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How rapidly did Mars accrete? Uncertainties in the Hf–W timing of core formation

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Abstract

Estimates for the martian core formation timescale based on the hafnium–tungsten (Hf–W) isotopic system have varied by almost an order of magnitude, because of uncertainties in the martian mantle Hf/W ratio. Here we argue that the Hf/W ratio is ∼4 but is uncertain by ∼25%, resulting in (instantaneous) martian core formation timescales ranging from 0 to 10 Myr; accordingly, Hf–W isotope observations currently have limited utility in distinguishing between scenarios in which Mars formed as a stranded embryo and scenarios in which Mars suffered a prolonged accretion history.

Keywords: Mars; Accretion; Planetary formation; Impact processes; Interiors

1. Introduction

The manner in which the terrestrial planets accreted probably played a major role in determining their ultimate geological and atmospheric evolution. The different planets' accretion histories are thus of considerable interest, and have been investigated using two very different techniques. One technique is to simulate the growth history of an evolving distribution of protoplanets using numerical techniques (e.g. Chambers and Wetherill, 1998; Kokubo and Ida, 1998; Agnor et al., 1999; Morbidelli et al., 2000; Raymond et al., 2006); the other is to infer planetary core formation timescales using geochemical observations, particularly those of the hafnium–tungsten (Hf–W) system (e.g., Harper and Jacobsen, 1996; Kleine et al., 2002; Yin et al., 2002; Schoenberg et al., 2002). Both techniques, when applied to the Earth, yield very similar results, suggesting that the final large impact occurred 30–50 Myr after Solar System formation (cf. Chambers, 2001; Kleine et al., 2005a). The purpose of this Note is to point out that the accretion history of Mars is currently less well-constrained by the Hf–W system than is generally appreciated. For instance, using similar samples, Kleine et al. (2004) concluded that the core formation age of Mars was 12 ± 5 Myr, while Jacobsen (2005) obtained a core formation age of 3.3 Myr.

As we will show below, uncertainties in the Hf/W ratio for the martian mantle, and the stochastic nature of late-stage accretion, permit an extended (∼10 Myr) accretion history for Mars, as well as one in which accretion happens rapidly (<1 Myr). These different timescales have different consequences for martian evolution. If Mars formed via runaway growth (Chambers and Wetherill, 1998) then its accretion timescale was ∼1 Myr. Such rapid accretion allows the possibility of significant heating by short-lived radio-isotopes such as ^{26}Al (cf. Ghosh and McSween, 1998), though the low mass of the majority of individual impactors likely resulted in restricted accretional heating of the interior (Senshu et al., 2002). On the other hand, Mars may have suffered a more protracted accretion history, involving large impacts, similar to the histories of the larger terrestrial planets (Agnor et al., 1999; Raymond et al., 2006). Such large impacts are likely to have resulted in widespread melting and magma ocean formation (Elkins-Tanton et al., 2003; Reese and Solomatov, 2006), though the geochemical evidence

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for such processes is weak (e.g., Righter, 2003). Large impacts may also have exerted a significant influence on the volatile budget of the planet (Lunine et al., 2003) and the evolution of its magnetic field (Williams and Nimmo, 2004).

The rest of the note is organized as follows. We will first briefly discuss the theory on which the estimation of core formation timescales from observations of Hf and W isotopes is based. We will then discuss the observations and demonstrate how uncertainties in these observations generate uncertainties in the core formation timescale. In particular, we will show that the uncertainty in the Hf/W ratio of the martian mantle is a significant cause of uncertainty. Finally, we will investigate the additional uncertainty introduced by the stochastic nature of the late-stage accretion process.

2. Theory

Planetary accretion and core formation are intimately linked: as a planet grows, gravitational energy is deposited and the interior heats up. At some point, the planet is sufficiently hot (and probably molten) that differentiation occurs: its dense constituents (mainly iron) sink to the center and form a core (Stevenson, 1990; Tonks and Melosh, 1992). Although core formation in reality may be a protracted process, as material is brought in by successive impacts (cf. Nimmo and Agnor, 2006), the theory is simplified if core formation is modeled as a single and instantaneous process. In any event, the timing of core formation gives an indication of the time at which accretion was approximately complete.

The Hf–W system is well-suited to constrain the timing of core formation because Hf and W behave differently when metal segregation occurs, and because radioactive ^{182}Hf decays to stable ^{182}W with a half-life of 9 Myr, comparable to theoretical accretion timescales. Here we will first explain in a qualitative sense what happens during core formation, and then apply a quantitative analysis; our notation is based on the review by Jacobsen (2005). Our purpose in restating this material is simply to make it accessible to dynamicists and others who are not familiar with the geochemical vocabulary.

Assume that a planet is initially undifferentiated and has a chondritic composition (what exactly is meant by chondritic will be discussed below). At some time t_c the planet instantaneously differentiates into a core and mantle. Hafnium (Hf), being a lithophile element, will remain in the mantle; some tungsten (W) will be removed to the core. Thus, the planet's mantle will have more Hf and less W than would a chondritic sample.

If differentiation happens late (>50 Myr after Solar System formation), essentially all the live ^{182}Hf will already have decayed to ^{182}W. Since all tungsten isotopes behave in a chemically identical fashion, they will all be extracted into the core in the same proportion. Thus, the ratio of ^{182}W to ^{183}W will remain the same as for a chondritic (undifferentiated) sample.

If, however, differentiation happens early, some live ^{182}Hf will remain in the mantle. After differentiation, this remaining ^{182}Hf will decay to ^{182}W, resulting in a mantle which has more radiogenic tungsten than would a chondritic sample. The mantle thus possesses a positive tungsten anomaly. The earlier the core forms, and the more Hf there is relative to W, then the larger the tungsten anomaly will be. Conversely, if the tungsten anomaly and the ratio of Hf to W can be measured, then the core formation time can be inferred. As we will show below, the largest uncertainty in inferring the core formation time of the martian core derives from uncertainties in the Hf/W ratio.

Quantitatively, the tungsten anomaly relative to chondritic is defined by ϵ_W where

$$\epsilon_W = \left[\frac{(^{182}\mathrm{W}/^{183}\mathrm{W})}{(^{182}\mathrm{W}/^{183}\mathrm{W})_{\mathrm{CHUR}}} - 1\right] \times 10^4, \tag{1}$$

where CHUR (chondritic uniform reservoir) denotes a chondritic sample. The tungsten anomaly simply compares the tungsten isotopic ratio in the sample to the same ratio in a chondritic (undifferentiated) sample. A positive ϵ_W denotes excess ^{182}W, implying early core formation. Here we are defining ϵ_W relative to ^{183}W and to chondritic samples. This is useful for modeling purposes because chondrites are representative of the W isotope evolution of an undifferentiated body. Note however that most of the original W isotope data are reported as ϵ_W relative to ^{184}W and relative to Earth (which has $\epsilon_W = 1.9$ in our notation; Kleine et al., 2002), but the principles are the same.

For instantaneous core formation at time t_c, the tungsten anomaly is given by Jacobsen (2005):

$$\epsilon_W = 10^4 \left(\frac{^{180}\mathrm{Hf}}{^{182}\mathrm{W}}\right)^{\mathrm{now}}_{\mathrm{CHUR}} \left(\frac{^{182}\mathrm{Hf}}{^{180}\mathrm{Hf}}\right)^{T_0} f^{\mathrm{Hf/W}} e^{-\lambda t_c}, \tag{2}$$

where T_0 is the time of Solar System formation, now refers to the present day, λ is the decay constant for ^{182}Hf (=0.078 Myr^{-1}; Vockenhuber et al., 2004) and $f^{\mathrm{Hf/W}}$ is a parameter describing the Hf/W ratio and is described below.

The first factor in Eq. (2) arises because ϵ_W is defined relative to chondritic; thus, an increase in the amount of ^{182}W in the reference sample will, other things being equal, reduce the observed tungsten anomaly. The second factor describes the initial ratio of ^{182}Hf to ^{180}Hf and arises because more ^{182}Hf initially will lead to a larger tungsten anomaly. The first two factors do not depend on the particular sample being measured and will be referred to below as global variables. The third factor $f^{\mathrm{Hf/W}}$ is specific to the particular sample, and describes the Hf/W ratio relative to the chondritic reference. It is given by

$$f^{\mathrm{Hf/W}} = \frac{(\mathrm{Hf/W})}{(\mathrm{Hf/W})_{\mathrm{CHUR}}} - 1 = 0.94(\mathrm{Hf/W}) - 1, \tag{3}$$

where the second equality is obtained assuming a carbonaceous chondritic composition (e.g., Palme and Jones, 2003). A larger value of $f^{\mathrm{Hf/W}}$ means that more ^{182}Hf is present relative to W, resulting in more radiogenic ^{182}W production and thus a larger tungsten anomaly. The final factor in Eq. (2) shows that later differentiation results in a smaller tungsten anomaly, as expected.

In practice, to determine the age of core formation of a sample, we will rewrite Eq. (2) as follows:

$$\begin{aligned} t_c &= \frac{1}{\lambda}\ln\left[\frac{10^4\left(\frac{^{180}\mathrm{Hf}}{^{182}\mathrm{W}}\right)^{\mathrm{now}}_{\mathrm{CHUR}}\left(\frac{^{182}\mathrm{Hf}}{^{180}\mathrm{Hf}}\right)^{T_0} f^{\mathrm{Hf/W}}}{\epsilon_{\mathrm{W}}}\right] \\ &= \frac{1}{\lambda}\ln\left[\frac{1.5 f^{\mathrm{Hf/W}}}{\epsilon_{\mathrm{W}}}\right]. \end{aligned} \tag{4}$$

The second equality is derived for a carbonaceous chondritic composition described by the global variables discussed below and emphasizes that the main uncertainties in the core formation timescale derive from uncertainties in $f^{\mathrm{Hf/W}}$ and ϵ_{W}. Equation (4) is the key expression: given values of $f^{\mathrm{Hf/W}}$ and ϵ_{W}, the core formation time t_c can be derived. Assuming that the global variables are known, uncertainties in t_c arise from uncertainties in $f^{\mathrm{Hf/W}}$ and ϵ_{W}. We will next proceed to discuss the values of all these quantities for the specific case of Mars.

3. Parameter values

Although it is generally assumed that bulk planetary compositions resemble those of carbonaceous chondrites, in the case of Mars oxygen and nitrogen isotopic observations have been used to argue that the compositions of Mars more closely resembles that of H chondrites (Lodders and Fegley, 1997; Sanloup et al., 1999; Mohapatra and Murty, 2003; Burbine and O'Brien, 2004). Thus, as discussed below, the chondritic reference quantities for Mars are somewhat uncertain.

The global chondritic quantities $(\frac{^{180}\mathrm{Hf}}{^{182}\mathrm{W}})^{\mathrm{now}}_{\mathrm{CHUR}}$ and $(\mathrm{Hf/W})_{\mathrm{CHUR}}$ occur in the ratio 1.32:1 and we will therefore focus on the latter quantity. There is some uncertainty associated with this quantity because the Hf/W ratio is variable among different chondrites (Newsom et al., 1996; Kleine et al., unpubl. data). Precise isotope dilution data show that carbonaceous chondrites have a Hf/W ratio of ∼1.06 (Kleine et al., 2004). H chondrites have a lower Hf/W ratio of ∼0.7 while LL chondrites have higher values of ∼1.8 (Newsom et al., 1996; Kleine et al., unpubl. data). This variability in Hf/W among chondrites likely reflects the presence of W in both metal and a refractory component in the solar nebula (Newsom et al., 1996). Thus, variations in the Hf–W systematics of chondrites (i.e., the reference for the W isotope evolution of the undifferentiated planet) have an effect on the calculated core formation ages.

The global quantity $(\frac{^{182}\mathrm{Hf}}{^{180}\mathrm{Hf}})^{T_0}$ refers to the time of Solar System formation and must be inferred indirectly by Hf–W measurements on meteorites of independently known age. From Hf–W data for ordinary chondrites Lee and Halliday (2000) obtained an initial $(\frac{^{182}\mathrm{Hf}}{^{180}\mathrm{Hf}})^{T_0}$ of the Solar System of 2.75×10^{-4}, but more recently it was shown that $(\frac{^{182}\mathrm{Hf}}{^{180}\mathrm{Hf}})^{T_0}$ is significantly lower. From an Hf–W isochron for chondrites and Allende CAIs (thought to be the oldest solid objects formed in the Solar System) Yin et al. (2002) obtained a value of $(1.00 \pm 0.08) \times 10^{-4}$ and Kleine et al. (2002) obtained a value of $(1.09 \pm 0.09) \times 10^{-4}$ based on the H chondrite Ste. Marguerite. The most recent determination of the initial $(\frac{^{182}\mathrm{Hf}}{^{180}\mathrm{Hf}})^{T_0}$ of the Solar System is based on an internal Hf–W isochron for Allende CAIs and is $(1.07 \pm 0.10) \times 10^{-4}$ (Kleine et al., 2005b).

The parameter values appropriate to Mars introduce additional uncertainties. Apparent samples from Mars are represented by the shergottite, nakhlite and chassignite (SNC) classes of meteorites (McSween, 1994). These different classes appear to be sampling isotopically distinct reservoirs which have remained mutually isolated since they formed early in Solar System history (e.g., Halliday et al., 2001). In particular, the shergottite group has ^{182}W and ^{142}Nd characteristics distinct from the nakhlites and chassignites, and also from a third group represented by the meteorite DaG 476 (Foley et al., 2005; Kleine et al., 2004). The isotopic characteristics of the latter two groups are probably caused by silicate mantle differentiation (Kleine et al., 2004), which makes them unsuitable as chronometers of core formation. The correlation between ^{182}W and ^{142}Nd for the basaltic shergottites has been used to infer both the initial W isotope value of the martian mantle ($\epsilon_{\mathrm{W}} = 2.34 \pm 0.07$, relative to carbonaceous chondrites) and a silicate differentiation timing of 42^{+21}_{-19} Myr after Solar System formation (Foley et al., 2005). This estimate of ϵ_{W} agrees with the more conservative estimates of $\epsilon_{\mathrm{W}} = 2.3 \pm 0.2$ obtained by Kleine et al. (2004) and $\epsilon_{\mathrm{W}} = 2.4 \pm 0.5$ quoted by Jacobsen (2005).

It turns out that the initial ratio of Hf/W in the martian mantle is more uncertain. As described above (Eq. (4)), this ratio is important because it controls the magnitude of the tungsten anomaly for a given time of core formation. How is the Hf/W ratio of the martian mantle estimated? The problem is that martian meteorites are relatively young igneous rocks and their measured Hf/W ratios are the product of complex melting histories. During igneous processes, W is more incompatible (it goes into melts more readily) than Hf, resulting in Hf–W fractionation during partial melting; melts will have lower Hf/W ratio than their residues. The Hf/W ratio of the bulk martian mantle therefore cannot be measured directly but must be inferred by comparing the W concentrations in martian meteorites with another element (such as La or Th) that behaves similarly during silicate melting (i.e., has a similar incompatibility), tends to stay in the mantle and whose abundance relative to Hf is known. The latter two conditions are met by refractory lithophile elements (RLE) because their relative abundances in bulk planetary mantles are chondritic. This is because they are neither fractionated by core formation (because they are lithophile) nor by volatile element depletion (because they are refractory). The Hf/W ratio of a bulk planetary mantle can thus be calculated as follows:

$$(\mathrm{Hf/W})_{\mathrm{M}} = (\mathrm{RLE/W})_{\mathrm{M}} \times (\mathrm{Hf/RLE})_{\mathrm{CHUR}}, \tag{5}$$

where the subscripts M and CHUR denote mantle and chondritic, respectively.

To infer the Hf/W ratio of a bulk planetary mantle it is thus critical to find a refractory lithophile element whose incompatibility is similar to that of W. Trace element studies on lunar and terrestrial basalts show that their U/W and Th/W ratios are relatively constant, indicating that W is as incompatible as Th and U (e.g., Palme and Rammensee, 1981; Newsom et al., 1996). The U/W ratio of lunar basalts and the

Th/W of the bulk silicate Earth have been used to infer the Hf/W ratios of the lunar and terrestrial mantles (Newsom et al., 1996). For martian meteorites however there are no studies that report precise Th (or U) and W concentrations that are measured on the same sample aliquots. Therefore, another RLE that has been used to constrain the Hf/W ratio of bulk planetary mantles is La. Trace element studies on lunar basalts (Rammensee and Wanke, 1977) and basaltic eucrites (Palme and Rammensee, 1981) show good correlations between La and W. Jones and Palme (2000) however note that for lunar basalts the correlation of W with U is better than the one with La, most likely indicating that La and W behaved differently during igneous processes. This is consistent with trace element studies on terrestrial samples, which indicate a higher incompatibility of W compared to La (Newsom et al., 1996).

Kong et al. (1999) and Treiman et al. (1986) give chondrite-normalized La/W ratios for the martian mantle that correspond to Hf/W ratios of 5.1 and 3.7, respectively. The problem is that there is considerable scatter in the correlation diagrams of W to La, and thus considerable uncertainty in the La/W ratio. This uncertainty likely arises because W is more incompatible than La, as discussed above.

Fig. 1 summarizes most of the available Th and W concentration data for martian meteorites (see figure caption for data selection). There is no correlation between Th/W ratio and W concentration, indicating only minor or absent Th/W fractionation during igneous processes on Mars. The average Th/W ratio obtained from these data is 0.98 ± 0.13 (2 standard errors). One problem with these data is that the Th and W concentrations have been measured on different aliquots, in different laboratories and using different techniques, which may contribute to the considerable scatter seen in Fig. 1. For instance, although identical Th concentrations have been reported for Nakhla and Lafayette, their W contents differ by a factor of two. The observed scatter might thus reflect sample heterogeneities, alteration (on Mars and/or Earth), or analytical artefacts caused by interlaboratory bias, and limits the precision with which the Hf/W ratio of the martian mantle can be determined.

From the Th/W ratio of 0.98 ± 0.13 obtained from the Th and W data shown in Fig. 1 the Hf/W ratio of the martian mantle can be calculated using Eq. (5), provided the Hf/Th ratio of chondrites is known. In their compilation of trace element abundances in CI (carbonaceous) chondrites Palme and Jones (2003) report a Hf/Th ratio of 3.59 ± 0.40 (uncertainty calculated using uncertainties of 5 and 10% for Hf and Th concentrations as reported by Palme and Jones, 2003). Other chondrite classes show small variations in Hf/Th ratios. In the sequence of chondrite classes CI–CM–CV the Hf/Th ratio increases from 3.22 to 4.23 (Rocholl and Jochum, 1993) and the average Hf/Th is 3.70 ± 0.84 (2σ). Using this Hf/Th ratio for chondrites results in a Hf/W of the bulk martian mantle of 3.6 ± 1.0 (Eq. (5)) and $f^{\mathrm{Hf/W}} = 2.4 \pm 1.0$ (Eq. (3)).

There exist only limited Hf and Th concentration data for chondrites other than carbonaceous chondrites. This is a problem because several lines of evidence suggest that the composition of bulk Mars might differ from that of carbonaceous chondrites. For instance, based on the O isotope compositions of martian meteorites and different groups of chondrites, Lodders and Fegley (1997) suggested that Mars might consist of 85% H-, 11% CV-, and 4% CI-chondritic material. Sanloup et al. (1999) also used O isotopes to infer that Mars

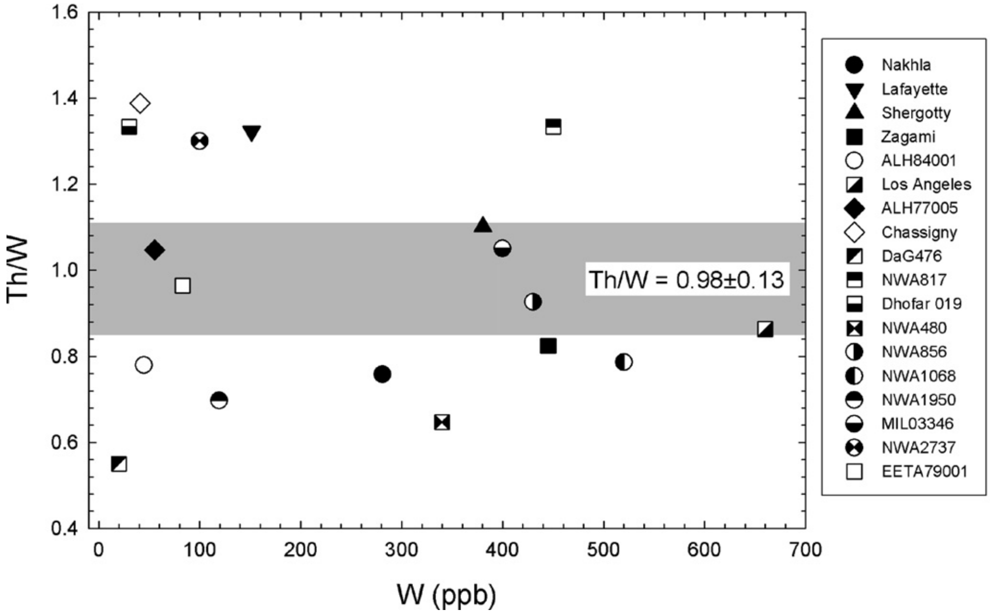

Fig. 1. Plot of Th/W ratio vs W concentration for martian meteorites. Data are summarized using the Mars Meteorite Compendium (Meyer, 2003). The gray shaded area indicates the average Th/W ratio of 0.98 ± 0.13 (2SE). Uncertainty on the Th/W ratio are standard errors (2σ). Assumed uncertainties for Th and W concentrations have no influence on the inferred Th/W ratio. For samples shown with filled symbols Th and W concentrations are determined using isotope dilution mass spectrometry [Th from Chen and Wasserburg (1986); W from Lee and Halliday (1997)]. For samples shown with open symbols W concentrations are also isotope dilution data from Lee and Halliday (1997), but Th data are from the compilation of Lodders (1998). For all other samples Th and W concentrations determined using ICP-MS (for references see Meyer, 2003).

consists of a mixture of H and EH chondrite material. Similar arguments have been presented based on a combination of O, N and Cr isotope data (Mohapatra and Murty, 2003; Burbine and O'Brien, 2004). We are not arguing here that Mars has an H-chondrite composition; we are simply pointing out that its composition is not well known, and is unlikely to exactly resemble that of carbonaceous chondrites. Hence, to determine the Hf/W ratio of the bulk martian mantle from Eq. (5), the Hf/Th ratio of chondrites other than carbonaceous chondrites must be known. To our knowledge however there are no studies that report precise data for both Hf and Th in ordinary and enstatite chondrites, rendering it difficult to precisely determine the Hf/Th of these meteorites. Combining precise Th concentration data determined by isotope dilution for the H chondrites Guarena and Pultusk (Hagee et al., 1990) with the average Hf content of H chondrites determined by isotope dilution (Patchett et al., 2004) yields $\mathrm{Hf/Th} = 4.3 \pm 0.4$ (the uncertainty on this ratio is difficult to assess and we assume an 10% uncertainty on this ratio). Within their relatively large uncertainties the Hf/Th ratios of carbonaceous and H chondrites are indistinguishable but H chondrites nevertheless appear to have a slightly higher Hf/Th ratio than carbonaceous chondrites. The Hf/Th ratio of other chondrite classes are difficult to assess because precise Hf and Th concentrations are not available. Hf/Th variations among chondrites, if they occur, have important consequences for estimating the Hf/W ratio of the bulk martian mantle. For instance, if the bulk martian mantle has a Hf/Th ratio similar to H chondrites, then its Th/W ratio obtained from the data in Fig. 1 translates into a Hf/W ratio of 4.2 ± 0.7 and $f^{\mathrm{Hf/W}} = 4.5^{+0.9}_{-1.0}$ (relative to $\mathrm{Hf/W} = 0.77$ in H chondrites; Kleine et al., unpubl. data).

An alternative approach to determining the Hf/W ratio of the martian mantle was adopted by Righter and Shearer (2003). Assuming that Mars went through a magma ocean stage early in its history these authors used the experimentally determined partition coefficient of W between liquid silicate and liquid metal to calculate the concentration of W in the mantle. Using this approach, Righter and Shearer (2003) obtained a Hf/W ratio of ~4, similar to the estimates deduced above.

In summary, with the currently available data the Hf/W ratio of the martian mantle is uncertain and might vary from 2.6 ($f^{\mathrm{Hf/W}} = 1.4$, relative to a carbonaceous chondrite composition) to 5.0 ($f^{\mathrm{Hf/W}} = 5.5$, relative to H-chondrite material). As will be shown below, this uncertainty results in a significant uncertainty in core formation timescales.

4. Results

Equation (4) may be used to investigate the effects of uncertainty in the Hf/W ratio on the inferred core formation age. This is illustrated in Fig. 2 for two sets of parameter values. For a carbonaceous chondrite composition of Mars the parameter values in Eq. (2) are: $\left(\frac{^{180}\mathrm{Hf}}{^{182}\mathrm{W}}\right)^{\mathrm{now}}_{\mathrm{CHUR}} = 1.4$; the W anomaly of the martian mantle is $\epsilon_{\mathrm{W}} = 2.34$; $(\mathrm{Hf/W})_{\mathrm{CHUR}} = 1.06$; and the bulk martian mantle has $(\mathrm{Hf/W}) = 3.6 \pm 1.0$. If, as outlined above, the bulk composition of Mars resembles those of H and EH chondrites these parameter values may be different. Enstatite (Lee and Halliday, 2000) and H chondrites (Kleine et al., unpubl. data) have slightly more negative ϵ_{W} values and lower Hf/W ratios than carbonaceous chondrites. For an EH–H chondrite-like composition of Mars the parameter values thus change to: $\left(\frac{^{180}\mathrm{Hf}}{^{182}\mathrm{W}}\right)^{\mathrm{now}}_{\mathrm{CHUR}} = 0.92$; the W anomaly of the martian mantle is $\epsilon_{\mathrm{W}} = 2.7$; $(\mathrm{Hf/W})_{\mathrm{CHUR}} = 0.69$; and a bulk mantle $(\mathrm{Hf/W}) = 4.3 \pm 0.7$.

Fig. 2 demonstrates that the uncertainty in the Hf/W ratio of the martian mantle leads to a range of core formation timescales from immediate to roughly 10 Myr. Assuming $\epsilon_{\mathrm{W}} = 2.34$ (appropriate for a carbonaceous chondritic composition), an $f^{\mathrm{Hf/W}}$ value of 3.3 (i.e., $\mathrm{Hf/W} = 4.6$) gives a core formation time of 9.6 Myr (Eq. (4)); for $f^{\mathrm{Hf/W}} = 1.4$ (i.e., $\mathrm{Hf/W} = 2.6$), a negative core formation time results. The difference in martian core

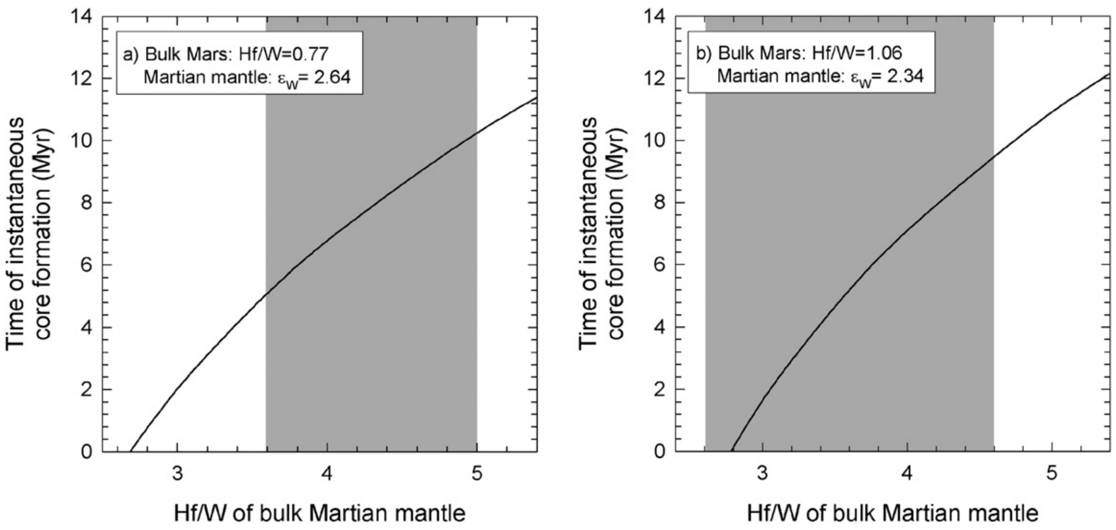

Fig. 2. Core formation timescale as a function of mantle Hf/W ratio calculated using Eq. (4) and assuming different bulk composition of Mars (see text). The shaded zone indicates our estimate of the martian mantle Hf/W ratio. In (a) it is assumed that the bulk composition of Mars resembles that of H chondrites; Hf–W systematics of H chondrites based on data from Kleine et al. (unpubl. data). (b) As for (a), except that the bulk martian composition is assumed to be that of carbonaceous chondrites.

formation timescales obtained by Kleine et al. (2004), Foley et al. (2005) and Jacobsen (2005) is due almost entirely to the different assumptions about $f^{\mathrm{Hf/W}}$: the latter used 2.0 ± 0.8 while the two other studies assumed $f^{\mathrm{Hf/W}} \sim 3.6$. Thus a small change in the assumed Hf/W ratio can lead to a large, and dynamically significant, change in the estimated core formation timescale.

Fig. 2 also illustrates that the lowest possible Hf/W ratio of the martian mantle is $\approx$2.8 because lower Hf/W ratios would result in negative core formation ages (i.e., the maximum possible ϵ_{W} under these circumstances would be less than the observed value). The martian mantle likely has a Hf/W ratio only slightly higher than $\approx$2.8 (see above), such that the Hf/W ratio must be determined very precisely to yield core formation ages of sufficient precision.

Fig. 2 additionally shows that assumptions regarding the composition of bulk Mars are relevant. If the chemical composition of Mars is actually dominated by H chondrite-like material, then the instantaneous core formation ages range from roughly 4 to 10 Myr. Given that these ages refer to the earliest possible time core formation can have ceased (Halliday et al., 1996; Kleine et al., 2004), this is a potentially very important result because it would preclude a very early accretion of Mars. However, the 0–10 Myr age range given by the carbonaceous assumption means that more precise Hf, Th and W concentration and W isotope data for chondrites and martian meteorites are needed to confidently constrain the formation time of the martian core. Note that the Hf/W ratio of the bulk martian mantle as estimated above is based on Hf and Th concentration data on a very small set of partly different samples. In addition it will be important to constrain the bulk composition of Mars (i.e., to determine which if any of the known chondrite classes most closely matches the material Mars is made off).

5. Discussion

Fig. 2 illustrates the fundamental problem, which is that the current uncertainties in the martian mantle Hf/W ratio permit a range of possible model ages for core formation (roughly 0–10 Myr). Thus, these geochemical observations currently only provide weak constraints for different models of how Mars accreted.

Other factors are likely to exacerbate this problem further. For instance, the real accretion process, at least for Earth-mass bodies, involves the delivery of large masses of core material at different times. Thus, the instantaneous core formation model is a simplification of the real process. A slightly more realistic approach is to assume that Mars grows at an exponentially decaying rate, where the time to reach 63% of the final mass is defined as $t_{63\%}$ (Jacobsen, 2005). For our best-guess chondritic value of $f^{\mathrm{Hf/W}} = 2.5$, $t_{63\%} = 3.4$ Myr, roughly half the instantaneous core formation timescale of 6 Myr (Eq. (4)).

N-body accretion simulations can be used to derive more realistic accretion scenarios, and to calculate the resulting isotopic signatures (Nimmo and Agnor, 2006). These simulations produce bodies having different "model" values for ϵ_{W} depending on the details of their accretion history and equilibration. Each model ϵ_{W} value may be used to calculate the instantaneous core formation timescale t_c using Eq. (4). Fig. 3 compares this calculated timescale against the simulation time at which the body reached 90% of its final mass ($t_{90\%}$, Fig. 3a) and 63% of its final mass ($t_{63\%}$, Fig. 3b). Fig. 3a shows that t_c is an underestimate of the time at which a body reaches 90% of its final mass, with the discrepancy in some cases exceeding a factor of 3. Hence, a body with an instantaneous core formation timescale of 6 Myr might in fact have suffered a large impact, delivering the final 10% of its mass, as late as 18 Myr. On the other hand, Fig. 3b shows that t_c is generally an overestimate of the time it takes for a body to reach 63% of its final

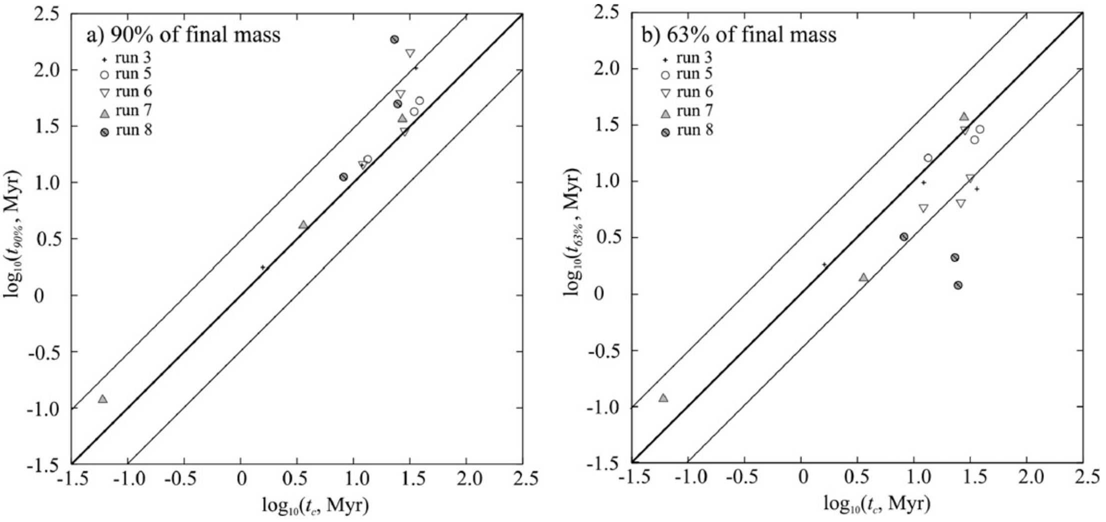

Fig. 3. (a) Comparison of different estimates of planetary formation timescales. The value of t_c is calculated using Eq. (4) and values for ϵ_{W} and $f^{\mathrm{Hf/W}}$ calculated from a series of N-body numerical simulations of late-stage planetary accretion and differentiation (Table 2 in Nimmo and Agnor, 2006). The quantity $t_{90\%}$ is the time required for each planet in the N-body simulation to reach 90% of its final mass. The bold line indicates $t_c = t_{90\%}$; thin lines are a factor of 3 higher or lower. Note that t_c underpredicts $t_{90\%}$. (b) As for (a), except comparing t_c with the time required for each planet to reach 63% of its final mass ($t_{63\%}$). Note that in general t_c overpredicts $t_{63\%}$.

mass. Again, in some cases the discrepancy exceeds a factor of 3. Thus, because of the stochastic nature of late-stage accretion, the instantaneous core formation timescale is likely to be only accurate to within a factor of ≈3 when used to infer the time it takes to assemble the terrestrial planets.

An additional uncertainty arises because the isotopic signature of accretion depends on the extent to which impactor cores re-equilibrate with the target mantle. In the extreme case of a collision between two equal mass bodies, if the cores do not equilibrate at all then the collision would have no effect on the isotopic signature. In practice, however, the measured ϵ_W values of silicate bodies agree most closely with numerical accretion model results if re-equilibration occurs even for the largest collisions (Nimmo and Agnor, 2006). Thus, this particular uncertainty is of less concern. A more serious problem is that the mantle oxygen fugacity, and thus the partitioning behavior of W, is likely to have changed as Mars accreted (cf. Wade and Wood, 2005). This process is likely to further complicate the interpretation of tungsten isotopic measurements.

Before the Hf–W timescale for the accretion of Mars can be assessed using more realistic models, it is critical to determine the Hf/W ratio of the martian mantle to higher precision. The most promising approach would be to determine Th, Hf and W concentrations on the same sample aliquot from a representative set of martian meteorites and different groups of chondrites by isotope dilution mass spectrometry. This technique can potentially provide elemental ratios with an uncertainty of ±1–2% or better. If the Hf/W ratio of the martian mantle is known to within ±2%, then the uncertainty of the Hf–W model age could be reduced to less than ±1 Ma. This improvement would significantly aid our understanding of the accretion history of Mars.

6. Conclusions

The accretion history of Mars is currently unclear. It may have finished accretion during the runaway growth stage of planetary accretion (Chambers and Wetherill, 1998), leading to a core formation timescale of ∼1 Myr. On the other hand, its accretion may have been more protracted and included late-stage giant impacts. Although Hf–W isotopic observations ought, in principle, to be able to place constraints on the timescale over which Mars accreted, the uncertainties are currently large. These uncertainties arise because the Hf/W ratio of the martian mantle is currently uncertain by ±25%, and permit (instantaneous) core formation timescales in the approximate range 0–10 Myr. An additional uncertainty factor of about 3 arises because the instantaneous core formation model does not take into account the stochastic nature of the late-stage accretion process.

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