The early differentiation of Mars inferred from Hf-W chronometry

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Abstract

Mars probably accreted within the first 10 million years of Solar System formation and likely underwent magma ocean crystallisation and crust formation soon thereafter. To assess the nature and timescales of these large-scale mantle differentiation processes we applied the short-lived ^{182}Hf–^{182}W and ^{146}Sm-^{142}Nd chronometers to a comprehensive suite of martian meteorites, including several shergottites, augite basalt NWA 8159, orthopyroxenite ALH 84001 and polymict breccia NWA 7034. Compared to previous studies the ^{182}W data are significantly more precise and have been obtained for a more diverse suite of martian meteorites, ranging from samples from highly depleted to highly enriched mantle and crustal sources. Our results show that martian meteorites exhibit widespread ^{182}W/^{184}W variations that are broadly correlated with ^{142}Nd/^{144}Nd, implying that silicate differentiation (and not core formation) is the main cause of the observed ^{182}W/^{184}W differences. The combined ^{182}W–^{142}Nd systematics are best explained by magma ocean crystallisation on Mars within ~20–25 million years after Solar System formation, followed by crust formation ~15 million years later. These ages are indistinguishable from the I-Pu-Xe age for the formation of Mars' atmosphere, indicating that the major differentiation of Mars into mantle, crust, and atmosphere occurred between 20 and 40 million years after Solar System formation and, hence, earlier than previously inferred based on Sm-Nd chronometry alone.

Key words: martian meteorites, Hf-W chronometry, Sm-Nd chronometry, planetary differentiation, magma ocean, crust fomation

1 Introduction

The early evolution of Mars probably involved large-scale melting and core formation, followed by magma ocean crystallisation and crust formation (e.g. Elkins-Tanton, 2005; Mezger et al., 2013). The timescales of these processes can be quantified through the application of the short-lived ^{182}Hf–^{182}W [half-life = 8.9 million years (Ma)] and ^{146}Sm–^{142}Nd (half-life = 103 Ma) systems to martian meteorites, which derive from compositionally distinct sources that were established during the early differentiation of Mars. The mantle sources of martian meteorites are thought to comprise mafic cumulates and late-stage crystallisation products of a magma ocean (Borg et al., 1997; Borg and Draper, 2003; Elkins-Tanton, 2008, 2005), as well as crust (Agee et al., 2013; Humayun et al., 2013). These distinct reservoirs have different Hf/W and Sm/Nd ratios, ultimately leading to variations in radiogenic ^{182}W and ^{142}Nd within the martian mantle and crust. Thus, the ^{182}W and ^{142}Nd compositions of martian meteorites from distinct sources reflect Hf/W and Sm/Nd fractionations during the earliest evolution of Mars and as such can be used to constrain the timescales of magma ocean processes and crust formation.

Several studies have shown that large radiogenic ^{182}W and ^{142}Nd variations exist within Mars (Borg et al., 2016, 1997; Brennecka et al., 2014; Caro et al., 2008; Debaille et al., 2007; Foley et al., 2005; Kleine et al., 2004; Lee and Halliday, 1997). For instance, nakhlites display some of the most radiogenic ^{142}Nd and ^{182}W compositions yet reported among martian meteorites, indicating source formation within ~25 Ma of Solar System formation (Harper et al., 1995; Kleine et al., 2004; Foley et al., 2005; Debaille et al., 2009). Similarly, early studies on shergottites suggested that Mars primordial differentiation occurred at about 20–60 Ma after Solar System formation (Borg et al., 2003; Kleine et al., 2004; Foley et al., 2005). However, mainly driven by improvements in the analytical precision of ^{142}Nd/^{144}Nd measurements, subsequent studies demonstrated that shergottites define a precise ^{142}Nd-^{143}Nd model age of 63±6 Ma after Solar System formation (Borg et al., 2016). The significance of this age, and whether the ^{142}Nd-^{143}Nd systematics of shergottites record a single differentiation event is debated, however. As such, the ^{142}Nd-^{143}Nd data for shergottites have also been interpreted to record a prolonged interval of magma ocean crystallisation on Mars, lasting between ~30–100 Ma after Solar System formation (Debaille et al., 2007).

One potential issue in the chronological interpretation of ^{142}Nd-^{143}Nd systematics is the presence of nucleosynthetic Nd isotope variations that arise through the heterogeneous distribution of presolar matter at the bulk meteorite and planetary scale (Burkhardt et al., 2016). For instance, recent studies have shown that the ~10–20 parts-per-million ^{142}Nd difference observed between chondrites and terrestrial samples (Boyet and Carlson, 2005) reflects nucleosynthetic Nd isotope heterogeneity between chondrites and the Earth (Burkhardt et al., 2016; Bouvier and Boyet, 2016), rather than an early Sm/Nd fractionation and subsequent radiogenic ingrowth from short-lived ^{146}Sm. The ^{142}Nd difference between terrestrial samples and chondrites, therefore, does not provide a record of an early differentiation of the silicate Earth. This example highlights that quantifying the extent of nucleosynthetic Nd isotope variations is essential for using the ^{146}Sm-^{142}Nd system to obtain meaningful ages for early differentiation processes. For Mars the extent of nucleosynthetic Nd isotope anomalies is not well known, however, and this may impact the chronology of Mars' early differentiation inferred from ^{146}Sm-^{142}Nd systematics. For instance, assuming an ordinary chondrite-like bulk ^{142}Nd/^{144}Nd for Mars provides a ~30 Ma model age for the formation of the source of depleted shergottites (Debaille et al., 2007), whereas this age changes to ~60 Ma if an Earth-like ^{142}Nd^{144}Nd is assumed for bulk Mars (Borg et al., 2016). Thus, the aforementioned uncertainties in the ^{146}Sm-^{142}Nd timescale for Mars' early differentiation at least partially reflect uncertainties in the ^{142}Nd composition of bulk Mars.

The Hf-W chronometer is ideally suited to investigate the duration of magma ocean differentiation on Mars and to distinguish between an early differentiation at ~30 Ma and a later differentiation at ~60 Ma after Solar System formation. This is because owing to the much shorter half-life of ^{182}Hf compared to ^{146}Sm, significant ^{182}W variations can only be produced within the first ~50 Ma of the Solar System (e.g., Kleine et al., 2009). Thus, if the martian magma ocean crystallized at ~60 Ma as suggested by a ^{142}Nd-^{143}Nd isochron for shergottites (Borg et al., 2016), then these meteorites should all have the same ^{182}W composition. Conversely, if Mars' early differentiation largely occurred at ~30 Ma, then there should be ^{182}W variations among the shergottites. Published ^{182}W data for shergottites do not show resolvable ^{182}W variations (Foley et al., 2005; Kleine et al., 2004; Lee and Halliday, 1997) and, therefore, seem to be consistent with differentiation of Mars at ~60 Ma after Solar System formation. However, the precision of the ^{182}W measurements achievable at the time of these earlier studies was significantly lower than at present and was insufficient for resolving potential ^{182}W variations among the shergottites formed from relatively young source regions.

To assess the extent of ^{182}W variations in the martian mantle, and to better constrain the timescales of Mars' early differentiation, we obtained high-precision ^{182}W data for a comprehensive suite of martian meteorites, including samples derived from some of the most enriched and depleted sources known on Mars. To help interpret the ^{182}W data in terms of differentiation timescales, we also obtained high-precision ^{142}Nd data for some of the same samples, coupled with data for non-radiogenic Nd isotopes to assess whether Mars shows a nucleosynthetic Nd isotope anomaly relative to Earth. Combined, these data provide new insights into the timescales of core formation, magma ocean crystallisation, and crust formation on Mars.

2 Samples and analytical methods

Samples selected for this study include several shergottites (5 enriched, 3 intermediate, 5 depleted), augite basalt Northwest Africa (NWA) 8159, orthopyroxenite Allan Hills (ALH) 84001, and polymict breccia NWA 7034. The last two samples derive from the most incompatible trace element–enriched sources, whereas Tissint and NWA 7635 derive from the most depleted sources known on Mars (Agee et al., 2013; Brennecka et al., 2014; Humayun et al., 2013; Lapen et al., 2017, 2010; Nyquist et al., 2016). Note that NWA 7034 is a breccia containing matrix and clasts of numerous different lithologies (Agee et al., 2013; Humayun et al., 2013). The bulk sample analysed here is relatively typical for NWA 7034, and represents a mixture of various clasts and matrix. All samples were received as rock fragments. Their surfaces were abraded to remove any potential terrestrial contamination, and the samples (~0.2-2.5 g) were then ultrasonically cleaned and rinsed with ethanol, and subsequently crushed and ground to a fine powder in an agate mortar.

The analytical techniques for sample digestion, chemical separation of W, and W isotope ratio measurements by MC-ICPMS are based on previously developed procedures (Kruijer et al., 2015, 2014) and are described in detail in the online Supplementary Material. In brief, the martian meteorite samples and terrestrial rock standards (~0.2-0.5 g) were digested in HF–HNO_3 (2:1) at 130-150 °C on a hotplate for 2-3 days. When samples quantities of >0.5g were needed to obtain sufficient W, powder splits of <0.5 g were digested in separate vials. Tungsten was separated from the sample matrix using a two-stage anion exchange chromatography in HCl-HF media (Kleine et al., 2012; Kruijer et al., 2015, 2014). Total procedural yields were ~75-100%, and total blanks correspond to ~50-100 pg W and were negligible given the amounts of W analysed (~30-150 ng).

The W isotope compositions were measured to high precision using a ThermoScientific® Neptune *Plus* MC-ICPMS in the Institut für Planetologie at the University of Münster (Kruijer et al., 2015, 2012). Instrumental mass bias was corrected by internal normalization to $^{186}W/^{184}W = 0.92767$ using the exponential law. Note that we only used $^{186}W/^{184}W$-normalised data and avoided normalisations involving ^{183}W; the latter can be biased by a small analytical effect on ^{183}W introduced during sample preparation (see Section 3 and Supplementary Material), as observed in this and multiple earlier studies (e.g., Cook and Schönbächler, 2016; Kruijer et al., 2012; Willbold et al., 2011). A single W isotope measurement comprised 200 cycles of 4.2 s integration time each. The W isotope analyses of samples are reported as -unit (*i.e.*, 0.01%) deviations from the mean values of the bracketing standards (Alfa Aesar® metal, batch no. 22312) obtained in one analytical session. The accuracy and reproducibility of the W isotope measurements were assessed by repeated analyses of terrestrial rock standards (BHVO-2, BCR-2), which were digested and processed through the full chemical separation and analysed alongside the martian samples. The mean ^{182}W obtained for multiple analyses of the terrestrial rock standards yields $^{182}W = 0.01 \pm 0.10$ (2s.d., *N*=42, Fig. 1), demonstrating the high level of precision achieved for a single W isotope analysis consuming as little as ~30 ng W. Note that the *external* reproducibility of ± 0.10 $\varepsilon^{182}W$ (2 s.d.) obtained here is significantly better than that reported in earlier W isotope studies of martian meteorites (Foley et al., 2005; Kleine et al., 2004), where the external precision was typically on the order of ± 0.5 $\varepsilon^{182}W$ (2 s.d.).

For the analyses of Nd isotope compositions in some of the same samples, we recombined the saved matrix aliquots from the W separation procedure described above. Neodymium was then separated through several ion exchange chromatography steps as described in Borg et al. (2016), and analysed using the Triton TIMS at Lawrence Livermore National Laboratory following previously established procedures (Borg et al., 2016; Burkhardt et al., 2016; more details given in the Supplementary Material, Section S5). Neodymium isotope compositions were corrected for instrumental mass fractionation by internally normalizing to $^{146}Nd/^{144}Nd = 0.7219$ using the exponential law, and are reported in ^{i}Nd as the parts-per 10^4 deviations from terrestrial standard values. Total procedural yields for Nd obtained using this procedure were 60-95% and total blanks were approximately 50 pg Nd, which is inconsequential given the amounts of Nd analysed (~500 ng Nd).

3 Results

The investigated samples shows large and well-resolved ^{182}W variations from approximately +0.1 (ALH 84001) to approximately +1.8 (NWA 7635) (Fig. 2a, Table 1), indicating that the total spread in ^{182}W is much larger than found for shergottites by previous studies (Fig. 2b; Foley et al., 2005; Kleine et al., 2004; Lee and Halliday, 1997). In particular, in contrast to earlier work, we find that different groups of shergottites exhibit distinct ^{182}W values. The enriched shergottites have a uniform ^{182}W of 0.37±0.05 (95% conf., n=5), whereas the depleted shergottites exhibit more elevated and more variable ^{182}W from *ca.* +0.8 to +1.8. The larger range of ^{182}W values not only reflects the higher precision of our measurements compared to previous investigations, but also the more diverse sample suite examined here that included several meteorites for which ^{182}W data had not previously been reported, such as NWA 7635, Tissint, NWA 8159 and NWA 7034 (Fig. 2). Both the terrestrial rock standards and some martian samples exhibit small deficits in measured ^{183}W (Tables S1, S2). These offsets have been observed in several previous studies and are attributed to a small mass-independent fractionation affecting only ^{183}W that is induced during sample preparation (e.g., Budde et al., 2015; Cook and Schönbächler, 2016; Kruijer et al., 2012; Willbold et al., 2011), most likely by a nuclear field shift effect induced during incomplete dissolution of W in Savillex beakers (Cook and Schönbächler, 2016). Nevertheless, this ^{183}W-effect does not modify ^{182}W values normalized to ^{186}W/^{184}W, which is the normalization used throughout this study.

The ^{142}Nd compositions of some of the same martian samples shows a similar spread as observed in previous work (Borg et al., 2016, 1997; Caro et al., 2008; Debaille et al., 2007; Foley et al., 2005) (Tables 1, S3). However, ^{142}Nd values obtained for ALH 84001 and NWA 7034 (*ca.* –0.30 and *ca.* –0.45), are the lowest values determined so far for martian meteorites; these unradiogenic ^{142}Nd compositions are consistent with derivation of these samples from the most enriched sources known on Mars. The non-radiogenic Nd isotope data (*i.e.*, isotope ratios not affected by radioactive decay) collected in this study and also in Borg et al. (2016) show considerable scatter (Fig. S1), making it difficult to reliably assess as to whether the Nd isotopic composition of Mars is different from that of the Earth. Nevertheless, when mean values and their associated 95% conf. limits are calculated (N=16, Table S3), hints of small excesses become apparent for ^{148}Nd (+0.05±0.02) and ^{150}Nd (+0.14±0.10), but not for ^{145}Nd (+0.02±0.03). The larger scatter of these data compared to previous work (Burkhardt et al., 2016) reflects the shorter duration and lower intensity of the Nd measurements of the present study, caused by the smaller mass of sample available. While this is inconsequential for resolving the large ^{142}Nd variations among martian meteorites, it makes detecting small nucleosynthetic Nd isotope anomalies more difficult.

4 Discussion

4.1 Origin of ^{182}W variations and Hf-W age of core formation

Utilizing the Hf-W system to date core formation on Mars requires knowledge of the ^{182}W composition of the bulk martian mantle, that is, the martian mantle composition set solely by core formation. Previous studies have estimated this value using the co-variation of ^{182}W and ^{142}Nd (Kleine et al., 2004; Foley et al., 2005; Mezger et al., 2013). Because silicate differentiation leads to correlated ^{182}W-^{142}Nd variations, the ^{182}W of samples having the ^{142}Nd of bulk Mars should represent the ^{182}W of the bulk martian mantle (Kleine et al., 2004; Foley et al., 2005). Despite demonstrating significant variations in ^{142}Nd isotopic compositions, previous data for shergottites did not show large ^{182}W variations (Foley et al., 2005; Kleine et al., 2004), yielding precise estimates of the ^{182}W of the bulk martian mantle, with values between 0.34±0.07 and 0.45±0.15 (Foley et al., 2005; Kleine et al., 2004). By contrast, the results obtained in the present study reveal significant ^{182}W variations among shergottites (Fig. 1) that show a general positive trend with ^{142}Nd (Fig. 3). In particular, meteorites with the most enriched source characteristics (as given e.g. by La/Sm) and lowest ^{182}W also show low ^{142}Nd (NWA 7034, ALH 84001), whereas those derived from depleted sources with higher ^{182}W show higher ^{142}Nd (NWA 7635, Tissint). Whereas variations in ^{182}W can be caused by both core formation and silicate differentiation, ^{142}Nd variations can only be produced by silicate differentiation. The positive trend between ^{182}W and ^{142}Nd, therefore, implies that these isotope variations are caused by the same process, so that the ^{182}W *differences* predominantly reflect silicate differentiation and not core formation. Nonetheless, in spite of this general ^{182}W *vs.* ^{142}Nd trend, there is considerable scatter about the trend, indicating that the ^{182}W *vs.* ^{142}Nd systematics cannot be caused by a single episode of differentiation within the martian mantle – this will be discussed in detail further below (Section 4.2).

As in previous studies, the ^{182}W of the bulk martian mantle can be determined from the ^{182}W-^{142}Nd variation combined with an estimate of the bulk martian mantle ^{142}Nd (e.g. Mezger et al., 2013). The latter is uncertain, however, due to nucleosynthetic Nd isotope heterogeneity among the terrestrial planets and chondrites (Burkhardt et al., 2016). Currently proposed ^{142}Nd values for bulk Mars range from ^{142}Nd = –0.06 (Borg et al., 2016) down to the composition measured for ordinary chondrites (*i.e.*, ^{142}Nd = –0.18) (Debaille et al., 2007). However, over this range of values there is essentially no variability in ^{182}W among the martian meteorites (*i.e.*, the enriched shergottites and NWA 7042) (Fig. 3). Thus, we take the mean ^{182}W = +0.37±0.04 (95% conf.) of these shergottites to represent the ^{182}W of the bulk martian mantle. This value is consistent with but more precise than the previous estimates summarized above (Foley et al., 2005; Kleine et al., 2004).

As the bulk martian mantle ^{182}W deduced in the present study is not different from those inferred previously, the calculated Hf-W model ages for core formation do not change. Nevertheless, core formation ages are briefly reviewed below to provide an estimate for the duration of Mars' accretion and core formation. Assuming that bulk silicate Mars has a ^{182}W value of +0.37±0.04 and a ^{180}Hf/^{184}W ratio of 4.0±0.5 (Dauphas and Pourmand, 2011) yields a two-stage model age for core formation of 4.1±2.7 Ma. The two-stage Hf-W model age assumes that core formation occurred in a single instant, but this assumption may not be valid for larger bodies like Mars, in which metal segregation likely occurred by several distinct events as accretion proceeded. In this case, a more realistic age is obtained by assuming continuous core formation and an exponentially decreasing accretion rate (Harper and Jacobsen, 1996). In this model, a mean life of accretion, corresponding to 63% growth, of $\tau = 2.4^{+1.3}_{-1.5}$ Ma is obtained, consistent with a previous estimate of $1.8^{+0.9}_{-1.0}$ Ma for 44% growth from

Dauphas and Pourmand (2011). In this model, ~90% of Mars' growth would have been completed by ~6 Ma after Solar System formation. These age calculations assume complete metal-silicate equilibration during core formation, but as to whether this has always been the case is not known. For instance, if Mars formed as a stranded planetary embryo, then most of its mass was added by small planetesimals, in which case complete metal-silicate equilibration seems likely. If, however, Mars' accretion involved giant impacts, then it is possible that the metal cores of these impactors did not fully equilibrate within the martian mantle before entering the core (e.g., Morishima et al., 2013). In this case the true core formation time would be younger than the ages calculated above (Mezger et al., 2013; Nimmo and Kleine, 2007). For instance, assuming the degree of metal-silicate equilibration was only 50%, then would change to ~5 Ma, meaning that ~90% of Mars' mass would have accreted by ~10 Ma after Solar System formation (Mezger et al., 2013). Taken together, the Hf-W systematics indicate that most of Mars' accretion history was probably completed within the first ~10 Ma of Solar System history. This age provides a quite robust estimate for the accretion rate of Mars, unless the Hf/W ratio of the martian mantle is significantly higher than currently estimated. Although currently available data seem to preclude this possibility, the data upon which this estimate is based were obtained on only a small number of samples and using different analytical techniques. As such it would be useful for future studies to determine the Hf/W ratio of the martian mantle on a larger set of samples and using a common high-precision analytical method.

4.2 Using combined ^{182}W–^{142}Nd systematics to date silicate differentiation

In order to utilize the ^{182}W and ^{142}Nd data for determining differentiation timescales, we assessed the extent of Hf/W and Sm/Nd fractionations within the martian mantle using magma ocean crystallisation models (Borg and Draper, 2003; Debaille et al., 2008; Elkins-Tanton, 2005). In this modelling the generation of *depleted* martian mantle sources was simulated through the sequential crystallisation of several cumulate packages from the magma ocean (Lodders and Fegley, 1997; Borg and Draper, 2003; Supplementary Material). In this model, the residual liquid left behind after magma ocean crystallisation then represents the *enriched* mantle end member composition. The bulk martian mantle, *i.e.*, the starting composition of the model, was assumed to have a chondritic ^{147}Sm/^{144}Nd of

0.1960 (Jacobsen and Wasserburg, 1980; Bouvier et al., 2008) and a $^{180}Hf/^{184}W$ of 4.0±0.5 (Dauphas and Pourmand, 2011). For the modelling we used published crystal-melt partition coefficients for Sm, Nd, Hf, and W (Borg and Draper, 2003; Righter and Shearer, 2003; Snyder et al., 1992) (Table S4), and the high-pressure (~15 GPa) cumulate crystallisation assemblage from Borg and Draper (2003), corresponding to a magma ocean depth of ~1350 km (Borg and Draper, 2003; Righter and Chabot, 2011; Righter and Shearer, 2003). The modelling shows that the cumulate packages have $^{147}Sm/^{144}Nd$ ratios from 0.282 to 0.528 and $^{180}Hf/^{184}W$ ratios from 12 to 23, corresponding to 5 to 98% crystallised solids (Table S5). The weighted mean values for the cumulate packages used here correspond to $^{147}Sm/^{144}Nd$ • 0.291 and $^{180}Hf/^{184}W$ • 14, in good agreement with previous estimates (Borg and Draper, 2003; Debaille et al., 2008; Foley et al., 2005; Righter and Shearer, 2003). For the range in enriched end-member compositions, we used the $^{147}Sm/^{144}Nd$ of 0.157-0.170 and $^{180}Hf/^{184}W$ of 1.19-1.83 modelled for 98 to 99.5% trapped liquid. Using the $^{180}Hf/^{184}W$ and $^{147}Sm/^{144}Nd$ ratios obtained, the ^{182}W and ^{142}Nd evolution were calculated for enriched and depleted mantle sources formed at different times after Solar System formation.

The results of the modelling demonstrate that the ^{182}W variations as well as the coupled ^{142}Nd–$\varepsilon^{182}W$ variations of martian meteorites are reproduced for differentiation ages between ~20 and ~40 Ma after Solar System formation (Fig. 3, 4), where the isotopic compositions of ALH 84001, Tissint, and NWA 7635 require differentiation as early as ~20–25 Ma after Solar System formation. Note that especially the large ^{182}W variations observed among the martian meteorites require such an early differentiation of Mars. For instance, producing the $\varepsilon^{182}W$ excess of ~+1.8 for NWA 7635 at 60 Ma after Solar System formation (*i.e.*, the age for martian differentiation previously inferred from ^{146}Sm-^{142}Nd systematics of shergottites) would require a $^{180}Hf/^{184}W$ ratio of ~135 for the source of this sample (Fig. 4). By contrast, our modelling, as well as previous work (Foley et al., 2005; Kleine et al., 2004; Righter and Shearer, 2003), shows that mafic cumulates of a martian magma ocean have $^{180}Hf/^{184}W$ ratios that are much lower and typically are between ~12 and ~23; only garnet/majorite has a higher $^{180}Hf/^{184}W$ ratio of ~128 (Table S5). However, a mantle source consisting exclusively of garnet is not appropriate for the shergottites, whose source consists of a mixture of olivine, orthopyroxene, clinopyroxene, garnet and ilmenite (Borg and Draper, 2003; Debaille et al., 2008), yielding a bulk

^{180}Hf/^{184}W ratio of only ~14. Thus, for the modelled range of ^{180}Hf/^{184}W ratios in the shergottite sources, the large ^{182}W variations observed among the shergottites require source formation much earlier than previously inferred solely based on ^{142}Nd systematics. Of note, using different bulk martian mantle ^{182}W compositions (from +0.25 to +0.5), crystallisation sequences and/or cumulate packages yields very similar silicate differentiation ages for Mars (see Supplementary material, Fig. S2). Furthermore, using individual cumulate packages as the depleted end member composition in the magma ocean model (Fig. S3, Table S5) yields differentiation ages that are consistent with those derived when the weighted mean cumulate compositions is used (Fig. 3). Thus, the differentiation ages for the martian mantle inferred here do not depend on a particular magma ocean model or bulk composition.

Further evidence for an early differentiation of Mars comes from the incompatible trace element –enriched nature of the sources of ALH 84001 and NWA 7034. These meteorites exhibit lower ^{182}W and ^{142}Nd than the bulk martian mantle and so must derive from sources with Hf/W and Sm/Nd ratios below those of the bulk mantle (Fig. 3, 4). Note that although NWA 7034 is a breccia that contains a meteoritic component added during impacts on the martian surface (Humayun et al., 2013), the effect of this meteorite contamination is very small, <0.03 ^{182}W (see Supplementary Material). Thus, the low ^{182}W of NWA 7034 cannot reflect meteorite contamination, but instead indicates derivation from a source (or sources) characterized by low-Hf/W ratios. Since the ^{180}Hf/^{184}W of the bulk martian mantle is only 4.0±0.5 (Dauphas and Pourmand, 2011), there is only a very limited range of possible Hf/W ratios for the sources of ALH 84001 and NWA 7034, and so the inferred source formation ages are essentially independent on the partition coefficients and bulk mineralogy used for modelling magma ocean crystallisation. This makes the formation ages for the ALH 84001 and NWA 7034 sources of ~25-40 Ma quite robust (Fig. 3, 4). Note that because NWA 7034 is a breccia, its isotopic composition may not reflect derivation from a single source (Nyquist et al., 2016). Consequently, the bulk sample of NWA 7034 measured here could potentially represent a mixture of components with lower and higher ^{182}W and ^{142}Nd than that measured for the bulk sample. If this is the case, then the component with lower ^{182}W and ^{142}Nd would require an even earlier source formation time than the bulk sample. Thus, W isotope analyses of individual clasts from NWA 7034 may allow even more precise determination of the timing of crust formation on Mars.

An important observation from the new isotopic data is that the martian meteorites analysed here do not define a single mixing array in ^{142}Nd *vs.* ^{182}W space (Fig. 3). Such ^{182}W-^{142}Nd systematics can potentially be explained by variable mixing between intermediate magma ocean differentiation products (*i.e.,* individual cumulate packages) formed contemporaneously (Table S5; Fig. S3). However, mixing lines for some individual cumulate packages fail to reproduce the alignment of the data in ^{142}Nd-^{182}W space, and also cannot explain the ^{142}Nd-^{182}W composition of ALH 84001 (Fig. S3, see Supplementary Material). Instead, rather than by instantaneous differentiation, the ^{182}W-^{142}Nd systematics are most easily explained by a more prolonged interval of differentiation between ~20 and ~40 Ma after Solar System formation (Fig. 3). For instance, the combined ^{182}W-^{142}Nd systematics of ALH 84001 appear to require source formation at ~20-25 Ma after CAI formation, whereas the source of NWA 7034 appears to have formed later at ~40 Ma after CAIs. It is noteworthy that combined ^{147}Sm-^{143}Nd and ^{176}Lu-^{176}Hf systematics have been used to argue that the source of ALH 84001 contains trapped residual liquid of a magma ocean (Lapen et al., 2010), whereas the source of NWA 7034 is thought to be martian crust rather than residual liquid of a magma ocean (Agee et al., 2013; Humayun et al., 2013; Nyquist et al., 2016). Thus, one possibility to account for the disparate ^{182}W-^{142}Nd systematics of ALH 84001 and NWA 7034 is that the formation age of the ALH 84001 source inferred here records the timing of the final stage of magma ocean crystallisation at ~20–25 Ma after Solar System formation, whereas the later formation age of the NWA 7034 source at ~40 Ma inferred here reflects crust formation by means of re-melting of the mantle, perhaps triggered by cumulate overturn (Debaille et al., 2009; Elkins-Tanton, 2005). Similarly, re-melting and cumulate overturn in the mantle also provides an explanation for the slightly younger source formation ages of some depleted shergottites (DaG 476, SaU 005) and augite basalt NWA 8159 in comparison to the most depleted shergottites Tissint and NWA 7635 (Fig. 3, 4). A corollary of the above is that the initial solidification of the martian mantle must have preceded these re-melting and crust formation events, and so regardless of whether the enriched sources reflect trapped liquid of a magma ocean or martian crust, our results indicate that magma ocean crystallisation on Mars occurred •20–25 Ma after Solar System formation.

This age for magma ocean crystallisation is similar to the ~23 Ma source formation age of nakhlites as inferred from their ^{182}W-^{142}Nd composition (Debaille et al., 2009; Foley et al., 2005). The nakhlites are thought to derive from deep mantle sources comprised of cumulates formed during the onset of magma ocean solidification (Debaille et al., 2009). Thus, these data considered together suggest that deep and shallow regions of the magma ocean crystallized about contemporaneously at ~20–25 Ma, followed by crust formation until at least ~40 Ma after Solar System formation (Fig. 5). Finally, the differentiation timescales for Mars inferred here are also consistent with ^{129}I-^{244}Pu-Xe systematics of martian meteorites that indicate an early I/Pu fractionation related to intensive, large-scale magmatic activity in the martian mantle within ~35 Ma of Solar System formation leading to degassing into the atmosphere (Marty and Marti, 2002).

4.3 Comparison to ^{142}Nd-^{143}Nd systematics of shergottites

Previous studies have used the coupled ^{142}Nd-^{143}Nd chronometry of shergottites to argue for a prolonged interval of martian silicate differentiation and magma ocean crystallisation of up to ~60–100 Ma (Borg et al., 2016; Debaille et al., 2007). Such a late differentiation of Mars contrasts with the evidence for earlier differentiation at ~25–40 Ma inferred in the present study, raising the question as to why these two estimates disagree. Differentiation ages from ^{142}Nd-^{143}Nd data are typically calculated using two different approaches. First, the ^{142}Nd-^{143}Nd systematics of *individual* rock samples can be used to calculate three-stage model ages. This approach requires an assumption about the bulk ^{142}Nd/^{144}Nd of Mars. For instance, assuming that bulk Mars has a ^{142}Nd of –0.06 (*i.e.*, similar to the Earth's mantle) results in model ages of ~60 Ma for the shergottites (Borg et al., 2016). By contrast, assuming an ordinary chondrite-like bulk ^{142}Nd for Mars results in ^{142}Nd model ages of ~30 Ma for the depleted shergottites, and of >100 Ma after Solar System formation for the enriched shergottites (Debaille et al., 2007). Of note, the 30 Ma model age for the depleted shergottites would be consistent with the timescale of Mars' differentiation inferred above using combined ^{142}Nd-^{182}W systematics (Section 4.2). However, in this case enriched and depleted shergottites would not define a single isochron, that is, their sources would not have formed contemporaneously.

In the second approach, *several* rock samples are combined to calculate a single age from a combined ^{142}Nd-^{143}Nd isochron. Based on this approach, the shergottites define a ^{142}Nd-^{143}Nd age of 63±6 Ma after Solar System formation (Borg et al., 2016). An important underlying assumption of the ^{142}Nd-^{143}Nd isochron method is that the enriched and depleted shergottites derive from two complementary and co-genetic sources that had formed contemporaneously and subsequently underwent binary mixing. Supporting evidence for this assumption comes from the geochemical characteristics of the shergottite sources, which are consistent with derivation from a common reservoir (Borg et al., 2003; Borg and Draper, 2003; Elkins-Tanton et al., 2003). However, the results of the present study demonstrate that shergottites do not plot on a single mixing array in ^{142}Nd *vs.* ^{182}W space (Fig. 3), precluding that the shergottites derive from mantle sources that formed concurrently and subsequently mixed. Instead, the ^{182}W-^{142}Nd systematics of the shergottites require a more protracted interval of source formation between ~20-25 and ~40 Ma after Solar System formation (Fig. 3). A corollary of this is that the ^{142}Nd-^{143}Nd correlation is not an isochron, but instead a mixing line between sources that likely did not form contemporaneously.

Further support for this protracted interval of source formation comes from the ^{182}W-^{142}Nd systematics of NWA 7034 and ALH 84001. As is evident from their less radiogenic ^{182}W and ^{142}Nd compositions (Fig. 3,4), both ALH 84001 and NWA 7034 derive from sources that were either more strongly enriched or formed earlier than the source of the enriched shergottites. Moreover, the ALH 84001 and NWA 7034 sources formed at different times (Fig. 3), demonstrating there is no single enriched component in Mars. As such, the enriched shergottite source may neither be directly related to the residual liquid of a magma ocean, nor to a single enriched component formed at a well-defined point in time during Mars' primordial differentiation. Figure 3 shows that the W and Nd isotopic composition of the enriched shergottites may instead reflect a mixture of depleted and enriched components formed between ~25 and ~40 Ma after Solar System formation. This implies that the isotopic composition of the enriched shergottites themselves does not provide direct information on the timing of Mars' early differentiation.

4.4 Nucleosynthetic Nd isotope anomaly in martian meteorites

A further complication in the chronological interpretation of ^{142}Nd data is the potential presence of nucleosynthetic Nd isotope variations. Such variations have recently been demonstrated to exist at the bulk planetary scale, leading for instance to different ^{142}Nd compositions of chondrites and the Earth's mantle (Burkhardt et al., 2016). It is currently unknown, however, to what extent Mars exhibits a nucleosynthetic Nd isotope anomaly. Of note, several of the martian samples analysed in this study and in Borg et al. (2016) exhibit small excesses in ^{145}Nd, ^{148}Nd, and ^{150}Nd (Fig. S1; Table S3). However, for individual data points, these apparent excesses are not resolved from the terrestrial standard when taking into account the external reproducibility of the Nd isotope analyses (Section S5). Nevertheless, given that Mars is a differentiated planetary body, any nucleosynthetic isotope signature should be homogeneously distributed within the planet. Thus, in case of Mars, we can pool the non-radiogenic Nd isotope data for individual martian meteorites together to obtain a mean composition for Mars. This approach results in weighted mean values for Mars of ^{148}Nd = +0.05±0.02 and ^{150}Nd = +0.14±0.10, ^{145}Nd = +0.02±0.03 (95% conf., N=16). The relative magnitude of these variations is generally consistent with those predicted for nucleosynthetic Nd isotope heterogeneity (Fig. 6; see also Burkhardt et al., 2016). As a result, the Nd isotope composition of Mars may be intermediate between those of enstatite and ordinary chondrites (Fig. 6), consistent with evidence from O and Cr isotopes (Trinquier et al., 2007).

The potential presence of nucleosynthetic Nd isotope anomalies in Mars complicates the chronological interpretation of the ^{142}Nd-^{143}Nd systematics. Although the ^{142}Nd-^{143}Nd isochron method does not directly depend on an assumed bulk composition of Mars, the assumption of contemporaneous source formation requires that bulk Mars plots on the ^{142}Nd-^{143}Nd isochron defined by the shergottites (Fig. 7a). By contrast, if Mars had a Nd isotope composition that is intermediate between the compositions of enstatite and ordinary chondrites (as inferred above), then the ^{142}Nd composition of bulk Mars would be between *ca.* –0.10 (enstatite chondrites) and *ca.* –0.18 (ordinary chondrites) (Burkhardt et al., 2016). This inferred bulk composition only marginally overlaps with the bulk Mars ^{142}Nd composition of –0.06±0.07 as inferred from intersection of the ^{142}Nd-^{143}Nd shergottite array with the chondritic ^{147}Sm/^{144}Nd ratio (Borg et al. 2016). In this case, the different groups of shergottites would not define a single isochron in ^{142}Nd *vs.* ^{143}Nd space, but instead be derived from sources that formed at slightly different times (Fig. 7b). Of note, Debaille et al. (2007) assumed an ordinary chondrite-like ^{142}Nd and with this assumption derived an ~30 Ma age for the formation of the depleted shergottite source, consistent with the timescale determined in the present study based on combined ^{182}W-^{142}Nd systematics. Thus, a nucleosynthetic Nd isotope anomaly for Mars provides an alternative way of reconciling the Sm-Nd data of shergottites with the early silicate differentiation of Mars required by the large ^{182}W variations among shergottites. Clearly, fully assessing the extent of nucleosynthetic Nd isotope anomalies in martian meteorites, and their bearing on Sm-Nd chronology, will be an important future task for applying ^{142}Nd-^{143}Nd systematics to date the early differentiation of Mars.

5 Conclusions

Large ^{182}W variations among martian meteorites require silicate differentiation on Mars within 20–40 million years after Solar System formation and, hence, earlier than previously inferred based on ^{146}Sm-^{142}Nd systematics of shergottites alone. The ^{182}W and ^{142}Nd compositions of ALH 84001 and NWA 7034 are the least radiogenic compositions yet reported for martian rocks, indicating that these samples derive from the most strongly enriched sources known from Mars. The combined ^{182}W-^{142}Nd systematics are inconsistent with a single differentiation event and provide evidence that the initial magma ocean crystallisation was followed by re-melting and crust formation, perhaps triggered by cumulate overturn in the martian mantle. As such the ^{182}W-^{142}Nd data indicate magma ocean crystallisation on Mars within 20–25 Ma, followed by on-going crust formation until at least ~40 Ma after Solar System formation (Fig. 5). These timescales are consistent with Xe isotopic evidence for large-scale degassing at ~35 Ma after Solar System formation. Thus, collectively these data demonstrate that Mars underwent a major episode of mantle differentiation, crust formation and atmosphere degassing between ~20 and ~40 Ma after Solar System formation.

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Tables and Figures

Table 1

Tungsten and Nd isotope data for martian meteorites.

Sample	*N*	$\varepsilon^{182}W$ (±2σ)		$\varepsilon^{142}Nd$ (±2σ)	
Enriched shergottites					
Zagami	3	0.35	±0.10	ND	
RBT 04262	2	0.42	±0.10	ND	
NWA 4864	1	0.35	±0.10	-0.19	±0.06
LAR 12011	2	0.33	±0.10	-0.13	±0.06
NWA 4468 *	3	0.40	±0.10	-0.17	±0.06
Mean (±95% conf., n=5)		0.37	±0.05	-0.16	±0.08
Intermediate shergottites					
EETA 79001B *	2	0.29	±0.10	0.23	±0.06
ALH 77005 *	1	0.51	±0.12	0.16	±0.07
NWA 7042	2	0.37	±0.10	0.03	±0.06
Depleted shergottites					
SaU 005 *	1	0.83	±0.10	0.57	±0.06
LAR 12095	1	0.90	±0.16	ND	
DaG 476 *	1	0.91	±0.10	0.65	±0.06
Tissint	1	1.48	±0.10	0.72	±0.06
NWA 7635 §	1	1.80	±0.13	0.92	±0.08
Orthopyroxenite					
ALH 84001	1	0.09	±0.10		
ALH 84001 *(replicate)*	1	0.08	±0.10		
ALH 84001 (Mean)		0.09	±0.10	-0.29	±0.06
Polymict breccia					
NWA 7034 (±95% conf.)	5	0.20	±0.05	-0.45	±0.06
Augite basalt					
NWA 8159	1	1.13	±0.10	0.77	±0.06

^{182}W data analysed by MC-ICPMS and ^{142}Nd data by TIMS (See Supplementary Material). N, number of W isotope measurements of each sample; ND, not determined. ^{182}W internally normalised to $^{186}W/^{184}W = 0.92767$, and ^{142}Nd to $^{146}Nd/^{144}Nd = 0.7219$. Uncertainties on ^{182}W and ^{142}Nd represent the external reproducibility (2s.d.) estimated from rock standard analyses from this study (Table S1), or the two-standard error (2s.e.) obtained from internal run statistics, whichever is larger. * ^{142}Nd data from Borg et al. (2016), in case of EETA 79001, determined on lithology A. § ^{142}Nd data from Lapen et al. (2017).

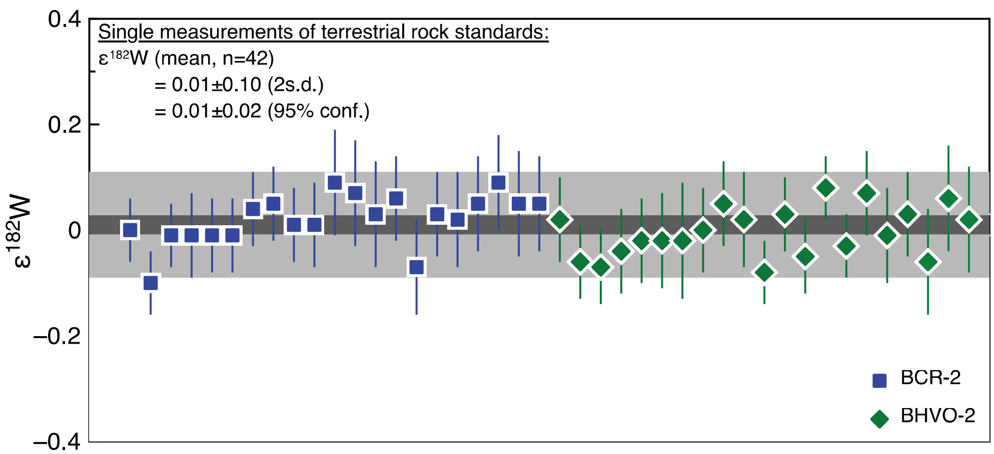

Fig. 1: ^{182}W data for the silicate rock standards analyzed in this study. Each data point represents a single W isotope measurement of a standard that was processed through the full chemical separation and error bars denote internal errors (2s.e.). The external uncertainty (2 s.d.), as inferred from replicate standard analyses, is shown as a light grey filled bar, and the corresponding 95% confidence interval as a dark grey bar.

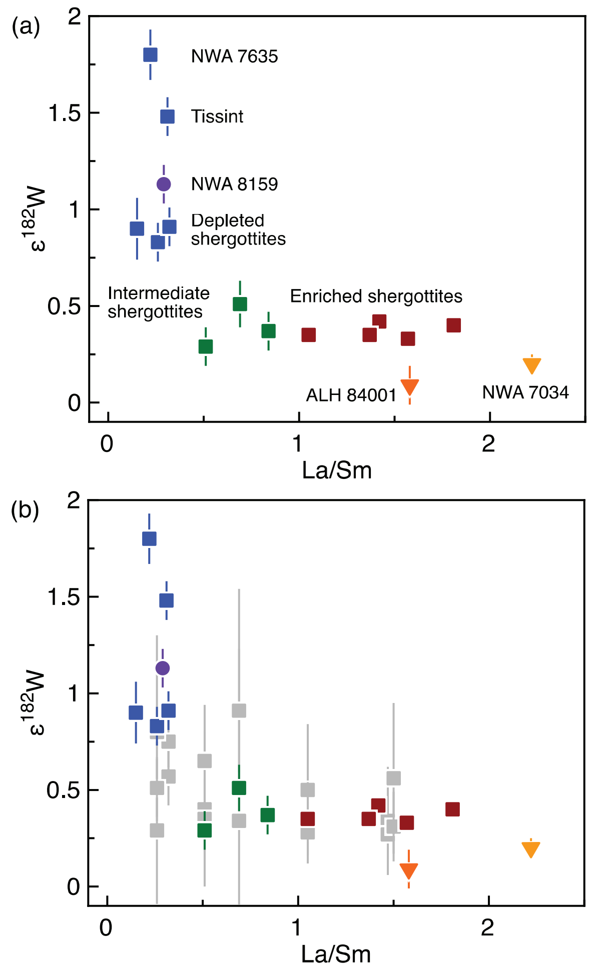

Fig. 2: ^{182}W data of martian meteorites plotted *vs.* La/Sm as an index for enrichment. (a) samples analysed in this study, and (b) data shown in comparison to literature ^{182}W data (light grey squares; Lee and Halliday, 1997; Kleine et al., 2004; Foley et al., 2005). Error bars indicate external uncertainties (2 , see Table S2 and Supplementary Material). Data sources for La/Sm ratios: The martian meteorite compendium (and references therein), Humayun et al. (2013), and Lapen et al. (2017).

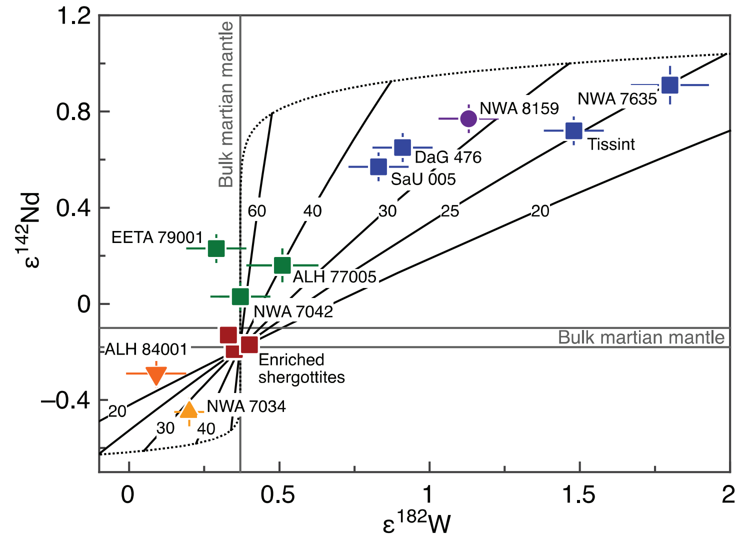

Fig. 3: Coupled ^{182}W *vs.* ^{142}Nd systematics of martian meteorites. The coupled ^{182}W– ^{142}Nd data are shown together with model results for magma ocean crystallisation (see Supplementary aterial). Dotted line shows ^{182}W– ^{142}Nd composition of the enriched (*lower left quadrant*) and the depleted mantle end member (*upper right quadrant*) after magma ocean crystallisation of a primordial mantle. Solid curved lines represent mixing lines between end member sources formed at different times after Solar System formation (*i.e.*, at 20, 25, 30, 40 and 60 Ma). Grey horizontal and vertical lines show the ^{182}W and ^{142}Nd compositions of the bulk martian mantle as inferred in this study. Existing data for nakhlites are not plotted because their source(s) had a more complex history, involving more than two stages of evolution (Righter and Shearer, 2003; Kleine et al., 2004; Foley et al., 2005; Debaille et al., 2009). As a consequence, no meaningful age information can be deduced for the nakhlites using the two-stage model illustrated here. Note that one sample (EETA 79001) plots outside the field of possible differentiation ages, either reflecting that ^{182}W and ^{142}Nd were not determined on the same lithologies, or that crustal contamination modified ^{182}W and ^{142}Nd to different degrees (Andreasen et al., 2015).

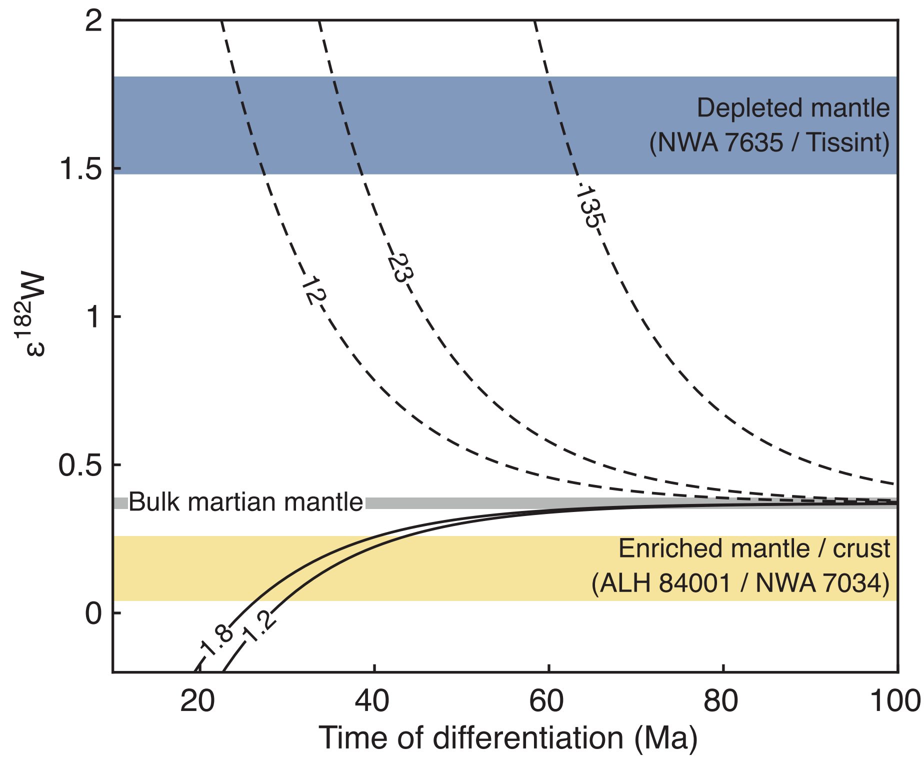

Fig. 4: Timescales of martian mantle differentiation inferred from Hf-W systematics. Shaded areas denote the range in ^{182}W measured for martian meteorites from enriched (ALH 84001, NWA 7034) and the most depleted mantle sources (NWA 7635, Tissint). Model curves show the possible range in ^{182}W of enriched (*solid lines*) and depleted (*dashed lines*) mantle sources produced by magma ocean crystallisation as a function of differentiation time. These model ^{182}W compositions were calculated using the range in Hf/W obtained for enriched (^{180}Hf/^{184}W = 1.2-1.8) and depleted (^{180}Hf/^{184}W = 12-23) end member sources from the magma ocean model (see Supplementary Material). The ^{182}W composition of the bulk martian mantle (*grey shaded bar*) is shown for reference.

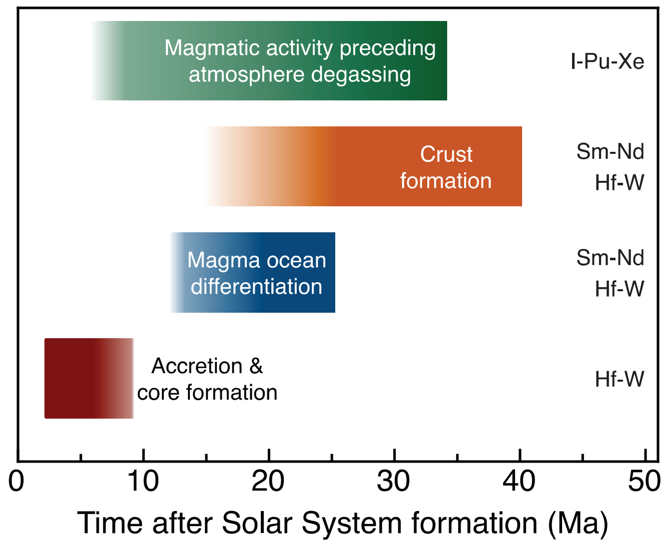

Fig. 5: Chronology for the early differentiation of Mars. Shown are the timing of accretion and core formation as inferred using Hf-W chronometry (Dauphas and Pourmand, 2011; Kleine et al., 2004; Nimmo and Kleine, 2007), the new estimates for the timescales of magma ocean differentiation and crust formation from this study, and the timing of magmatic activity as required to explain the I-Pu-Xe systematics of martian meteorites (Marty and Marti, 2002).

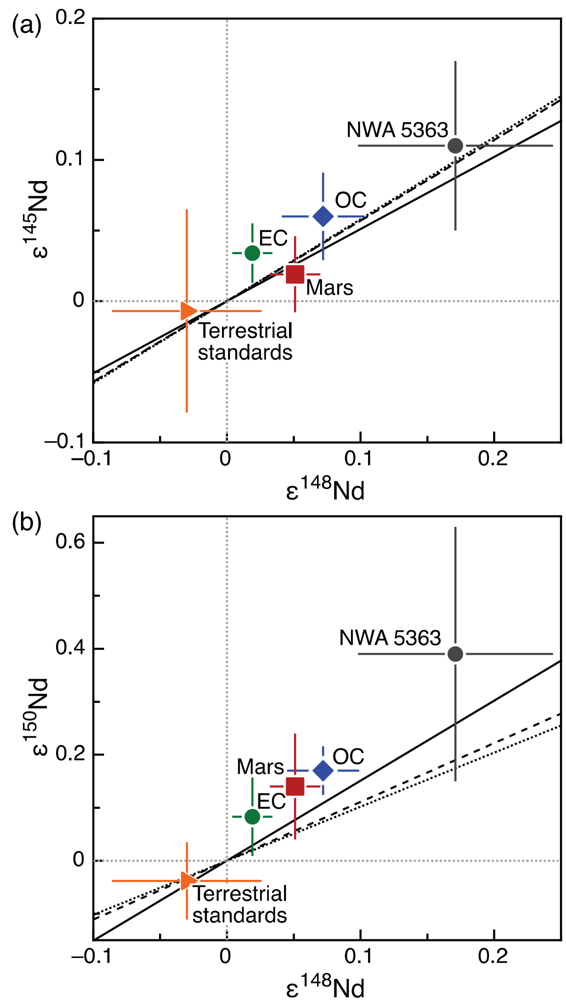

Fig. 6: Non-radiogenic Nd isotope compositions of meteorites**.** (a) ^{145}Nd *vs.* ^{148}Nd and (b) ^{150}Nd *vs.* ^{148}Nd. The data point for Mars represents the mean value obtained for martian meteorites from this study and from (Borg et al., 2016), while data for ordinary chondrites, enstatite chondrites and NWA 5363 are from Burkhardt et al. (2016). Also shown are mixing lines between *s*-process Nd and terrestrial Nd, as described in Burkhardt et al. (2016).

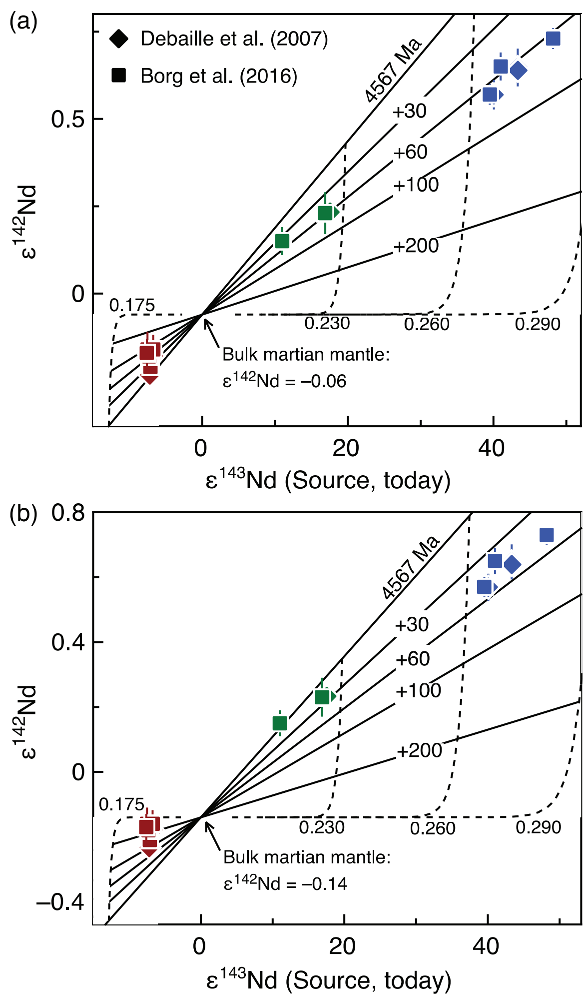

Fig. 7: ^{142}Nd– ^{143}Nd isochron diagram used to determine the age of shergottite source regions. Measured ^{142}Nd of shergotttites *(solid symbols*) are plotted *vs.* the ^{143}Nd of the present-day sources, calculated using the initial ^{143}Nd/^{144}Nd of each meteorite, and the approach described in Borg et al. (2016). Solid lines show model isochrons for source formation at 30, 60, 100, and 200 Ma after CAI formation. The model isochrons were calculated using two different ^{142}Nd values for the bulk martian mantle: (a) using ^{142}Nd of –0.06±0.07 (Borg et al. (2016), in the case that Mars has no nucleosynthetic Nd isotope anomaly relative to the Earth, and in (b) using ^{142}Nd of ~–0.14, in the case that Mars has a nucleosynthetic Nd isotope anomaly between that of enstatite and ordinary chondrites (see main text). Vertical dotted lines show the Nd isotope evolution for different source ^{147}Sm/^{144}Nd (0.175, 0.23, 0.26, and 0.29). Neodymium isotope data of shergottites are from Debaille et al. (2007) and Borg et al. (2016).