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Accretion Timescale and Impact History of Mars Deduced from the Isotopic Systematics of Martian Meteorites

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Abstract

High precision Sm−Nd isotopic analyses have been completed on a suite of 11 martian basaltic meteorites in order to better constrain the age of silicate differentiation of Mars and to evaluate the merits and disadvantages of various mathematical approaches that have been employed in previous work on this topic. Ages determined from the Sm−Nd isotopic systematics of individual samples are strongly dependent on the assumed Nd isotopic composition of the bulk planet. This assumption is problematic given differences observed between the Nd isotopic composition of Earth and chondritic meteorites and the fact that these materials are both commonly used to represent bulk planetary Nd isotopic compositions. Ages determined from ^{146}Sm–^{142}Nd whole rock isochrons are not dependent on the assumed ^{142}Nd/^{144}Nd ratio of the planet, but require the sample suite to be derived from complementary, contemporaneously-formed source regions. In this work we present a mathematical expression that defines the age of silicate differentiation based on the twin Sm−Nd decay chains that is independent of any *a priori* assumptions regarding the bulk isotopic composition of the planet. This expression is also applicable to mineral isochrons and has been used to successfully calculate ^{143}Nd–^{142}Nd model crystallization ages of early refractory solids as well as lunar samples. This permits ages to be obtained using only Nd isotopic measurements without the need for ^{147}Sm/^{144}Nd isotope dilution determinations. When used in conjunction with high-precision Nd isotopic measurements completed on martian meteorites this expression yields an age of differentiation of the martian basaltic meteorite source regions of 4504 ± 6 Ma. Because the Sm−Nd model ages for the formation of martian source regions are commonly interpreted to record the age of planetary differentiation associated with magma ocean solidification, the young age determined here implies that magma ocean solidification occurred late in the history of the Solar System. Recent thermal models, however, suggest that Mars-sized bodies cool rapidly in less than ~5 Ma after accretion ceases, even in the presence of a thick atmosphere. An extended period of accretion may therefore be necessary to provide a mechanism to keep portions of the martian mantle partially molten until 4504 Ma. Late accretional heating of Mars could either be associated with protracted accretion occurring at a quasi-steady state or alternatively be associated with a late giant impact. If this scenario is correct, then accretion of Mars-sized bodies takes up to 60 Ma and is likely to be contemporaneous with the core formation and possibly the onset of silicate differentiation. This further challenges the concept that isotopic equilibrium is attained during primordial evolution of planets, and may help to account for geochemical evidence implying addition of material into planetary interiors after core formation was completed.

1. INTRODUCTION

The planetesimal hypothesis is the favored model for explaining how terrestrial planets formed from the dust and gas that was present in the protoplanetary disk during the birth of our Solar System. This hypothesis describes how dust grains migrating toward the midplane of the disk accrete to form progressively larger planetesimals. Gravitational interactions between planetesimals produce a modest number of relatively large, Mars-sized, planetary embryos, which in turn randomly collide to form the terrestrial planets (Chambers, 2004). Accretion introduces significant quantities of heat into the newly forming terrestrial planets, resulting in broad scale melting and subsequent cooling. Elemental fractionation associated with melting and cooling are thought to produce mineralogically and chemically distinct reservoirs in the core, mantle, and crust resulting in primordial differentiation of the planet. Whereas isotopic dating of the earliest Solar System solids indicates that this process began at 4567 Ma (Amelin et al., 2010; Connelly et al., 2012), its duration is poorly defined.

The timescale of planetary differentiation is constrained by the systematics of daughter isotopes produced by short-lived radionuclide decay observed in planetary samples. Samples from the planet Mars are ideal for this purpose because they demonstrate obvious anomalies in several isotope systems, such as ^{182}Hf–^{182}W and ^{146}Sm–^{142}Nd. The suite of martian meteorites is comprised mostly of basalts, basaltic cumulates, and ultramafic rocks that have large systematic variations in trace element and isotopic compositions. The basaltic meteorites (shergottites) are the focus of this investigation. The inferred incompatible-element characteristics of the shergottite source regions have been identified and used as a basis to divide the shergottites into subgroups called “enriched”, “depleted”, and “intermediate” (Borg et al., 2003; Debaille et al., 2007; Symes et al., 2008). The initial Sr, Nd, and Hf isotopic systematics of the shergottites define mixing lines between incompatible-element enriched and incompatible-element depleted geochemical end-members (Borg et al., 2003; Borg and Draper, 2003) underscoring the close petrogenetic affinity between the shergottites. The second class of martian meteorites relevant to this investigation is the nakhlites. These meteorites are clinopyroxene cumulates with petrologic and geochemical characteristics that are nearly identical to one another. The nakhlites have ^{182}W isotopic compositions that are significantly more radiogenic than the shergottites (e.g., Foley et al., 2005), demonstrating that they are derived from a fundamentally different mantle source region than the shergottites.

Geochemical modeling of the shergottite source regions suggests that they could have formed as a result of solidification of a martian magma ocean (Blichert-Toft et al., 1999; Borg et al., 1997; 2003; Borg and Draper, 2003; Elkins-Tanton, 2003), although formation through interaction of mantle and crustal reservoirs has also been proposed (Borg et al., 1997; Herd et al., 2002). The age of this silicate differentiation event is best determined using the ^{146}Sm–^{142}Nd system of the shergottites due to the relatively short half-life of ^{146}Sm and the fact that Sm and Nd are both refractory lithophile elements. Ages derived from the ^{146}Sm–^{142}Nd system are based on one of two assumptions. The most precise ages are three-stage Nd evolution model ages for individual samples that assume ^{147}Sm/^{144}Nd and ^{142}Nd/^{144}Nd values for bulk Mars (Harper et al., 1995; Borg et al., 1997; Debaille et al., 2007). The ^{142}Nd/^{144}Nd value for bulk Mars was originally assumed to be represented by terrestrial rocks, but most recently has been assumed to be the average value measured for chondritic meteorites. Ages for individual samples are strongly dependent on the assumed ^{142}Nd/^{144}Nd ratio of bulk Mars, however, and vary by ~50 Ma depending on whether chondritic or terrestrial values are used in the calculation. This led to the development of whole rock isochron age determinations of martian differentiation based on the range of Sm−Nd isotopic compositions displayed by the shergottite meteorite suite. These ages are predicated on the hypothesis that the isotopic variability of the martian meteorite suite reflects mixing between complementary, contemporaneously-formed, isotopic reservoirs (Shih et al., 1982; Borg et al., 2003; Foley et al., 2005; Caro et al., 2008). However, previous ages determined using this approach are more imprecise than ages determined on individual samples. This is a reflection of the fact that uncertainty associated with ages defined by a suite of samples includes contributions from both analytical measurement and from scatter exhibited by the sample suite, whereas ages defined by single samples incorporate uncertainty associated only with individual measurements. The most accurate previous estimate of silicate differentiation is probably represented by the average of the published ages reported by (Borg et al., 1997; 2003; Foley et al., 2005; Debaille et al., 2007; Caro et al., 2008) which is 4530 ± 27 Ma (uncertainty defined by 2 standard deviations).

Tungsten isotopic measurements completed on the martian meteorites have been used to calculate model ages for Hf/W fractionation that was originally thought to be associated with core formation on Mars. These models are strongly dependent on the assumed Hf/W ratio for bulk Mars. Furthermore, more recent investigations note that silicate differentiation has the potential to fractionate Hf from W, whereas late accretion can modify ^{182}W through the addition of isotopically distinct W (e.g. Mezger et al., 2013). Thus, mechanisms to account for the difference between the ^{182}W isotopic compositions of shergottites ($\varepsilon^{182}W = \sim 0.65$) and nakhlites ($\varepsilon^{182}W = \sim 3.0$) are not well understood, leading Halliday and Kleine (2006) to suggest that caution should be used when interpreting W ages calculated from martian meteorite data. Nevertheless, evidence for fractionation of Hf from W in martian meteorites is irrefutable and this system still provides the best constraint for the timing of martian core formation. Numerous ages of core formation have been calculated based on a range of model parameters. The most conservative estimate of the age of martian core formation is probably the average of these ages which is 4559 ± 8 Ma (average ± 2 standard deviations of ages reported by Kleine et al., 2004; 2009; Foley et al., 2005; Halliday and Kleine, 2006; Nimmo and Kleine, 2007; Dauphas and Pourmand, 2011). This calculated Hf−W age of core formation is within uncertainty of the average Sm−Nd age of silicate differentiation of 4530 ± 27 Ma inferred from the shergottites indicating that the duration of martian differentiation could have been as short as 10 Ma or as long as 64 Ma after formation of the first Solar System solids. A short time interval between core formation and silicate differentiation would imply the martian core and mantle formed more or less simultaneously, whereas a long time interval would imply that the planet had a more protracted accretion and differentiation history. In order to more accurately define the duration of planetary accretion and differentiation on Mars, we have completed high-precision Sm−Nd isotopic measurements on a suite of shergottites and used these as a basis to rigorously evaluate and further develop various approaches to constrain the differentiation age of the shergottite source regions.

2. METHODS

High precision $^{147}Sm/^{144}Nd–^{143}Nd/^{144}Nd–^{142}Nd/^{144}Nd$ and $^{87}Rb/^{86}Sr–^{87}Sr/^{86}Sr$ isotopic measurements have been completed on 10 shergottites exhibiting trace element characteristics indicative of derivation from the observed range of enriched and depleted source regions. The high precision measurements were completed on 5 shergottites with enriched source regions (Los Angeles, NWA1068, Dho378, NWA4468, and NWA4878), 3 with depleted source regions (Tissint, DaG476, and SaU005) and 2 of intermediate composition (EET79001A and NWA480). An additional relatively small aliquot of the depleted shergottite Dhofar 019 has been analyzed for $^{147}Sm/^{144}Nd–^{143}Nd/^{144}Nd$ and $^{87}Rb/^{86}Sr–^{87}Sr/^{86}Sr$ only. Fractions of these samples were dissolved after washing in water and 0.1M acetic acid in a Class 100 laboratory at Lawrence Livermore National Laboratory (LLNL). Small fractions were spiked using mixed $^{149}Sm–^{150}Nd$ tracer and $^{87}Rb–^{84}Sr$ tracers to obtain whole rock $^{147}Sm/^{144}Nd$ and $^{87}Rb/^{86}Sr$ values. These concentration data are presented in Table 1.

Both spiked and unspiked samples were purified using a combination of ion-exchange chromatographic procedures. Rubidium, strontium, and rare earth elements (REE) were purified using 2N HCl, 2N HNO_3, and 6N HCl acids and AG 50W-X8 200-400 mesh resin in quartz columns. Strontium was further purified using Sr-Spec resin in 100 µL Teflon columns with 1 N HNO_3 and H_2O. The Sm and Nd were separated in pressurized quartz columns using 0.2M alpha-hydroxyisobutyric acid buffered to pH = 4.4 and AG 50W-X8 200-400 mesh resin converted to NH_4 form. Unspiked Nd fractions analyzed for $^{142}Nd/^{144}Nd$ ratios were put through this procedure twice to remove Ce. Total procedural blanks including digestions were Rb = 9 pg, Sr = 21 pg, Sm = 8 pg and Nd = 22 pg.

Isotopic analyses were obtained using a ThermoScientific Triton thermal ionization mass spectrometer at LLNL. Neodymium and samarium were loaded in 2N HCl onto zone refined Re double filaments. High precision $^{142}Nd/^{144}Nd$ ratios were obtained through multi-dynamic analyses at high intensity (up to 4.9×10^{-11} amperes ^{144}Nd) and long duration (up to 13.5 hours) on the unspiked Nd fractions. Neodymium was corrected for instrumental mass fractionation using $^{146}Nd/^{144}Nd = 0.7219$. Isobaric interferences on Nd were monitored using ^{140}Ce and ^{149}Sm. Cerium corrections ranged from 0 to 3.6 ppm, whereas Sm interference corrections were less than 2 ppm. Average values determined on Nd and Sm isotopic standards are presented in Table 2. Replicate $^{142}Nd/^{144}Nd$ analyses completed on shergottites and terrestrial standards during the course of this investigation agreed within 3 ppm. The maximum difference between four samples analyzed by both Debaille et al. (2007) and in this investigation was also 3 ppm. Neodymium isotope dilution measurements were completed using static acquisition in which 200 eight-second integrations were collected. The isotopic composition of Sm was obtained from unspiked fractions of the samples using a static acquisition routine consisting of 200 eight-second integrations. The intensity of these runs ranged from 1.0 to 1.8×10^{-11} amperes of ^{149}Sm. Samarium was corrected for mass fractionation assuming $^{147}Sm/^{152}Sm = 0.56081$. Isobaric interferences for Sm were monitored using ^{155}Gd and ^{146}Nd and were less than 2 ppm for all but two samples. The Sm isotopic data obtained during this investigation is presented in Table 3.

Rubidium was loaded on single zone refined Re filaments in 2N HCl with a 99.999% pure Ta_2O_5 emitter suspended in 0.5M H_3PO_4. Fractionation was corrected using runs of NBS-984 completed during the course of the investigation. Strontium was also loaded on single zone refined Re filaments in 2N HCl with the Ta_2O_5 emitter and run at 3 to 6 x 10^{-11} amps ^{88}Sr for 200 ratios of 16 second integrations. Fractionation was corrected assuming $^{86}Sr/^{88}Sr = 0.1194$. Although ^{85}Rb was monitored during the analyses, it was not detected during Sr measurements. Strontium isotopic compositions of samples and standards completed during the course of this investigation are presented in Table 2.

3. RESULTS

3.1. Samarium isotopic compositions

The Sm isotopic composition of the shergottites was determined in order to assess if they have been modified by the capture of thermal neutrons on the martian surface (Table 3). This phenomenon is well known on the Moon where galactic cosmic rays produce thermal neutrons that are captured by isotopes, such as ^{149}Sm, that have exceedingly large neutron capture cross sections (Russ, 1972). Such modification of the ^{149}Sm abundance of a sample will affect the $^{147}Sm/^{144}Nd$ ratio if undetected. An excessively large thermal neutron fluence, such as is observed on the Moon, can even affect $^{142}Nd/^{144}Nd$ ratios of the samples (Nyquist et al., 1995). Our data indicate, however, that the Sm isotopic compositions of the shergottites are within analytical uncertainty of values obtained on terrestrial rock and isotopic standards. The slight excesses reported in ^{150}Sm determined for Los Angeles and Tissint are most likely caused by isobaric interferences from ^{150}Nd in these samples ($^{146}Nd/^{152}Sm$ up to 0.0016) because these samples demonstrate no evidence for corresponding deficits in ^{149}Sm. Thus, the ^{149}Sm data suggest that levels of thermal neutron radiation have been low near the martian surface over the past ~600 Ma so that $^{147}Sm/^{144}Nd$ and $^{142}Nd/^{144}Nd$ ratios determined on the shergottites require no corrections.

3.2 Neodymium and strontium isotopic compositions

The $^{87}Rb/^{86}Sr$ and $^{147}Sm/^{144}Nd$ ratios of the shergottites have been determined using the isotope dilution technique and are presented in Table 1, whereas the $^{87}Sr/^{86}Sr$, $^{143}Nd/^{144}Nd$, and $^{142}Nd/^{144}Nd$ isotopic compositions of the shergottites are presented in Table 2. The isotopic compositions of terrestrial rock and mass spectrometry standards are also presented in Table 2. In general, the shergottite data is similar to that previously reported for similar martian meteorites (see summary in Nyquist et al., 2001; as well as Borg et al., 2003; Foley et al., 2005;

Debaille et al., 2007; Caro et al., 2008). The $^{87}Rb/^{86}Sr$ ratios determined for the suite of shergottites is highly variable ranging from 0.006 to 0.35. Although the range of $^{87}Rb/^{86}Sr$ generally correlates with shergottite subgroup (depleted, intermediate, enriched) there is some overlap. The $^{147}Sm/^{144}Nd$ ratios measured for this suite of shergottites is also typical ranging from 0.23 to 0.51 and mostly correlating with shergottite subgroup. The depleted subgroup, however, demonstrates a large range of $^{147}Sm/^{144}Nd$ ratios from 0.38 to 0.51 overlapping the range defined by the intermediate group. As expected the Sr and Nd isotopic compositions correlate well with the shergottite subgroup because they are used to define the subgroups. The depleted shergottites have $^{87}Sr/^{86}Sr$ = 0.701−0.708, $^{143}Nd/^{144}Nd$ = 0.5151−0.5155, and $^{142}Nd/^{144}Nd$ = 1.141911−1.141920 ($\varepsilon^{142}Nd$ = +0.57 to +0.72). The intermediate shergottites have $^{87}Sr/^{86}Sr$ = 0.710−0.713, $^{143}Nd/^{144}Nd$ = 0.5134−0.5137, and $^{142}Nd/^{144}Nd$ = 1.141854−1.141863 ($\boldsymbol{\varepsilon}^{142}Nd$ = +0.15 to +0.23). The isotopic composition of the enriched shergottites are remarkably consistent with $^{87}Sr/^{86}Sr$ = 0.718−0.723, $^{143}Nd/^{144}Nd$ = 0.51231-0.51235, and $^{142}Nd/^{144}Nd$ = 1.141813-1.141819 ($\varepsilon^{142}Nd$ = −0.21 to −0.16). The Rb−Sr isotopic systematics of the shergottites analyzed in this study are quite variable reflecting both compositional differences inherited from their source regions and addition of terrestrial Sr during weathering in the desert localities where many of these samples were found. The desert meteorites display Sm−Nd isotopic systematics that are essentially identical to those determined from non-desert meteorites indicating that the Sm−Nd isotopic system has not been affected by weathering.

4. MODEL AGE CALCULATIONS

4.2. Samarium−neodymium ages

4.2.1 $^{147}Sm/^{144}Nd$ of basalt source regions

The Sm−Nd isotopic system provides a powerful tool with which to constrain the timing of silicate differentiation. This stems from the fact that it is comprised of two decay chains. The first is $^{147}Sm \rightarrow {}^{143}Nd$ with a half-life of 106 Ga. This decay chain provides a record of the long-term, time-integrated, elemental fractionation of Sm/Nd that occurred over the entire history of the planet beginning at 4567 Ma until the present. This system is therefore ideal to estimate the average $^{147}Sm/^{144}Nd$ ratio of individual meteorite source regions. The second decay chain is $^{146}Sm \rightarrow {}^{142}Nd$. Although the half-life for this system was recently determined to be 68 Ma (Kinoshita et al., 2012), the traditional half-life of 103 ± 5 Ma (Friedman et al., 1966; Meissner et al., 1987) appears to best reproduce the absolute ages of most planetary samples (Borg et al., 2014; Marks et al., 2014a). Therefore, the 103 Ma half-life is used in the calculations presented here. The relatively short half-life of ^{146}Sm allows this decay chain to record the timing of geologic processes that fractionated Sm from Nd in the earliest stages of planetary history. When both Sm−Nd decay chains are used together in an iterative fashion, they can define the $^{147}Sm/^{144}Nd$, $^{143}Nd/^{144}Nd$, and $^{142}Nd/^{144}Nd$ ratios of planetary-scale source regions and the age of differentiation of these sources.

There are three ways to calculate Sm–Nd model ages for the formation of the shergottite source region using the measured Sm–Nd isotopic compositions of bulk samples. These model age calculations are discussed separately below in the following sections. All three approaches used to determine the age of differentiation require the present-day $^{147}Sm/^{144}Nd$ ratio of the shergottite source regions to be known. This can be estimated in two ways. In the first, the $^{147}Sm/^{144}Nd$ ratio of the bulk rock is used as a proxy for the $^{147}Sm/^{144}Nd$ of the source region. This assumes that Sm is minimally fractionated from Nd during the partial melting event that produced the basaltic parental melts and that the accumulation of mineral phases in the basalts has not changed their Sm/Nd ratios. It has been demonstrated, however, that these assumptions may not be valid for Mars (Borg et al., 1997; 2003; Debaille et al., 2007; 2008). The $^{147}Sm/^{144}Nd$ ratios of the shergottites indicate that they are derived from more depleted source regions than is suggested by their $^{143}Nd/^{144}Nd$ ratios. For example, the $^{147}Sm/^{144}Nd$ ratios of the shergottites from the enriched subgroup are significantly higher (0.23-0.25) than the chondritic value of 0.1967, yet the meteorites have initial $\varepsilon^{143}Nd$ values that range from −6 to −8 (Tables 1-2). Estimating the $^{147}Sm/^{144}Nd$ of the shergottite source region from the bulk rock $^{147}Sm/^{144}Nd$ values is therefore unlikely to be accurate.

The second way to calculate the present-day $^{147}Sm/^{144}Nd$ ratio of basalt sources was published by Nyquist et al. (1995) and is presented in Equation 1. The equation uses the age, as well as the $^{147}Sm/^{144}Nd$ and $^{143}Nd/^{144}Nd$ ratios of the basalts, and assumes that the Nd isotopic systematics reflect growth in three stages of evolution (Figure 1). The first stage of growth occurs in an undifferentiated reservoir that is assumed to have present-day $^{147}Sm/^{144}Nd = 0.1967$ and $^{143}Nd/^{144}Nd = 0.512638$ (Jacobsen and Wasserburg, 1980). The second stage occurs in the differentiated reservoir that formed at T_1 (calculated below to be 4504 Ma) until the age of eruption (i.e., crystallization) of the samples. The final stage occurs in the rock itself until the present time. Table 4 presents a summary of variables used in the following equations.

(Eq. 1)

$$\left(\frac{^{147}Sm}{^{144}Nd}\right)^{S} = \frac{\left[\left(\frac{^{143}Nd}{^{144}Nd}\right)^{M3} - \left(\frac{^{143}Nd}{^{144}Nd}\right)^{SSI} - \left(\frac{^{147}Sm}{^{144}Nd}\right)^{Ch}\left(e^{\lambda^{147}T_0} - e^{\lambda^{147}T_1}\right) - \left(\frac{^{147}Sm}{^{144}Nd}\right)^{M1}\left(e^{\lambda^{147}T_2} - 1\right)\right]}{\left(e^{\lambda^{147}T_1} - e^{\lambda^{147}T_2}\right)}$$

The present-day $^{147}Sm/^{144}Nd$ ratio of the meteorite source regions is calculated assuming they evolved in three-stages of evolution and is therefore analogous to the models used determine the ages of the source regions below. The $^{147}Sm/^{144}Nd$ of the source, however, is also dependent on the age of differentiation. Thus, the $^{147}Sm/^{144}Nd$ of the source and the age of the source must be derived simultaneously (see equations 2, 3, 4b, and 4c below).

4.2.2. Three stage model age for individual samples

The simplest approach to determine the age of differentiation of the shergottite source regions is to calculate three-stage model ages on single samples using Equations 1 and 2. Note that Equation 2 is structurally identical to the equation used for other short-lived chronometers, such as Hf–W model ages (e.g., Kleine et al., 2009). Like many other model ages derived from short-lived isotopic systems, Equation 2 is referenced to the age of CAIs of 4567 Ma (Amelin et al., 2010; Connelly et al., 2012).

(Eq. 2)

$$Age\ of differentiation\ (T_1) = T_0 - \left(\frac{1}{\lambda^{146}}\right) ln \left\{ \left(\frac{^{146}Sm}{^{144}Sm}\right)^{SSI} \frac{\left(\frac{^{147}Sm}{^{144}Nd}\right)^{S}\left(\frac{^{144}Sm}{^{147}Sm}\right)^{Std} - \left(\frac{^{147}Sm}{^{144}Nd}\right)^{Ch}\left(\frac{^{144}Sm}{^{147}Sm}\right)^{Std}}{\left(\frac{^{142}Nd}{^{144}Nd}\right)^{M2} - \left(\frac{^{142}Nd}{^{144}Nd}\right)^{B}} \right\}$$

Ages calculated using Equation 2 must incorporate the Sm/Nd ratio of the shergottite source regions (expressed in equation 2 as $\left(\frac{^{147}Sm}{^{144}Nd}\right)^{S}$), and as well as an estimate of the Nd isotopic composition of the bulk planet (expressed as $\left(\frac{^{142}Nd}{^{144}Nd}\right)^{B}$). The advantage of the Sm–Nd system over other short-lived chronometers is that the Sm/Nd ratio of the shergottite source regions can be determined from $^{143}Nd/^{144}Nd$ isotopic measurements of the samples, rather than estimated from their bulk chemistry which is influenced by magma production (partial melting) and magma differentiation (crystallization and mineral accumulation) processes. Thus, the $\left(\frac{^{147}Sm}{^{144}Nd}\right)^{S}$ of the source used in Equation 2 is calculated from Equation 1. However, because calculation of the $\left(\frac{^{147}Sm}{^{144}Nd}\right)^{S}$ ratio requires the age of differentiation to be known, Equations 1 and 2 must be solved iteratively until they converge. This age calculation is therefore considered to be a three-stage model age despite the fact that the third stage of $^{142}Nd/^{144}Nd$ growth in the shergottites is ignored because of their young crystallization ages (Figure 1).

The model ages derived from Equation 2 are dependent on the $\left(\frac{^{142}Nd}{^{144}Nd}\right)^{B}$ ratio used in the expression. If Mars is assumed to have a chondritic $^{142}Nd/^{144}Nd$ value of 1.141813 (equivalent

ε^{142}Nd = -0.21 relative to our terrestrial standard value; e.g., Boyet and Carlson, 2005), the measured Sm−Nd isotopic compositions of the enriched shergottite subgroup do not permit Equations 1 and 2 to converge. The average age of the depleted shergottite subgroup is 4531 ± 7 Ma, whereas the intermediate shergottites yield average ages that are older than the Solar System (4589 ± 50 Ma). The variation in the three-stage model ages for the depleted and intermediate shergottites, combined with the lack of convergence demonstrated by the Nd isotopic systematics of the enriched shergottites, is inconsistent with the assumption that shergottites evolved from a planet with a present-day bulk ^{142}Nd/^{144}Nd ratio of chondritic meteorites in three stages of evolution. However, if the present-day ^{142}Nd/^{144}Nd of the bulk planet is assumed be the same as the terrestrial value measured in our laboratory (1.141837) then the equations converge for all three subgroups of shergottites and yield an average age of 4526 ± 87 Ma.

4.2.3. Whole rock ^{146}Sm−^{142}Nd isochron age

Constraining the age of planetary differentiation using the whole rock isochron method is based on the predication that the source regions of the samples formed contemporaneously from a common reservoir and thus have the same initial isotopic compositions. The age of martian differentiation was originally defined using the Rb-Sr system to be approximately 4.5 Ga (Shih et al., 1982) because the initial ^{87}Sr/^{86}Sr ratio for the model isochron was very close to the initial ^{87}Sr/^{86}Sr value estimated for the Solar System. Borg et al. (2003) noted that the enriched and depleted shergottites source regions had ^{87}Rb/^{86}Sr, ^{147}Sm/^{144}Nd, and ^{176}Lu/^{177}Hf ratios that closely approximated values determined for lunar magma ocean cumulates by Snyder et al. (1992), and suggested the Sm-Nd whole rock isochron could be used to constrain the differentiation age of Mars. Subsequent investigations of major and trace element compositions of the shergottite source regions confirmed that they are a close match to compositions of martian magma ocean cumulates that formed by crystallization of a common reservoir of chondritic composition (Borg and Draper, 2003; Elkins-Tanton et al., 2003). Thus, the shergottite source regions have geochemical characteristics that are consistent with derivation from a common reservoir at the same time and are therefore potentially in isotopic equilibrium.

The second approach used to determine the age of martian source differentiation is based on ^{146}Sm–^{142}Nd whole rock isochrons constructed using the ^{147}Sm/^{144}Nd ratios of the source regions, calculated for each meteorite using Equation 1, and the ^{142}Nd/^{144}Nd ratio measured in the bulk meteorite samples. This approach has been extensively used in the geochemical community (e.g., Nyquist et al. 1995; Rankenburg et al., 2006; Boyet and Carlson, 2007; Caro et al., 2008; Brandon et al., 2009). The age of differentiation (T_1) is expressed as:

(Eq. 3) $$T_1 = 4567 - \left(\frac{1}{-\lambda^{146}}\right) ln\left[\frac{m}{\left(\frac{^{146}Sm}{^{144}Sm}\right)^{SSI}\left(\frac{^{144}Sm}{^{147}Sm}\right)^{Std}}\right]$$

The slope m, and hence age, defined by the $^{147}Sm/^{144}Nd$–$^{142}Nd/^{144}Nd$ isochron is dictated by the $^{147}Sm/^{144}Nd$ ratios of the shergottite source region calculated from Equation 1 and plotted on the x-axis of Figure 2. Because Equation 1 requires the age of differentiation to be known, Equations 1 and 3 must be solved iteratively. The ^{147}Sm isotope is used to represent Sm concentrations on the x-axis of this plot instead of the traditional ^{144}Sm isotope because this ratio is calculated from the $^{143}Nd/^{144}Nd$ ratio (Eq. 1). As a consequence, the slope derived from the isochron presented in Figure 2 yields an initial $^{146}Sm/^{147}Sm$ ratio rather than a $^{146}Sm/^{144}Sm$ ratio. Therefore, Equation 3 is formulated to yield an age from a slope in the form $^{146}Sm/^{147}Sm$. Importantly, the $^{147}Sm/^{144}Sm$ ratios of individual samples were measured and found to match the ratio determined on terrestrial rock standards as well as the AMES Sm isotope standard (Table 3). Therefore this formulization yields results that are identical to results based on the slope determined from a $^{144}Sm/^{144}Nd$–$^{142}Nd/^{144}Nd$ isochron plot.

Equation 3 is used to calculate ages from the slope of the $^{147}Sm/^{144}Nd$–$^{142}Nd/^{144}Nd$ isochron plot (Figure 2). Slopes are regressed through the data using IsoPlot 4.15. The model age of silicate differentiation determined from our data using this approach is 4504 ± 8 Ma. A slightly more precise age is calculated if the Sm−Nd isotopic data obtained by Debaille et al. (2007) are included in this calculation. In this case, an age of 4503 ± 6 Ma is determined (MSWD = 0.48). Other published data sets increase the scatter on Figure 2 and do not help to better constrain the age of shergottite source formation. This is our preferred age of silicate differentiation determined using this approach. Uncertainties in the age calculation do not incorporate uncertainties associated with the initial $^{146}Sm/^{144}Sm$ of the Solar System of 0.00828 ± 43 (Marks et al., 2014a) or with the half-life of ^{146}Sm of 103 ± 5 Ma (Friedman et al., 1966; Meissner et al., 1987). It is calculated however, that the uncertainty associated with the initial $^{146}Sm/^{144}Sm$ ratio and ^{146}Sm half-life translate to uncertainties on the final age of 8 and 3 Ma, respectively.

It should be noted that the difference in age reported here and the age of 4535 ± 7 Ma reported by Debaille et al. (2007) does not reflect significant differences in the measured Sm−Nd isotopic data. Instead, the difference reflects the fact that Debaille et al. (2007) calculated an age from the average Sm–Nd isotopic composition of three depleted shergottites assuming bulk Mars has a chondritic $^{142}Nd/^{144}Nd$ ratio. However, unlike the three-stage model ages determined for individual samples using Equation 2, the age defined by the isochron (Figure 2) is not dependent on the assumed $^{142}Nd/^{144}Nd$ ratio for bulk Mars. As discussed above, the underlying assumption associated with this age is that meteorite sources formed from a common reservoir at the same time. Although the geochemical and isotopic systematics of the shergottites support this contention (e.g., Borg et al., 2003; Elkins-Tanton, 2003; Symes et al., 2008) this remains an assumption. Nevertheless, if this assumption is correct, this isochron represents the age at which the shergottite sources formed from a common reservoir. The initial $^{142}Nd/^{144}Nd$ defined by the isochron therefore represents the composition of this reservoir at the time of shergottite source formation at 4504 Ma. The initial $^{142}Nd/^{144}Nd$ ratio determined from the ^{146}Sm–^{142}Nd isochron is 1.141615 ± 8. A reservoir with a $^{142}Nd/^{144}Nd$ ratio of 1.141615 at 4504 Ma would have a present-day $^{142}Nd/^{144}Nd$ ratio 1.141830 ± 8 if it also had a present-day $^{147}Sm/^{144}Nd$ ratio of chondritic meteorites of 0.1967. In other words, the initial $^{142}Nd/^{144}Nd$ ratio determined from this whole rock isochron falls on an evolution curve for a reservoir with present-day $^{147}Sm/^{144}Nd$ and $^{142}Nd/^{144}Nd$ ratios of 0.1967 and 1.141830 (Figure 1).

4.2.4. Whole rock $^{142}Nd/^{144}Nd$–$^{143}Nd/^{144}Nd$ isochron age

The third approach used to constrain the age of differentiation of the shergottite source region uses the present-day $^{142}Nd/^{144}Nd$ and $^{143}Nd/^{144}Nd$ ratios of the shergottite sources and is presented in Figure 3. The $^{142}Nd/^{144}Nd$ of the source region today is the same as is measured for the shergottite whole rocks, whereas the $^{143}Nd/^{144}Nd$ ratio of the source today is calculated from the initial $^{143}Nd/^{144}Nd$ ratio of the sample at the time of crystallization and the $^{147}Sm/^{144}Nd$ calculated for the source using Equation 1. This approach is based on the fact that the slope on a $^{143}Nd/^{144}Nd$ versus $^{142}Nd/^{144}Nd$ diagram (or $\varepsilon^{143}Nd$–$\varepsilon^{142}Nd$ plot) corresponds to a three-stage model age (Borg et al., 2003; Foley et al., 2005).

The slope of a line on a $^{143}Nd/^{144}Nd$–$^{142}Nd/^{144}Nd$ plot is related to the differentiation age of the shergottite source region (T_1) by the equation:

(Eq. 4a)

$$m = \frac{\left(\frac{^{146}Sm}{^{144}Sm}\right)^{SSI} \left(\frac{^{144}Sm}{^{147}Sm}\right)^{Std} \left[e^{\left(-\lambda^{146}(T_0-T_1)\right)}\right]}{\left(e^{\lambda^{147}T_1} - 1\right)}$$

where $\left(\frac{^{146}Sm}{^{144}Sm}\right)^{SSI}$ is the initial Solar System value of 0.00828 (Marks et al. 2014a), $\left(\frac{^{144}Sm}{^{147}Sm}\right)^{Std}$ is the Sm isotopic composition of the AMES standard of 0.202419 (Table 4), and T_0 is the age of the Solar System of 4567 Ma. Rearranging and taking the natural logs allows this equation to be expressed in terms of age of source formation:

(Eq. 4b)

$$T_1 = \left\{(-\lambda^{146}T_0) - ln\left[(e^{\lambda^{147}T_1} - 1)\frac{(m)}{\left(\frac{^{146}Sm}{^{144}Sm}\right)^{SSI}\left(\frac{^{144}Sm}{^{147}Sm}\right)^{Std}}\right]\right\}\left(\frac{1}{-\lambda^{146}}\right)$$

Note that T_1 is on both sides of the equation so that it must be solved iteratively. Solving the equation only takes a single iteration, however. The cancelation of terms in this derivation results in an age equation that is independent of the $^{142}Nd/^{144}Nd$ isotopic composition of the bulk planet.

If the slope *m* is determined through regression on an $\varepsilon^{143}Nd$–$\varepsilon^{142}Nd$ plot instead of a $^{143}Nd/^{144}Nd$–$^{142}Nd/^{144}Nd$ plot, the expression is easily modified to solve for T_1 by simply multiplying the slope by the ratio of values used to convert isotopic ratio measurements to epsilon notation.

(Eq. 4c) $$T_1 = \left\{(-\lambda^{146}T_0) - ln\left[(e^{\lambda^{147}T_1} - 1)\frac{\frac{\left(\frac{^{142}Nd}{^{144}Nd}\right)^{Calc}}{\left(\frac{^{143}Nd}{^{144}Nd}\right)^{Calc}}(m)}{\left(\frac{^{146}Sm}{^{144}Sm}\right)^{SSI}\left(\frac{^{144}Sm}{^{147}Sm}\right)^{Std}}\right]\right\}\left(\frac{1}{-\lambda^{146}}\right)$$

Thus, for Nd measurements completed in our laboratory this ratio is expressed as:

(Eq. 4d) $$\frac{\left(\frac{^{142}Nd}{^{144}Nd}\right)^{Calc}}{\left(\frac{^{143}Nd}{^{144}Nd}\right)^{Calc}} = \frac{1.141837}{0.512638}$$

The slope determined from a line regressed through the combination of our data and the data of Debaille et al. (2007) in Figure 3 is 0.01641 ± 62 (MSWD = 0.57). This corresponds to an age of 4504 ± 6 Ma. This age agrees with the age determined by the ^{146}Sm–^{142}Nd method and is our preferred age for the formation of the shergottite source regions.

4.2.5. Relationship between age calculations

Although calculation of ages using the three approaches outlined in Equations 2, 3, and 4b-4c have been derived separately, the results are not independent for all applications. The shergottite differentiation ages derived from the isochrons on Figure 2 and 3 represent a case where the ages are not independent. This stems from the fact that the ^{147}Sm/^{144}Nd ratio used in the ^{147}Sm/^{144}Nd–^{142}Nd/^{144}Nd isochron calculation is derived from the measured ^{143}Nd/^{144}Nd ratio that represents the x-axis on the ^{143}Nd–^{142}Nd isochron diagrams. Furthermore, ages derived for individual samples using Equation 2 are only independent if the ^{142}Nd/^{144}Nd ratio used in the equation is defined by terrestrial or chondritic materials. On the other hand, ages calculated from Equation 2 will agree with those defined by the isochrons if the ^{142}Nd/^{144}Nd ratio used in the equations is assumed to be the same as the initial ^{142}Nd/^{144}Nd values defined by the isochrons. Thus, the average of the three-stage model ages determined on individual samples is 4504 ± 42 Ma, assuming that Mars had a bulk planet ^{142}Nd/^{144}Nd ratio of 1.141830 (Table 2).

The most significant difference between the shergottite model age calculations is associated with how sensitive each age is to the values of variables used in the equations. As noted earlier, the ages determined on individual samples are extremely sensitive to the ^{142}Nd/^{144}Nd ratio of assumed for the bulk planet, whereas the isochron ages are independent of this parameter. If the bulk planet is assumed to have a present-day ^{142}Nd/^{144}Nd ratio that differs by more than ~3 ppm, the ages calculated for individual shergottites shift outside analytical uncertainty associated with the isotopic measurements. The strong dependence of three-stage model ages determined for individual shergottites on the assumed ^{142}Nd/^{144}Nd ratio of the bulk planet, combined with observations that suggest that the chondritic ratio may be a poor proxy for other planetary bodies (Borg et al., 2011, 2013, 2014; Marks et al., 2014b) illustrates the main weakness of using this approach to calculate differentiation ages. Ages calculated using Equation 2 are also sensitive to the ^{147}Sm/^{144}Nd value used to represent the source composition. For example, an uncertainty on the ^{147}Sm/^{144}Nd ratio of the source of 1%, corresponds to an uncertainty in age of ~10 Ma. In contrast, the ages determined using the isochron methods are not dependent on the isotopic composition of the bulk planet and are less sensitive to uncertainty in the ^{147}Sm/^{144}Nd ratios than are ages calculated for individual meteorites. For example, a 1% uncertainty in the ^{147}Sm/^{144}Nd ratio of the source region corresponds to ~1 Ma uncertainty on the ^{147}Sm/^{144}Nd–^{142}Nd/^{144}Nd and ^{143}Nd–^{142}Nd isochron ages.

Finally it is important to note that both the ^{147}Sm/^{144}Nd–^{142}Nd/^{144}Nd and ^{143}Nd–^{142}Nd isochron methods are applicable to age determinations from mineral isochrons of any planetary sample demonstrating evidence for live ^{146}Sm. However, unlike the case for whole rock isochrons, these age determinations are not calculated using the same measured parameters and so are not dependent on each other. This stems from the fact that the ^{147}Sm/^{144}Nd of the mineral fractions is measured, not calculated from their ^{143}Nd/^{144}Nd ratios as is done for the shergottite whole rock isochrons. The ^{147}Sm/^{144}Nd versus ^{142}Nd/^{144}Nd mineral isochron ages require the ^{147}Sm/^{144}Nd ratio to be determined, whereas ^{143}Nd/^{144}Nd versus ^{142}Nd/^{144}Nd isochron age are defined without even measuring the ^{147}Sm/^{144}Nd ratio. This is demonstrated in Table 5 in which ages calculated from equation 4b using only Nd isotopic measurements of mineral fractions are compared to ^{147}Sm–^{143}Nd and ^{146}Sm–^{142}Nd mineral isochron ages we have recently published for lunar samples and an Allende CAI Al3S4. Because the ages derived from equations 3 and 4b depend on different measured parameters, the Nd-Nd isochron approach can potentially be applied to materials with recently disturbed Sm/Nd ratios.

4.2.6. ^{142}Nd/^{144}Nd ratio of bulk Mars

Whereas limited fractionation of Sm/Nd in geologic environments allows the ^{147}Sm/^{144}Nd ratios of bulk planets to be fairly well constrained by the analysis of chondritic meteorites, the bulk ^{142}Nd/^{144}Nd ratio appears to be more variable in planetary materials (e.g., Boyet et al., 2005; Andreasen and Sharma, 2006; Boyet and Carlson, 2010; Gannoun et al., 2011). The present-day ^{142}Nd/^{144}Nd ratio of bulk Mars can be estimated from the Sm−Nd isochron diagram presented in Figure 2 assuming Mars has a ^{147}Sm/^{144}Nd value of 0.1967 (Figure 1). A present-day ^{142}Nd/^{144}Nd ratio of 1.141830 ± 8 (ε^{142}Nd = −0.06 ± 0.07) is derived from the initial ^{142}Nd/^{144}Nd defined by the y-intercept value of ^{142}Nd/^{144}Nd = 1.1416154 ± 75 on the whole rock isochron in Figure 2. The ε^{142}Nd−ε^{143}Nd isochron plot presented in Figure 3 also provides an estimate of the present-day ^{142}Nd/^{144}Nd ratio of Mars that is based on the assumption that bulk Mars has a present day bulk ^{143}Nd/^{144}Nd ratio of chondritic meteorites of 0.512638. In this case, the present-day ^{142}Nd/^{144}Nd ratio is defined by the intercept of the whole rock isochron with ^{143}Nd/^{144}Nd = 0.512638 (Figure 3). The present-day ^{142}Nd/^{144}Nd of bulk Mars estimated from Figure 3 is 1.141830 ± 2 (ε^{142}Nd = −0.06 ± 0.02), and as expected, agrees with the value defined by the ^{146}Sm-^{142}Nd isochron in Figure 2.

The initial ^{142}Nd/^{144}Nd ratio calculated for bulk Mars here is dependent, to some small degree, on the assumption that Mars has a chondritic ^{147}Sm/^{144}Nd ratio of 0.1967. For example, if bulk Mars is assumed to have a present-day ^{147}Sm/^{144}Nd ratio of 0.206, as proposed by Caro et al. (2008), the ^{147}Sm/^{144}Nd ratios calculated for the shergottite sources using equation 1 would change slightly. This would shift the initial ^{142}Nd/^{144}Nd ratio determined from the ^{146}Sm-^{142}Nd isochron in Figure 2 from 1.141615 ± 8 to 1.141607 ± 8. The age would also shift slightly from 4503 Ma to 4501 Ma. Note, however, that the initial ^{142}Nd/^{144}Nd ratio of 1.141607 would correspond to a present-day ^{142}Nd/^{144}Nd of 1.141830 ± 8 assuming growth between 4567 Ma and 4501 Ma occurred in a reservoir with a ^{147}Sm/^{144}Nd = 0.206. Thus, the initial ^{142}Nd/^{144}Nd ratio derived from the ^{146}Sm/^{144}Nd isochron is not strongly affected by the values of the ^{147}Sm/^{144}Nd ratio assumed for the bulk planet.

The initial ^{142}Nd/^{144}Nd of 1.141830 ± 8 calculated for bulk Mars today corresponds to a value of 1.141496 ± 8 at 4567 assuming a bulk ^{147}Sm/^{144}Nd ratio of 0.1967. This value is identical to the initial ^{142}Nd/^{144}Nd isotopic composition derived from the internal isochron of the Type B CAI Al3S4 from the Allende meteorite (Marks et al., 2014a). Furthermore, the present-day ^{142}Nd/^{144}Nd ratio estimated for bulk Mars from the isochron plots is within uncertainty of the values measured in our laboratory on terrestrial Nd and whole rock standards (Table 1), suggesting that the Sm−Nd isotopic systematics of Mars, Earth and the CAI source region are very similar. As discussed above, the initial Nd isotopic compositions determined here for Mars are based on the simplifying assumption that Nd evolution of the shergottites occurred in three stages. Note however, that not all martian igneous samples are likely to have evolved in 3 stages of evolution. The fact that the Nakhlites fall off the isochrons defined by the shergottites (Debaille et al., 2009), therefore, likely reflects the fact that these samples had a more complex evolutionary history than the shergottites, and not necessarily that initial Nd isotopic composition estimated for Mars from the shergottites is inappropriate.

4.3. Rubidium-strontium model age calculation

The conclusion that Mars underwent planetary differentiation at ~4.5 Ga was originally proposed by Shih et al. (1982) on the basis of whole rock Rb−Sr systematics of the shergottites. These authors noted that the bulk rock $^{87}Rb/^{86}Sr$–$^{87}Sr/^{86}Sr$ compositions of the Shergotty, Zagami, and ALH77005 fell near a 4.5 Ga reference line that passed through the initial Sr isotopic composition of the Solar System derived from basaltic achondrites (Basaltic Achondrite Best Initial, BABI) by Papanastassiou and Wasserburg (1969). Shih et al. (1982) argued that the fact that the Rb−Sr systematics scattered around a ~4.5 Ga model isochron reflected the fact that the bulk rock $^{87}Rb/^{86}Sr$ ratios are a rough approximation of the ratios of the meteorite source regions.

Figure 4 is a plot of bulk rock Rb−Sr isotopic compositions of the shergottites for which we measured Sm-Nd isotopic compositions. The Rb−Sr data demonstrate significant scatter about a 4.5 Ga BABI reference line. The basaltic lithologies from non-desert environments fall closest to the reference line, whereas meteorites from desert environments generally fall to the left of this line. This likely reflects the fact that many of the meteorites found in desert environments have undergone terrestrial weathering that has resulted in the addition of Sr. The presence of calcite in several of these samples (e.g., DaG 476) further supports this hypothesis (Zipfel et al., 2000). Note that not all meteorites found in desert environments lie to the left of the 4.5 Ga reference line, indicating that weathering has been relatively mild in some samples such as Dhofar 019, NWA 4468, and NWA 856. Likewise, not all non-desert meteorites line on the 4.5 Ga reference line. Deviation of these samples from the 4.5 Ga reference line indicates that the bulk rock $^{87}Rb/^{86}Sr$ ratio is not a perfectly faithful representation of the $^{87}Rb/^{86}Sr$ ratio of the source regions of the meteorites. Slight accumulation of plagioclase, for example, will drive the ratio to the left in Figure 4 and accumulation of small amounts of trapped liquid will drive the whole rocks to the right. Despite these disturbances, the Rb−Sr isotopic systematics of the shergottites support the original hypothesis put forth by Shih et al. (1982) that the shergottite source regions formed at ~4.5 Ga and is consistent with the more precise age obtained from the Sm−Nd isotopic system.

5. DISCUSSION

5.1. Age of silicate differentiation

The age of 4504 ± 6 Ma calculated for the formation of the shergottite source regions is in good agreement with most of the previous age determinations for martian silicate differentiation. These include 4525 ± 18 Ma (Borg et al., 1997), 4513 $^{+27}/_{-33}$ Ma (Borg et al. 2003), 4525 $^{+19}/_{-21}$ (Foley et al., 2005), and 4527 ± 18 Ma (Caro et al., 2008). Although the Sm−Nd isotopic data obtained in this study and by Debaille et al. (2007) are in excellent agreement, the ages calculated from the data differ outside analytical uncertainty. This reflects the fact that the age of 4535 ± 7 Ma calculated by Debaille et al. (2007) for three depleted shergottite source regions is a three-stage model age that assumes Mars had a chondritic $^{142}Nd/^{144}Nd$ isotopic composition (Eq. 2). As noted above, model ages calculated for individual samples assuming a chondritic $^{142}Nd/^{144}Nd$ isotopic composition fail to converge for all shergottites, suggesting that either the model calculation uses an incorrect parameter, or that the enriched and intermediate shergottites have had a more complex evolutionary history than the depleted shergottites.

Debaille et al. (2007) do in fact suggest that the enriched and intermediate shergottites contain a younger component that is absent from the depleted shergottites. The existence of the younger enriched reservoir is based on the observation that the $^{147}Sm/^{144}Nd$ ratios of the shergottites are higher than those calculated for their sources; a feature that is inconsistent with partial melting of olivine-pyroxene cumulates assumed to be representative of the shergottite sources. Debaille et al (2007) calculated the model age of the enriched source to be 4457 Ma from the $^{147}Sm/^{144}Nd$ and $^{142}Nd/^{144}Nd$ ratios inferred for this source. They defined the $^{147}Sm/^{144}Nd$ ratio of this enriched reservoir to be ≤0.159 from the intersection of a line regressed through the $^{147}Sm/^{144}Nd$ ratios measured for the bulk rocks versus $^{147}Sm/^{144}Nd$ ratios calculated for the meteorite sources and a 1:1 line on Figure 5. The present-day $^{142}Nd/^{144}Nd$ of the source was defined by the intersection of a line regressed through a plot of the shergottite Nd−Nd isotopic data and a Nd isotope growth curve modeled from a chondritic starting composition for a reservoir with a $^{147}Sm/^{144}Nd$ ratio of ≤0.159. The age was calculated from these parameters assuming bulk Mars had a chondritic Nd bulk isotopic composition.

Figure 5 is a reproduction of the $^{147}Sm/^{144}Nd$ whole rock versus $^{147}Sm/^{144}Nd$ source region plot that uses all currently available data. Whereas the older data were more or less linear, several newer data points for Tissint (Brennecka et al., 2014), Dhofar 019 (Caro et al., 2008; this study) and NWA 480 (this study) lie to the left of the line used to define the $^{147}Sm/^{144}Nd$ ratio of the enriched source by Debaille et al. (2007). The fact that shergottites derived from source regions with similar $^{147}Sm/^{144}Nd$ ratios have different $^{147}Sm/^{144}Nd$ ratios suggests the $^{147}Sm/^{144}Nd$ of the bulk rocks does not reflect binary mixing between enriched and depleted source regions and therefore cannot be used to constrain the $^{147}Sm/^{144}Nd$ ratio of the enriched source region. Consequently the significance of the 4457 Ma age derived for a source with $^{147}Sm/^{144}Nd$ of 0.159 is not clear.

5.2. Differentiation of Mars

Any petrogenetic model for martian differentiation must account for three observations: (1) ^{182}W isotopic compositions of the shergottites and nakhlites range from ~+0.65 to +3 epsilon units, respectively, (2) silicate differentiation of the shergottite source region occurs at 4504 ± 6 Ma, and (3) the fact that the nakhlites fall to the left of the 4567 Ma Nd-Nd isochron on Figure 3. If the Hf−W and Sm−Nd isotopic data are interpreted to record silicate differentiation at 4504 Ma alone, then the Hf/W ratios of the shergottite and nakhlite source regions must range from approximately 50 to 300. Partition coefficients for W and Hf determined by Shearer and Righter (2003) suggest that Hf is 3 to 7 times more compatible in clinopyroxene and 30 to 70 times more compatible in garnet. Nevertheless, these authors demonstrate that it is unlikely that even a garnet and clinopyroxene bearing mantle will have high enough Hf/W ratio to yield W isotopic composition radiogenic enough to serve as the nakhlite source region if it formed at 4504 Ma. Another problem with the hypothesis that W isotopic differences between the nakhlites and shergottites reflect silicate differentiation at 4504 Ma is the observation that the ^{142}Nd isotopic composition of the nakhlites falls to the right of the 4567 Ma Nd-Nd isochron on Figure 3 indicating that the nakhlite Nd isotopic compositions did not evolve in only 3 stages. Although a unique differentiation history for the nakhlites probably cannot be derived from their Nd isotopic systematics, late incompatible-element enrichment of the nakhlite source occurring between 4504 Ma and the ~1.3 Ga crystallization age of the nakhlites is perhaps the simplest explanation for their Nd isotopic systematics. In any case, the variation in W and Nd isotopic compositions of the shergottites and nakhlites cannot result from differences in source mineralogy produced by silicate differentiation occurring at 4504 Ma alone.

Alternatively, the ^{182}W and ^{142}Nd isotopic compositions of the shergottites and nakhlites might reflect a combination of fractionation events associated with core formation and silicate differentiation. A relatively simple scenario associated with this hypothesis is that the ^{182}W of the shergottites reflects an early core formation event that imparted a ~0.65 ε^{182}W anomaly on the entire silicate mantle. In this case the best estimate of the age of core formation may be the average shergottite Hf-W age of 4559 ± 8 Ma. If this is correct, then there must be an extended period of 55 ± 13 Ma between core formation at 4559 Ma and silicate differentiation at 4504 Ma (Figure 6, Option 1). A nakhlite source region forming from a homogeneous mantle with the same W isotopic composition as inherited by the shergottite source regions must have an Hf/W ratio of ~200 if the source region formed at 4504 Ma. This ratio is higher than those predicted for mantle cumulates based on partition studies of Hf and W (Shearer and Righter, 2003). Thus, in order to account for the difference in W isotopic compositions between the shergottites and nakhlites, the nakhlite source must form substantially before the shergottite source regions, requiring the martian magma ocean to cool slowly. Although some thermal modeling initially suggested that a shallow terrestrial magma ocean would cool in 100 Ma to 200 Ma in the presence of a thick atmosphere (e.g. Abe, 1997), more recent thermal modeling, incorporating additional constraints such as complete compositional information, mineralogy, and internal dynamics of the Mars (Elkins-Tanton; 2008; Labrun et al. 2013) demonstrates that mantle solidification likely occurred in less than 5 Ma even in the presence of a thick atmosphere. Thus, the discrepancy between the Hf−W and Sm−Nd model ages is difficult to attribute to slow cooling of a magma ocean without an additional source of heat.

Another possibility is that Hf/W ratios of the martian mantle were highly variable reflecting either heterogeneous core formation or late addition of material with variable ^{182}W isotopic compositions. In this case it is difficult to place firm constraints on the timing of core formation from the Hf-W isotopic system (Kleine and Halliday, 2006). Likewise, the 4504 Ma Nd model age of shergottite source formation almost certainly would not constrain the timing of a planet-wide differentiation event. Instead, the 4504 Ma age would likely record the age at which a portion of the mantle differentiated in isolation from other mantle regions. This scenario of martian differentiation (Figure 6, Option 2) is consistent with protracted accretion of a heterogeneous body that occurs contemporaneously with localized melting and differentiation. If accretion occurred over an extended interval, then solidification of portions of Mars could be delayed despite rapid heat flow from the planet as implied by thermal modeling (Figure 5; Option 2). Late accretion is expected to add heat into the system locally and could, in principle, help to maintain molten, undifferentiated, domains on the planet. If this scenario is correct, then accretion must have lasted ~60 Ma in order to postpone differentiation of the shergottite mantle source regions until 4504 Ma. In this case, the metal/silicate segregation event recorded by the ^{182}Hf–^{182}W isotopic system may reflect Hf/W fractionation that occurred on planetesimals prior to accretion, during martian core formation, and during martian silicate differentiation. This scenario is appealing not only because it satisfies the thermal modeling, but also because it accounts for elevated abundances of highly siderophile elements (HSE) observed in the martian mantle. High abundances of these elements in terrestrial mantles are inconsistent with formation of metallic cores in closed geochemical systems because HSEs are strongly partitioned into the metal phase (e.g., Brandon et al., 2012). Accretion that occurred after core formation terminated could replenish the martian mantle in HSEs. Heterogeneous distribution of the later accreting material in the martian mantle might also contribute to the observed isotopic variation of ^{182}W in the different classes of martian meteorites.

A variation of this accretion scenario involves a late giant impact on Mars (Figure 6, Option 3). Such an impact has been suggested to be responsible for the formation of the northern lowlands of Mars (Wilheims and Squires, 1984; Andrews-Hanna et al., 2008; Marinova et al., 2008; Nimmo et al., 2008). Geophysical modeling of a martian giant impact event suggests that: (1) both Mars and the impactor are likely to be differentiated at the time of impact (Yoshino et al., 2003; Neumann et al., 2012), (2) the impact could heat a significant portion of the planet and induce melting (Tonks and Melosh, 1993; Monteux et al., 2007; Arkani-Hamed and Ghods, 2011), and (3) chemical global equilibrium between Mars and the impactor was probably not attained after the impact (Monteux and Arkani-Hamed, 2013). The Sm−Nd age could therefore record a differentiation event associated with cooling of a large, but not globally extensive, portion of the mantle after the impact. This hypothesis is consistent with the fact that the shergottites fall into a few young crystallization age groups (Nyquist et al., 2001; Borg and Drake, 2005) and many have identical cosmic ray exposure ages (Nishiizumi et al., 2011) suggesting that they probably do not represent an extensive sampling of the martian surface. Several authors have suggested that the shergottites sample only a handful of sites on the martian surface (Nyquist et al., 2001; Borg and Drake, 2005; Brennecka et al., 2014). If this hypothesis is correct, then the age recorded in the Sm−Nd systematics of the shergottites might reflect a local, rather than a global, differentiation event. The Sm−Nd age would not define the age of martian silicate differentiation, but instead would place temporal constraints on the timing of a martian giant impact. Differences in ^{182}W isotopic compositions observed in martian meteorites could reflect a combination of the heterogeneous distribution of W derived from Mars and the impactor in the martian mantle, as well as a variable extents and ages of Hf/W fractionation associated with silicate differentiation. This hypothesis implies that planet formation is a stochastic process in which accretion and differentiation occur contemporaneously over tens of millions of years, to produce numerous compositionally distinct geochemical reservoirs. If this scenario is correct, then neither ^{142}Nd nor ^{182}W constrain the timing of planetary scale differentiation events. The Sm−Nd age of 4504 ± 6 Ma therefore only provides a minimum estimate for the time when accretion terminated.

6. CONCLUSIONS

A mathematical expression to calculate an age from the slope defined by the regression on the ^{142}Nd/^{144}Nd−^{143}Nd/^{144}Nd isochron is presented and used to calculate the age of shergottite source formation of 4504 ± 6 Ma from Sm−Nd isotopic data obtained on 11 martian meteorite samples. This age agrees with ages calculated assuming three stage Nd evolution for individual samples, as well as with the age determine from a ^{146}Sm−^{142}Nd whole rock isochron provided bulk Mars is assumed to have a near terrestrial ^{142}Nd/^{144}Nd value of 1.141830 (ε^{142}Nd = −0.06). The Nd−Nd method is the preferred method to establish the age of the shergottite mantle source regions because it is not dependent on the assumed ^{142}Nd/^{144}Nd ratio of bulk Mars nor strongly influenced by uncertainties associated with estimates of ^{147}Sm/^{144}Nd ratios of the shergottite source regions. The young age for the formation of the shergottite source regions requires that either solidification of the primordial martian magma ocean occurred relatively late in Solar System history or that the Hf−W and Sm−Nd fractionation recorded in the meteorites does not reflect a global differentiation process. Prolonged cooling of the magma ocean is not consistent with thermal modeling that suggests that this process requires only a few million years to complete. If the thermal modeling is correct, then an additional heat source appears to be required to keep the martian interior hot until 4504 Ma. Protracted accretion occurring more or less continuously for ~60 Ma or a giant impact occurring just prior to 4504 Ma might provide such heat and could account for some of the isotopic compositions of the shergottite suite. Such an impact could also produce a mantle that is compositionally heterogeneous on a planetary scale. In this case, the 4504 ± 6 Ma Sm−Nd model age recorded in the shergottites would reflect differentiation associated the cooling of the mantle following a giant impact.

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Table 1. Rb, Sr, Sm, and Nd concentration data

Sub-group	Sample	Weight (g)	Rb (ppm)	Sr (ppm)	$\left(\frac{^{87}Rb}{^{86}Sr}\right)^{b}$	Sm (ppm)	Nd (ppm)	$\left(\frac{^{147}Sm}{^{144}Nd}\right)^{c}$
Enriched	Los Angeles	0.231				2.161	5.576	0.23432 ± 23
	Dho 378	0.498	4.42	79.29	0.1612 ± 16	1.149	2.859	0.24301 ± 24
	NWA 856	0.207	5.19	41.99	0.3581 ± 36	0.9542	2.379	0.24247 ± 24
	NWA 4878	0.561	4.92	71.64	0.1989 ± 20	1.274	3.177	0.24245 ± 24
	NWA 1068	0.433	5.37	63.67	0.2441 ± 21	1.348	3.516	0.23182 ± 23
	NWA 4468	0.430				0.7559	1.917	0.23835 ± 24
	NWA 4468	0.394	3.06	26.39	0.3360 ± 33	0.5306	1.301	0.24650 ± 25
Inter-mediate	EET79001A	0.738	0.896	13.66	0.1898 ± 19	0.6183	0.892	0.41890 ± 42
	NWA 480	0.240	2.31	46.40	0.1440 ± 14	1.198	2.457	0.29478 ± 29
Depleted	DaG 476	1.812	0.531	57.95	0.02652 ± 27	0.3659	0.425	0.51689 ± 51
	SaU 005	1.839	0.298	79.30	0.01089 ± 11	0.4387	0.540	0.49071 ± 49
	Tissint	0.460	0.229	25.62	0.02590 ± 26	0.7159	1.116	0.38332 ± 38
	Dhofar 019 [a]	0.016	0.652	307.1	0.00615 ± 70	0.6698	1.079	0.37534 ± 38

[a] Isotope dilution measurement only.
[b.] Error limits apply to last digits and include a minimum uncertainty of 1% plus 50% of the blank correction for Rb and Sr added quadratically.
[c.] Error limits apply to last digits and include a minimum uncertainty of 0.1% plus 50% of the blank correction for Sm and Nd added quadratically.

Table 2. Sm−Nd Isotopic Data

Sub-group	Sample	Age Sample (Ma) [a]	$\left(\frac{^{87}Sr}{^{86}Sr}\right)^{d}$	$\left(\frac{^{143}Nd}{^{144}Nd}\right)^{e}$	$\left(\frac{^{142}Nd}{^{144}Nd}\right)^{e}$	ε_{Nd}^{142}	$\left(\frac{^{147}Sm}{^{144}Nd}\right)^{f}$	Model Age (Ma) [g]
Enriched	Los Angeles	170		0.512327 ± 1	1.141815 ± 3	−0.20	0.1844	4530 ± 23
	Dho 378	157	0.720922 ± 5	0.512335 ± 1	1.141813 ± 2	−0.21	0.1846	4549 ± 17
	NWA 856	170	0.723390 ± 7	0.512321 ± 2	1.141819 ± 6	−0.16	0.1839	4475 ± 61
	NWA 4878	170	0.720626 ± 6	0.512331 ± 1	1.141817 ± 2	−0.17	0.1842	4498 ± 24
	NWA 1068	185	0.717949 ± 5	0.512352 ± 1	1.141819 ± 2	−0.16	0.1852	4493 ± 23
	NWA 4468	187		0.512316 ± 1	1.141818 ± 4	−0.17	0.1837	4485 ± 39
	NWA 4468	187	0.720852 ± 5	0.512323 ± 1	1.141818 ± 3	−0.17	0.1836	4482 ± 27
	Average (2SD)							**4504 ± 55**
Inter-mediate	EET79001A	173	0.712979 ± 5	0.513724 ± 2	1.141863 ± 7	+0.23	0.2257	4507 ± 36
	NWA 480	343	0.709702 ± 5	0.513380 ± 1	1.141854 ± 4	+0.15	0.2156	4522 ± 26
	Average (2SD)							**4515 ± 23**
Depleted	DaG 476	474	0.707158 ± 6	0.515516 ± 1	1.141911 ± 4	+0.65	0.2670	4507 ± 8
	SaU 005	445	0.707034 ± 5	0.515324 ± 1	1.141902 ± 3	+0.57	0.2645	4495 ± 7
	Tissint	580	0.701039 ± 7	0.515506 ± 1	1.141920 ± 3	+0.72	0.2794	4498 ± 5
	Dhofar 019 [c]	574	0.707756 ± 9	0.515106 ± 25			0.2654	
	Ave, (2SD)							**4503 ± 13**
	Shergottite Average (2SD)							**4504± 42**
Terrestrial Standards	BCR-2		0.705000 ± 4	0.512621 ± 1	1.141831 ± 3	−0.05		
	BCR-2		0.705003 ± 4	0.512622 ± 1	1.141835 ± 3	−0.02		
	BCR-2		0.705003 ± 9					
	BHVO-2			0.512978 ± 2	1.141836 ± 3	−0.01		
	NBS-987 [b]		0.710249 ± 8					
	LaJolla [b]			0.511845 ± 8	1.141839 ± 6	+0.02		
	JNdi [b]			0.511201 ± 6	1.141837 ± 7	≡0.00		

a. Age of samples summarized in Nyquist et al. (2001), Borg and Drake (2005) and from Borg et al. (2001), Brennecka et al. (2014), and Marks et al. (2010).

b. Long-term average values obtained on standards. Uncertainties refer to last digits and are $2\sigma_p$ (2 x standard deviation of population of mass spectrometry runs on isotopic standard). NBS-987 standard average of N = 55 runs, BCR-2 standard average of N = 14 runs, JNdi standard average of N = 40 runs, LaJolla standard average of N = 12 runs.

c. Isotope dilution measurements only.

d. Measured value normalized to $^{86}Sr/^{88}Sr = 0.1194$. Uncertainties refer to last digits and are $2\sigma_m$ (2 x standard error of measured isotopic ratios)

e. Measured value normalized to $^{146}Nd/^{144}Nd = 0.7219$. Uncertainties refer to last digits and are $2\sigma_m$ (2 x standard error of measured isotopic ratios).

f. Value calculated from value equation 1.

g. Value calculated from Equation 2 assuming bulk Mars has present-day $^{142}Nd/^{144}Nd = 1.141830$ (derived from the y-axis value in Fig. 2 at a $^{147}Sm/^{144}Nd = 0.1967$). Uncertainties on individual model ages reflect the precision of the measured $^{142}Nd/^{144}Nd$ ratios, whereas the uncertainties on average model ages are 2× the standard deviation of respective ages

Table 3. Samarium isotopic compositions

Sub-group	Sample	$\left(\frac{^{144}Sm}{^{152}Sm}\right)$	$\left(\frac{^{148}Sm}{^{152}Sm}\right)$	$\left(\frac{^{149}Sm}{^{152}Sm}\right)$	$\left(\frac{^{150}Sm}{^{152}Sm}\right)$	$\left(\frac{^{154}Sm}{^{152}Sm}\right)$	ε_{Sm}^{149}	ε_{Sm}^{150}
Enriched	Los Angeles	0.114977 ± 2	0.420437 ± 2	0.516847 ± 2	0.276002 ± 2	0.850797 ± 4	−0.08	+0.33
	NWA 856	0.114971 ± 3	0.420438 ± 3	0.516842 ± 3	0.275997 ± 2	0.850765 ± 5	−0.17	+0.14
	NWA 4878	0.114976 ± 2	0.420437 ± 2	0.516841 ± 2	0.275994 ± 2	0.850771 ± 6	−0.19	+0.04
	NWA 4468	0.114976 ± 2	0.420437 ± 3	0.516841 ± 3	0.275994 ± 2	0.850771 ± 5	−0.19	+0.04
Inter-mediate	EET79001A	0.114974 ± 2	0.420437 ± 2	0.516846 ± 3	0.275990 ± 2	0.850774 ± 5	−0.10	−0.11
	NWA 480	0.114971 ± 2	0.420436 ± 2	0.516848 ± 3	0.275991 ± 1	0.850766 ± 3	−0.06	−0.07
Depleted	DaG 476	0.114974 ± 2	0.420440 ± 3	0.516846 ± 3	0.275992 ± 2	0.850772 ± 5	−0.10	−0.04
	SaU 005	0.114973 ± 2	0.420437 ± 2	0.516849 ± 2	0.275991 ± 1	0.850775 ± 4	−0.04	−0.07
	Tissint	0.114953 ± 3	0.420447 ± 3	0.516850 ± 3	0.276001 ± 2	0.850762 ± 5	−0.02	+0.29
Terrestrial Standards	BCR-2	0.114975 ± 2	0.420438 ± 6	0.516851 ± 3	0.275992 ± 2	0.850795 ± 7	0.00	−0.03
	BCR-2	0.114977 ± 2	0.420440 ± 6	0.516854 ± 3	0.275994 ± 2	0.850793 ± 6	0.06	+0.04
	AMES [a]	0.114976 ± 7	0.420438 ± 8	0.516851 ± 8	0.275993 ± 3	0.850798 ± 9	≡0.00	≡0.00

Measured value normalized to $^{147}Sm/^{152}Sm = 0.56801$. Uncertainties refer to last digits and are $2\sigma_m$ (2× standard error of measured isotopic ratios).

[a]. Long-term average value obtained on AMES Sm standard (N=25). Uncertainties refer to last digits and are $2\sigma_p$ (2× standard deviation of population of mass spectrometry runs on isotopic standard).

Table 4. Variables used in equations 1-4

Variable	Description	Value
$(^{143}Nd/^{144}Nd)^{M3}$	Present-day whole rock Nd isotopic ratio	Measured
$(^{142}Nd/^{144}Nd)^{M2}$	Present-day whole rock Nd isotopic ratio	Measured
$(^{143}Nd/^{144}Nd)^{SSI}$	Solar System initial Nd isotopic ratio	0.506674 [a]
$(^{142}Nd/^{144}Nd)^{B}$	Bulk Mars Nd isotopic composition	1.141830
$(^{147}Sm/^{144}Nd)^{Ch}$	Present-day bulk planet ratio (determined from analysis of chondritic meteorites)	0.1967[a]
$(^{147}Sm/^{144}Nd)^{M1}$	Present-day whole rock ratio	Measured
$(^{146}Sm/^{144}Sm)^{SSI}$	Solar System initial Sm isotopic composition	0.00828 [b]
T_0	Age of Solar System (determined from CAIs)	4567 Ma [c]
T_1	Differentiation age of Mars	Solved for
T_2	Internal isochron age of martian meteorite	Measured
λ^{147}	^{147}Sm decay constant	6.54×10^{-6} Ma^{-1}
λ^{146}	^{146}Sm decay constant	0.0067296 Ma^{-1} [b]
$(^{144}Sm/^{147}Sm)^{Std}$	Sm isotopic composition determined from terrestrial standards	0.202419
$(^{147}Sm/^{144}Nd)^{S}$	Sm/Nd isotopic composition of shergottite source regions	Solved for
$(^{142}Nd/^{144}Nd)^{Calc}$	Value used as denominator for calculating $\varepsilon^{142}Nd$	1.141837
$(^{143}Nd/^{144}Nd)^{Calc}$	Value used as denominator for calculating $\varepsilon^{143}Nd$	0.512638

[a.] Jacobsen and Wasserburg (1980)
[b.] Marks et al. (2014a)
[c.] Amelin et al. (2010); Connelly et al. (2012)

Table 5. Examples of Sm−Nd ages calculated using different methods

Sample	$^{147}Sm–^{143}Nd$ age (Ma)	$^{146}Sm–^{142}Nd$ age (Ma)	$^{142}Nd–^{143}Nd$ age (Ma)	Reference
60025	4367 ± 15	$4318\ ^{+30}/_{-38}$	$4319\ ^{+30}/_{-38}$	Borg et al. (2011)
76535	4307 ± 11	$4300\ ^{+29}/_{-36}$	$4299\ ^{+29}/_{-36}$	Borg et al. (2013)
60016	4300 ± 32	$4298\ ^{+57}/_{-94}$	$4296\ ^{+58}/_{-97}$	Marks et al. (2014b)
77215	4283 ± 23	$4348\ ^{+59}/_{-100}$	$4350\ ^{+58}/_{-96}$	Carlson et al (2014)
CAI Al3S4[A]	4560 ± 34	$4564\ ^{+7.9}/_{-8.4}$	$4565\ ^{+8.0}/_{-8.4}$	Marks et al. (2014a)

Ages calculated using ^{146}Sm t½ = 103 Ma and $^{146}Sm/^{144}Sm$ = 0.00828 following Marks et al. (2014a). CAI Al3S4 age calculated using $^{146}Sm/^{144}Sm$ = 0.0084 obtained from eucrite meteorites (Boyet et al., 2010). Slopes determined by regression of $^{143}Nd/^{144}Nd–^{142}Nd/^{144}Nd$ data are: 60025 = 0.0112 ± 0.0025; 76535 = 0.098 ± 0.0021; 60016 = 0.0096 ± 0.0046; 77215 = 0.0137 ± 0.0065; CAI Al3S4 = 0.0561 ± 0.0031.

Figure Captions

Figure 1. Plots of $^{143}Nd/^{144}Nd$ and $^{142}Nd/^{144}Nd$ versus age illustrating Nd evolution in three stages (circled numbers) as discussed in the text. Stage 1 is growth in an undifferentiated reservoir, stage 2 is growth in a differentiated reservoir, and stage 3 represents growth in the meteorites after they solidified. Present-day whole rock Nd isotopic values are represented by open squares, whereas initial $^{143}Nd/^{144}Nd$ ratios are represented by solid squares. The upper panel illustrates Nd growth in an undifferentiated reservoir with present-day $^{147}Sm/^{144}Nd = 0.1967$ and $^{143}Nd/^{144}Nd = 0.512638$ (Jacobsen and Wasserburg, 1980). The growth curves for a depleted shergottite (Tissint; $^{147}Sm/^{144}Nd = 0.2974$) and an enriched shergottite (NWA 4468; $^{147}Sm/^{144}Nd = 0.1836$) are calculated using equation 1 assuming differentiation occurred at 4504 Ma. Lower panel depicts growth of $^{142}Nd/^{144}Nd$ starting from the composition of Allende CAI Al3S4 (Marks et al. 2014a). Growth of $^{142}Nd/^{144}Nd$ is modeled in two stages because ^{146}Sm is extinct before stage 3 begins. The position of the SNC whole rock initial $^{142}Nd/^{144}Nd$ (^{146}Sm-^{142}Nd isochron) point (open circle) is defined by the age and y-intercept of the ^{146}Sm-^{142}Nd isochron from Figure 2. The SNC whole rock initial $^{142}Nd/^{144}Nd$ (^{143}Nd-^{142}Nd isochron) point (partially filled circle) is derived from the intersection of the whole rock Nd-Nd isochron (Figure 3) with the chondritic $^{143}Nd/^{144}Nd$ value of 0.512638. The point representing the initial $^{142}Nd/^{144}Nd$ ratio inherited by Mars at 4567 Ma is the filled circle labeled Mars Initial (calculated). It is derived from the initial $^{142}Nd/^{144}Nd$ on Figure 2 assuming the planet has a bulk $^{147}Sm/^{144}Nd$ of 0.1967 to be 1.141496 ± 7. This value is the same as the initial value determined from the isochron from CAI Al3S4 by Marks et al (2014a).

Figure 2. A ^{146}Sm–^{142}Nd isochron plot used to determine the age of differentiation of the shergottite source regions. Data from this study are open circles and data reported by Debaille et al. (2007) are filled squares. The measured bulk meteorite $^{142}Nd/^{144}Nd$ ratios are plotted versus the $^{147}Sm/^{144}Nd$ of martian meteorite source regions calculated from the measured $^{143}Nd/^{144}Nd$ ratios (Eq. 1). This isochron yields a $^{146}Sm/^{147}Sm$ slope of 0.001089 ± 43 (MSWD = 0.48) that corresponds to an age of 4503 ± 6 Ma (Eq. 3). Uncertainties plotted on diagram are internal uncertainties associated with the mass spectrometry measurements ($2\sigma_m$), whereas uncertainty on the regression is calculated using two times the standard deviation of mass spectrometry runs on the standard ($2\sigma_p$). The uncertainty on the $^{147}Sm/^{144}Nd$ ratios is assumed to be 0.1%. The initial $^{142}Nd/^{144}Nd$ of this isochron is 1.141615 ± 8, which corresponds to a present-day $^{142}Nd/^{144}Nd$ of 1.141830, assuming bulk Mars has a $^{147}Sm/^{144}Nd$ similar to that of chondritic meteorites of 0.1967, and the initial Solar System $^{146}Sm/^{144}Sm$ of 0.00828 ± 43 (Marks et al., 2014a).

Figure 3. An $\varepsilon^{142}Nd$– $\varepsilon^{143}Nd$ isochron plot used to determine the age of differentiation of the shergottite source regions. The measured bulk meteorite $\varepsilon^{142}Nd$ value is plotted against the

ε^{143}Nd value of the present-day source region calculated from the initial ^{143}Nd/^{144}Nd of the meteorite. An isochron regressed through the data (thick solid line) yields a slope of 0.01636 ± 52 (MSWD = 0.57), which corresponds to an age of 4504 ± 6 Ma (Eq. 4b). A slope of 0.0364 ± 0.0014 is calculated from the regression of the ^{142}Nd/^{144}Nd-^{143}Nd/^{144}Nd plot. Vertical dashed lines are Nd isotopic growth curves calculated at different ages using ^{147}Sm/^{144}Nd of 0.17, 0.1967, 0.23, 0.26, and 0.29. Thin solid lines are model isochrons calculated at common ages using different ^{147}Sm/^{144}Nd ratios. These isochrons are spaced at 50 Ma intervals starting at 4200 Ma, excluding 4500 Ma, but including 4567 Ma. The present-day initial ^{142}Nd/^{144}Nd value determined by the y-intercept is 1.141830 ± 2 and is consistent with the value determined from Figure 2. The relationship of the present-day martian ^{142}Nd/^{144}Nd values to bulk Earth (open star) suggests that the Nd isotopic composition of Mars and Earth are very similar, and it remains possible that the shergottite source region represents a mixing relationship between the terrestrial Nd isotopic composition and the chondritic Nd isotopic composition. Chondritic Nd isotopic composition (solid star) is from Boyet and Carlson (2007).

Figure 4. A Rb−Sr isochron plot of shergottite whole rock data. Reference line has a slope corresponding to an age of 4.50 Ga and passes through Basaltic Achondrite Best Initial (BABI) ^{87}Sr/^{86}Sr = 0.69906 (Papanastassiou and Wasserburg, 1969). Data from this study, Borg et al. (1997, 2001, 2002, 2003, 2005); Brennecka et al. (2014); Marks et al. (2010); Nyquist et al. (1979); and Symes et al. (2008). Samples from desert environments generally fall to the left and above reference line as a result of terrestrial weathering and addition of Sr.

Figure 5. A plot of ^{147}Sm/^{144}Nd measured in the bulk meteorite versus the ^{147}Sm/^{144}Nd calculated for the source region from the bulk rock ^{143}Nd/^{144}Nd using Equation 1. Solid line to the right of the 1:1 line is from Debaille et al. (2007) and was used to define the ^{147}Sm/^{144}Nd ratio of 0.159 for their enriched shergottite source region. The data are from this study, Borg et al. (1997, 2002, 2003, 2005); Brennecka et al. (2014); Caro et al. (2008); Debaille et al. (2007); and Shih et al. (1982); Symes et al. (2008) and fall to the right of the 1:1 line indicating the bulk meteorites are more depleted in light rare earth elements than their source regions. Note that these data do not define a linear array on this diagram indicating that compositional variation does not appear to reflect simple two-component mixing. Instead, several meteorites with variable ^{147}Sm/^{144}Nd ratios are derived from source regions with similar ^{147}Sm/^{144}Nd ratios suggesting that bulk rock chemistry is not related to long-term fractionation of Sm/Nd in the source regions.

Figure 6. A schematic illustration of the early evolution of Mars. The petrogenetic models are based on: (1) silicate differentiation of the shergottites source regions occurring at 4504 ± 6 Ma and (2) thermal modeling that suggest magma ocean solidification occurred rapidly after accretion terminated (Elkins-Tanton, 2008). Option 1 depicts rapid accretion and rapid

early cooling of the martian magma ocean. It does not account for the young age of silicate differentiation determined for the shergottite source regions, nor provide an obvious mechanism to preserve ^{182}W isotopic differences between various martian meteorites. Option 2 depicts a prolonged period of accretion that is sufficient to extend the period of cooling of some portions of the martian mantle until 4504 Ma. Option 3 depicts rapid initial accretion and magma ocean cooling followed by a giant impact. In this case the silicate differentiation age recorded in the shergottites reflects cooling of a portion of the mantle following melting by the impact event. Both options 2 and 3 imply significant accretion on Mars for ~60 Ma.