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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 crystallization 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 crystallization 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.

1. Introduction

The early evolution of Mars probably involved large-scale melting and core formation, followed by magma ocean crystallization and crust formation (e.g. Elkins-Tanton, 2005; Mezger et al., 2013). The timescales of these processes can be quantified through 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 crystallization products of a magma ocean (Borg et al., 1997; Borg and Draper, 2003; Elkins-Tanton, 2005, 2008), 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

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(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 crystallization 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 crystallization, 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., 2010, 2017; 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 analyzed 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., 2014, 2015) 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 >0.5 g 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., 2014, 2015). Total procedural yields were ∼75–100%, and to-

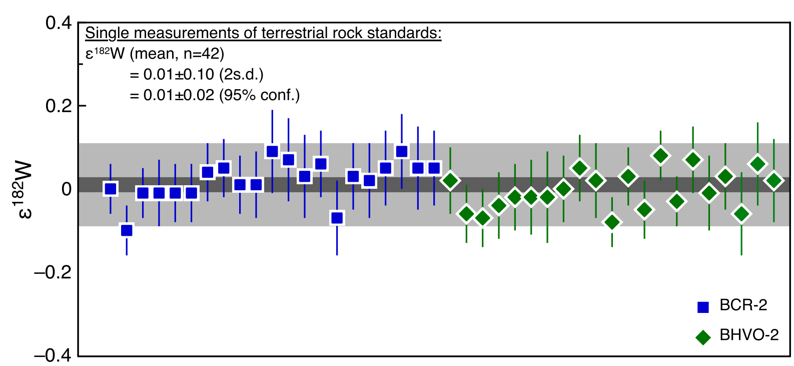

Fig. 1. ε^{182}W data for the silicate rock standards analyzed in this study. Each data point represents a single W isotope measurement of a standard that was processed through the full chemical separation and error bars denote internal errors (2 s.e.). The external uncertainty (2 s.d.), as inferred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

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