26Al, which is determined by their accretion age. Impact-related processes were important in the subsequent evolution of asteroids but do not appear to have induced large-scale melting. For instance, Hf–W ages for eucrite metals postdate CAI formation by / C24 20 Myr and may reflect impact-triggered thermal metamorphism in the crust of the eucrite parent body. Likewise, the Hf–W systematics of some non-magmatic iron meteorites were modified by impact-related processes but the timing of this event(s) remains poorly constrained.

The strong fractionation of lithophile Hf from siderophile W during core formation makes the Hf–W system an ideal chronometer for this major differentiation event. However, for larger planets such as the terrestrial planets the calculated Hf–W ages are particularly sensitive to the occurrence of large impacts, the degree to which impactor cores re-equilibrated with the target mantle during large collisions, and changes in the metal-silicate partition coefficients of W due to changing fO2 in differentiating planetary bodies. Calculated core formation ages for Mars range from 0 to 20 Myr after CAI formation and currently cannot distinguish between scenarios where Mars formed by runaway growth and where its formation was more protracted. Tungsten model ages for core formation in Earth range from ~30 Myr to >100 Myr after CAIs and hence do not provide a unique age for the formation of Earth. However, the identical 182W/184W ratios of the lunar and terrestrial mantles provide powerful evidence that the Moon-forming giant impact and the final stage of Earth’s core formation occurred after extinction of 182Hf (i.e., more than ~50 Myr after CAIs), unless the Hf/W ratios of the bulk silicate Moon and Earth are...
identical to within less than ~10%. Furthermore, the identical $^{182}$W/$^{184}$W of the lunar and terrestrial mantles is difficult to explain unless either the Moon consists predominantly of terrestrial material or the W in the proto-lunar magma disk isotopically equilibrated with the Earth’s mantle.

Hafnium–tungsten chronometry also provides constraints on the duration of magma ocean solidification in terrestrial planets. Variations in the $^{182}$W/$^{184}$W ratios of martian meteorites reflect an early differentiation of the martian mantle during the effective lifetime of $^{182}$Hf. In contrast, no $^{182}$W variations exist in the lunar mantle, demonstrating magma ocean solidification later than ~60 Myr, in agreement with $^{147}$Sm–$^{143}$Nd ages for ferroan anorthosites. The Moon-forming giant impact most likely erased any evidence of a prior differentiation of Earth’s mantle, consistent with a $^{146}$Sm–$^{142}$Nd age of 50–200 Myr for the earliest differentiation of Earth’s mantle. However, the Hf–W chronology of the formation of Earth’s core and the Moon-forming impact is difficult to reconcile with the preservation of $^{146}$Sm–$^{142}$Nd evidence for an early (~30 Myr after CAIs) differentiation of a chondritic Earth’s mantle. Instead, the combined $^{182}$W–$^{142}$Nd evidence suggests that bulk Earth may have superchondritic Sm/Nd and Hf/W ratios, in which case formation of its core must have terminated more than ~42 Myr after formation of CAIs, consistent with the Hf–W age for the formation of the Moon.© 2009 Elsevier Ltd. All rights reserved.

1. INTRODUCTION

The formation of asteroids and terrestrial planets began with the accumulation of dust grains to kilometer-sized planetesimals, which is thought to have occurred in less than ~10⁶ years at 1 AU (e.g., Chambers, 2004). Gravity and gas drag caused these planetesimals to collide and form increasingly larger bodies in a period of runaway growth, the products of which include numerous Moon- to Mars-sized planetary embryos that are thought to have formed within ~10⁶ years (Weidenschilling et al., 1997). Collisions among these bodies mark the late stages of accretion, culminating in the formation of a few terrestrial planets that sweep up all the other bodies. Numerical simulations suggest that this stage may have taken 10⁷–10⁸ years (Chambers and Wetherill, 1998; Agnor et al., 1999; Chambers, 2001). The Moon probably formed during this period and involves a ‘giant impact’ of a Mars-sized body with proto-Earth at the very end of Earth’s accretion (Canup and Asphaug, 2001).

Collisions among the planetary embryos and the decay of short-lived radioactive isotopes (especially $^{26}$Al) caused the planetary interiors to heat up and eventually melt and differentiate. As a consequence, all major bodies of the inner solar system and also many smaller bodies are chemically differentiated into a metallic core and a silicate mantle (e.g., Walter and Trones, 2004). However, some objects such as the parent bodies of chondritic meteorites remained undifferentiated.

Determining the timescales for the accretion of asteroids and terrestrial planets is essential for evaluating planetary accretion models and, hence, is key to constraining the nature of the planet formation process. Similarly, determining the timescales for the early, high-temperature evolution of planetary bodies (i.e., chemical differentiation and thermal metamorphism) provides essential information for constraining the initial conditions that controlled the subsequent evolution of planets. Short-lived nuclides have proven particularly useful for obtaining such age constraints and, depending on their half-lives, can provide information on different stages of early planetary accretion and evolution. While the $^{26}$Al–$^{26}$Mg chronometer ($t_{1/2}$ ~0.71 Myr) is suitable for dating processes in the first ~5 Myr of the solar system to high precision, the $^{182}$Hf–$^{182}$W system, owing to its longer half-life of 8.9 ± 0.1 Myr, can potentially be used to date processes in the first ~60 Myr. This timescale is most relevant to the formation and early differentiation of the terrestrial planets, processes that are thought to have been largely completed in the first ~100 Myr of the solar system (Chambers, 2004).

In the past ~15 years $^{182}$Hf–$^{182}$W chronometry has successfully been applied to date a variety of processes associated with the formation and earliest evolution of planetary bodies. The main interest in the HF–W system was initially related to its potential for dating core formation (Lee and Halliday, 1995; Harper and Jacobsen, 1996) but HF–W fractionations also occur during mantle melting processes (Shearer and Newsom, 2000; Righter and Shearer, 2003). This allows the timescales of early mantle differentiation (e.g., magma ocean crystallization) to be determined. There is also an increasing number of applications that use internal HF–W isochrons for meteorites to date the timing of HF–W closure in meteorites and their components and constrain the thermal evolution of their parent bodies (Markowski et al., 2007; Burkhard et al., 2008; Kleine et al., 2008b). Here we review the chronology of the accretion and earliest evolution of asteroids and terrestrial planets as obtained by applying HF–W chronometry to meteoritic and planetary samples.

2. THE $^{182}$Hf–$^{182}$W CHRONOMETER

Hafnium-182 is produced by both the r- and s-processes and decays to $^{182}$W with a half-life of 8.9 ± 0.1 Myr (Voekenhuber et al., 2004). Given the range in Hf/W ratios in planetary reservoirs and meteorite components, $^{182}$Hf was sufficiently abundant to create resolvable $^{182}$W differences in the first ~60 Myr of the solar system and HF–W chronometry can be used to date chemical and physical processes that fractionated Hf from W during this period. This time span is most appropriate for studying the formation and early differentiation of planetary objects in the inner solar system, processes that are generally thought to have been completed within the first ~100 Myr of the solar system (Chambers, 2004). Due to the different geo- and cosmochemical properties of Hf and W, these two elements are
fractionated by a variety of processes that occurred during the accretion, differentiation and early evolution of planetary bodies. This makes the Hf–W system an extremely useful chronometer for the early solar system.

2.1. Hf–W fractionation during planetary differentiation and in meteorites

Hafnium and W are refractory elements and as such should occur in chondritic relative abundances in most bulk planetary objects. The Hf–W systematics of chondrites therefore provide an estimate for the W isotope composition of a bulk planetary object and serve as a reference for calculating Hf–W ages of core formation. During core formation lithophile Hf is entirely retained in the mantle, whereas siderophile W is preferentially partitioned into the metal core, resulting in Hf/W ~ 0 in the core and correspondingly high Hf/W ratios in the silicate mantle. The extend to which W partitions into the core is determined by its metal-silicate partition coefficient, which depends on several parameters including pressure, temperature, oxygen fugacity, and silicate melt composition (Walter and Thibault, 1995; Walter et al., 2000). Therefore, depending on the conditions of core formation, the depletion of W in the silicate mantle can vary among different planetary objects but also during core formation within a single object.

Following core formation, additional fractionation of Hf from W may occur in the silicate part of differentiated planetary objects and in this case is related to the higher incompatibility of W relative to Hf (Righter and Shearer, 2003). Whereas W is one of the most incompatible elements (with a similar bulk distribution coefficient in mantle melting to those of Th and U), Hf can be incorporated into several rock-forming minerals such as high-Ca pyroxene and ilmenite. Crystallization of these two minerals – e.g. during solidification of a magma ocean or during basalt crystallization – can result in the formation of reservoirs with fractionated Hf/W ratios. In some cases, these fractionations can exceed those induced by core formation. For instance, because of the presence of ilmenite and high-Ca pyroxene in their source, lunar high-Ti mare basalts have Hf/W ratios as high as ~100, whereas KREEP-rich samples have much lower Hf/W ratios of ~20 (Kleine et al., 2005c). Such large fractionations greatly enhance the application of the Hf–W system as a chronometer of mantle differentiation.

The Hf/W ratio that is characteristic of the entire mantle of a differentiated planetary body cannot be measured directly in most cases because substantial Hf–W fractionations occurred during mantle melting (Righter and Shearer, 2003). The bulk mantle Hf/W ratio must thus be inferred by comparing the W concentrations in mantle-derived samples with the abundance of a refractory lithophile element that is as incompatible as W and whose abundance relative to Hf is known. Trace element studies of lunar, terrestrial, and meteoritic basalts indicate that Th, U, and W have similar incompatibilities (Palme and Rammensee, 1981; Newsom et al., 1996), such that Th/W and U/W ratios in silicate mantles in conjunction with Hf/Th and Hf/U ratios in chondrites can be used to estimate the Hf/W ratios in bulk planetary mantles.

Table 1 summarizes current best estimates for the Hf/W ratios in the bulk mantles of Mars, the Earth, and Moon. Nimmo and Kleine (2007) estimated the Th/W ratio of the martian mantle to be 0.98 ± 0.13. Using the Hf/Th ratio of 3.1 ± 0.1 of carbonaceous chondrites (Kleine et al., 2007) this Th/W translates into Hf/W = 3.0 ± 0.4. However, ordinary chondrites have higher Hf/Th ratios of 4.0 ± 0.2 (Kleine et al., 2007), in which case the calculated Hf/W ratio of the martian mantle would be 3.9 ± 0.6. As shown below, uncertainties and variations in the Hf/Th ratio of chondrites have a significant effect on the calculated core formation ages for Mars because the Hf/W ratio of the martian mantle is only three to four times higher than the Hf/W ratio of chondrites (Treiman et al., 1986; Nimmo and Kleine, 2007). Furthermore, the range in Th/W ratios among martian meteorites is large (0.6–1.4), such that it is currently unclear whether there is one Th/W ratio that is representative of the entire martian mantle.

The Hf/W ratio of the bulk silicate Earth can be inferred from its Th/W ratio of 5.5 ± 1.6 (Newsom et al., 1996), which, using Hf/Th = 3.1 ± 0.1 for carbonaceous chondrites, corresponds to Hf/W = 17 ± 5. Similarly, the Hf/W ratio of the bulk lunar mantle can be estimated from its U/W ratio of 1.93 ± 0.08 (Palme and Rammensee, 1981). Using Hf/U = 13.7 ± 0.7 for chondrites (Rocholl and Jouchum, 1993) this corresponds to an Hf/W ratio of the lunar mantle of 26 ± 2. A slightly lower Hf/W of 25 ± 2 is obtained if Th/U = 4.2 ± 0.2 for the Moon and Hf/Th = 3.1 ± 0.1 for chondrites are used. The differences in these estimates reflect uncertainties and/or variations in the Hf, U, and Th concentrations of chondrites as well as uncertainties in the trace element composition of the lunar and terrestrial mantles. Additional uncertainties may arise if planetary bodies have non-chondritic relative abundances of refractory lithophile elements (in this case Hf, Th, and U). For instance, Pb isotope data for terrestrial mantle rocks were used to estimate the Th/U ratio of the bulk terrestrial mantle to 4.2 ± 0.2 (Allègre et al., 1986), slightly higher than Th/U ~ 3.8 in chondrites (Rocholl and Jouchum, 1993). Moreover, Caro et al. (2008) proposed that
Earth, Moon, and Mars have superchondritic Sm/Nd ratios.

The fractionation of Hf from W is not restricted to planetary differentiation but also occurs among the constituent minerals of many meteorites and some of their components. Table 1 summarizes measured Hf/W ratios in mineral separates from various meteorites along with the ratios of mineral–melt partition coefficients for Hf and W (Righter and Shearer, 2003). The high Hf/W ratios in high-Ca pyroxene make it possible to obtain precise internal isochron for meteorites because high-Ca pyroxene is an important constituent of numerous meteorites and their components, such as eucrites, angrites, and CAIs. Almost all meteorites contain some metal, which has Hf/W ~ 0 and allows direct measurement of the initial 182W/184W of a sample. Precise Hf–W ages can thus be obtained from Hf–W isochrons involving high-Ca pyroxene and other silicates (e.g., olivine, melilitie), such as for CAIs (Burkhardt et al., 2008) and angrites (Markowski et al., 2007; Kleine et al., 2008a), or co-genetic metal and silicate fractions, such as for H chondrites (Kleine et al., 2008b). Table 2 summarizes initial 182Hf/180Hf ratios for meteorites that have been obtained from internal isochrons.

### 2.2. Notation and Hf–W isotope systematics

Tungsten isotope data are commonly expressed in 182W, which is defined as follows:

\[
e^{182\text{W}} = \left( \frac{(182\text{W} / 184\text{W})_{\text{sample}}}{(182\text{W} / 184\text{W})_{\text{standard}}} - 1 \right) \times 10^4
\]  

(1)

Note that similarly to other short-lived chronometers such as the 53Mn–53Cr and 26Al–26Mg systems, e182W values are calculated relative to the 182W/184W of the terrestrial standard. However, for modeling purposes some authors (Harper and Jacobsen, 1996; Jacobsen, 2005; Nimmo and Agnor, 2006) also expressed 182W/184W relative to CAIs (Amelin et al., 2002, 2006); D’Orbigny (Amelin, 2008); NWA 2999, 4590, 4801 (Amelin and Irving, 2007); Sahara 99555 (Burkhardt et al., 2008) as eucrites, angrites, and CAIs. Almost all meteorites contain some metal, which has Hf/W ~ 0 and allows direct measurement of the initial 182W/184W of a sample. Precise Hf–W ages can thus be obtained from Hf–W isochrons involving high-Ca pyroxene and other silicates (e.g., olivine, melilitie), such as for CAIs (Burkhardt et al., 2008) and angrites (Markowski et al., 2007; Kleine et al., 2008a), or co-genetic metal and silicate fractions, such as for H chondrites (Kleine et al., 2008b). Table 2 summarizes initial 182Hf/180Hf ratios for meteorites that have been obtained from internal isochrons.

### Table 2

Summary of initial 182Hf/180Hf and calculated Hf–W ages as obtained from internal isochrons.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(182Hf/180Hf)i × 10^5</th>
<th>Δt_{CAI} (Ma)</th>
<th>t (Ma)</th>
<th>207Pb–206Pb age (Ma)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAIs</td>
<td>9.72 ± 0.44</td>
<td>=0</td>
<td>4568.3 ± 0.7</td>
<td>4567.11 ± 0.16</td>
<td>Burkhardt et al. (2008)</td>
</tr>
<tr>
<td>Ste. Marguerite (H4)</td>
<td>8.50 ± 0.23</td>
<td>1.7 ± 0.7</td>
<td>4566.5 ± 0.5</td>
<td>—</td>
<td>Kleine et al. (2008b)</td>
</tr>
<tr>
<td>Richardson (H5)</td>
<td>6.23 ± 0.30</td>
<td>3.7 ± 0.9</td>
<td>4562.6 ± 0.8</td>
<td>—</td>
<td>Kleine et al. (2008b)</td>
</tr>
<tr>
<td>ALH84009 (H5)</td>
<td>6.12 ± 0.62</td>
<td>5.9 ± 1.4</td>
<td>4562.5 ± 1.4</td>
<td>—</td>
<td>Kleine et al. (2008b)</td>
</tr>
<tr>
<td>Kurnouou (H6)</td>
<td>4.66 ± 0.34</td>
<td>9.4 ± 1.1</td>
<td>4558.8 ± 1.0</td>
<td>—</td>
<td>Kleine et al. (2008b)</td>
</tr>
<tr>
<td>Estacado (H6)</td>
<td>4.43 ± 0.53</td>
<td>10.1 ± 1.7</td>
<td>4559.2 ± 1.6</td>
<td>—</td>
<td>Kleine et al. (2008b)</td>
</tr>
<tr>
<td>Vaca Muerta clast</td>
<td>7.69 ± 0.82</td>
<td>3.0 ± 1.5</td>
<td>4565.3 ± 1.4</td>
<td>—</td>
<td>Schönächler et al. (2002)</td>
</tr>
<tr>
<td>D’Orbigny</td>
<td>7.20 ± 0.21</td>
<td>3.8 ± 0.7</td>
<td>4564.42 ± 0.12</td>
<td>4564.42 ± 0.12</td>
<td>Markowski et al. (2007)</td>
</tr>
<tr>
<td>Sahara 99555</td>
<td>6.89 ± 0.18</td>
<td>4.4 ± 0.7</td>
<td>4563.9 ± 0.5</td>
<td>4564.58 ± 0.14</td>
<td>Markowski et al. (2007)</td>
</tr>
<tr>
<td>NWA 2999 (px-metal)</td>
<td>5.38 ± 0.48</td>
<td>7.6 ± 1.3</td>
<td>4560.7 ± 1.2</td>
<td>4561.79 ± 0.42</td>
<td>Markowski et al. (2007)</td>
</tr>
<tr>
<td>NWA 4590</td>
<td>4.65 ± 0.17</td>
<td>9.5 ± 0.8</td>
<td>4558.8 ± 0.6</td>
<td>4558.86 ± 0.30</td>
<td>Kleine et al. (2008a)</td>
</tr>
<tr>
<td>NWA 4801</td>
<td>4.34 ± 0.23</td>
<td>10.3 ± 0.9</td>
<td>4557.9 ± 0.8</td>
<td>4558.06 ± 0.15</td>
<td>Kleine et al. (2008a)</td>
</tr>
<tr>
<td>Camel Donga</td>
<td>1.7 ± 0.7</td>
<td>22 ± 5</td>
<td>4546 ± 5</td>
<td>—</td>
<td>Kleine et al. (2005b)</td>
</tr>
</tbody>
</table>

\(^{a}\) All initial 182Hf/180Hf ratios were re-calculated from Hf–W data given in the original references using the model 1 fit of IsoPlot and 180Hf/184W = 1.18 × Hf/W (note that most of the previous study used 180Hf/184W = 1.14 × Hf/W). The Pb–Pb ages are from the following references: CAIs (Amelin et al., 2002, 2006); D’Orbigny (Amelin, 2008); NWA 2999, 4590, 4801 (Amelin and Irving, 2007); Sahara 99555 (Connelly et al., 2008b).
of CAIs, and $T_0$ is the age of the solar system. Note that we distinguish age $T$ defined as time before present, from time $t$ elapsed since the start of the solar system, which is assumed to be the formation of CAIs. Therefore, the time of core formation is given by $t_{cf} = T_0 - T$. An equivalent set of equations for calculation two-stage model ages for core formation was introduced by Harper and Jacobsen (1996) and as follows:

$$\Delta \epsilon_W(t) = Q_{182W}/f_H/W \left( \frac{182Hf}{180Hf} \right) \frac{e^{-\lambda t}}{t_w}$$

where $Q_{182W} = 10^{4} \left( \frac{182Hf}{180Hf} \right)_{CHUR} = 1.42 \times 10^{4}$ (see below and Table 3). The Hf/W fractionation in reservoir $j$ relative to CHUR is defined by

$$f_H/W = \left( \frac{Hf/W}{Hf/W}_{j} \right)_{CHUR} - 1$$

For the present-day, i.e., $t = T_0$, and we obtain:

$$\Delta \epsilon_W(0) = Q_{182W}/f_H/W \left( \frac{182Hf}{180Hf} \right)_{T_0} e^{-\lambda t_{cf}}$$

In practice, to determine the age of core formation of a sample or reservoir, we will rewrite Eq. (8) as follows:

$$t_{cf} = \frac{1}{\lambda} \ln \left( \frac{Q_{182W}/f_H/W \left( \frac{182Hf}{180Hf} \right)_{T_0}}{\Delta \epsilon_W(0)} \right) = \frac{1}{\lambda} \ln \left[ \frac{1.38 f_H/W}{\Delta \epsilon_W(0)} \right]$$

Note that the second equality is derived by assuming a carbonaceous chondritic composition, i.e., $Q_{182W} = 10^{4} \left( \frac{182Hf}{180Hf} \right)_{CHUR} = 1.42 \times 10^{4}$.

Eqs. (5) and (9) reveal that core formation ages can be calculated from the $182W/184W$ and $180Hf/184W$ ratios of a mantle or core once the Hf–W systematics of chondrites and the $182Hf/180Hf$ at the time of CAI formation are known. However, as shown below the calculation of realistic core formation ages requires more complex models, at least for Earth-sized bodies (Section 6).

### 2.3. Reference parameters for Hf–W chronology

**2.3.1. Hf–W systematics of chondrites**

The first W isotope data for chondrites appeared to indicate that Earth’s mantle and chondrites have identical $182W/184W$ ratios (Lee and Halliday, 1995, 1996). However, in 2002 it was shown that carbonaceous chondrites have a $182W/184W$ ratio $\sim 2\epsilon_1$ units lower than that of the silicate Earth (Kleine et al., 2002; Schoenberg et al., 2002a; Yin et al., 2002). The currently most precise determination of the chondritic $182W/184W$ ratio is based on 14 carbonaceous chondrites that have an average $e_{182W}$ of $-1.9 \pm 0.1$ (Kleine et al., 2004a). There are no resolvable differences in the $182W/184W$ among the carbonaceous chondrite groups (Fig. 1), consistent with their limited spread in $180Hf/184W$ ratios ($180Hf/184W = 1.18 \times Hf/W$) from $\sim 1.1$ to $\sim 1.6$ (Kleine et al., 2004a). Ordinary chondrite groups exhibit a larger range in $180Hf/184W$ ratios and $e_{182W}$ values (Fig. 1). H chondrites have lower $180Hf/184W$ ratios (from $\sim 0.6$ to $\sim 1.1$) and $e_{182W}$ values (from $\sim 2.5$ to $\sim 2.0$), whereas LL chondrites have higher $180Hf/184W$ ratios (from $\sim 1.6$ to $\sim 2.1$) and $e_{182W}$ values (from $\sim 1.7$ to $\sim 1.5$) (Kleine et al., 2007). Likewise, enstatite chondrites have $180Hf/184W$ ratios and $e_{182W}$ values that are similar to those of the H chondrites (Lee and Halliday, 2000).

The different Hf/W ratios among the chondrite groups most likely reflect metal-silicate and refractory element fractionation in the solar nebula. Therefore, in principle, bulk planetary objects may have different Hf/W ratios, at least to the extent present in the different chondrite groups. However, the broad provenance and large scale mixing of components associated with the accretion of larger planets probably reduced the total spread. Furthermore, in most cases the variations of the Hf/W ratios among bulk chondrites are small compared those produced during planetary differentiation (Section 2.1).

#### 2.3.2. Initial $^{182}Hf/^{180}Hf$ and $^{182}W/^{184}W$ of CAIs

Precise knowledge of the $182Hf/180Hf$ and $182W/184W$ at the time of CAI formation is essential for making full use of the time constraints provided by Hf–W chronometry. This is because CAIs are the oldest yet dated material formed in the solar system (Gray et al., 1973) and as such are the most suitable reference point for constraining the duration of processes in the early solar system. Moreover, intervals relative to CAIs determined with the Hf–W chronometer can be directly compared to $^{26}Al/^{27}Mg$ ages that are also commonly expressed as time intervals calculated based on the initial $^{26}Al/^{27}Al$ of CAIs.

**Table 3**

Reference parameters for Hf–W chronology.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{182}Hf/^{180}Hf$</td>
<td>$(9.72 \pm 0.44) \times 10^{-5}$</td>
<td>Internal isochron for CAIs</td>
</tr>
<tr>
<td>$^{182}Hf/^{180}Hf$</td>
<td>$(7.20 \pm 0.21) \times 10^{-5}$</td>
<td>Internal isochron for D’Orbigny</td>
</tr>
<tr>
<td>$^{182}W/^{184}W$</td>
<td>$0.864579 \pm 0.000014$</td>
<td>Initial $^{182}W/^{184}W$ of CAI isochron</td>
</tr>
<tr>
<td>$^{182}W/^{184}W$</td>
<td>$\epsilon_{182W} = -3.28 \pm 0.12$</td>
<td>$^{182W}/^{184}W$ of terrestrial standard as measured at ETH Zurich</td>
</tr>
<tr>
<td>$^{180}Hf/^{184}W$</td>
<td>$0.864863 \pm 0.000018$</td>
<td>Average $^{182W}/^{184}W$ of carbonaceous chondrites</td>
</tr>
<tr>
<td>$^{180}Hf/^{184}W$</td>
<td>$\epsilon_{182W} = -1.9 \pm 0.1$</td>
<td>Calculated using the initial $^{182}W/^{184}W$ and $^{182}Hf/^{180}Hf$ of CAIs and the present-day $^{182}W/^{184}W$ of carbonaceous chondrites. Note that this value agrees with the measured $^{182}Hf/^{184}W$ for carbonaceous chondrites</td>
</tr>
<tr>
<td>$Q_{182W}$</td>
<td>$1.42 \times 10^{4}$</td>
<td>Calculated for a carbonaceous chondrite composition</td>
</tr>
</tbody>
</table>
Several approaches have been used to determine the initial $^{182}$Hf/$^{180}$Hf and $^{182}$W/$^{184}$W ratios of the solar system and for this task Hf–W data for meteorites can be utilized in three different ways (Table 4). The first approach is to assume that the lowest $^{182}$W/$^{184}$W measured in iron meteorites represents the initial W isotope composition of the solar system (Lee and Halliday, 1995; Quitté and Birck, 2004). The difference between this assumed initial value and the present-day $^{182}$W/$^{184}$W of chondrites then represents ingrowth from decay of $^{182}$Hf in a reservoir with a chondritic $^{180}$Hf/$^{184}$W ratio. However, the $^{182}$W/$^{184}$W of most iron meteorites have been lowered by the interaction with cosmic rays (Masarik, 1997; Leya et al., 2003) and the lowest $^{182}$W/$^{184}$W reported for iron meteorites does not provide a robust estimate for the initial $^{182}$W/$^{184}$W of the solar system but rather reflects the effects of interaction with thermal neutrons (Masarik, 1997; Leya et al., 2003; Kleine et al., 2005b; Markowski et al., 2006b; Schérsen et al., 2006). Therefore, using the lowest $^{182}$W/$^{184}$W ratio reported for iron meteorites results in estimates for the initial $^{182}$Hf/$^{180}$Hf of the solar system (Quitté and Birck, 2004) that are too high.

The second approach uses internal Hf–W isochrons for meteorites with a well-defined absolute age and relies on two assumptions: (i) the absolute age determined for a sample corresponds to the time of Hf–W closure, and (ii) the absolute age of CAIs is known. The first assumption is strictly valid only for rapidly cooled samples such as angrites or CAIs (see below). One problem with this approach is that the absolute age of CAIs is not known with sufficient precision, with Pb–Pb ages ranging from 4567.11 ± 0.16 Myr (Amelin et al., 2002, 2006) to 4568.5 ± 0.5 Myr (Bouvier et al., 2007). This introduces some uncertainty when the $^{182}$Hf/$^{180}$Hf at any point in time is back-calculated to the time of CAI formation. This approach was employed by Kleine et al. (2002) using Hf–W data for the H4 chondrite Ste. Marguerite and an initial $^{182}$Hf/$^{180}$Hf of (1.09 ± 0.09) × 10^-4 at the time of CAI formation was calculated (assuming a CAI age of 4566 Ma). The main reason for using this sample was that at that time no precise Hf–W isochrons for rapidly cooled samples were available. Similarly, Yin et al. (2002) used Hf–W data for one CAI and two equilibrated ordinary chondrites to determine an initial $^{182}$Hf/$^{180}$Hf of (1.00 ± 0.08) × 10^-4 at the time of CAI formation. This approach is based on the assumption that closure of the Hf–W system in those equilibrated ordinary chondrites occurred at the time of CAI formation.

The third and most direct approach to determine the initial $^{182}$Hf/$^{180}$Hf of the solar system is to obtain Hf–W data for the first solids that formed in the solar system. Ireland and Bukovanska (2003) reported ion probe Hf–W data for zircons from the H5 chondrite Simmern. These zircons have an ultrarefractory-enriched trace element pattern and their initial $^{182}$Hf/$^{180}$Hf of (7.2 ± 4.5) × 10^-3 might be close to the initial value of the solar system. The initial $^{182}$Hf/$^{180}$Hf of the solar system is most reliably and directly determined from internal isochrons for CAIs because these are the oldest known objects that formed in the solar system. Hafnium–tungsten data are available for 5 bulk CAIs and these exhibit a narrow range in Hf/W and $^{182}$W/$^{184}$W, which are slightly elevated relative to carbonaceous chondrites (Burkhardt et al., 2008). However, in type B CAIs fassaites have high $^{180}$Hf/$^{184}$W ratios, mainly reflecting the compatibility of Hf in fassaites. These high $^{180}$Hf/$^{184}$W resulted in radiogenic $^{182}$W/$^{184}$W ratios, which makes it possible to obtain precise internal Hf–W isochrons for CAIs (Burkhardt et al., 2008). Whole-rocks and mineral separates from eight CAIs from the Allende and NWA 2364 CV3 chondrites plot on a well-defined isochron corresponding to an initial c$^{182}$W of ~3.28 ± 0.12 and an initial $^{182}$Hf/$^{180}$Hf of (9.72 ± 0.44) × 10^-5 (Burkhardt et al., 2008). As discussed in detail by Burkhardt et al. (2008), parent body processes such as aqueous alteration or thermal metamorphism had no detectable effect on the Hf–W systematics of these CAIs, such that the CAI
isochron provides the initial $^{182}\text{Hf}/^{180}\text{Hf}$ ratios at the time of CAI formation.

### 2.3.3. Calibration of the $^{182}\text{Hf}$–$^{182}\text{W}$ chronometer and conversion to absolute ages

The accurate application of Hf–W chronometry to constrain timescales in the early solar system requires that relative Hf–W ages between different early solar system materials are consistent with the differences in their absolute ages. This criterion is strictly applicable only to those samples that cooled rapidly, such that potential differences in closure temperatures could not result in resolvable age differences among various chronometers. This requirement is met by angrites. Furthermore, these volatile depleted meteorites exhibit high U/Pb ratios, such that precise Pb–Pb ages are available (Lugmair and Galer, 1992; Amelin, 2008) and the available Pb–Pb ages for angrites reveal an age range of \(\approx 7\text{ Myr}\), which makes it possible to intercalibrate the Hf–W and U–Pb system.

In angrites, fassaites have high $^{180}\text{Hf}/^{184}\text{W}$ ratios whereas the other constituents – olivine, plagioclase and in one case metal – have low $^{180}\text{Hf}/^{184}\text{W}$ ratios (see Table 1), resulting in variations in W isotope compositions of up to \(\sim 15\text{ e}_{182}\text{W}\). This spread makes it possible to obtain precise Hf–W isochrons for angrites (Markowski et al., 2007; Kleine et al., 2008a) and the initial $^{182}\text{Hf}/^{180}\text{Hf}$ ratios obtained from the slopes of these isochrons are summarized in Table 2. The comparison of $^{207}\text{Pb}–^{206}\text{Pb}$ and Hf–W ages can be made for several angrites including D’Orbigny, Sahara 99555 and Northwest Africa 2999, 4590, and 4801. In Fig. 2, the initial $^{182}\text{Hf}/^{180}\text{Hf}$ ratios of these angrites are plotted against their Pb–Pb ages. This plot reveals that four of the angrites (D’Orbigny, Sahara 99555, Northwest Africa 4590 and 4801) plot on a straight line, whose slope is identical to the one predicted from the $^{182}\text{Hf}$ half-life. Northwest Africa 2999 plots slightly below but within uncertainty of this line and this probably reflects a slight disturbance of the Hf–W system in this sample. This is evident from the Hf–W data for one of the whole-rock and the fines fraction of Northwest Africa 2999, which plot off the isochron (Markowski et al., 2007). An important feature of Fig. 2 is that the calibration of the Hf–W system onto an absolute timescale yields consistent results regardless of which of the four angrites D’Orbigny, Sahara 99555, Northwest Africa 4590

### Table 4

Summary of estimates for the initial $^{182}\text{Hf}/^{180}\text{Hf}$ of the solar system.

<table>
<thead>
<tr>
<th>Initial $^{182}\text{Hf}/^{180}\text{Hf}$</th>
<th>Reference</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\sim 2 \times 10^{-5})</td>
<td>Harper and Jacobsen (1996)</td>
<td>Models for $^{182}\text{Hf}$ nucleosynthesis</td>
</tr>
<tr>
<td>(&gt; 2.6 \times 10^{-4})</td>
<td>Lee and Halliday (1995)</td>
<td>Hf–W data for chondrites, iron meteorites</td>
</tr>
<tr>
<td>((2.75 \pm 0.24) \times 10^{-4})</td>
<td>Lee and Halliday (2000)</td>
<td>Isochrons for Ste. Marguerite, Forest Vale</td>
</tr>
<tr>
<td>((1.00 \pm 0.08) \times 10^{-4})</td>
<td>Yin et al. (2002)</td>
<td>Isochron for Dalgety Downs (L4), Dhurmusal (LL6)</td>
</tr>
<tr>
<td>((1.09 \pm 0.09) \times 10^{-4})</td>
<td>Kleine et al. (2002)</td>
<td>Isochron for Ste. Marguerite (H4)</td>
</tr>
<tr>
<td>((7.4 \pm 4.5) \times 10^{-4})</td>
<td>Ireland and Bukovanska (2003)</td>
<td>Hf–W data for zircons from Simmern (H5)</td>
</tr>
<tr>
<td>((1.60 \pm 0.25) \times 10^{-4})</td>
<td>Quitté and Birck (2004)</td>
<td>Iron meteorites</td>
</tr>
<tr>
<td>((1.07 \pm 0.10) \times 10^{-4})</td>
<td>Kleine et al. (2005a)</td>
<td>Isochron for CAIs</td>
</tr>
<tr>
<td>((9.72 \pm 0.44) \times 10^{-5})</td>
<td>Burkhardt et al. (2008)</td>
<td>Mineral isochrons for CAIs</td>
</tr>
</tbody>
</table>

Fig. 2. Initial $^{182}\text{Hf}/^{180}\text{Hf}$ ratios vs. Pb–Pb for angrites. Slightly modified from Burkhardt et al. (2008). References are given in Table 2. Solid lines are decay lines calculated using the $^{182}\text{Hf}$ half-life of 0.078 Myr. Note that the Hf–W ages for angrites would be inconsistent with their $^{207}\text{Pb}–^{206}\text{Pb}$ ages if the 4567.11 Ma $^{207}\text{Pb}–^{206}\text{Pb}$ age for CAI E60 were used as the time anchor. Note that the Hf–W system in Northwest Africa 2999 is disturbed and the initial $^{182}\text{Hf}/^{180}\text{Hf}$ plotted here is higher than originally reported in Markowski et al. (2007). This higher value is obtained from excluding the Hf–W data for the whole-rock, fines and leached fractions.
2.4. Closure temperature of the Hf–W system

The interpretation of Hf–W ages in comparison to results from other chronometers and within the framework of models for the thermal evolution of asteroids requires knowledge of the closure temperature \( T_c \) for diffusive exchange of Hf and W among the constituent minerals in a rock (Dodson, 1973; Ganguly and Tirone, 2001). Closure temperatures can be calculated from diffusion rates of W in the appropriate minerals but such data are not available yet. Nevertheless, using the model developed by Van Orman et al. (2001), Kleine et al. (2008b) estimated the diffusion parameters of W in high-Ca pyroxene, the major host of radiogenic \( ^{182}\)W in most meteorites, and obtained an activation energy of 453 kJ/mol and a pre-exponential factor of \( 9.53 \times 10^{-5} \) m²/s. These parameters can be used to calculate \( T_c \) for the Hf–W system as a function of cooling rate and effective grain size. Fig. 3 presents Hf–W closure temperatures as a function of cooling rate, calculated for a 10 \( \mu \)m grain size and using the analytical model from Dodson (1973). Also shown are closure temperatures for the U–Pb system in clinopyroxene (Cherniak, 1998) and phosphates (Cherniak et al., 1991) and for the Al–Mg system in anorthite (LaTourrette and Wasserburg, 1998). Fig. 3 reveals that for a wide range of cooling rates (and grain sizes), \( T_c \) for the Hf–W system is always higher than closure temperatures of the U–Pb system in high-Ca pyroxene and in phosphates and the Al–Mg system in anorthite. Consequently, in slowly cooled samples (e.g., in most metamorphosed meteorites) the Hf–W system will have closed at higher temperatures than other chronometers and Hf–W ages are expected to be older than Pb–Pb and \(^{26}\)Al–\(^{26}\)Mg ages. Hence, Hf–W chronometry has the potential to date processes associated with the earliest evolution of meteorite parent bodies and is less susceptible to resetting by later thermal events than any other chronometer commonly used in cosmochronology.

The analytical models for closure temperature presented by Dodson (1973) and Ganguly and Tirone (2001) make several assumptions that do not necessarily apply to short-lived chronometers. For example, the Dodson (1973) and Ganguly and Tirone (2001) models assume (i) an infinite sink for radiogenic daughters (which in the case of the Hf–W system is valid for metal-rich meteorites but possibly not for other samples); (ii) a decay time that is very long compared to the cooling time (which may not be valid for short-lived chronometers); and (iii) that heating at peak metamorphic conditions was sufficient to homogenize any pre-existing isotopic heterogeneity. By contrast, the model of Van Orman et al. (2006) does not rely on these assumptions, and is thus a more realistic model for the production and exchange of radiogenic daughters in short-lived isotope systems. This model was applied by Kleine et al. (2008b) to numerically simulate the production and diffusive exchange of radiogenic W between high-Ca pyroxene and metal in H chondrites. These simulations show that for highly metamorphosed rocks, such as the H6 and H5 chondrites peak metamorphic temperatures were sufficiently high to homogenize any pre-existing W isotope heterogeneity. In this case, the calculated closure temperatures are identical to those calculated using the Dodson (1973) model. By contrast, in case of the H4 chondrites, the assumption that peak metamorphic conditions were sufficient to reset the Hf–W system is not valid. Consequently, for such samples the Hf–W closure temperature cannot be calculated using the Dodson (1973) model and assessing the effects of metamorphism on the Hf–W system in H4 chondrites requires a model that can simulate the prograde path, such as the model of Van Orman et al. (2006).
3. TIMESCALES FOR THE ACCRETION AND EARLY EVOLUTION OF PLANETESIMALS

3.1. Magmatic iron meteorites – remnants of the first planetesimals

The first comprehensive investigation of the W isotope composition of iron meteorites was performed by Horan et al. (1998), who showed that iron meteorites have $\varepsilon^{182\text{W}}$ values between $\sim-5$ and $\sim-3$. More recently, the W isotope compositions of a large number of iron meteorites were determined to higher precision than was obtainable during the earlier study and these studies confirmed the range in $\varepsilon^{182\text{W}}$ values obtained by Horan et al. (1998) (Kleine et al., 2005b; Markowski et al., 2006b; Schersten et al., 2006; Qin et al., 2008). With the higher precision obtained in these more recent studies variations within groups of iron meteorites became apparent. Moreover, non-magmatic iron meteorites (i.e., irons with unfractured trace element patterns) appear to have slightly higher $\varepsilon^{182\text{W}}$ values than the magmatic irons.

The $\varepsilon^{182\text{W}}$ values of iron meteorites become more negative with increasing exposure ages and values lower than $\sim-4.0$ are only observed for samples having exposure ages as old as $\sim1\text{ Ga}$ (Fig. 4). This decrease in $\varepsilon^{182\text{W}}$ reflects burnout of W isotopes by capture of thermal neutrons produced during cosmic-ray exposure of the iron meteoroids (Masarik, 1997; Leya et al., 2003). The production rate of thermal neutrons depends on the pre-atmospheric size of and the location within the meteoroid, such that cosmogenic effects on the W isotope composition can vary within a single meteorite. This was demonstrated for the two iron meteorites Grant and Carbo. In both meteorites, $^{182\text{W}}/^{184\text{W}}$ ratios were lower in samples close to the pre-atmospheric center compared to samples closer to the pre-atmospheric surface of the meteoroid (Markowski et al., 2006a).

There is currently no direct proxy available for precisely determining the flux of thermal neutrons in iron meteorite parent bodies. Thus, the effects of thermal neutrons on W isotopes can only be estimated from the concentrations of cosmogenic noble gases in particular samples (Markowski et al., 2006a; Qin et al., 2008). However, cosmogenic noble gases are produced by high-energy primary protons and secondary neutrons whereas the effects on W isotopes are caused by low-energy thermal neutrons, which reach deeper inside the meteoroid. Therefore, cosmogenic noble gases do not provide a direct measure of the production rate of thermal neutrons and the estimated thermal neutron fluxes are model-dependent (Masarik, 1997; Leya et al., 2003). Consequently, there is not yet a reliable method to correct for cosmogenic effects on W isotopes in iron meteorites. Therefore, the currently most reliable age information regarding core formation in iron meteorite parent bodies is provided by the W isotope compositions of magmatic iron meteorites that have not or only slightly been exposed to thermal neutrons, either because they have young exposure ages or because they were large enough for their interior to have been shielded from thermal neutrons. Among the analyzed iron meteorites, this is only the case for Negrillos (IIAB) and Gibeon (IVA). Negrillos has an exposure age of $\sim50\text{Myr}$ (Leya et al., 2000) and several authors have reported W isotope data for the IIAB Negrillos averaging at $\varepsilon^{182\text{W}}=-3.42\pm0.08\text{ (2\sigma)}$ (Kleine et al., 2005b; Lee, 2005; Markowski et al., 2006b). From the exposure age a downward shift of $\varepsilon^{182\text{W}}$ of $\sim0.03$ is calculated (Leya et al., 2003), resulting in a corrected $\varepsilon^{182\text{W}}$ of $-3.39\pm0.08$ (assuming a 50% uncertainty on the correction). In view of the discussion above we note however that the accuracy of this correction is difficult to assess. The IVA iron meteorite Gibeon has $\varepsilon^{182\text{W}}=-3.38\pm0.05$ (Qin et al., 2007) and the low concentrations of cosmogenic noble gases in this meteorite indicate that it is derived from the inner part of a larger body. Therefore, Gibeon probably

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**Fig. 4.** $\varepsilon^{182\text{W}}$ vs. exposure ages for magmatic iron meteorites. W isotope data are from Kleine et al. (2005a), Lee (2005), Markowski et al. (2006b), Schersten et al. (2006), and Qin et al. (2008). For exposure ages see these references. The three lines indicate the calculated $^{182\text{W}}$ burnout using different correction procedures (Leya et al., 2003; Qin et al., 2008), assuming that the pre-exposure $\varepsilon^{182\text{W}}$ of the magmatic irons is identical to the initial $\varepsilon^{182\text{W}}$ of CAIs (Burkhardt et al., 2008). KASKAD and JEF are two different libraries for cross sections of neutron induced reactions that were used by Qin et al. (2008) and for which reasonable agreement between the predicted effects and those measured in Grant and Carbo (Markowski et al., 2006a) were observed.
was largely shielded from thermal neutrons produced by the cosmic rays. As noted above, however, cosmonogenic noble gases are produced by high-energy protons and neutrons whereas the effects on W isotopes are caused by low-energy thermal neutrons, which may reach deeper inside the meteoroid.

The estimates based on exposure ages indicate that in iron meteorites the $^{182}\text{W}/^{184}\text{W}$ ratio might have been lowered by $\sim 0.1$ $^{182}\text{W}$ per $\sim 100$ Myr of cosmic-ray exposure and for an “average” shielding. This decrease in $^{182}\text{W}$ is similar to the radiogenic $^{182}\text{W}$ ingrowth that is achieved during the first Myr in a chondritic reservoir. Therefore, even in iron meteorites that were exposed to very low thermal neutron fluxes the effects of $^{182}\text{W}$ burnout can be significant but are essentially undetectable with current analytical techniques. It will thus be important to develop a monitor for the thermal neutron flux in the energy range that is relevant for W isotopes.

The corrected $^{182}\text{W} = -3.39 \pm 0.08$ for Negrillos and the measured $^{182}\text{W} = -3.38 \pm 0.05$ for Gibeon correspond to W model ages for core formation of $-1.0 \pm 1.2$ (2σ) and $-0.9 \pm 1.2$ (2σ) Myr after crystallization of type B CAIs. The uncertainties of these ages were calculated by propagating the uncertainties on the $^{182}\text{W}$ values of the iron meteorites, the initial $^{182}\text{W}$ of CAIs, and the present-day $^{182}\text{W}$ of carbonaceous chondrites. A more conservative approach is to calculate the range of ages obtained from the minimum and maximum $^{182}\text{W}$ differences between iron meteorites and CAIs. This approach results in W model ages that range from $-2.8$ to $+0.8$ for Negrillos and from $-2.5$ to $+0.6$ Myr for Gibeon. Note that the uncertainties of these ages do not include any uncertainty introduced by cosmic-ray effects, which may be present but are essentially undetectable with current analytical techniques. This makes it difficult to exactly determine the time of core formation based on W isotope data. Table 5 summarizes W model ages for different groups of magmatic iron meteorites that are based on $^{182}\text{W}$ values that were corrected for cosmic-ray effects using noble gas isotope systematics (Qin et al., 2008). The range of ages obtained from these corrected $^{182}\text{W}$ values is similar to the ages obtained for Negrillos and Gibeon, which have minor to absent cosmic-ray effects. However, for the IVB iron meteorites negative ages are obtained, most likely implying that the correction procedure did not fully account for the cosmic-ray effects on their $^{182}\text{W}/^{184}\text{W}$ ratios. Likewise, the $^{182}\text{W}/^{184}\text{W}$ ratios for several splits of the IID iron meteorite Carbo, after correction for cosmogenic effects using $^3\text{He}$ data (Markowski et al., 2006a), still show a slight trend between $^{182}\text{W}/^{184}\text{W}$ and $^3\text{He}$ and are still lower that the initial $^{182}\text{W}/^{184}\text{W}$ of Allende CAIs. This highlights the uncertainties associated with relying on noble gas systematics for quantifying the thermal neutron flux in iron meteorites (see Table 5).

In spite of the presence of cosmogenic effects on W isotopes in iron meteorites and difficulties in reliably quantifying them, it can be stated with confidence that core formation in the parent bodies of magmatic iron meteorites predated the formation of chondrules, most of which have Al–Mg and Pb–Pb ages of $\sim 2$–$3$ Myr after CAI formation (Kita et al., 2000; Amelin et al., 2002; Kunihiro et al., 2004; Rudraswami and Goswami, 2007). For instance, the estimated cosmogenic effect on the W isotope composition of Negrillos is $\sim 0.03$ c, corresponding to an age correction of $\sim 0.3$ Ma. Therefore, the correction would need to be $\sim 10$ times larger for the core formation age to be younger than the chondrule ages. However, it seems unlikely that the correction equations (Leya et al., 2003) are incorrect by one order of magnitude because they predict the observed effects to within $\sim 50\%$.

The finding that the parent bodies of magmatic iron meteorites accreted and differentiated before chondrules formed perhaps is the single most significant result of W isotope investigations in meteorites. This result has several far-reaching implications and it is therefore important to consider cases in which the W isotope composition of iron meteorites would not reflect the timing of core formation: (i) iron meteorite parent bodies did not contain $^{182}\text{Hf}$, such that their $^{182}\text{W}/^{184}\text{W}$ never evolved over time; (ii) temperatures during core formation were too low to allow diffusion of radiogenic W from silicates into the metal; (iii) there are nucleosynthetic W isotope anomalies in iron meteorites. As discussed in detail by Burkhardt et al. (2008), these scenarios are inconsistent with the Hf–W data for meteorites, such that the most straightforward interpretation of the low $^{182}\text{W}/^{184}\text{W}$ ratios of iron meteorites is an early metal segregation in their parent bodies.

The W isotopes in iron meteorites provide two important constraints for the formation and earliest evolution of planetesimals. First, the assembly of iron meteorite parent bodies prior to chondrule formation is inconsistent with the standard model for asteroid accretion, in which chondrules represent the precursor material from which asteroids accreted and then differentiated. Instead, chondrules appear to derive from relatively late formed planetesimals, whereas iron meteorites are remnants of some of the earliest planetesimals. Nevertheless, the latter might have ultimately
accrated from material resembling chondrites but the early melting and differentiation of the earliest planetesimals has erased evidence for this. It is important to note that the early formation of iron meteorite parent bodies is consistent with results from numerical simulations, which predict accretion of planetesimal in less than 1 Myr (e.g., Chambers, 2004). Second, the parent bodies of iron meteorites formed so early that heating by decay of $^{26}$Al must have been an important heat source. Thermal modeling indicates that for planetesimals that formed within 2 Myr after CAI formation and that are larger than $\sim 20$ km in diameter, heating by $^{26}$Al decay was sufficient to cause melting and core formation (Hevey and Sanders, 2006). The implications of these results will be discussed in more detail below (Section 3.6).

3.2. Chronology of non-magmatic iron meteorites

In contrast to the magmatic iron meteorites, the IAB–IIICD and IIE irons show little evidence for trace element fractionation and probably do not sample a planetary core (Scott and Wasson, 1975; Wasson and Kallemeyn, 2002). Moreover, metal-silicate separation was less efficient in the non-magmatic iron meteorites, as is evident from abundant silicate inclusions. Some authors have suggested that the IAB–IIICD iron meteorites formed in localized impact-melt pools in the megaregolith of a chondritic parent asteroid (Choi et al., 1995; Wasson and Kallemeyn, 2002), whereas others proposed formation of the IAB–IIICD irons by impact disruption of a partially differentiated body (Benedix et al., 2000) or incomplete differentiation of a chondritic planetesimal (Takeda et al., 2000).

Horan et al. (1998) were the first to show that most IAB–IIICD iron meteorites have slightly elevated $\epsilon^{182}$W values compared to magmatic irons. This was confirmed by later studies (Kleine et al., 2005b; Markowski et al., 2006b; Schersten et al., 2006). Whereas most magmatic iron meteorites have $\epsilon^{182}$W values below the initial $\epsilon^{182}$W of CAIs, all the non-magmatic irons have $\epsilon^{182}$W values similar to or slightly higher than the CAI initial (Fig. 5). Both groups of iron meteorites have a similar range in exposure ages, such that the higher $\epsilon^{182}$W of the IAB–IIICD irons compared to the magmatic irons cannot be caused by cosmic-ray effects on W isotopes in magmatic irons (see Section 3.1). They rather reflect a later event on the IAB–IIICD parent asteroid. Due to the presence of cosmic-ray effects on W isotopes the exact difference in the $^{182}$W/$^{184}$W ratios of non-magmatic and magmatic irons is difficult to assess but can be estimated from samples that were not exposed to substantial thermal neutron fluxes. This is the case for the non-magmatic iron Caddo County, whose $\epsilon^{182}$W/$^{184}$W is $0.2 \pm 0.1 \epsilon$ units more radiogenic than values for the magmatic irons Gibeon and Negrillos.

The W isotope composition of the Caddo County metal can be interpreted in different ways. It may represent the W isotope composition at the time of metal-silicate separation during (partial) melting of a chondritic source, in which case its two-stage model age of $\Delta t_{CAI} = 0.9 \pm 2.2$ Myr would date this event. An alternative interpretation is that the W isotope composition was partially or completely reset during thermal metamorphism and partial melting of the IAB silicates or during impact disruption of the parent body (Benedix et al., 2000). This requires diffusion of radiogenic W from the silicate inclusions into the metal. The metamorphic temperature of IAB silicates is similar to those of H6 chondrites [i.e., $\sim 900$ °C (Beneditx et al., 2000)], which, depending on the grain sizes of the silicates and the cooling rate might be sufficiently high to cause W diffusion in silicates (Kleine et al., 2008b). The metal of some IAB irons have $\epsilon^{182}$W values that are higher than those of the Caddo County metal (Fig. 5) and this could reflect diffusion of radiogenic $^{182}$W in the metals during thermal metamorphism.

Partial resetting of the Hf–W systematics after metal segregation renders a chronological interpretation of the W isotope data difficult. Nevertheless, the W isotope composition of the Caddo County metal provides important age information. Partial (or complete) resetting of the Hf–W system during thermal metamorphism and partial melting of the silicate inclusions would result in an increase of the $^{182}$W/$^{184}$W ratio of the metal. In this case the two-stage model time of $0.9 \pm 2.2$ Myr would be too young. Consequently, metal segregation in the IAB parent body must have occurred before the time given by this model age, i.e., within the first $\sim 3$ Myr after CAI formation. At such an early time, $^{26}$Al was sufficiently abundant to cause global melting of asteroids, indicating that melting and...
separation of the IAB metals was caused by internal heating from $^{26}$Al decay, as proposed by Benedix et al. (2000).

The $^{182}\text{W}/^{184}\text{W}$ ratios of metals from some IIE iron meteorites are higher than those of the IAB–IIICD iron meteorites (Snyder et al., 2001; Markowski et al., 2006b; Qin et al., 2008). Metal from the IIE iron Watson has the highest $^{182}\text{W}/^{184}\text{W}$ ratio (average $\varepsilon ^{182}\text{W} = -2.3 \pm 0.3$) among all iron meteorites measured for W isotopes so far and has a relatively young cosmic-ray exposure age of ~8 Ma (Bogard et al., 2000). The $^{180}\text{Hf}/^{184}\text{W}$ ratio of the Watson metal, therefore, is not affected significantly by cosmic-ray effects and provides evidence for a relatively late event on the IIE iron meteorite parent body. The two-stage model age of the Watson metal is $\Delta_{\text{CAI}} = 15 \pm 6$ Myr but it is unclear if this age dates a real event or if the W isotope composition of the Watson metal rather reflects incomplete resetting of the Hf–W system during impact-triggered mixing of metal and silicates on the IIE parent asteroid (Qin et al., 2008). In case of the latter option, the impact(s) must have occurred later than $15 \pm 9$ Myr.

### 3.3. Chronology of the eucrite parent body

#### 3.3.1. Accretion and primordial differentiation

The first W isotope data for eucrites were obtained by Lee and Halliday (1997) and Quitte et al. (2000) presented the first comprehensive investigation of the Hf–W systematics of basaltic eucrites. Subsequently, Yin et al. (2002) reported Hf–W data for one Juvinas whole-rock, Kleine et al. (2004a) reported Hf–W data for several additional basaltic eucrites and Kleine et al. (2005b) determined the W isotope composition of eucrite metals. Most recently, the W isotope composition of zircons in eucrites was determined (Srinivasan et al., 2007) and the Hf–W systematics of bulk-rock eucrites re-investigated (Touboul et al., 2008).

Most basaltic eucrites exhibit high $^{180}\text{Hf}/^{184}\text{W}$ and radiogenic $^{182}\text{W}/^{184}\text{W}$ ratios (Lee and Halliday, 1997; Quitte et al., 2000; Kleine et al., 2004a). Quitte et al. (2000) reported a large range in $^{180}\text{Hf}/^{184}\text{W}$ from ~0.1 to ~46 and $\varepsilon ^{182}\text{W}$ values from ~0 to ~39. In contrast, Kleine et al. (2004a) found a much narrower range in $^{180}\text{Hf}/^{184}\text{W}$ from ~12 to ~32 and $\varepsilon ^{182}\text{W}$ from ~14 to ~26. The Hf–W data for eucrites define a linear trend in a plot of $^{182}\text{W}/^{184}\text{W}$ vs. $^{180}\text{Hf}/^{184}\text{W}$, which yields a slope of $(7.25 \pm 0.05) \times 10^{-6}$ and an initial $\varepsilon ^{182}\text{W}$ of $-0.5 \pm 0.3$. If interpreted as an isochron, this slope corresponds to an age of ~4 Myr after CAIs. Quitte et al. (2000) initially interpreted the Hf–W data for eucrites as indicating differentiation of the eucrite parent body at ~11 Myr after CAI formation. However, this age was obtained using an initial $^{182}\text{Hf}/^{180}\text{Hf}$ of ~$2.75 \times 10^{-4}$ for CAIs but this value was later corrected to ~$1 \times 10^{-4}$ (Kleine et al., 2002; Yin et al., 2002). Subsequently, Quitte and Birck (2004) used the Hf–W data for eucrites to infer an age of ~8 Myr for parent body differentiation but this age was obtained using an initial $^{182}\text{Hf}/^{180}\text{Hf}$ of ~$1.6 \times 10^{-4}$ derived from the $^{182}\text{W}/^{184}\text{W}$ of the iron meteorite Tlacotepec. However, the $^{182}\text{W}/^{184}\text{W}$ of this sample has been lowered by the interaction with cosmic rays, such that the age estimate from Quitte and Birck (2004) is too young.

Recently, Touboul et al. (2008) showed that the Hf–W data for basaltic eucrites do not define an isochron. The correlation line is mainly defined by three samples [Serra de Magé and Jonzac (Quitte et al., 2000) and Juvinas (Yin et al., 2002)] that have anomalously high W contents. Using larger samples sizes, Touboul et al. (2008) were not able to reproduce the Hf–W data for these three samples and obtained much lower W contents and much higher $^{182}\text{W}/^{184}\text{W}$. Moreover, these authors could show that, in a plot of $\varepsilon ^{182}\text{W}$ vs. $1/W$ (Fig. 6a), the earlier reported W data for these three samples plot on mixing lines between terrestrial W and the W data obtained by Touboul et al. (2008). This relationship sheds doubt on the usefulness of the W data for these three samples to constrain the age of eucrite differentiation.

The Hf–W data for basaltic eucrite may nevertheless be used to extract age information on the differentiation of the eucrite parent body. The narrow range in $\text{Sm}/\text{Nd}$ and $\text{Lu}/\text{Hf}$ ratios as obtained from the combined $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{176}\text{Lu}/^{176}\text{Hf}$ isotope systematics of basaltic eucrites indicate that they may have formed as large degree melts from a source having chondritic relative abundances of refractory lithophile elements (Blichert-Toft et al., 2002). The lack of substantial variations in $^{176}\text{Hf}/^{177}\text{Hf}$ ratios among the basaltic eucrites rules out a significant role of ilmenite in their sources because this would have resulted in substantial $\text{Lu}/\text{Hf}$ fractionations and, hence, variations in the present-day $^{176}\text{Hf}/^{177}\text{Hf}$ ratios of these eucrites. Therefore, only limited fractionation of Hf and W is expected during formation of the basaltic eucrites. If this is correct, the $^{180}\text{Hf}/^{184}\text{W}$ and $^{182}\text{W}/^{184}\text{W}$ ratios of basaltic eucrites may closely reflect that of their sources and the Hf–W data can be used to constrain the timing of the earliest differentiation of the eucrite parent body. However, there is substantial variation in the $^{180}\text{Hf}/^{184}\text{W}$ and $^{182}\text{W}/^{184}\text{W}$ ratios reported for basaltic eucrites, which likely at least in part reflect Hf/W and W isotope heterogeneities in the small samples (~1 g) used for these analyses. Therefore, the average $^{180}\text{Hf}/^{184}\text{W}$ ratio and $\varepsilon ^{182}\text{W}$ value of basaltic eucrites are rather imprecisely defined and are $^{180}\text{Hf}/^{184}\text{W} = 27 \pm 8$ and $\varepsilon ^{182}\text{W} = 22 \pm 8$ [calculated using the data reported in Kleine et al. (2004a) and Kleine et al. (2005a)]. Using these values a two-stage model time for core formation of $\Delta_{\text{CAI}} = 3 \pm 6$ Myr is calculated (Fig. 6b). The large uncertainty on this age reflects uncertainties in the Hf/W ratio and W isotope composition of the bulk mantle of the eucrite parent body. Using larger sample sizes (~7 g), Touboul et al. (2008) reported Hf–W data for several basaltic eucrites and obtained model ages for core formation ranging from ~1 to ~4 Myr after CAI formation.

#### 3.3.2. Magmatism and thermal metamorphism

Basaltic eucrites have magmatic textures similar to those of terrestrial and lunar basalts, indicating formation as lava flows at or near the surface of their parent body, presumably the asteroid Vesta. As a result of rapid cooling near the surface, the pyroxenes in terrestrial and lunar basalts are chemically zoned. In contrast, pyroxenes in most eucrites show no chemical zoning and contain exsolution lamellae, indicating slow cooling and/or a protracted
thermal metamorphism after crystallization (Takeda and Graham, 1991). In addition to this thermal overprint, most eucrites are brecciated as a result of impacts on the surface of their parent body Vesta (e.g., Yamaguchi et al., 1996).

Most basaltic eucrites contain some zircons, which owing to their very high Hf/W ratios (up to ~17,000) can be dated with the Hf–W system (Ireland and Bukovanska, 2003; Srinivasan et al., 2007). Srinivasan et al. (2007) reported ion probe Hf–W data for zircons and pyroxenes from basaltic eucrites Asuka 881388 and Asuka 881467. The zircon–pyroxene isochrons yield \(^{182}\text{Hf}/^{180}\text{Hf}\) ratios of \((7.5 \pm 0.9) \times 10^{-5}\) and \((6.0 \pm 1.4) \times 10^{-5}\), corresponding to Hf–W ages of \(\Delta_{\text{CAI}} = 3 \pm 2\) and 6 ± 3 Myr and absolute ages of 4565 ± 2 Myr and 4562 ± 3 Ma, respectively.

All eucrites contain at least some metal (typically <0.5%) that formed either during crystallization of the basalts or during later metamorphism (Duke, 1965). The low Ni contents of these metals exclude a meteoritic origin by impacts on the surface of Vesta. The Camel Donga eucrite has the highest metal contents among eucrites and the metal in this meteorite evidently formed by reduction of FeO and FeS during thermal metamorphism (Palme et al., 1988). Metals from five basaltic eucrites (Camel Donga, Juvinas, Bereba, Bouvante, and Ibitira) have radiogenic W isotope compositions ranging from ~11 to ~16 \(\epsilon^{182}\text{W}\) but only for Camel Donga could a metal-silicate isochron be obtained (Kleine et al., 2005a). This isochron yields an initial \(^{182}\text{Hf}/^{180}\text{Hf}\) of \((1.7 \pm 0.7) \times 10^{-4}\), corresponding to an age of \(\Delta_{\text{CAI}} = 22 \pm 5\) Myr and an absolute age of 4546 ± 5 Ma (Kleine et al., 2005a) (Fig. 6b). The W model ages for the metals from the other basaltic eucrites, calculated relative to the average \(^{180}\text{Hf}/^{184}\text{W}\) and \(^{182}\text{W}/^{184}\text{W}\) of basaltic eucrites, yield similar ages (Kleine et al., 2005a).

The major hosts of radiogenic W in basaltic eucrites are high-Ca pyroxene, ilmenite and zircon. Identifying which of these minerals is the source of the radiogenic \(^{182}\text{W}\) in the metals requires knowledge of their respective closure temperatures for W diffusion as well as of the peak metamorphic temperatures of eucrites. Based on the diffusion profiles in pyroxenes the metamorphic temperatures of eucrites were ~800–900 °C (Takeda and Graham, 1991). There are no experimental data available for diffusion of W in high-Ca pyroxene, ilmenite, or zircon that could be used to calculate closure temperatures. However, the Hf–W closure temperature in a high-Ca pyroxene-metal system has been estimated using the numerical model of Van Orman et al. (2001) [see Section 2.4 and Kleine et al., 2008b] and, for an assumed starting temperature of 1000 °C, closure temperatures of 750–900 °C were obtained for a wide range of grain sizes and cooling rates (Kleine et al., 2008b).

It therefore seems likely that post-crystallization heating of basaltic eucrites resulted in W diffusion from high-Ca pyroxenes into metals. In contrast, W diffusion out of zircons probably did not occur because their Hf–W closure temperature is most likely very high. If W diffusion in zircon is slower than Pb diffusion, as is the case in other silicates such as high-Ca pyroxene (Kleine et al., 2008b), then the Hf–W closure temperature in zircons will be higher than the Pb closure temperature of ~1000 °C (Mezger and Krogstad, 1997). This is higher than the crystallization temperature of zircons in basaltic melts, indicating that...
the zircons crystallized below the Hf–W closure temperature but were not reset during later thermal metamorphism. This is consistent with the higher initial $^{182}$Hf/$^{180}$Hf of the zircons compared to the metal (see below) and indicates that the Hf–W zircon ages most likely dates the crystallization of basaltic eucrites.

Obtaining an age for crystallization from the Hf–W zircon data, however, requires Hf–W data for another phase that is co-genetic with the zircons and remained a closed system for Hf and W after crystallization. Srinivasan et al. (2007) used their Hf–W data for pyroxenes in the isochron calculations but the Hf–W closure temperature for high-Ca pyroxene in conjunction with temperature estimates for the thermal metamorphism of basaltic eucrites indicate that high-Ca pyroxene did not remain closed for W diffusion during thermal metamorphism (see above). In this case, the slope of the zircon–pyroxene isochron might be too steep because the high-Ca pyroxene exchanged its W with less radiogenic W from the metals, which would yield an apparent age that is too old (Fig. 6c). More reliable age information may then be obtained from a zircon-whole-rock isochron, provided that the eucrite whole-rocks remained closed systems with regard to Hf and W. Using the average $^{180}$Hf/$^{182}$W and $^{182}$W/$^{184}$W of basaltic eucrites in the regression of the zircon data results in Hf–W ages of $\Delta_{\text{CAI}} = 6 \pm 2$ Myr and $9 \pm 5$ Myr for the Asuka 881467 and Asuka 881388 zircons, corresponding to absolute ages of 4562 ± 2 Myr and 4560 ± 5 Myr (Fig. 6b).

An important observation is that eucrite metals plot above the regression line defined by the zircon and whole-rock Hf–W data (Fig. 6b). This is consistent with a significant time gap between zircon crystallization and the time of metal closure during thermal metamorphism. However, the metal and zircon data were not obtained on the same samples and a comprehensive assessment of the effects that thermal metamorphism had on the Hf–W system in eucrites will require Hf–W data for all major constituents of the same eucrite.

The similarity of Hf–W closure temperature in high-Ca pyroxene and metamorphic temperature for basaltic eucrites suggests that the Hf–W metal age corresponds closely to the time of the thermal peak and hence provides an age for the thermal metamorphism. This event occurred ~15 Myr after crystallization of Asuka 881467 zircons and may reflect slow cooling following magmatism, impact heating, burial of basaltic eucrites under hot interior material that was excavated by impacts, or a combination of these processes (Kleine et al., 2005a).

3.4. Timing of magmatism on the angrite and mesosiderite parent bodies

The angrites D’Orbigny and Sahara 99555 formed by rapid cooling of basaltic magmas. Therefore, their Hf–W ages of $\Delta_{\text{CAI}} = 3.8 \pm 0.7$ Myr and $\Delta_{\text{CAI}} = 4.4 \pm 0.7$ Myr reflect the crystallization ages of these basaltic rocks. The angrites NWA 2999, NWA 4590, and NWA 4801 have significantly younger Hf–W ages ranging from ~8 to ~10 Myr after CAI formation. This may reflect protracted cooling of more deeply buried igneous bodies inside the angrite parent body. Evidence for such a protracted cooling is provided by the annealed textures of NWA 2999 and NWA 4801 and the coarse plutonic texture of NWA 4590 and NWA 4801. The absence of chemical zoning in the pyroxenes of NWA 2999 and NWA 4801 provides evidence for annealing at temperatures above ~700–800 °C (Takeda and Graham, 1991), consistent with olivine-spinel temperatures of ~870 °C for NWA 2999 (Kuehner et al., 2006). The chronological data combined with the petrologic evidence therefore suggest that extrusion of basalt occurred at ~4 Myr and that interior parts of the angrite parent body cooled below ~800 °C (i.e., $T_c$ of the Hf–W system) in less than ~10 Ma, as constrained by the Hf–W ages for NWA 4801 and NWA 4590.

Schönbächler et al. (2000) reported a Hf–W isochron for a basaltic clast from the mesosiderite Vaca Muerta. The plagioclase–pyroxene isochron corresponds to an age of $\Delta_{\text{CAI}} = 3.0 \pm 1.5$ Myr and an absolute Hf–W age of 4565.3 ± 1.4 Ma. This age is similar to Hf–W ages for the quenched angrites D’Orbigny and Sahara 99555 as well as to Hf–W zircon ages for basaltic eucrites. These Hf–W ages suggest that extrusion of basaltic melts on the eucrite, angrite and mesosiderite parent bodies occurred within a narrow time interval of ~3–10 Myr after CAI formation. This is an important observation because it is consistent with results from numerical simulations for the thermal evolution of planetesimals heated by decay of $^{26}$Al and $^{60}$Fe. These simulations show that on bodies that accreted within the first 2–3 Myr of CAI formation magmatism began within the first ~4 Myr after CAI formation and that the last melting occurred before 10 Myr after CAI formation (Sahijpal et al., 2007).

3.5. Chronology of the H chondrite parent body

The early formation of the parent bodies of iron meteorites contrasts with the relatively late formation of chondrules. Based on $^{26}$Al–$^{26}$Mg and Pb–Pb ages it is well established that most chondrules formed ~2–3 Myr after CAIs (Kita et al., 2000; Amelin et al., 2002; Kunihiro et al., 2004; Rudraswami and Goswami, 2007; Connelly et al., 2008a; Kurahashi et al., 2008; Rudraswami et al., 2008). Chondrules must have formed prior to the assembly of chondrite parent bodies, such that the formation ages of chondrules provide the earliest possible time of parent body accretion. Furthermore, the distinct physical and chemical characteristics of chondrules from each chondrite group suggest that parent body accretion occurred shortly after chondrule formation. In a turbulent solar nebula, chondrules would be efficiently mixed on short timescales (Cuzzi et al., 2005), such that a characteristic population of chondrules with its distinct size distribution and chemical composition could only be preserved if this chondrule population is accreted into larger bodies soon after chondrule formation. This was quantified by Alexander (2005), who estimated that material in a 1 AU wide area could be mixed within less than ~0.5 Ma. Since asteroid feeding zones probably were smaller, these mixing times become even shorter. If these estimates are correct, chondrite accretion must have occurred almost instantaneously after chondrule
formation at ~2–3 Myr after CAI formation (Alexander, 2005). This timescale for the accretion of chondrite parent bodies is also consistent with results from thermal modeling, which suggest that the parent bodies of chondrites accreted more than ~2 Myr after CAIs because otherwise they would have differentiated due to heating from abundant $^{26}$Al. The question then arises as to whether this timescale for accretion is consistent with the long-term thermal evolution of chondrite parent bodies. Although the thermal evolution of carbonaceous chondrites is difficult to constrain—because except for CK chondrites there are only a few metamorphosed samples—the thermal evolution of ordinary chondrites can be investigated in detail because these samples exhibit a wide range of metamorphic grades (Dodd, 1969). Many ordinary chondrites are brecciated and shocked, such that a signature of their earliest thermal evolution—which is of main interest here—might have partly been erased. However, relatively unshocked H chondrites appear to have preserved their earliest cooling history (Trieloff et al., 2003).

Kleine et al. (2008b) presented Hf–W ages for such H chondrites and the selected meteorites cover the range of metamorphic conditions characteristic for H4–H6 chondrites. The Hf–W ages of the H chondrites become younger with increasing metamorphic grade and range from $\Delta t_{\text{CAI}} = 1.7 \pm 0.7$ Myr for the H4 chondrite Ste. Marguerite to $\Delta t_{\text{CAI}} = 9.6 \pm 1.0$ Myr for the H6 chondrites Kernejouvé and Estacado (Fig. 7a). The closure temperature of the Hf-W system in H4 chondrites is $800 \pm 50 \, ^\circ\text{C}$ and thus higher than the peak metamorphic temperature of H4 chondrites. Therefore, parent body metamorphism did not result in significant diffusion of radiogenic W from silicates into metals, such that the Hf–W age for Ste. Marguerite is much shorter than intervals obtained from Rb–Sr and Pb–Pb chronometry (Wasserburg et al., 1969; Göpel et al., 1994). Combined with previously published chronological data (Trieloff et al., 2003) the Hf-W ages reveal that shortly after their thermal peak H6 chondrites cooled at ~10 °C/Myr, H5 chondrites at ~30 °C/Myr and H4 chondrites at ~55 °C/Myr (Kleine et al., 2008b). This inverse correlation of cooling rate and metamorphic grade is most consistent with an onion-shell structure of an H chondrite parent body that was heated internally by $^{26}$Al decay (Kleine et al., 2008b). Therefore, heating by $^{26}$Al decay not only accounts for the peak temperatures reached inside the H chondrite parent body but is also consistent with its long-term thermal evolution. For planetesimals other than the H chondrite parent body, the thermal evolution is less well constrained and it will be important to investigate whether their thermal evolutions are also consistent with heating by $^{26}$Al decay.

3.6. Accretion and early thermal evolution of planetesimal and the importance of $^{26}$Al heating

Hafnium–tungsten chronometry of meteorites as summarized above indicates that melting and differentiation occurred in bodies that accreted within the first ~1 Myr. These are the parent bodies of some magmatic iron meteorites and possibly also the eucrites and angrites, as indicated by their $^{26}$Al–$^{26}$Mg systematics (Bizzarro et al., 2005). In contrast, thermal metamorphism with peak temperatures of 900–1000 °C is characteristic for the ordinary chondrite parent body. Therefore, heating was not an important factor determining the change in most ordinary chondrites.
bodies that formed shortly after ~2 Myr. The thermal histories of these meteorite parent bodies are consistent with heating by decay of $^{26}\text{Al}$ as the dominant heat source. This is illustrated in Fig. 8, where the peak temperature in the center of an asteroid is plotted against its (instantaneous) accretion age for parent body radii of 10 and 100 km. Also shown are the Hf–W ages for iron meteorites, which provide the latest possible time of accretion of their parent bodies, as well as ages for chondrules from various chondrite parent bodies, which provide the earliest possible time of parent body accretion. Note that parent body accretion must have postdated the formation time of the youngest chondrule from a given population. Fig. 8 predicts that, if $^{26}\text{Al}$ was the dominant heat source in meteorite parent bodies, then the parent bodies of the weakly metamorphosed carbonaceous chondrites (such as the CR chondrites) should have accreted more than ~3 Myr after CAI formation.

Recent applications of Al–Mg chronometry to chondrules suggest that this indeed may be the case. These studies show that chondrules from L and LL chondrites formed in a narrow interval of 1–2.5 Myr after CAI formation and that younger ages for L and LL chondrules reflect partial resetting by parent body metamorphism (Rudraswami and Goswami, 2007; Rudraswami et al., 2008). By contrast, chondrules from carbonaceous chondrites show no evidence for resetting by thermal metamorphism but their ages extend to more than ~3 Myr after CAI formation (Rudraswami et al., 2008; Hutcheon et al., 2009). For instance, chondrules from the CO3.0 chondrite Yamato 81020 have Al–Mg ages ranging from 1.7 to 3.0 Myr (Kunihiro et al., 2004; Kurahashi et al., 2008) and many chondrules from CR chondrites appear to have formed more than ~3 Myr after CAIs (Nagashima et al., 2008; Hutcheon et al., 2009). If these young chondrule ages do not reflect resetting by low-temperature aqueous alteration on chondrite parent bodies, then the Al–Mg ages for chondrules from carbonaceous chondrites require that their parent bodies accreted more than ~3 Myr after CAI formation and, hence, later than the ordinary chondrite parent bodies. In this case, $^{26}\text{Al}$ had decayed to a level too low to cause significant heating, consistent with the scarcity of highly metamorphosed specimens among the carbonaceous chondrites (Fig. 8).

The chronological data summarized above combined with results from thermal modeling (Hevey and Sanders, 2006; Sahijpal et al., 2007) indicate that the abundance of $^{26}\text{Al}$ present at the time of parent body accretion is the essential factor controlling the early evolution of planetesimals: $^{26}\text{Al}$ was sufficiently abundant to melt early-formed (<1 Myr) planetesimals, whereas in the late-formed (>2 Myr) chondrite parent bodies too little $^{26}\text{Al}$ remained to raise the temperatures high enough to cause large-scale melting and differentiation (Kleine et al., 2005b; Schéresten et al., 2006). Moreover, heating that caused the thermal metamorphism of ordinary chondrites is consistent with energy release from $^{26}\text{Al}$ decay, as is the scarcity of metamorphosed carbonaceous chondrites, whose parent bodies accreted more than ~3 Myr after CAI formation (Fig. 8). Finally, crystallization ages of meteoritic basalts from the eucrite, angrite and mesosiderite parent bodies are remarkably consistent with the timescale for basaltic magmatism predicted by thermal models for asteroids heated by decay of $^{26}\text{Al}$ (Sahijpal et al., 2007). Differences in the thermal evolution of meteorite parent bodies therefore largely reflect their initial $^{26}\text{Al}$ abundance, which, due to the rapid decay of $^{26}\text{Al}$, is controlled by the time of parent body accretion.

These observations can be rationalized if the variation of accretion time across the asteroid belt is of the order of several $^{26}\text{Al}$ half-lives (Grimm and McSween, 1993). Due to longer orbital periods and a decrease in surface density, the accretion time increases with increasing distance to the Sun (e.g., Weidenschilling, 1977) and this may account for the heliocentric zoning of the asteroid belt in igneous, metamorphic and unaltered asteroids, with igneous asteroids being located closest to the Sun (Gradie and Tedesco, 1982). Grimm and McSween (1993) considered the variation of accretion time as a function of semimajor axis and calculated the subsequent thermal histories for these planetesimals. The results show that the zonation of the asteroid belt and the thermal histories of meteorite parent bodies can be achieved by heating from $^{26}\text{Al}$ decay. The results of these calculations are remarkably consistent with the chronological constraints for asteroid accretion and evolution as summarized above. Bottke et al. (2006) proposed
that the parent bodies of iron meteorites initially accreted within the terrestrial planet region, where the fast accretion rates led to early melting even of small planetesimals, and were later scattered in the main asteroid belt. The Hf–W evidence for early core formation in the parent bodies of magmatic iron meteorites is consistent with this scenario and it should be noted that the Bottke et al. (2006) model was in part designed to account for the early formation of the iron meteorite parent bodies.

It is remarkable that chondrites, which represent some of the most primitive material that has been preserved in the meteorite record, were accreted and processed last. Although this seems somewhat paradoxical at first glance, it reflects the fact that due to the intense heating by $^{26}$Al decay only late-formed material could remain undifferentiated. Whether early-formed planetesimals accreted from material resembling those of the chondrite parent bodies is unknown because the early differentiation of the former erased any evidence of this.

In addition to $^{26}$Al heating, the decay of $^{60}$Fe may have been an important heat source in early planetesimals but uncertainties in the initial $^{60}$Fe abundance of the solar system make it difficult to calculate the contribution of $^{60}$Fe decay to planetesimal heating. Hevey and Sanders (2006) found that for an initial $^{60}$Fe/$^{56}$Fe of $\sim 1.8 \times 10^{-6}$, the contribution of $^{60}$Fe heating would have been only one-eights of that due to $^{26}$Al decay and, hence, has no significant influence on the thermal models for early-formed planetesimals. However, due to its longer half-life compared to $^{26}$Al, $^{60}$Fe may have been an important heat source for planetesimals that accreted more than 1.5–2 Myr after CAI formation but the energy provided by the decay of both $^{26}$Al and $^{60}$Fe is still insufficient to cause melting in planetesimals that accreted more than 2–3 Myr after CAI formation (Sahijpal et al., 2007).

Heating by impacts may have also been important in the thermal evolution of asteroids but the chronological data summarized above indicate that they probably played only a minor role in the early high-temperature evolution of asteroids. This is because the Hf–W ages for high-temperature events such as core formation, magmatism and parent body-wide thermal metamorphism summarized above are entirely consistent with $^{26}$Al as the sole heat source. Nevertheless, impact-related processes were important in the subsequent evolution of asteroids. For instance, Hf–W ages for eucrite metals postdate CAI formation by $\sim 20$ Myr and may reflect impact-triggered thermal metamorphism in the crust of the eucrite parent body, and the variable and slightly elevated $^{182}$W/$^{184}$W ratios of non-magmatic iron meteorites suggest a relatively late, impact-triggered resetting of the Hf–W systematics.

4. TIMESCALES FOR CORE FORMATION AND EARLY MANTLE DIFFERENTIATION IN MARS

4.1. $^{182}$W–$^{142}$Nd systematics of the martian mantle

The first W isotope data for martian meteorites were presented by Lee and Halliday (1997) and additional more precise analyses were reported by Kleine et al. (2004a) and Foley et al. (2005). The $^{182}$W/$^{184}$W ratios of martian meteorites mainly fall into two groups (Fig. 9). Basaltic shergottites have $^{182}$W/$^{184}$W $\sim 0.3–0.6$ and nakhlites and Chassigny (hereafter NC group) have $^{182}$W/$^{184}$W $\sim 2–3$ (Lee and Halliday, 1997; Kleine et al., 2004a; Foley et al., 2005). The only lherzolitic shergottite that has been analyzed for W isotopes so far is ALHA 77005 and its $^{182}$W/$^{184}$W value of 0.91 ± 0.32 appears to be slightly higher but is not well resolved from the basaltic shergottites (Foley et al., 2005). Orthopyroxenite ALH 84001 has $^{182}$W/$^{184}$W = 0.49 ± 0.33, similar to the values for basaltic shergottites (Foley et al., 2005). The W isotope data provide two important constraints. First, all martian meteorites have elevated $^{182}$W/$^{184}$W ratios relative to chondrites. This is not surprising because Hf and W can be strongly fractionated by large-scale parent body processes such as core formation and mantle melting. Second, there are $^{182}$W variations within the martian mantle, indicating that, in spite of relatively young crystallization ages for most martian meteorites (e.g., Nyquist et al., 2001), a signature of an early mantle differentiation (i.e., $\sim 60$ Myr after CAI formation) has been preserved.

The observed $^{182}$W heterogeneity in the martian mantle is consistent with variations in $^{142}$Nd/$^{144}$Nd ratios among martian meteorites that also require mantle differentiation within the first $\sim 60$ Myr of the solar system. All samples from the NC group studied so far have relatively constant $^{142}$Nd values of $\sim 0.6$ (Harper et al., 1995; Caro et al., 2008). In contrast, shergottites show $^{142}$Nd ranging from $\sim -0.3$ to $\sim +0.9$ (Borg et al., 1997; Debaille et al., 2007; Caro et al., 2008) (Fig. 9).

4.2. Age of the martian core

Dating core formation in Mars requires knowledge of the $^{182}$W/$^{184}$W ratio of the bulk martian mantle and for estimating this value W isotope variations that are due to early mantle differentiation must be distinguished from those that reflect core formation. The $^{142}$Nd variations among martian meteorites show that silicate mantle differentiation occurred.

![Fig. 9. $^{142}$Nd vs. $^{182}$W for martian meteorites. Nd isotope data are from Caro et al. (2008) and Debaille et al. (2007), W isotope data from Lee and Halliday (1997), Kleine et al. (2004a), and Foley et al. (2005). S = Shergotty, LA = Los Angeles, Z = Zagami.](image-url)
sufficiently early to have resulted in W isotope variations, such that the effects of silicate mantle differentiation on W isotopes need to be taken into account in any attempt to derive the $^{182}\text{W}/^{184}\text{W}$ of the bulk martian mantle. Kleine et al. (2004a) and Foley et al. (2005) used the $^{142}\text{Nd}/^{144}\text{Nd}$ ratios of shergottites for this task, mainly because the Nd isotope data available at that time suggested that at least some of the shergottites have $^{142}\text{Nd}/^{144}\text{Nd}$ identical to that of the bulk martian mantle, assumed to be $^{142}\text{Nd} = 0$ (i.e., identical to the terrestrial standard). However, recent high precision $^{142}\text{Nd}$ data sets for meteorites require a reassessment of this approach. Firstly, it was shown that chondrites, assumed to be representative for the bulk composition of Mars and other terrestrial planets, have $^{142}\text{Nd}$ values $\sim 20$ ppm below those for the terrestrial standard (Boyet and Carlson, 2005).

Secondly, new highly precise $^{142}\text{Nd}$ data for shergottites show that the $^{142}\text{Nd}/^{144}\text{Nd}$ ratios of all shergottites deviate from $^{142}\text{Nd} = 0$ (Debaille et al., 2007; Caro et al., 2008). Although some shergottites have $^{142}\text{Nd}$ values similar to those of ordinary chondrites [$^{142}\text{Nd} \sim -0.2$ (Boyet and Carlson, 2005)], their $^{143}\text{Nd}$ and $^{176}\text{Hf}$ values are negative, indicating that these are crustal samples (Bourdon et al., 2008; Caro et al., 2008). Therefore, the similar $^{142}\text{Nd}$ values of these shergottites and chondrites seem fortuitous.

The $^{142}\text{Nd}$ data for chondrites and shergottites show that, as a result of early mantle differentiation, the $^{142}\text{Nd}/^{144}\text{Nd}$ ratios of all shergottites deviate from that of the bulk martian mantle. It is therefore difficult to assess whether the $^{182}\text{W}/^{184}\text{W}$ ratio of any of the shergottites is representative for the bulk martian mantle. However, in spite of their different $^{142}\text{Nd}$ values, basaltic shergottites have very similar $^{182}\text{W}$ values ranging from $\sim 0.3$ to $\sim 0.6$ (Foley et al., 2005), indicating that the event that caused the $^{142}\text{Nd}$ variations among the shergottites did not result in significant $^{182}\text{W}$ variations.

The two-stage W model ages for the formation of the martian core reported in the recent literature range from $\sim 3$ to $\sim 12$ Myr after CAI formation (Kleine et al., 2004a; Foley et al., 2005; Nimmo and Kleine, 2007). This range primarily reflects the use of different Hf/W ratios for the bulk martian mantle (Nimmo and Kleine, 2007). Based on Hf, Th and W concentrations of martian meteorites and chondrites the currently best estimate for the Hf/W ratio of the bulk martian mantle is $\text{Hf}/\text{W} \sim 3.4$ (see Section 2.1). Using this value and $^{182}\text{W} \sim 0.3$–0.6 for the bulk martian mantle results in two-stage model ages for core formation ranging from $\sim 0$ Myr to $\sim 8$ Myr after CAI formation (Fig. 10a). As is evident from Fig. 10a, the uncertainty in these model ages is largely due to uncertainty in the Hf/W ratio of the bulk martian mantle. Fig. 10a also demonstrates that the lowest possible Hf/W ratio of the martian mantle is $\sim 3$ because lower Hf/W ratios would result in negative core formation ages. The martian mantle likely has a Hf/W ratio that is only slightly higher than this minimum value of $\sim 3$, such that the Hf/W ratio must be determined very precisely to yield core formation ages of higher precision.

A different approach for determining the age of the martian core was employed by Halliday and Kleine (2006), who argued that core formation in Mars might have started within the first Myr of CAI formation. These authors observed that the $^{152}\text{W}/^{184}\text{W}$ ratios of SNC meteorites are broadly correlated with their Th/W, which they used as a proxy for the Hf/W ratio in the sources. If this is correct, then the W isotope heterogeneity in the martian mantle might be due to different degrees of siderophile element depletion in the shergottite and NC sources. Later work by Nimmo and Kleine (2007), however, could not identify a systematic difference between the Th/W ratios of shergottites and nakhlites (+chassignites) but showed that there is a large range in Th/W ratios of martian meteorites, which make it difficult to precisely define the Hf/W ratio of the martian mantle and its distinct geochemical reservoirs.

Fig. 10. Hf–W chronology of Mars. (a) Two-stage model age for core formation as a function of Hf/W ratio in the bulk martian mantle. The gray hatched area indicates the best estimate for the Hf/W ratio of bulk silicate Mars. The solid line represents ages calculated using $^{182}\text{W} = 0.4$ for the bulk martian mantle. The dashed lines indicate ages calculated using $^{182}\text{W}$ values that are 0.2 higher and lower, respectively. (b) Model for the W isotope evolution of martian mantle reservoirs. In this model it is assumed that bulk silicate Mars has $^{180}\text{Hf}/^{184}\text{W} \sim 4$ (i.e., $\text{Hf}/\text{W} \sim 3.5$) and $^{182}\text{W} \sim 0.4$. W isotope evolution curves for depleted (DS) and enriched shergottites (ES) are shown for a differentiation age of $\sim 40$ Myr, as suggested based on their $\text{Sm}/\text{Nd}$ systematics. In this model, Hf–W fractionations in the shergottite sources were modest, consistent with the limited range in $^{182}\text{W}$ of shergottites. For the NC source two previously proposed scenarios are shown that can account for both the elevated $^{142}\text{Nd}/^{144}\text{Nd}$ and $^{182}\text{W}/^{184}\text{W}$ ratios of these rocks.
Nimmo and Kleine (2007) showed that in the case of Mars two-stage model ages may underestimate the time Mars reached ~90% of its final mass by a factor of more than 3. For instance, for a two-stage model time of ~6 Myr, which is at the upper end of the age range shown in Fig. 10a, Mars might have completed 90% of its accretion as late as at ~20 Myr. Therefore, Hf–W chronometry cannot currently distinguish between scenarios in which Mars formed within 1 Myr during the runaway growth stage of planetary accretion (Halliday and Kleine, 2006) and scenarios in which accretion was more protracted (Nimmo and Kleine, 2007). Clearly, a more precise determination of the age of the martian core requires better estimates of the Hf/W ratios of the martian mantle and its reservoirs.

### 4.3. Early mantle differentiation in Mars

The different $^{182}$W/$^{184}$W ratios of the shergottites and the NC group can in principle be used for constraining the timing of early silicate differentiation in the martian mantle but this requires knowledge of the Hf/W fractionation associated with these differentiation processes. This information is difficult to obtain and a more powerful approach is to use the W isotopes in conjunction with the combined $^{146,147}$Sm/$^{142,143}$Nd systematics.

The shergottites define a planetary isochron in the $^{143}$Nd/$^{142}$Nd two-stage evolution diagram, which was interpreted to indicate differentiation at 40 ± 18 Myr (Foley et al., 2005; Caro et al., 2008) or, alternatively, differentiation in the interval from 30 to ~100 Myr after CAI formation (Debaille et al., 2007). The elevated $^{142}$Nd/$^{144}$Nd ratio of the NC group corresponds to a two-stage model age of ~25 Myr after CAI formation (Harper et al., 1995; Foley et al., 2005) but the NC group plots outside the two-stage evolutionary field, indicating that their source(s) had a more complex history, such that the two-stage model age may have no chronological meaning (Borg et al., 2003; Caro et al., 2008). The NC group has $^{146,147}$Sm/$^{142,143}$Nd systematics similar to the depleted shergottites, whereas the $^{143}$Sm/$^{144}$Nd systematics reveal differences. This indicates a disturbance of the Sm–Nd system after extinction of $^{146}$Sm, possibly related to the addition of a LREE-enriched fluid (Borg et al., 2003; Foley et al., 2005).

The range of $^{182}$W values observed in martian meteorites combined with the constraints provided by their $^{146,147}$Sm/$^{142,143}$Nd systematics can be used to infer a possible (but certainly not unique) scenario for the W isotope evolution of the martian mantle (Kleine et al., 2004a; Foley et al., 2005). This scenario is illustrated in Fig. 10b, where it is assumed that the bulk martian mantle has a present-day $^{182}$W ~ 0.4 and $^{180}$Hf/$^{184}$W = 4 (Fig. 10b). The corresponding two-stage model age for core formation is ~4 Myr. The enriched and depleted shergottites might have slightly different W isotope compositions and these could have been produced by Hf–W fractionation during mantle differentiation at ~40 Myr. The inferred $^{180}$Hf/$^{184}$W ratio for the source of the depleted shergottites is ~8, whereas this ratio is ~2 in the source region of the enriched shergottites (Fig. 10b). This is consistent with $^{176}$Lu–$^{176}$Hf constraints on the evolution of shergottites, which were interpreted to indicate the presence of garnet in the source of the enriched shergottites and derivation of the depleted shergottites from an already depleted source (Blichert-Toft et al., 1999). Garnets have $D_{Hf}/D_{W}$ ~ 30 (Righter and Shearer, 2003), such that residual garnet in the source will result in low Hf/W ratios in the melts, as observed for the enriched shergottites. Likewise, elevated $^{180}$Hf/$^{184}$W in the source of the depleted shergottites are consistent with derivation from an already depleted source.

For the NC group several source compositions were proposed that could account for the observed Hf–W and $^{146,147}$Sm–$^{142,143}$Nd systematics (Borg et al., 2003; Righter and Shearer, 2003; Kleine et al., 2004a; Foley et al., 2005) and Fig. 10b shows the W isotope evolution for of two of these proposed compositions of the NC source. In the first model differentiation of the NC source occurred at ~25 Myr (i.e., at the time given by its two-stage $^{144}$Sm/$^{142}$Nd model age), in which case the NC source would have developed with $^{180}$Hf/$^{184}$W ~ 20 and $^{146}$Sm/$^{144}$Nd ~ 0.266 to reach the present-day $^{182}$W and $^{142}$Nd of the NC group (e.g., Foley et al., 2005). In the second model, the NC source formed at the same time as the shergottite source(s) and in this case the NC must have evolved with very high $^{180}$Hf/$^{184}$W ~ 56 and $^{146}$Sm/$^{144}$Nd ~ 0.303 to reach their present-day $^{182}$W and $^{142}$Nd values (e.g., Foley et al., 2005). The inferred $^{180}$Hf/$^{184}$W ratio of ~20 and ~56 are consistent with those that were calculated for a garnet-bearing shallow mantle and a majorite-rich garnet-bearing deep mantle, respectively, based on mineral–melt partition coefficients for Hf and W (Righter and Shearer, 2003). However, the problem with both of these NC source compositions is that the nakhlites themselves have low Hf/W and Sm/Nd ratios, which would require small degrees of partial melting during formation of the nakhlite and chassigny melts. Borg et al. (2003) suggested that the low Sm/Nd ratio of nakhlites may reflect a late addition of LREE-enriched fluids to the NC source but the effects this would have on its $^{146}$Nd/$^{144}$Nd ratio has not been investigated.

In summary, the preservation of $^{182}$W and $^{142}$Nd heterogeneities in the martian mantle demonstrate (i) that the martian mantle has differentiated within the first ~60 Myr of the solar system and (ii) that the reservoirs formed during this early differentiation have remained isolated since then. However, the exact timing of this earliest differentiation remains poorly constrained, as is the timing of core formation in Mars, which probably occurred in the first ~20 Myr of the solar system. Finally, it should be noted that the uncertainties inherent in the age estimates summarized above are too large to distinguish between scenarios in which core formation and early mantle differentiation occurred contemporaneously and those in which there was a significant time gap between these two differentiation events.

### 5. The Age of the Moon and Lifetime of Its Magna Ocean

The leading theory for the formation of the Moon involves the collision of a Mars-sized body with proto-Earth,
which probably was the last major event in Earth’s accretion (e.g., Canup and Asphaug, 2001). The high energies released by the Moon-forming impact led to the formation of a lunar magma ocean (LMO), the crystallization of which was the dominant process in the early evolution of the Moon (e.g., Shearer and Papike, 1999). The first minerals to crystallize from the LMO were mainly olivine and orthopyroxene and were followed by plagioclase that floated to the surface, forming the ferroan anorthosites. Towards the end of the crystallization sequence ilmenite and clinopyroxene precipitated, until the residual liquid of the magma ocean, termed KREEP (for its enrichment in K, REE, and P), solidified. Subsequent melting and mixing among these primary components produced the variety observed in the lunar sample suite. For example, mare basalts formed by remelting of early mafic cumulates, which in the case of high-Ti mare basalts included assimilation of ilmenite and clinopyroxene. The redistribution of KREEP during impacts on the lunar surface resulted in the contamination of the lunar highlands with various amounts of the KREEP-component.

Lee et al. (1997) reported the first W isotope data for lunar whole-rock samples and found variations in $^{182}$W/$^{184}$W ranging from ~0 to ~7 $^{182}$W. These were interpreted to indicate formation of the Moon ~54 Myr after formation of CAIs (Lee et al., 1997), mainly because the presence of $^{182}$W variations in the Moon was thought to require lunar formation within the effective lifetime of $^{182}$Hf. Later work, however, revealed that elevated $^{182}$W/$^{184}$W ratios in lunar samples largely reflect the presence of cosmogenic $^{182}$W. Nevertheless, small $^{182}$W variations that were attributed to $^{182}$Hf decay were thought to be present and implied formation of the Moon within the first ~60 Myr after CAI formation (Leya et al., 2000; Lee et al., 2002; Kleine et al., 2005c). However, Touboul et al. (2007, 2009) showed that all their measured lunar samples have constant $^{182}$W/$^{184}$W ratios and that elevated $^{182}$W/$^{184}$W ratios in lunar samples entirely reflect cosmogenic $^{182}$W production.

### 5.1. $^{182}$Hf–$^{182}$W systematics of the Moon

#### 5.1.1. Cosmogenic vs. radiogenic $^{182}$W in lunar samples

Lunar samples collected during the Apollo and Luna missions all derive from the surface of the Moon and during their residence at the lunar surface these rocks were exposed to cosmic rays that could have produced $^{182}$W via the reaction $^{181}$Ta(n,$\gamma$)$^{182}$Ta followed by $\beta^-$ decay to $^{182}$W (Leya et al., 2000). Thus, elevated $^{182}$W/$^{184}$W ratios of lunar whole-rock samples can reflect contribution from two sources: decay of $^{182}$Hf and cosmogenic production of $^{182}$W. Cosmogenic $^{182}$W production is significant in lunar samples because of their long exposure times to cosmic rays combined with their high Ta/W ratios, making cosmogenic $^{182}$W a dominant component in lunar samples (Fig. 11). Lee et al. (2002) showed that in some high-Ti mare basalts the $^{182}$W of mineral separates is correlated with their Ta/W ratios, providing clear evidence for the presence of cosmogenic Ta-derived $^{182}$W in these samples (Fig. 11). Lee et al. (2002) regressed their Ta–W data to determine the purely radiogenic $^{182}$W/$^{184}$W at Ta/W = 0. Although this
approach yielded rather imprecise corrected $^{182}\text{W}/^{184}\text{W}$ ratios with uncertainties of $\sim 2$–3ε units, these corrected $^{182}\text{W}/^{184}\text{W}$ ratios revealed variations among the investigated mare basalts that possibly could be as large as $\sim 7\epsilon$ units (Lee et al., 2002).

The most direct method to determine the $^{182}\text{W}/^{184}\text{W}$ of lunar samples devoid of any cosmogenic $^{182}\text{W}$ is to analyze minerals that do not contain any Ta and hence no Ta-derived cosmogenic $^{182}\text{W}$. Metals, which are found in trace amounts in most lunar samples, have Ta/W $\sim 0$ and hence are ideally suited for this task (Kleine et al., 2005c). While metals do not contain any Ta-derived cosmogenic $^{182}\text{W}$, the interaction with cosmic rays can nevertheless have altered their $^{182}\text{W}/^{184}\text{W}$ ratio by neutron-capture reactions of W isotopes. This is similar to what has been documented for iron meteorites but these effects are small compared to the cosmogenic $^{182}\text{W}$ production in samples with elevated Ta/W ratios. Kleine et al. (2005c) reported W isotope data for metals from lunar samples with relatively long exposure times of $\sim 500$ Myr and found that the $^{182}\text{W}/^{184}\text{W}$ ratio of the metal is lowered by $\sim 0.1\epsilon$ per 100 Myr of exposure. The most recent and comprehensive investigation of W isotopes in lunar metals focused on samples that have exposure ages of less than $\sim 100$ Ma, such that the effects of W burnout are negligible (Touboul et al., 2007).

### 5.1.2. Indigenous $^{182}\text{W}/^{184}\text{W}$ ratios in lunar samples

Relatively high Ni and Ir contents in metals from highland samples indicate that these are meteoritic metals added to the lunar surface by impacts. Unlike meteoritic metals, however, the metals from KREEP–rich highland rocks have extremely high contents of W ($\sim 30$ ppm (Kleine et al., 2005c)). The chondrite-normalized concentration of W in these metals exceeds those of highly siderophile elements (Os, Ir, etc.) by more than one order of magnitude, indicating that the W enrichment in the lunar highland metals has a lunar origin and reflects the strong enrichment of W in KREEP. Partitioning of W from KREEP into these metals occurred by impact-induced thermal metamorphism, melting, and brecciation during redistribution of KREEP on the lunar surface. In contrast to the highland rocks, mare basalts contain small amounts of native Fe which is Ni-poor. The composition of these metals, particularly their low Ni contents, distinguishes them from meteoritic metal added to the lunar surface by impacts. The mare basalt metals formed by crystalization from a silicate melt under reducing conditions.

Kleine et al. (2005c) reported the first W isotope data for lunar metals and found small variations in the $^{182}\text{W}/^{184}\text{W}$ ratios of metals from high-Ti mare basalts and KREEP-rich samples. However, Touboul et al. (2007) recently presented W isotope data for high-purity metal separates from a comprehensive set of lunar mare basalts. These new data reveal that low- and high-Ti mare basalts have identical W isotope compositions that are also identical to the $^{182}\text{W}/^{184}\text{W}$ of KREEP (Fig. 12). This result is inconsistent with the earlier reported W isotope data for magnetic separates for two high-Ti mare basalts (Kleine et al., 2005c) but Touboul et al. (2007) showed that the magnetic separates analyzed earlier contained a small fraction of ilmenite with high Ta/W and hence cosmogenic $^{182}\text{W}$. After correction for cosmogenic $^{182}\text{W}$, these high-Ti mare basalts have $^{182}\text{W}/^{184}\text{W}$ indistinguishable from the metals of all other mare basalts (Touboul et al., 2007).

Mineral separates from low-Ti mare basalt 15555, in spite of having variable Ta/W ratios, show no resolvable difference in their $\epsilon^{182}\text{W}$ values averaging at $1.4 \pm 0.4$ (Lee et al., 2002). This elevated $^{182}\text{W}/^{184}\text{W}$ appears inconsistent with $\epsilon^{182}\text{W} \sim 0$ for all metals from mare basalts but Touboul et al. (2009) reported somewhat lower $\epsilon^{182}\text{W}$ of $0.9 \pm 0.4$ and Ta/W $\sim 4.6$ for sample 15555 (Fig. 11b). Using correction equations (Leya et al., 2000) and the Sm isotope composition of sample 15555 (Nyquist et al., 1995; Rankenburg et al., 2006) to estimate the effective thermal neutron flux, the calculated cosmogenic $^{182}\text{W}$ at Ta/W $\sim 4.6$ is $\sim 0.9$, and agrees with the measured W isotope composition as reported by Touboul et al. (2009), and is consistent with the $\epsilon^{182}\text{W}$ value and Ta/W ratio reported for a 15555 whole-rock analysis by Kleine et al. (2005c). This indicates that the W isotope composition of mare basalts 15555 is indistinguishable from $\epsilon^{182}\text{W} \sim 0$, i.e., the composition of other mare basalts as based on W isotope data for their metals (Fig. 11b). The reason for the systematic offset reported by Lee et al. (2002) for sample 15555 remains unclear.

Similarly, Lee et al. (1997) reported a positive $^{182}\text{W}$ anomaly of $3.1 \pm 1.7 \epsilon^{182}\text{W}$ in ferroan anorthosites 60025. This sample has an exposure age of $\sim 2$ Ma, such that its elevated $^{182}\text{W}/^{184}\text{W}$ cannot reflect the presence of cosmogenic $^{182}\text{W}$. However, more recently Touboul et al. (2009) obtained new W isotope data for pure plagioclase separates from the two ferroan anorthosites 60025 and 62255 and in contrast to the earlier study by Lee et al. (1997) did not find any resolvable $^{182}\text{W}$ excess in these samples (Fig. 12). The reason for this discrepancy is not known but could...
potentially reflect the presence of cosmogenic $^{182}$W in a mafic component of anorthosite 60025, which is not present in the pure plagioclase separates analyzed by Touboul et al. (2009). Therefore, all the major lunar geochemical reservoirs – ferroan anorthosites, mare basalts and KREEP – have indistinguishable W isotope compositions that are also indistinguishable from that of the terrestrial mantle (Fig. 12).

5.2. Earth–Moon equilibration and the age of the Moon-forming impact

The identical $^{182}$W/$^{184}$W ratios of the Moon and bulk silicate Earth provide important constraints on models of lunar formation and on the time at which the giant Moon-forming impact occurred. This is important not only for understanding the formation and early history of the Moon but also provides information on the accretion rate of Earth because most theories for the formation of the Moon suggest that the giant Moon-forming impact was the last major event in Earth’s accretion. The implications of the latter will be discussed in more detail below (Section 6).

5.2.1. Earth–Moon equilibration

If, as numerical simulations suggest, the Moon mainly consist of impactor mantle material (Canup, 2004), then its W isotope composition should reflect the accretion and differentiation history of the impactor. Therefore, that two such different objects as the proto-Earth and impactor would evolve to identical W isotope compositions in their mantles seems highly unlikely, given the evidence for widely different W isotope signatures in the meteorite record. This is also exemplified in the two accretion simulations shown in Figs. 19 and 20, where, regardless of the degree of re-equilibration and accretion history, impactor and Earth have very different $^{182}$W anomalies at the time of the Moon-forming impact. Therefore, the identical W isotope compositions of the lunar and terrestrial mantles could indicate that the Moon is largely derived from terrestrial mantle material but this is inconsistent with results from numerical simulations, all of which indicate that the Moon predominantly consists of impactor material. If this is correct, then equilibration of W isotopes between the Earth’s mantle and proto-lunar material during or after the giant impact seems to be required. Such equilibration processes could involve metal-silicate re-equilibration between the impactor mantle and core, which would reduce a radiogenic W isotope signature in the proto-lunar material (Bourdon et al., 2008) but it is unlikely that this process fortuitously resulted in a $^{182}$W/$^{184}$W that is identical to that of the Earth’s mantle. Therefore, the equilibration should have involved the Earth’s mantle and could potentially have occurred via a shared silicate vapor atmosphere of the lunar magma disk and the terrestrial magma ocean, as has been proposed to account for the identical O isotope compositions of the Earth and Moon (Pahlevan and Stevenson, 2007). This requires that W became efficiently vaporized to enter the atmosphere of the magma disk but the efficiency to which this is possible and hence W isotopes could equilibrate remains to be investigated.

5.2.2. Tungsten model age of the Moon-forming impact

The two-stage Hf–W model time for separation of the Moon from a chondritic reservoir is $\sim 37$ Myr (Touboul et al., 2007). This model age could either date formation of a small lunar core or, if the Moon does not possess a metal core, the isolation of the Moon from the proto-lunar circumterrestrial magma disk. In any case, this model age should correspond closely to the time of the giant impact. Note that this age cannot correspond to the time of core formation in the impactor – which might be expected if the Moon predominantly consists of impactor material – because the identical $^{182}$W/$^{184}$W of the lunar and terrestrial mantles require either formation of the Moon from terrestrial material or Moon–Earth equilibration. Although the formation of the Moon occurred by a single event, such that the timing of this event can in principle be calculated using a two-stage model, the initial W isotope composition of the Moon most likely was higher than chondritic. This is because the Moon is predominantly derived from silicate mantle material having high Hf/W and therefore most likely radiogenic $^{182}$W/$^{184}$W ratios (see for instance Fig. 19). Therefore, the Moon probably formed later than given by its two-stage model age of $\sim 37$ Myr.

Fig. 13 shows the difference in $^{182}$W/$^{184}$W between the lunar and terrestrial mantles that would have developed as a function of age and difference in Hf/W. As is evident from this figure, core formation in Earth could have terminated as early as $\sim 30–40$ Myr only if the difference in Hf/W between the bulk silicate Moon and Earth is less than $\sim 10\%$. The current best estimates for these Hf/W ratios (Table 1) indicate that this difference might be as high as $\sim 50\%$ (i.e., $f_{\text{Hf/W}} = 0.5$ in Fig. 13), in which case the Moon would have formed later than $\sim 50$ Myr after CAI formation. Combined with the age of the oldest lunar rocks

![Fig. 13. Difference in $\delta^{182}$W between bulk silicate Moon (BSM) and Earth (BSE) as a function of time (slightly modified from Touboul et al., 2007). The dotted area indicates the W isotope composition of the lunar mantle. Assuming that BSM and BSE had identical initial $^{182}$W/$^{184}$W ratios, the time of their formation can be calculated from their present-day $^{182}$W/$^{184}$W and Hf/W ratios. The current best estimates for the Hf/W ratios in BSM and BSE indicate a difference of $\sim 50\%$. If this is correct, the Moon must have formed more than $\sim 50$ Myr after CAI formation.](image-url)
tion by plagioclase flotation occurs after crystallization was achieved later than at 112 ± 40 Myr., entirely consistent with the Hf–W constraints.

Although the revised Hf–W chronology of the LMO (Touboul et al., 2007, 2009) now appears to be consistent with the ~200–250 Myr 146Sm–142Nd age of the lunar mantle isochron (Nyquist et al., 1995; Rankenburg et al., 2006; Boyet and Carlson, 2007), the latter probably does not reflect the timing of magma ocean solidification. Bourdon et al. (2008) recently showed that cumulate overturn, magma mixing and melting following lunar magma ocean crystallization at 50–100 Myr could produce an array in the 142Nd/144Nd–147Sm/144Sm diagram that yields a ~200–250 Myr model age. Therefore, the crystallization timescale of the LMO appears to be best constrained by the combined Hf–W and 147Sm–143Nd isotope systems that indicate that ~70% crystallization could have been achieved at ~60 Myr at the earliest and at ~150 Myr at the latest (Touboul et al., 2007, 2009).

This age estimate for ~70% LMO crystallization can potentially be used to constrain the duration of magma ocean solidification but the uncertainty of this time estimate combined with uncertainties in the age of the Moon currently hamper a precise determination of the duration of magma ocean solidification and the available age constraints are consistent with both an almost immediate crystallization and a more protracted timescale of ~100 Myr.

6. TIMESCALES FOR ACCRETION AND DIFFERENTIATION OF EARTH

The application of the 182Hf–182W system as a chronometer for the formation of Earth’s core goes back to the pioneering work of Harper and Jacobsen (1996) and Halliday et al. (1996). At that time, however, important parameters for calculating core formation ages were unknown. These include the 182W/184W ratio of chondrites and the initial 182Hf/180Hf at the time of CAI formation (or another well-defined point in time). These parameters were first determined by Lee and Halliday (1995, 1996) but their results were revised in 2002 (Kleine et al., 2002; Schoenborn et al., 2002a; Yin et al., 2002). Since then Hf–W chronometry has been utilized in various accretion and core formation models, which are summarized in Table 6.

In the simplest model of core formation it is assumed that the core formed instantaneously and an age for core formation can then be calculated by assuming a two-stage model. Using the 182W excess of Earth’s mantle of ε182W = +1.9 ± 0.1 relative to chondrites and a Hf/W ratio of ~17 for the bulk silicate Earth (see Section 2.1), results in a two-stage model time for core formation of ~30 Myr (Eq. (5); Section 2.2). However, at least for bodies as large as the Earth, core formation did not occur as a single event but took place episodically during planetary growth, which probably lasted several tens of millions of years (Halliday et al., 1996; Harper and Jacobsen, 1996; Halliday, 2004; Kleine et al., 2004b; Jacobsen, 2005; Nimmo and Agnor, 2006). Thus, for the Earth the assumption of instantaneous
Hf-W chronology of asteroids and terrestrial planets

6.1. Models of core formation and metal-silicate equilibration

6.1.1. Mechanisms of core formation

Two lines of evidence suggest that Earth accreted mostly from planetesimals and planetary embryos already differentiated into mantle and core. First, the Hf–W data for meteorites reveal that differentiation of planetesimals (e.g., the parent bodies of migmatic iron meteorites, eucrites, and angrites) occurred within the first few Myr of the solar system. Second, current models for the accretion of terrestrial planets suggest that planetary embryos formed within the first Myr of the solar system, in which case they will have differentiated owing to heating from decay of then abundant $^{26}$Al. Therefore, there are two endmember models for the formation of Earth’s core during growth from pre-differentiated bodies: either Earth’s core formed by merging of metal cores from pre-differentiated objects or core formation is not justified, and the two-stage model time of ~30 Myr would only date core formation if during this event the entire core was first remixed and homogenized with the entire mantle before final segregation of metal to form the present core. This seems physically implausible.

The two-stage model time nevertheless provides an important age constraint. It assumes that Earth’s mantle had a chondritic W isotope composition at the time of its formation. This corresponds to the minimum $^{182}$W/$^{184}$W ratio. Therefore, the two-stage model age corresponds to the earliest time core formation could have ceased before ~30 Myr after CAI formation.

In models of continuous evolution of a reservoir, such as the core, there is no single “age” for core formation and the reported ages rather correspond to a certain growth stage of the core. In this regard, two different ages have been used: (i) the mean time of core formation, $\langle t_c \rangle$, which corresponds to ~63% of the core (in the case of an exponentially decaying rate of accretion) (cf. Harper and Jacobsen, 1996), and (ii) the time of the Moon-forming impact, which most likely determines the termination of the major stage of Earth’s accretion and core formation. Obtaining these age constraints requires an understanding of the mechanisms of core formation in Earth because the magnitude of the W isotope effects in the bulk silicate Earth depend on the type of mechanism by which metal is transported to the core and the degree to which isotopic equilibrium is achieved during metal segregation. This has been addressed in several W isotope evolution models for Earth (Halliday, 2004; Kleine et al., 2004b; Jacobsen, 2005; Nimmo and Agnor, 2006) but these models yield different apparent timescales for formation of the Earth’s core that largely reflect different assumptions regarding the degree and processes of metal-silicate re-equilibration during core formation and the mechanisms and rate of Earth’s growth.

### Table 6

Summary of proposed Hf–W ages for the formation of Earth’s core.

<table>
<thead>
<tr>
<th>Age</th>
<th>Based on</th>
<th>Accretion/core formation model</th>
<th>Metal-silicate re-equilibration</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_{100%}$</td>
<td>$\Delta W(BSE) = +1.9$</td>
<td>Two-stage</td>
<td>n.a.</td>
<td>Kleine et al. (2002); Schönberg et al. (2002a); Yin et al. (2002)</td>
</tr>
<tr>
<td>$t_{32%}$</td>
<td>$\Delta W(BSE) = +1.9$</td>
<td>Continuous core formation during exponentially decreasing accretion</td>
<td>100%</td>
<td>Yin et al. (2002)</td>
</tr>
<tr>
<td>$t_{100%}$</td>
<td>$\Delta W(BSE) = +1.9$</td>
<td>Continuous core formation during exponentially decreasing accretion</td>
<td>60–100%</td>
<td>Kleine et al. (2004b)</td>
</tr>
<tr>
<td>$t_{25%}$</td>
<td>$\Delta W(BSE) = +1.9$</td>
<td>Multiple giant impacts that occur at an overall exponentially decreasing rate</td>
<td>100% before the Moon-forming impact; 26% during the Moon-forming impact; batch equilibration</td>
<td>Halliday (2004)</td>
</tr>
<tr>
<td>$t_{75%}$</td>
<td>$\Delta W(BSE) = +1.9$</td>
<td>Multiple giant impacts that occur at an overall exponentially decreasing rate</td>
<td>100% before the Moon-forming impact; 4% during the Moon-forming impact; batch equilibration</td>
<td>Halliday (2004)</td>
</tr>
<tr>
<td>$t_{100%}$</td>
<td>$\Delta W(BSE) = +1.9$</td>
<td>Exponentially decreasing accretion, terminated by Moon-forming impact</td>
<td>100%; fully equilibrative plumbing</td>
<td>Jacobsen (2005)</td>
</tr>
<tr>
<td>$t_{100%}$</td>
<td>$\Delta W(BSE) = +1.9$</td>
<td>Independent on the accretion/core formation model</td>
<td>n.a.</td>
<td>Touboul et al. (2007)</td>
</tr>
<tr>
<td>$t_{100%}$</td>
<td>$\Delta W(BSE) = +1.9$</td>
<td>Exponentially decreasing accretion until ~40 Myr; no accretion until final Moon-forming impact at ~100 Myr</td>
<td>100%; batch equilibration</td>
<td>Halliday (2008)</td>
</tr>
<tr>
<td>$t_{50%}$</td>
<td>$\Delta W(BSE) = +1.9$</td>
<td>Multiple stochastic giant impacts</td>
<td>Variable</td>
<td>This study</td>
</tr>
<tr>
<td>$t_{75%}$</td>
<td>$\Delta W(BSE) = +1.9$</td>
<td>Multiple stochastic giant impacts</td>
<td>Variable</td>
<td>This study</td>
</tr>
</tbody>
</table>

* BSE, bulk silicate Earth; BSM, bulk silicate Moon; BSI, bulk silicate impactor; GI, giant impact (i.e., the Moon-forming impact).
the cores of these objects dispersed as small metal droplets in the terrestrial magma ocean prior to sinking to join the existing core.

Which of these scenarios is most appropriate for a given collision depends on the relative size of the two colliding bodies. Collisions in which the impactor is much smaller than the target result in vaporization of the impactor, in which case the impactor material can efficiently mix and homogenize within the magma ocean of the target. In this case any information on the differentiation of the impactor is lost, such that the chemical and isotopic consequences for Earth’s mantle are identical to those for addition of an undifferentiated, chondritic body.

What happens in detail during larger collisions, however, is less well understood. Hydrocode simulations of giant impacts (Canup and Asphaug, 2001) show that the cores of target and impactor merge rapidly although more recent simulations indicate that some re-equilibration might occur (Canup, 2004). The problem is that these simulations currently provide a resolution on the order of 100 km, whereas the length-scale on which chemical and isotopic re-equilibration occurs is probably on the order of centimeters (Stevenson, 1990; Rubie et al., 2003). An alternative approach for constraining the degree of re-equilibration is provided by the abundances of siderophile elements in Earth’s mantle. The observed depletions of several siderophile elements in Earth’s mantle are consistent with metal-silicate equilibration at high temperatures and pressures in a terrestrial magma ocean (cf. Rubie et al., 2003). This equilibration can be achieved if the metal cores of the impactor emulsified as small metal droplets in a magma ocean (Rubie et al., 2003; Hoinik et al., 2006) and can occur during the descent of iron diapirs that originated from metal ponds that formed at the bottom of the magma ocean (Samuel and Tackley, 2008). However, Sasaki and Abe (2007) observed that re-equilibration might not have been complete if the metal droplets were not distributed throughout the entire mantle. Furthermore, full equilibration may have been limited if the terrestrial magma ocean was not global.

The $^{182}$W/$^{184}$W ratio of Earth’s mantle at time $t_2$ immediately after accretion of a new object at $t_1$ can be expressed as a mixture of three components as follows:

$$R_{\text{BSE}}(t_2) = \frac{y_{\text{BSE}} + y_{\text{mantle Imp}} + k \times y_{\text{core Imp}}}{y_{\text{BSE}} + y_{\text{mantle Imp}} + k \times y_{\text{core Imp}}}$$

(10)

where $\text{BSE}$ and $\text{Imp}$ denote bulk silicate Earth and impactor, $R_i$ is the $^{182}$W/$^{184}$W ratio, $y_i = m_i C_W$ is the amount of W in an object $i$, and $k$ is the fraction of the impactor’s core that first equilibrates with the Earth’s mantle before entering Earth’s core. Fig. 15 schematically illustrates the W isotope evolution of Earth’s mantle in the different modes of core formation. In the core-merging model ($k = 0$) (Fig. 15c), metal-silicate re-equilibration does not occur and the W isotope composition of the target’s mantle immediately after the impact results from addition of impactor mantle material to the target’s mantle. The result-

Fig. 15. Schematic illustration of different processes of core formation and their effect on the W isotope evolution of the bulk silicate Earth. For metal-silicate equilibration in a magma ocean, two different equilibration scenarios are shown. For details see text.
ing $^{182}\text{W}^{184}\text{W}$ ratio will always be higher than chondritic because no core material (with subchondritic $^{182}\text{W}^{184}\text{W}$) is involved in these mixing processes (Eq. (10)). In the case of core merging, no isotopic record of the collision was generated and the W isotope effect in Earth’s mantle would largely reflect the timing of core formation in the pre-merged objects. In contrast, small metal droplets in a magma ocean could have equilibrated efficiently with the surrounding molten silicates (Fig. 15a and b). If re-equilibration was complete (i.e., $k = 1$), this is equivalent to adding an undifferentiated object to Earth’s mantle, followed by metal segregation. In this case the resulting W isotope effect reflects the rate of accretion and timing of core formation.

6.1.2. Metal-silicate equilibration in a magma ocean

An additional complication is that the process by which re-equilibration occurs is not well understood and two different models have been used to calculate the effects of full equilibration. Here we summarize the important equations governing these two different equilibration scenarios and then evaluate the reduction in W isotope effects that is achieved in both equilibration models during giant impacts. The derivation of these equations is given in the Appendix.

In the fully equilibrative plumbing model (Harper and Jacobsen, 1996), which was termed magma ocean differentiation model by Jacobsen (2005), a single impactor is treated as an infinite number of small impactors, which are added to Earth’s mantle, re-equilibrate and join the core one after the other. This is similar to modeling the growths of different objects to Earth’s mantle, followed by metal segregation. In this case the resulting W isotope effect reflects the rate of accretion and timing of core formation.

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The derivation of these equations is given in the Appendix.
in the terrestrial magma ocean (by the batch equilibration process described above). This is a reasonable assumption if accretion occurred by the incremental growth of small mass fractions but a more realistic view is that much of the Earth accreted by several distinct large collisions that may have occurred at an exponentially decaying rate. In this case, the degree of metal-silicate equilibration is less well constrained (see above).

Fig. 17b reveals that the present-day $\Delta_{182}W$ of Earth’s mantle of $+1.9$ can be produced if the mean time of accretion is $\approx 11$ Myr. This corresponds to $\approx 63\%$ growth at $\approx 11$ Myr and $\approx 90\%$ growth at $\approx 25$ Myr. Note that in these models the end of accretion is not well defined because there is a small exponential tail of accretion that is technically still continuing today (Harper and Jacobsen, 1996).

6.2.1.1. Effects of incomplete metal-silicate re-equilibration. Fig. 17b also illustrates the effect of incomplete metal-silicate re-equilibration on the W isotope evolution of Earth’s mantle. Metal-silicate re-equilibration during core formation results in a decrease of the $^{182}W$ excess in Earth’s mantle that had previously accumulated due to $^{182}Hf$ decay. For a given accretion rate, a decreasing degree of metal-silicate re-equilibration (i.e., decreasing $k$ values) will result in an increasingly radiogenic W isotope composition of Earth’s mantle. For instance, if 75% instead of 100% of the newly accreted core material first equilibrated with Earth’s mantle before entering Earth’s core, the $\Delta_{182}W$ value of Earth’s mantle would be $+2.8$ instead of $+1.9$ (for a given $t$ of 11 Myr). Thus, to match the present-day W isotope composition of Earth’s mantle, a decreasing degree of metal-silicate re-equilibration must be accompanied by longer accretion timescales. This is illustrated in Fig. 18a, where the calculated age of core formation is plotted as a function of the degree of metal-silicate re-equilibration $k$. As is evident from this figure, the calculated core formation ages strongly depend on the assumed value for $k$.

6.2.1.2. Changes in metal-silicate partition coefficient of W. Similar effects are observed if it is assumed that the Hf/W ratios in the mantles of the newly accreted planetary embryos were different from the value observed in Earth’s mantle today. This is likely because the metal-silicate distribution coefficient for W ($D_W$) is sensitive to many parameters such as pressure, melt compositions, and particularly oxygen fugacity (see Section 2.1). These parameters likely were different in the various objects that accreted to Earth and also probably changed over time, such that considerable variability in the mantle Hf/W ratios is expected (Righter, 2003; Wade and Wood, 2005). Halliday (2004) suggested that Earth may have accreted from relatively oxidized planetesimals having low Hf/W ratios, similar to the present-day values observed for the martian mantle. Such a scenario has important consequences for interpreting the W isotope record of Earth’s mantle because a mantle with a relatively low Hf/W ratio will never develop a large $^{182}W$ excess. Therefore, upon accretion of such objects to Earth, the W isotope composition of Earth’s mantle can stay at a relatively low value even without significant metal-silicate re-equilibration. Thus, changes in the Hf/W ratios of the mantles of newly accreting objects and different values of $k$ have similar effects on the W isotope evolution of the Earth’s mantle. This is illustrated in Fig. 18b, where for a given core formation age (calculated assuming an exponentially decaying rate of accretion) the Hf/W ratio in the mantle of the accreting planetesimals is plotted against the degree of metal-silicate re-equilibration $k$. This plot reveals that, for a given core formation age (in this case $t = 11$ Myr), the present-day $^{182}W/^{184}W$ of Earth’s mantle can be obtained by assuming several distinct pairs of these two parameters. For instance, assuming $k = 1$ and Hf/W = 20 in the mantles of the accreting planetesimals yields the same result as assuming $k = 0.7$ and Hf/W = 4 (Fig. 18b). Therefore, W isotope systematics alone cannot distinguish between scenarios involving a high degree of metal-silicate re-equilibration and those involving low Hf/W ratios in early-formed proto-planets.

Wade and Wood (2005) found the best match to the observed mantle depletions in siderophile elements if the oxygen fugacity of Earth’s mantle increased during accretion. In their model, $D_W$ started off at values $>10^4$ and decreased...
to \( \sim 20 \) at the end of accretion. A similar prediction is made by models that predict that the composition of the material accreted to Earth changed over time (heterogeneous accretion) and that Earth was initially highly reducing and became more oxidized by the late addition of volatile-rich material (Wänke and Dreibus, 1988).

6.2.2. Tungsten isotope evolution in N-body simulations of planetary accretion

In the models discussed above, it is assumed that accretion of the Earth occurred at an exponentially decreasing accretion rate. Dynamical modeling, however, suggests that the final stages of terrestrial planet formation are characterized by multiple and stochastic impacts that bring in large core masses at once (Agnor et al., 1999; Chambers, 2001). Jacobsen (2005) and Nimmo and Agnor (2006) presented a framework for implementing the evolution of W isotopes in N-body simulations of planetary accretion. Nimmo and Agnor (2006) showed that the physical and isotopic characteristics of Earth can be reproduced with the last large impact occurring at \( \sim 30 \) Myr. This result is similar to those of Jacobsen (2005), who showed that the W isotope composition of Earth’s mantle is consistent with most of Earth’s growth taking place in \( \sim 10 \) Myr and a final giant impact at \( \sim 32 \) Myr. At the time of these studies it was thought that the Moon-forming impact occurred earlier than \( \sim 50 \) Myr (cf. Lee et al., 2002; Kleine et al., 2005a,b,c) but a more recent study of the Hf–W systematics of the Moon showed that a later date is much more likely (Touboul et al., 2007).

Therefore, we applied the approach of Nimmo and Agnor (2006) to two accretion simulations from Raymond et al. (2006) that were selected mainly on the basis that they are characterized by a relatively late formation of the Moon. In the first of these simulations, a giant impact resembling the Moon-forming collision occurs at \( \sim 125 \) Myr after CAI formation (Fig. 19a), in the second simulation it occurs at \( \sim 75 \) Myr after CAI formation (Fig. 20a). These are near the upper and lower end of the \( 62^{+10}_{-90} \) Myr age for the giant impact as proposed by Touboul et al. (2007) (see also Section 5.2.2). Another important difference between these two simulations is the history of the impactor, whose collision resulted in the formation of the Moon. In the first simulation the silicate part of the impactor had, at the time of its collision with proto-Earth, a W isotope composition that was less radiogenic than that of proto-Earth’s mantle. This results from a relatively late collision of the impactor with another body at \( \sim 40 \) Myr (Fig. 19b). In the second simulation the impactor has highly radiogenic \( ^{182}\text{W} \) at the time it collided with proto-Earth.
because this impactor was largely accreted and differentiated within the first few Myr (Fig. 20b).

In the simulations both a high and low degree of metal-silicate equilibration were assumed (Figs. 19b and 20b) and in the case of full equilibration the effects of both batch equilibration and fully equilibrative plumbing were calculated (Figs. 19c and 20c). These simulations reveal that, if the degree of metal-silicate equilibration was low throughout accretion, Earth’s mantle should exhibit a much more radiogenic $^{182}\text{W}$ anomaly than observed, consistent with earlier conclusions (e.g., Kleine et al., 2004b). This suggests that substantial metal-silicate re-equilibration occurred but at what stage of accretion this occurred is less well constrained. In both simulations, the present-day $\Delta \varepsilon_{\text{W}}$ of

Fig. 19. Growth curves and $\text{W}$ isotope evolution for a model Earth and Moon-forming impactor from accretion simulations of Raymond et al. (2006). (a) Growth curves are from run 2b of the $N$-body accretion simulations of Raymond et al. (2006), which track the evolution of 1054 planetesimals as they orbit and collide. The Moon-forming impact occurs at $\sim 125$ Myr and the impactor itself underwent a large impact at $\sim 40$ Myr. (b) W isotope evolution of these bodies and considering the two extreme cases of core merging and full metal-silicate re-equilibration (batch equilibration). Silicate mass fraction of bodies is variable; W partition coefficient is fixed at $D_{\text{W}} = 29.4$ (i.e., $\text{Hf}/\text{W}_{\text{BSE}} \sim 17$). Other parameter values and methods are as in Nimmo and Agnor (2006). Note that the isotopic evolution of all planetesimals is tracked in these calculations. (c) As for (b) but both fully equilibrative plumbing and batch equilibration were considered.
Earth’s mantle of +1.9 can be obtained for both a high and low degree of metal-silicate re-equilibration prior to the final, Moon-forming impact (Figs. 19b and 20b). Thus, the conditions of metal-silicate separation during most of Earth’s growth are only poorly constrained by the W isotope data and most of this information is erased by the final giant impact. In the two exemplary accretion scenarios considered here, the degree of metal-silicate re-equilibration must have been high during the final impact because otherwise the $^{182}$W anomaly of the bulk silicate Earth would be larger than observed. Whether this is a common feature of all accretion simulations that can reproduce the physical properties of Earth is unclear. In the case of full equilibration, fully equilibrative plumbing results in a stronger reduction of the W isotope effects (Figs. 19c and 20c), as expected from the discussion above.

The results of the two exemplary accretion simulations reveal that the physical and isotopic characteristics of Earth can be reproduced in a variety of accretion and differentiation scenarios. Therefore, the $^{182}$W excess of Earth’s mantle relative to chondrites cannot be used to firmly establish an age of core formation and rate of accretion and models can
be constructed that indicate that Earth’s core had entirely formed as early as ~30 Myr or as late as ~125 Myr, for example. Knowing the degree of metal-silicate re-equilibration in particular and the processes by which equilibration occurred is critical for interpreting the W isotope record of Earth’s mantle and for distinguishing among different scenarios for Earth’s accretion. Furthermore, an assumption made in many W isotope models of Earth’s growth is that the rate of accretion decreased exponentially while the size of the impactors increased. However, dynamical modeling of planetary accretion suggests that, while the early growth might have been roughly exponential, the late stages of accretion are characterized by the stochastic occurrence of large impacts that bring in large amounts of mass. As is evident from the variation in the timing of the last large collision (i.e., the Moon-forming impact) there can be a significant time gap between the exponential part of the growth curve and the last large impact (see for instance Fig. 19a). Thus the final stage of accretion is not well-represented by an exponential function but appears to be most significant for defining the present-day W isotope composition of Earth’s mantle (see above). Thus, different assumptions regarding the growth curve for Earth can lead to significant differences in the estimated core formation timescale, even for a given degree of metal-silicate equilibration. For instance, for full metal-silicate equilibration throughout accretion, Earth’s core might have been completely formed as early as ~30 Myr (Jacobsen, 2005) or as late as ~125 Myr (Fig. 19).

6.3. Early mantle differentiation and implications of a non-chondritic bulk Earth

6.3.1. Early differentiation of Earth’s mantle

Hafnium–tungsten chronometry cannot be directly applied to constrain the timescales of early mantle differentiation in Earth because no 182W variations have yet been detected in terrestrial samples. A possible exception are low 182W/184W ratios in a few Archean metasediments from the Earth’s mantle has a 182W/184W ratio of ~1.4 times the BSE (Boy et al., 2003; Caro et al., 2003, 2006). This differentiation probably occurred too late to have resulted in resolvable W isotope variations because these can only be produced in the first ~60 Myr. This is also consistent with the absence of resolvable 182W variations among lunar samples, which indicate differentiation later than ~60 Myr after CAI formation.

However, Boyet and Carlson (2005) observed that the accessible Earth’s mantle has a ~20 ppm 142Nd excess relative to chondrites and that this could be explained by an early mantle differentiation prior to ~30 Myr that generated an early depleted reservoir (EDR) and an early enriched reservoir (EER) that since its formation has remained hidden. This model has important consequences for interpreting the Hf–W record of Earth’s core formation because (i) the W isotope composition of terrestrial samples would not reflect the composition of the bulk silicate Earth (BSE) but rather that of the EDR and (ii) the estimate for the Hf/W ratio of the BSE is incorrect because it assumes a chondritic Hf/W ratio. The EDR will have a Hf/W ratio higher than chondritic because it formed by an early melt depletion. Carlson and Boyet (2008) estimated that the Hf/W ratio of the EDR would be ~1.4 times higher than the chondritic ratio, such that the Hf/W ratio of the EDR would be 1.4 times the Hf/W ratio of BSE, i.e., ~1.4 × 17 = 24. Therefore, the EDR would be characterized by ΔHfW = +1.9 and Hf/W ~ 24 and the two-stage model time at which the EDR separated from a chondritic reservoir is ~41 Myr after CAI formation. Thus, in the model for early Earth differentiation the earliest point in time at which core formation could have been complete is ~41 Myr.

Therefore, the combination of the 146Sm–142Nd and 182Hf–182W constraints for the early differentiation of a non-chondritic Earth suggests that an early mantle differentiation that resulted in the formation of the EDR and EER occurred earlier (<30 Myr) than the completion of core formation (>41 Myr). This problem is further exacerbated by the observation that, to generate the present-day Nd isotope systematics of the observable Earth by an early differentiation of a chondritic mantle, the mass balance of Nd isotopes in the bulk silicate Earth requires formation of the EDR and EER well within the first ~10 Myr of the solar system (Bourdon et al., 2008). Therefore, a significant part of Earth’s core must have formed after the EER, implying that the latter must have remained isolated from the remainder of the bulk silicate Earth while at the same time metal melts separated and segregated into Earth’s core. The EER must also have remained isolated during the giant Moon-forming impact, although this event resulted in a mean temperature rise of Earth of ~4000 K (e.g., Stevenson, 2008). Such a scenario seems implausible and, consequently, modeling the 142Nd excess of Earth’s mantle relative to chondrites in terms of an early mantle differentiation is difficult to reconcile with the Hf–W constraints on the timescale of the early differentiation of the Earth.

6.3.2. Hf–W chronometry of core formation in a non-chondritic Earth

The 146Sm–142Nd and 182Hf–182W constraints on the chronology of Earth’s early differentiation provide a consistent picture if Earth’s mantle is characterized by ε142Nd = 0, as proposed by Caro et al. (2008), implying that bulk Earth has a non-chondritic Sm/Nd ratio. If this is true, then the Hf/W ratio of bulk Earth most likely also is not chondritic, such that one of the basic assumptions for calculating core formation timescales may not be valid. The magnitude of this effect is difficult to assess and depends on the process(es) that were responsible for generating non-chondritic ratios of refractory elements in bulk Earth. If this is related to impact erosion of an early-formed crust (O’Neill and Palme, 2008) or explosive volcanism (Warren, 2008), then W, due to its higher incompatibility relative to Hf, would be preferentially lost.
Based on the observation that bulk Earth has a Fe/Mg ratio that is significantly higher than those of chondrites, O’Neill and Palme (2008) proposed that the composition of the Earth was modified by collisional erosion during accretion of the Earth. The erosion led to preferential loss of the differentiated crust from planetary embryos, such that the effects on the composition of the Earth would depend on the incompatibility of the elements during silicate melting. O’Neill and Palme (2008) quantified these effects by assuming that collisional erosion modified the Sm/Nd ratio of the BSE to an extent that can account for the observed ~20 ppm $^{142}$Nd excess of the BSE relative to chondrites (i.e., $^{142}$Sm/$^{144}$Nd ~ 0.21). In this case the Hf/Ti ratio of the BSE would be ~1.5 times higher than chondritic (O’Neill and Palme, 2008) and this affects the Hf–W chronology of Earth’s core in two ways. First, the estimate for the Hf/W ratio of the BSE is based on the assumption that the BSE has a chondritic Hf/Ti ratio. Consequently, if the Hf/Ti ratio of the BSE is ~1.5 times higher than chondritic, then its Hf/W ratio also will be ~1.5 times higher, i.e., ~25.5 instead of ~17. Note that the Th/W ratio of the BSE, on which the estimate for its Hf/W ratio is based, remains unaffected by collisional erosion because Th and W have similar incompatibilities. Second, the Hf/W ratio of bulk Earth would be ~1.5 times higher than that of chondrites. Therefore, if the collisional erosion took place in the first Myr of the solar system, bulk Earth would have an $\varepsilon^{182}$W value of ~−1.2. Note that if the $^{144}$Sm–$^{142}$Nd evidence is interpreted in terms of a superchondritic Sm/Nd of bulk Earth, then the Sm–Nd fractionation should have occurred in the first Myr of the solar system (Caro et al., 2008).

Consequently, in the collisional erosion model, core formation ages are more appropriately calculated relative to a bulk Earth composition of $^{180}$Hf/$^{184}$W ~ 1.85 and $\varepsilon^{182}$W ~ −1.2, rather than to a chondritic composition. Furthermore, a Hf/W ratio of the bulk silicate Earth of ~25.5 rather than ~17 should be used. This is illustrated in Fig. 21, which compares two-stage model times for core formation calculated assuming a chondritic bulk composition and a bulk composition modified by collisional erosion. In the latter case the model time is ~42 Myr, i.e., ~12 Myr later than the two-stage model age for core formation in a chondritic Earth. Thus, collisional erosion has a significant effect on the calculated core formation ages. As has been discussed in detail above, the two-stage model age corresponds to the earliest time core formation can have been complete, such that in the collisional erosion model formation of Earth’s core could not have ceased before ~42 Myr. Thus, if the $^{142}$Nd deficit in chondrites does not reflect a heterogeneous distribution of Nd and/or Sm isotopes in the early solar nebula, then the combined $^{142}$Nd–$^{182}$W record of early Earth’s differentiation requires that core formation had been complete at ~42 Myr at the earliest. Note that the age of the Moon and the final stage of Earth’s core formation estimated using the identical $\varepsilon^{182}$W values of the terrestrial and lunar mantles (Touboul et al. (2007) and Section 5.2) is insensitive to the actual bulk composition of the Earth and thus provides a more reliable estimate for the termination of Earth’s accretion.

Hafnium–tungsten chronometry of meteorites provides age constraints on several key events in the early evolution of the solar system and its planetary objects, and has led to the establishment of a new model for the accretion and early evolution of asteroids. Important events that are being dated using the Hf–W chronometer include the formation of CAIs and chondrules as well as core formation, magmatism and thermal metamorphism in meteorite parent bodies (Fig. 22). The chronological data indicate that melting and differentiation was prevalent in planetesimals that accreted within the first ~1 Myr (parent bodies of the iron meteorites and possibly eucrites and angrites), thermal metamorphism is characteristic for bodies formed shortly after ~2 Myr (ordinary chondrite parent bodies), and aqueous alteration is the dominant parent body process in asteroids that formed more than ~3 Myr after CAI formation (some carbonaceous chondrite parent bodies). These accretion ages for asteroids are inversely correlated with the peak temperature reached in their interiors, indicating that the different thermal histories of meteorite parent bodies reflect their accretion ages, which determine their initial $^{26}$Al abundance. This is most consistent with a model that involves decreasing accretion rates across the asteroid-forming region that is of the order of several $^{26}$Al half-lives. Moreover, thermal models for asteroids heated by energy release from $^{26}$Al decay not only reproduce the peak temperatures reached inside the meteorite parent bodies but are also consistent with the timescales of thermal metamorphism and cooling of chondrite parent bodies as well as with the time span of basaltic magmatism on asteroids.

For terrestrial planets, the timescales of accretion and primordial differentiation are much longer, and determined by different parameters. This is consistent with dynamical models of planetary accretion that indicate that the final
stage of terrestrial planet formation is characterized by multiple large and stochastic impacts. Although the Hf–W timescale for the formation of Mars is currently uncertain and would allow core formation ages ranging from 0 to 20 Myr, Mars clearly formed much earlier than the Earth and Moon. The Hf–W ages for termination of Earth's accretion and core formation range from ~30 Myr to more than ~100 Myr after CAI formation. This range in ages primarily reflects different assumptions regarding the mechanisms of accretion and core formation and highlights the uncertainties inherent in applying Hf–W chronometry to date core formation in large planetary bodies. Determining the age of the Moon provides an alternative way for dating the termination of core formation in Earth because the Moon-forming impact most likely was the last major event in Earth’s accretion. The identical $^{182}$W/$^{184}$W ratios of the lunar and terrestrial mantles, combined with the age of the oldest lunar rocks, provide evidence that the Moon formed 50–150 Myr after CAI formation. This age estimate is valid, unless the Hf/W ratios of the bulk silicate Moon and Earth are identical to within less than ~10%. Termination of Earth’s core formation later than 50 Myr after CAI formation is consistent with the U–Pb age for the formation of Earth (e.g., Allègre et al., 1995; Galer and Goldstein, 1996) and with I–Pu–Xe constraints for the formation of Earth’s atmosphere (Podosek and Ozima, 2000; Yokochi and Marty, 2005; Pepin and Porcelli, 2006). In this case, the Hf–W, U–Pb, and I–Pu–Xe systematics converge to provide indistinguishable ages for what might have been the complete accretion and major early differentiation of the Earth at ~4.50–4.42 Ga.

The preservation of $^{182}$W heterogeneities in the martian mantle contrasts with the constant $^{182}$W/$^{184}$W ratios of lunar and terrestrial rocks and provides constraints on the timing of early mantle differentiation in Mars as well as the Earth and Moon. Variable $^{182}$W abundances in SNC meteorites indicate that differentiation of the martian mantle occurred when $^{182}$Hf was still extant and that any later process was not sufficiently efficient to re-homogenize the martian mantle. This is consistent with $^{146,147}$Sm–$^{142,143}$Nd systematics of martian rocks. In contrast, solidification of the lunar and terrestrial magma ocean occurred later, after extinction of $^{182}$Hf, consistent with $^{147}$Sm–$^{143}$Nd ages for lunar anorthosites and the $^{146,147}$Sm–$^{142,143}$Nd constraints for differentiation of Earth’s mantle between 50 and 200 Myr. However, the Hf–W chronology for the formation of Earth’s core is difficult to reconcile with $^{146}$Sm–$^{142}$Nd evidence for an early (<30 Myr after CAIs) differentiation of a chondritic Earth’s mantle. Instead, the combined $^{182}$W–$^{142}$Nd evidence suggests that bulk Earth may have superchondritic Sm/Nd and Hf/W ratios, in which case formation of its core must have terminated more than ~42 Myr after formation of CAIs.

The Hf–W timescale of planetary accretion as summarized here is remarkably consistent with predictions from dynamical simulations. That is, the first planetary objects formed within less than 1 Myr, whereas the final assembly of the terrestrial planets may have taken as long as ~100 Myr. Moreover, implementation of Hf–W systematics in N-body simulations of planetary accretion indicates that the physical and isotopic characteristics of Earth can successfully be reproduced in such simulations.
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APPENDIX A

A.1. Effects of metal-silicate equilibration on the W isotope composition of the bulk silicate Earth

Fully equilibrative plumbing. The fully equilibrative plumbing model of Harper and Jacobsen (1996) was termed magma ocean differentiation model by Jacobsen (2005). In this model the reservoir content \( N_j \) of a stable species \( j \) in the magma ocean is given by Eq. (37) of Jacobsen (2005):

\[
\frac{dN_{j2}}{dt} = C_j M_2 \left( 1 - \gamma \right) D_{j}^{m/s} M_2 N_{j2}
\]

(A1)

Here the subscripts 1, 2, and 3 refer to bulk, mantle, and core (not given in the equation), \( C_j \) is the bulk Earth concentration, \( D_j^{m/s} \) is the metal/silicate partition coefficient (considered constant), \( \gamma \) is the core mass fraction (also considered constant), \( M_2 \) is the mass of the mantle and \( M_2 = dM_2/dt \). With these simplifying assumptions, the concentration of \( j \) in the mantle is

\[
C_j = \frac{1}{C_j} \left( \frac{dN_{j2}}{dt} \right) \left( 1 - \gamma \right)
\]

(A2)

This is equivalent to the expression for static models of trace element partitioning (cf. Righter and Drake, 1997) and is also identical to that for a batch equilibration model (see Eq. (3) in Nimmo and Agnor, 2006). Jacobsen (2005) showed that the W isotopic evolution of the magma ocean (Eq. (72) in Jacobsen, 2005) can, for a very short interval (i.e., no decay) such as directly after an impact, be simplified to

\[
\frac{d\Delta_{W}(t_f)}{dt} = -(1 + f^{182/W}) \frac{M_2}{M_2} \Delta_{W}
\]

(A3)

Thus, the difference between the initial \( (t_i) \) and final states \( (t_f) \) after an impact is given by

\[
\frac{\Delta_{W}(t_f)}{\Delta_{W}(t_i)} = \left( \frac{M_2(t_f)}{M_2(t_i)} \right)^{1 + f^{182/W}}
\]

(A4)

Batch equilibration model. Consider a collision between two bodies of mass \( m_A \) and \( m_B \), respectively, where \( m_B \leq m_A \). The core mass fraction in each case is \( \gamma \) and the ratio \( m_B/d_{pr} = g \). During the collision, it is assumed that the metal + silicates of body B are completely homogenized with the silicates of body A, and that the metallic fraction from body B then separates from this reservoir. During this separation process elements are partitioned according to the metal/silicate partition coefficient, \( D_j^{m/s} = C_j^{met}/C_j^{sil} \), where \( C_j^{met} \) and \( C_j^{sil} \) are the concentrations in the metal and silicate fractions, respectively. From mass balance considerations, it can be shown that the final concentration of an element \( j \) in the mantle of the resulting object \( C_{j2}^{f} \) is given by

\[
C_{j2}^{f} = \frac{(1 - \gamma) C_{j1}^{f} + g C_{j1}^{f}}{1 - \gamma + g \left( 1 + \gamma D_j^{m/s} - 1 \right)}
\]

(A5)

where \( C_{j1}^{f} \) is the initial concentration of the element \( j \) in the mantle of body A, and \( C_{j1}^{f} \) is the bulk concentration of the element in body B (assumed chondritic).

If \( D_j^{m/s} = 1 \) then Eq. (A5) shows that the final concentration is just the mass-weighted average of the initial concentrations, as required. In the limit as \( g \to 0 \) the final concentration equals the initial concentration, as required. In the limit as \( g \to \infty \) (i.e., the pre-existing silicate reservoir is vanishingly small), we recover Eq. (39) of Jacobsen (2005).

After some additional algebra, it may be shown that the final \( 182 \text{W} \) anomaly, \( \Delta_{W}(t_f) \), immediately after the impact, is given by

\[
\frac{\Delta_{W}(t_f)}{\Delta_{W}(t_i)} = \frac{\Delta_{W}(t_i)}{1 + g (1 + f^{182/W})}
\]

(A6)

where \( \Delta_{W}(t_i) \) is the \( 182 \text{W} \) anomaly of the silicate portion of body 1 immediately prior to the impact.

Recognizing that \( f^{182/W} = D_j^{m/s} \gamma (1 - \gamma) \) (Jacobsen, 2005; Eq. (49)) we may rewrite Eq. (A6) as

\[
\frac{\Delta_{W}(t_f)}{\Delta_{W}(t_i)} = \frac{1}{1 + g (1 + f^{182/W})}
\]

(A7)

which for \( g \ll 1 \) yields

\[
\frac{\Delta_{W}(t_f)}{\Delta_{W}(t_i)} \approx 1 - g (1 + f^{182/W}) + \cdots
\]

(A8)

Similarly, recognizing that \( M_2(t_f)/M_2(t_i) = 1/(1 + g) \), Eq. (11) (i.e., the reduction of the W isotope effects in the fractional equilibration model) may be written

\[
\frac{\Delta_{W}(t_f)}{\Delta_{W}(t_i)} \approx \frac{1}{1 + g} \left( 1 + f^{182/W} \right) \approx 1 - g (1 + f^{182/W}) + \cdots
\]

(A9)

where the approximation is appropriate for \( g \ll 1 \). Thus, in the limit of small \( g \) the two approaches give the same answer, as required.

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*Associate editor:* Richard J. Walker