The Early Differentiation History of Mars from New Constraints on ^{182}W-^{142}Nd Isotope Systematics in the SNC Meteorites

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Abstract

We report here the results of an investigation of W and Nd isotope systematics in the SNC (martian) meteorites that reveal new constraints on the time scales of early planetary differentiation on Mars. Assuming a two-stage model, the metallic core is estimated to have formed at approximately 11 Myr after the beginning of solar system formation, but continuous accretion models suggest that core formation extended for millions of years beyond this time. Core formation was followed by major silicate differentiation which established the shergottite source reservoirs at 4525^{+19}_{-21} Ma and the nakhlite source reservoir before ~4542 Ma. These ages imply that, within the uncertainties afforded by the ^{182}Hf-^{182}W and ^{146}Sm-^{142}Nd chronometers, the silicate differentiation events that established the source reservoirs of the shergottite and nakhlites may have occurred contemporaneously, possibly during crystallization of a global magma ocean. The distinct ^{182}W-^{142}Nd systematics in the shergottites and the nakhlites imply the presence of at least three isotopically distinct silicate reservoirs on Mars, two of which are depleted and the third is enriched. The two depleted silicate reservoirs most likely reside in the martian mantle while the enriched one could be either in the crust or the mantle. The ^{182}W-^{142}Nd systematics additionally indicate that the shergottites and the nakhlites originated from distinct source reservoirs and cannot be petrogenetically related. A further implication is that the source reservoirs of the shergottites and nakhlites on Mars have been isolated since their establishment prior to ~4.5 Ga. This implies that there has been no giant impact or global mantle convection to homogenize the martian mantle following the establishment of the SNC source reservoirs.

1. INTRODUCTION

The ^{182}Hf-^{182}W extinct chronometer ($t_{1/2}$ ~9 Myr) has previously been applied towards constraining the timing of early metal-silicate differentiation on Mars, the parent body of the shergottite-nakhlite-chassignite (SNC) meteorites (Lee and Halliday, 1997; Yin et al, 2002; Kleine et al., 2002; and Kleine et al., 2004). Both Hf and W are highly refractory and are assumed to be present in approximately chondritic relative abundances in the terrestrial planets. During core formation, the lithophile Hf preferentially partitions into the silicate reservoir, whereas the siderophile W partitions into the metallic core. If this event occurred during the lifetime of ^{182}Hf (i.e., within ~50 Myr of solar system formation), the bulk silicate reservoir is expected to have an excess of ^{182}W relative to chondritic meteorites. Moreover, silicate differentiation occurring within the first ~50 Myr of solar system history may result in further Hf-W fractionation (Righter and Shearer, 2003), producing silicate reservoirs with highly variable ^{182}W excesses.

The ^{146}Sm-^{142}Nd short-lived chronometer ($t_{1/2}$ ~ 103 Myr) has also been applied towards understanding early silicate differentiation on Mars (e.g., Harper et al., 1995; Borg et al., 1997, 2003). Since Sm and Nd are refractory lithophile elements, it is assumed that their abundances in the terrestrial planets are chondritic and that neither core formation nor volatile loss fractionated them. While both elements are incompatible in mafic silicate minerals, Nd is more so, resulting in Sm-Nd fractionation during silicate differentiation. Therefore, if major silicate differentiation occurred during the lifetime of ^{146}Sm (and provided there was minimal subsequent convective mixing), distinct martian silicate reservoirs are expected to have detectable ^{142}Nd excesses and deficits relative to chondrites. However, as discussed by Harper et al. (1995), given the initial abundance of ^{146}Sm in the early solar system, i.e., ^{146}Sm/^{144}Sm ~0.008 (e.g., Lugmair and Galer 1992; Prinzhofer et al., 1992; Nyquist et al., 1994; Stewart et al., 1994), and the limited range of Sm-Nd fractionation in large-scale silicate reservoirs, the range of expected excesses and deficits in the ^{142}Nd/^{144}Nd ratio relative to chondrites is only on the order of ~1 ε-unit (one part in 10^4).

The earliest reported W and Nd isotopic analyses of the SNCs showed that their whole rock ε^{182}Wvalues (defined as deviations of the ^{182}W/^{183}W or ^{182}W/^{184}W ratio from the terrestrial standard value in parts per 10^4) vary from ~0 to +3 (Lee and Halliday, 1997), while their ε^{142}Nd values (defined as deviations of ^{142}Nd/^{144}Nd ratios from the terrestrial standard value in parts per 10^4) vary from –0.2 to +0.9 (Harper et al., 1995). These data further indicated a possible correlation between ε^{182}W and ε^{142}Nd in the SNC meteorites, from which it was inferred that core formation and silicate differentiation processes on Mars were "coeval and co-genetic" and occurred while both ^{182}Hf and ^{146}Sm were extant (Lee and Halliday, 1997). However, it has subsequently been shown that ε^{182}Win terrestrial samples is more radiogenic than in chondrites by ~2 ε units (Yin et al., 2002, Kleine et al., 2002; and Schoenberg et al., 2002). Therefore, the ε^{182}W in the SNCs is clearly superchondritic. The fact that several of the shergottites have superchondritic ε^{182}W and nearly chondritic ε^{142}Nd then suggests that core formation preceded silicate differentiation and occurred within the first ~12-13 Myr of solar system formation (Yin et al., 2002, Kleine et al., 2002; and Schoenberg et al., 2002). Nevertheless, the suggested correlation between ε^{182}W and ε^{142}Nd in SNC meteorites still implied that the Hf-W and Sm-Nd systems must have fractionated together very early in Mars' history, most likely during a major global silicate differentiation event.

Since the first W isotope data were reported (Lee and Halliday, 1997), many new samples of the SNCs have been recovered, the parent melts of which may be derived from a wider range of source reservoirs on Mars. A more recent study of W isotope systematics in the SNCs (Kleine et al., 2004) included two of these more recently discovered ones, but was limited to only three shergottite samples (i.e., EETA79001, Dar al Gani 476 and Sayh al Uhaymir 051, of which the latter two were recovered recently). This study indicated that the linear correlation between ε^{182}W and ε^{142}Nd in the SNCs, previously suggested by Lee and Halliday (1997), could be tenuous.

The goal of the present study is to rigorously evaluate the relationship between the W and Nd isotope systematics in the SNC meteorites to elucidate the timing and nature of differentiation of martian mantle reservoirs. Therefore, we have determined ^{182}W-^{142}Nd systematics in a greater variety of shergottite and nakhlite samples than those analyzed in previous such investigations. Specifically, we report here the ^{182}W/^{183}W isotopic compositions of several SNCs that show the range of petrologic and geochemical diversity currently represented within this group. The sample suite investigated here includes eight shergottites: the lherzolitic shergottite ALHA77005, the light rare earth element (LREE) enriched basaltic shergottites Shergotty, Zagami and Los Angeles (LA), and the LREE-depleted basaltic shergottites EETA79001 lithology A (EETA) and lithology B (EETB), Dar al Gani 476 (DaG 476) and Sayh al Uhaymir 008 (SaU 008) (considered paired with SaU 005/051; Meyer, 2003, and references therein); three nakhlites: Governador Valadares (GV), Lafayette, and Northwest Africa 998 (NWA 998); and the orthopyroxenite ALH84001. We also report the ^{142}Nd/^{144}Nd isotopic compositions of six of the shergottites: ALHA77005, Shergotty, Zagami, EETA, DaG 476 and SaU 008. The results reported here on this sample suite represent the most comprehensive study of ^{182}W-^{142}Nd isotopic systematics in the SNCs since the work of Lee and Halliday (1997) and Harper et al. (1995).

2. ANALYTICAL TECHNIQUES

2.1. Sample Preparation and Chemical Procedures

Samples were first examined for the presence of any weathering products and/or fusion crust. In all cases, interior chips devoid of fusion crust and containing minimal weathering products were used for the W and Nd isotopic analyses. Bulk samples for W analyses were leached in 0.5 N HNO_3 while those for Nd analyses were rinsed in ultrapure water (18 mΩ/cm), both in ultrasonic baths for ~10-15 minutes. Following ultrasonication, each sample was washed three times in ultrapure water. The samples were then dried and crushed with a clean agate mortar and pestle. Dissolution of silicate samples was performed by treatment with a 3:1 mixture of concentrated $HF:HNO_3$, followed by concentrated HNO_3 and concentrated HCl. Dissolution of Toluca and Allende required the additional use of aqua regia and perchloric acid, respectively.

Column chemistry to isolate W from the samples was performed at the Field Museum's Isotope Geochemistry Laboratory. In preparation for the separation of W, the dissolved bulk samples were dried down and brought into a solution of 1N HCl-0.5 N HF. Isolation of W was performed using a column chromatography procedure (Table 1) similar to that used by previous investigators (Kraus et al., 1955; Horan et al., 1998; Münker et al., 2001; Schoenberg et al., 2002). For silicate samples, ~0.25-1 g of sample was loaded on the column. The W cut from the first pass through this column was put through the same procedure described in Table 1 a second time, using the same resin as was used for the first pass for a given sample. Two passes were necessary for the silicate samples to reduce the amount of Ti in the W cut from the first pass through the column. For most silicate samples, Ti was eluted in the first pass through the column using the higher volume of the HCl-HF acid mixture (45 ml) shown in Table 1, and was subsequently eluted using the lower volume of the acid mixture (7.5 ml) during the second pass. The only exception was the AGV-2 terrestrial andesite, which has the lowest Ti/W ratio of all silicate samples analyzed here and in the case of which Ti was eluted using only 7.5 ml of the HCl-HF acid mixture during each of the two passes through the column. The column chemistry for iron-rich samples (like the Toluca IA iron meteorite) is also shown in Table 1. ~0.2 g of Toluca was loaded on the column, and only a single pass through the column was necessary to isolate the W from the sample matrix. However, a second pass was also performed to assure reduction of the amount of matrix elements present. In order to keep the separated W in solution, 20 μl of perchloric acid was added to the W cut before drying down and a final drop of ~2 μl was brought into a solution of 0.5 N HNO_3-0.05 N HF for isotopic analyses.

To minimize the W blank, only new Savillex (Teflon PFA) beakers were used for the processing of samples for W isotopic analyses. Prior to being used, the new beakers were boiled twice in 50% HNO_3 and then in ultrapure water (for a minumum of six hours each). Following this, W was further leached from the beakers by filling them with a few ml of 7N HCl-1N HF acid solution, closing them tightly and heating them at 90^{o}C for a minimum of 3 hours, followed by a thorough and immediate rinse with ultrapure water; this procedure was repeated twice for each beaker. The resin for W column chemistry was pre-cleaned prior to being loaded on the column by rinsing first with ~2 resin-volumes of ultrapure water, followed by ~2 resin-volumes of 0.5N HCl-0.5N HF acid solution, ~12.5 resin-volumes of 7N HCl-1N HF acid solution, and finally again with ~2 resin-volumes of ultrapure water. Following these protocols and with the exclusive use of Optima-grade acids containing <0.5 pg/g W, our total procedural blanks were typically ≤200 pg per gram of sample processed and were negligible compared to the amount of W in the samples.

Column chemistry for separation of Nd was performed at the Radiogenic Isotope Laboratory at the University of New Mexico, using procedures broadly similar to those described by Borg et al. (1997). Specifically, the separation of Nd from the sample matrix consisted of the following steps: (1) separation of the REE from the rock matrix using cation resin, (2) purification of the REE cut using an RE-spec resin, (3) separation of Nd from the other REE using a methylactic column, (4) removal of the methylactic acid from the Nd cut using a cation clean-up column, and (5) removal of any remaining Ce from the Nd cut using two Ln-spec clean-up columns. To ensure good separation of Ce from Nd, the methylactic column separation was repeated twice for some samples. Total procedural blanks were ~7 pg Nd for the samples analyzed here, and were negligible compared to the amount of Nd in the samples.

2.2. Mass Spectrometry

Tungsten and neodymium isotopic analyses were made using a Micromass IsoProbe multicollector ICPMS in the Isotope Geochemistry Laboratory at the Field Museum. For W isotopic measurements, sample solutions of 10-50 ppb W were introduced into the plasma using a CETAC Aridus microconcentric nebulizer (MCN). The array of 9 Faraday collectors allowed simultaneous collection of all W isotopes as well as ^{188}Os (which was monitored to estimate the contribution from Os at mass 186). For all samples analyzed here, with the exception of Toluca, the Os contribution on mass 186 was negligible. However, in the case of Toluca, there was a minor Os contribution at mass 186, which required a correction of 0.09 ε units on the measured $^{182}W/^{183}W$ ratio.

Each W isotope measurement was comprised of 20-40 cycles of 10 second integrations, and was preceded by a 10-minute washout and a 45 second integration of the background. Measurement of each sample was bracketed with multiple measurements of the NIST 3163 W standard. For each sample, at least 2 repeat measurements were performed interspersed with measurements of the NIST 3163 W standard. The normalizing ratio used to correct the raw $^{182}W/^{183}W$ ratio for instrumental mass fractionation was the $^{186}W/^{184}W$ ratio in the terrestrial standard of 0.927633 (Lee and Halliday, 1997). As a check, we also determined the fractionation corrected $^{182}W/^{183}W$ ratio by normalizing to the $^{184}W/^{183}W$ ratio in the terrestrial standard of 2.139758 (Harper and Jacobsen, 1996). For all samples the corrected $^{182}W/^{183}W$ ratios were the same using either one of these normalization schemes, within 2σ errors. All $^{182}W/^{183}W$ ratios measured in the samples are reported here relative to the terrestrial standard in parts per 10^4, i.e., as $\varepsilon^{182}W$ values, defined as follows:

$$\varepsilon^{182}W = \left(\frac{\left(\frac{^{182}W}{^{183}W}\right)_{Sample} - \left(\frac{^{182}W}{^{183}W}\right)_{Standard}}{\left(\frac{^{182}W}{^{183}W}\right)_{Standard}} \right) \bullet 10^4 \qquad (1)$$

The measurement protocol for Nd isotopic analyses was similar to that used for W isotopic analyses. Sample solutions of 35-50 ppb Nd were introduced into the plasma using a CETAC Aridus MCN. We measured all Nd isotopes, except for ^{150}Nd. In addition to the Nd isotopes, ^{140}Ce and ^{149}Sm were monitored to estimate the Ce and Sm contributions at mass 142 and mass

144, respectively; typical corrections for Ce and Sm on the measured ^{142}Nd/^{144}Nd ratios were negligible for all samples except for DaG 476 and SaU 008, for which the Sm correction was ~0.2 ε units.

Measurements of samples, with at least three repeats, were bracketed with multiple measurements of the Geological Survey of Japan JNDi-1 Nd standard. The normalizing ratio used to correct the raw ^{142}Nd/^{144}Nd ratio for instrumental mass fractionation was the ^{146}Nd/^{144}Nd ratio in the terrestrial standard of 0.7219. All ^{142}Nd/^{144}Nd ratios measured in the samples are reported here relative to the terrestrial standard in parts per 10^4, i.e., as ε^{142}Nd values, defined as follows:

$$\varepsilon^{142}Nd = \left(\frac{\left(\frac{^{142}Nd}{^{144}Nd}\right)_{Sample} - \left(\frac{^{142}Nd}{^{144}Nd}\right)_{Standard}}{\left(\frac{^{142}Nd}{^{144}Nd}\right)_{Standard}} \right) \bullet 10^4 \qquad (2)$$

Measurements of the W isotopic composition of NIST 3163 and the Nd isotopic composition of JNDi-1 standards were performed over the course of several months. Figures 1a and b show the results of these analyses. Each data point is an average calculated from 5 to 10 brackets of repeat measurements of the standards performed on a single day. The reproducibility of the repeat measurements of standards on any given day (illustrated in Fig. 1 as the errors on individual data points) was typically better than or equal to ±0.3 ε units (2σ). The long-term reproducibility of W and Nd isotopic measurements is significantly better than ± 0.2 εunits (2σ (Fig. 1; Table 2).

3. RESULTS

The results of our W and Nd isotopic analyses are given in Table 2 and illustrated in Fig. 2. The accuracy of our W isotopic analyses for silicate and metal-rich samples is demonstrated by the results obtained for the terrestrial rock standards BCR2 and AGV2, the carbonaceous chondrite Allende and the IA iron meteorite Toluca. As can be seen in Table 2, ε^{182}W in the terrestrial rock standards BCR2 and AGV2 is identical to that in the NIST W standard. The ε^{182}W values determined for Allende and Toluca are, within uncertainties, similar to those reported by several investigators (Kleine et al., 2002, 2004; Schoenberg et al., 2002; Yin et al., 2002).

Tungsten isotopic compositions are reported here for several basaltic shergottites, i.e., the LREE-enriched basalts Shergotty, Zagami, and LA, and the LREE-depleted basalts EETA, EETB, DaG 476, and SaU 008. The ε^{182}W values of these basaltic shergottites have a rather limited range, from 0.27 ± 0.13 (Shergotty) to 0.66 ± 0.11 (DaG 476). The lherzolitic shergottite ALHA77005 has an ε^{182}W value of 0.91 ± 0.32, only marginally higher (although not outside of 2σ errors) than the highest value in the basaltic shergottites. The orthopyroxenite ALH84001 has an ε^{182}W value of 0.49 ± 0.33, which falls within the range of ε^{182}W in the basaltic shergottites. The three nakhlites analyzed here (GV, Lafayette and NWA 998) have W isotopic compositions that are quite distinct from, and significantly more radiogenic than, those of the shergottites and the orthopyroxenite ALH84001. Within uncertainties, all three nakhlites analyzed here have identical ε^{182}W values, with an average of 3.07 ± 0.14.

The ε^{142}Nd values we measured in six shergottites (five basaltic and one lherzolitic) show a range of ~1 ε unit. The LREE-enriched shergottites Shergotty and Zagami have the lowest

ε^{142}Nd values that are identical, within errors, and have an average of –0.19 ± 0.08. The LREE-depleted shergottites DaG 476 and SaU 008 have the highest ε^{142}Nd values that are also identical, within errors, and have an average of 0.86 ± 0.20. The ε^{142}Nd values in the LREE-depleted basaltic shergottite EETA (0.36 ± 0.10) and the lherzolitic shergottite ALHA77005 (0.29 ± 0.10) are intermediate between those of Shergotty and Zagami, on the one hand, and DaG 476 and SaU 008, on the other.

Figure 2 shows a plot of ε^{182}W versus ε^{142}Nd for the SNCs in which all the W isotopic data are from this work; some of the Nd isotopic data (solid symbols) are from this study, but others (open symbols) are from previous investigations (Harper et al., 1995; Carlson and Irving, 2004). In this figure, shergottites define a linear compositional array with near-uniform ε^{182}W but wide-ranging ε^{142}Nd, while nakhlites define a distinct compositional group with uniform ε^{182}W and ε^{142}Nd (within 2σ errors).

4. DISCUSSION

4.1. ^{182}W-^{142}Nd Systematics in the SNCs: Comparison with Previous Results

Of the SNC samples analyzed here, the W isotopic compositions of several have previously been reported (Lee and Halliday, 1997; Kleine et al, 2004) and are shown in Table 2 for comparison. As can be seen in this table, the majority of our W data agree with these previous results. There are a few instances, however, where our results do not agree with previous ones. In particular, Lee and Halliday (1997) had reported an ε^{182}W for EETA79001 of 2.21 ± 0.60. More recently, Kleine et al. (2004) reported a significantly lower ε^{182}W for this shergottite of 0.4

± 0.4. This shergottite contains two distinct lithologies in igneous contact (i.e., lithology A which contains olivine-orthopyroxene megacrysts in a basaltic groundmass of pyroxenes and plagioclase, and lithology B which consists of pyroxenes and plagioclase). Neither of these previous studies identified the particular lithology that was analyzed. In this work, we have reported ε^{182}W for both lithologies of EETA79001 (i.e., 0.65 ± 0.29 for lithology A and 0.35 ± 0.21 for lithology B). These values are distinctly lower than that reported by Lee and Halliday (1997), but agree within uncertainties with that reported by Kleine et al. (2004). Additionally, the ε^{182}W values we determined for the LREE-depleted shergottite DaG 476 (0.66 ± 0.11) and the nakhlite Lafayette (2.87 ± 0.12) are both somewhat higher than those reported by Kleine et al. (2004) and Lee and Halliday (1997), respectively, for these meteorites (Table 2). Finally, Lee and Halliday (1997) also reported ε^{182}W for two SNCs that were not analyzed in this study. Specifically, these authors reported ε^{182}W for two splits of Nakhla (that give an average value of 3.00 ± 0.20), which agrees well with the values reported here for the three other nakhlites, GV, Lafayette and NWA 998. They also reported ε^{182}W for the unique dunitic SNC meteorite, Chassigny (2.14 ± 0.62); although the analytical uncertainty is high, this value is marginally lower than the average of the values reported here for three nakhlites (i.e., 3.07 ± 0.14).

The ε^{142}Nd values for the six shergottites for which we have obtained Nd isotopic data have been reported previously (Harper et al., 1995; Jagoutz et al., 2000, 2003), but are in question for four of the six samples (specifically, ALHA77005, Shergotty, DaG 476 and SaU 008). Allan Hills 77005 and Shergotty do not fall on the ε^{142}Nd-ε^{143}Nd isochron defined by other shergottites (Fig. 5 of Borg et al., 2003). In the case of ALHA77005, it is possible that this lherzolitic shergottite underwent a more complex petrogenesis than the other shergottites or alternatively, the previously determined ε^{142}Nd value for this meteorite may be in error (Borg et al., 2003). In the case of Shergotty, given that it is similar to Zagami not only in its petrologic and geochemical characteristics but also in its initial ε^{143}Nd, the difference in the ε^{142}Nd between these two samples, coupled with the fact that the Shergotty data point falls off the ε^{142}Nd-ε^{143}Nd isochron, made the previously determined ε^{142}Nd value for this meteorite questionable. Jagoutz et al. (2000) had initially reported an ε^{142}Nd of ~0.8 for DaG 476 and SaU 005. Subsequently, these authors have revised their estimates of the ε^{142}Nd values for these two samples to the substantially lower ones shown in Table 2 (Jagoutz et al., 2003).

For the two shergottites, Zagami and EETA, for which the previously reported ε^{142}Nd values are not disputed, the ε^{142}Nd values determined by us agree with the values reported earlier by Harper et al. (1995) (Table 2). However, our ε^{142}Nd value for ALHA77005 is higher than that reported earlier by Harper et al. (1995). Moreover, our ε^{142}Nd value for Shergotty is lower than that reported by Harper et al. (1995), although it is identical, within errors, to that for Zagami (this work; Harper et al., 1995). These new ε^{142}Nd values reported here for ALHA77005 and Shergotty fall along the ε^{142}Nd-ε^{143}Nd isochron defined by other shergottites (see Fig. 3, implications of which are discussed in more detail in section 4.2.1.).

The ε^{142}Nd values presented here for DaG 476 and SaU 008 are systematically higher than those reported by Jagoutz et al. (2003). The higher ε^{142}Nd values that we determined for these two LREE-depleted shergottites are consistent with that of the LREE-depleted shergottite QUE94201 (ε^{142}Nd = 0.92 ± 0.11; Borg et al., 1997), which is considered to have similar Rb-Sr and Sm-Nd isotopic systematics to these meteorites (Borg et al., 2003). It has been shown by previous studies that the Saharan shergottites contain variable amounts of an LREE-enriched terrestrial weathering component that can affect the Sm-Nd systematics in these rocks (e.g., Wadhwa et al., 2001; Crozaz et al., 2003). Given the precautions taken to avoid any terrestrial weathering component in the samples analyzed here, we believe it is likely that our samples of DaG 476 and SaU 008 contain a smaller amount of this terrestrial component compared to the samples analyzed by Jagoutz et al. (2003). Terrestrial contamination will lower the apparent ε^{142}Nd values of the samples and, therefore, may account for this apparent discrepancy between our data and that of Jagoutz et al. (2003).

4.2. Implications for the Early Differentiation History of Mars

Given the distinct geochemical affinities of parent-daughter element pairs in the ^{182}Hf-^{182}W and ^{146}Sm-^{142}Nd systems, the combined ^{182}W-^{142}Nd systematics in the SNCs offer a uniquely powerful means of constraining the timing of the earliest episodes of metal-silicate and silicate-silicate differentiation on Mars. As can be seen in Fig. 2, the shergottites and nakhlites have distinct ε^{182}W-ε^{142}Nd systematics. This has implications for the timing of the differentiation events that established the mantle source reservoirs of these two types of SNC meteorites. Furthermore, these isotope systematics indicate that the source mantle reservoirs of the shergottites and the nakhlites in the martian mantle were distinct from each other and have remained isolated since they were established. Thus, petrogenetic models that attempt to relate the shergottites and the nakhlites by mixing processes (e.g., Shih et al., 1982; Jones, 1989; Jagoutz, 1991) are not valid in light of the ^{182}W-^{142}Nd systematics presented here. Detailed implications of the ε^{182}W-ε^{142}Nd systematics in the SNC meteorites are discussed in more detail in the sections below.

4.2.1. Implications of ^{182}W-^{142}Nd systematics in the shergottites and the ancient orthopyroxenite ALH84001

There is evidence from whole rock Rb-Sr (e.g., Shih et al., 1982; Jagoutz, 1991; Borg et al., 1997) and Pb-Pb (e.g., Chen and Wasserburg, 1986; Misawa et al., 1997) isotope systematics in the shergottites that these meteorites formed as a result of a relatively simple two-stage evolutionary history on Mars, where the first stage involved major silicate differentiation at ~4.5 Ga that established their silicate source reservoirs and the second stage corresponded to the later partial melting event that produced their parent melt. Given this, it is possible to apply the long-lived ^{147}Sm-^{143}Nd ($t_{1/2}$ ~106 Gyr) and the short-lived ^{146}Sm-^{142}Nd ($t_{1/2}$ ~103 Myr) chronometers in conjunction with each other to these shergottites to define the age of silicate differentiation (Borg et al., 1997; 2003). Assuming the two-stage evolutionary history, the independent decay equations for these two chronometers make it possible to solve for the formation age and the ^{147}Sm/^{144}Nd ratio of their source reservoir. Borg et al. (1997) had applied this method for determining the time of source formation for the QUE94201 shergottite and had obtained a model age of ~4525 Ma. As pointed out by Borg et al. (2003), however, a model age estimate based on a single data point is inherently imprecise. Therefore, these authors applied the isochron approach to constraining the formation age of the shergottite source reservoirs on Mars. In this approach, the initial ε^{143}Nd of the samples at 175 Ma were plotted against their present-day ε^{142}Nd (Fig. 5 of Borg et al., 2003), and this ε^{142}Nd-ε^{143}Nd isochron yielded a model age of planetary differentiation of 4513^{+27}_{-33} Ma. However, as is evident from Fig. 5 of Borg et al. (2003), a few of the shergottites (specifically, Shergotty and ALHA77005) did not fall on the isochron and were not used to define the age.

Using the new ε^{142}Nd values reported here for Shergotty, Zagami, EETA, DaG 476 and ALHA77005, including the previously measured values for EETB (Harper et al., 1995) and QUE94201 (Borg et al., 1997), and using previously determined initial ε^{143}Nd values for all these samples (Borg et al., 2003; and references therein), we have replotted the ε^{142}Nd-ε^{143}Nd isochron for the shergottites (Fig. 3). As can be seen in Fig. 3, all the shergottites for which both ε^{142}Nd and ε^{143}Nd are determined fall on a well-defined isochron that corresponds to a model age of planetary differentiation, when the shergottite source reservoirs were established, of 4525^{+19}_{-21} Ma (calculated using the same assumptions as those made by Borg et al., 2003). This is the most precise estimate obtained so far for the timing of this major silicate differentiation event on Mars.

The ε^{142}Nd-ε^{143}Nd isochron for the shergottites passes through the chondritic Nd isotopic values, implying that the bulk silicate portion of Mars has a chondritic Sm/Nd ratio. In Fig. 3, the (0,0) point is characterized by a present-day chondritic ^{147}Sm/^{144}Nd ratio of 0.1967. Shergottites plotting above this point were derived from LREE-depleted sources with superchondritic ^{147}Sm/^{144}Nd ratios (e.g., 0.285 for the QUE94201 source, the most depleted among the shergottite sources; Borg et al., 2003), while those plotting below this chondritic point were derived from LREE-enriched sources with subchondritic ^{147}Sm/^{144}Nd ratios (e.g., 0.182 for the Shergotty source, the most enriched among the shergottite sources; Borg et al., 2003). It has previously been suggested that the parent melts of the various shergottites resulted from different degrees of mixing of components derived from depleted and enriched reservoirs that formed contemporaneously (e.g., Shih et al., 1982; Jones, 1989; Borg et al., 1997; Borg and Draper, 2003). Therefore, although the linear trend defined by the various shergottites in Fig. 3 is probably a mixing line, it still defines the time of contemporaneous formation of the end-member (depleted and enriched) source reservoirs for the shergottite parent melts. In such a case, the depleted end-member reservoir had a minimum ^{147}Sm/^{144}Nd ratio of ~0.285, while the enriched end-member reservoir had a maximum ^{147}Sm/^{144}Nd ratio of ~0.182.

In addition to the tighter constraints on the timing of shergottite source formation provided by the new ε^{142}Nd values reported here, the combined ^{182}W-^{142}Nd systematics in the shergottites provide information on the timing of core formation on Mars and the nature of their source reservoirs. Specifically, the relationship between ε^{182}W and ε^{142}Nd in the shergottites shown in Fig. 4 can be used to place limits on the timing of core formation. The ε^{182}W value in the primitive martian mantle (PMM) may be obtained from the intercept of the best-fit line to the shergottite data shown in Fig. 4 (i.e., the ε^{182}W value corresponding to a chondritic ^{142}Nd), and is estimated to be 0.37 ± 0.07. This value is similar to, but more tightly constrained than, that estimated recently for the PMM by Kleine et al., (2004) (i.e., 0.4 ± 0.2). Therefore, using the ε^{182}W value of 0.37 ± 0.07 and an Hf/W ratio of 5.1 for the PMM (from the La/W ratio estimated for the PMM and the chondritic La/Hf ratio; Palme and Beer, 1993; Kong et al., 1999), and assuming an initial solar system ^{182}Hf/^{180}Hf ratio of $\sim 1 \times 10^{-4}$ (Kleine et al., 2002; Yin et al., 2002), we calculate a two-stage model age for core formation on Mars of 10.9 ± 0.4 Myr after solar system formation. However, a simple two-stage model of core formation may not be a realistic one for the actual process of metal segregation on a planetary body. In fact, it has been argued that the processes of planetary accretion and core formation are continuous and likely extend over millions of years (e.g., Harper and Jacobsen, 1996; Jacobsen and Harper, 1996; Halliday and Lee, 1999; Halliday, 2000; Halliday et al., 2003). In this case, the two-stage model age provides only a lower limit on the time elapsed between solar system formation and completion of metal segregation.

From the relationship between ε^{182}W and ε^{142}Nd in the shergottites it is also possible to constrain the geochemical characteristics of the shergottite source reservoirs. From the slope and intercept of the best-fit line to the shergottite data shown in Fig. 4, we determine that an ε^{142}Nd of ~—0.2 (in the LREE-enriched shergottites such as Shergotty and Zagami) corresponds to an ε^{182}W of ~0.3, while an ε^{142}Nd of ~0.9 (in the LREE-depleted shergottites such as DaG 476 and SaU 008) corresponds to an ε^{182}W of ~0.6. As discussed earlier, the Nd isotopic systematics in the shergottites (specifically, the ε^{142}Nd-ε^{143}Nd isochron shown in Fig. 3) have been used to obtain a model age of planetary differentiation of 4525^{+19}_{-21} Ma and estimates of the minimum and maximum ^{147}Sm/^{144}Nd ratios for the depleted and enriched end-member shergottite source reservoirs of ~0.285 and ~0.182, respectively. The range of ε^{182}W in the shergottites can then be used to place constraints on the Hf/W ratios in their end-member (depleted and enriched) source reservoirs as follows:

$$\varepsilon^{182}W_{SSR} = Q_{182} f_{PMM}^{Hf/W} \left(\frac{^{182}Hf}{^{180}Hf} \right)_{T_1} \left(e^{-\lambda_{182}(T_1 - T_2)} - e^{-\lambda_{182}(T_1 - T_{3'})} \right) + Q_{182} f_{SSR}^{Hf/W} \left(\frac{^{182}Hf}{^{180}Hf} \right)_{T_1} e^{-\lambda_{182}(T_1 - T_{3'})} - 1.9 \qquad (3)$$

where $\varepsilon^{182}W_{SSR}$ is the present-day ε^{182}W in the shergottite source reservoir, T_1 is the absolute age of the solar system with respect to the present (assumed to be the age of formation of refractory inclusions in primitive meteorites , i.e., ~4567 Ma; Amelin et al., 2002), T_2 is the age of the core formation event (which we assume to be a single event that occurred ~11 Myr after solar system formation; see discussion above) and $T_{3'}$ is the age of the silicate differentiation event that established the shergottite source reservoirs (i.e., ~4525 Ma; see discussion above). Therefore, $(T_1 - T_2)$ = 11 Myr and $(T_1 - T_{3'})$ = 42 Myr; $Q_{182} = 10^4 \left({^{180}Hf} / {^{182}W} \right)_{CHUR}$ = 15,500, where

$\left({}^{180}Hf/{}^{182}W\right)_{CHUR}$ is the ratio in the present-day chondritic uniform reservoir (CHUR) (Harper and Jacobsen, 1996); $f_{PMM}^{Hf/W}$ is the Hf/W fractionation factor in the PMM and is given by $\left(\left({}^{180}Hf/{}^{183}W\right)_{PMM}/\left({}^{180}Hf/{}^{183}W\right)_{CHUR}-1\right)$ = 3.4; $f_{SSR}^{Hf/W}$ is the Hf/W fractionation factor in the shergottite source reservoir and is calculated in a similar fashion; $\left({}^{182}Hf/{}^{180}Hf\right)_{T_1}$ ~1 × 10^{-4} (Kleine et al., 2002; Yin et al., 2002); λ_{182} = 0.077 Myr^{-1}. Since $\varepsilon^{182}W$ in the PMM is estimated to be 0.37, equation (3) may be simplified to:

$$\varepsilon^{182}W_{SSR} = 0.37 - Q_{182}\left(f_{PMM}^{Hf/W} - f_{SSR}^{Hf/W}\right)\left(\frac{{}^{182}Hf}{{}^{180}Hf}\right)_{T_1}\left(e^{-\lambda_{182}(T_1-T_{3'})}\right) \tag{4}$$

From the above equation, we estimate that the depleted shergottite end-member source reservoir characterized by an $\varepsilon^{182}W_{SSR}$ of ≥ 0.6 (and with a minimum $^{147}Sm/^{144}Nd$ ~0.285, based on the $^{147,146}Sm$-$^{143,142}Nd$ systematics in the LREE-depleted shergottites such as QUE94201 and DaG 476; Borg et al., 2003) has an Hf/W ratio of ≥ 9.5 ($^{180}Hf/^{183}W$ ≥ 24). The enriched shergottite end-member source reservoir characterized by an $\varepsilon^{182}W_{SSR}$ of ≤ 0.3 (and with a maximum $^{147}Sm/^{144}Nd$ ~0.182, based on the $^{147,146}Sm$-$^{143,142}Nd$ systematics in the LREE-enriched shergottites such as Shergotty and Zagami) has an Hf/W ratio of ≤ 3.8 ($^{180}Hf/^{183}W$ ≤9.5). Given that W is more incompatible than Hf in silicate systems (Righter and Shearer, 2003), such minimum and maximum Hf/W ratios may be expected in depleted and enriched sources, respectively, derived from a PMM with a bulk Hf/W ratio of ~5.1. The Hf/W ratios estimated in the shergottite end-member source reservoirs are in the range of those expected for garnet-free shallow mantle sources on Mars (Righter and Shearer, 2003).

The fact that ε^{182}W in the orthopyroxenite ALH84001 (0.49 ± 0.33) is, within errors, similar to the ε^{182}W estimated for the PMM (0.37 ± 0.07) indicates that subsequent to core formation, the Hf/W ratio in the mantle source reservoir of ALH84001 did not fractionate significantly relative to the Hf/W ratio in the PMM. In fact, if one assumes that the mantle source for this ancient orthopyroxenite was established contemporaneously with the shergottite source reservoirs (i.e., at 4525^{+19}_{-21} Ma), its ε^{182}W of ~0.49 indicates that the Hf/W ratio in its source was ~7.4, somewhat higher than the Hf/W ratio in the PMM. This appears to be generally consistent with its Sm-Nd isotopic systematics, which indicate an ancient age (~4.5 Ga) and a slightly positive initial ε^{143}Nd (Jagoutz et al., 1994; Nyquist et al., 1995; Gleason et al., 1997). This suggests that the Hf/W and Sm/Nd ratios in the ALH84001 mantle source were fractionated relative to chondritic ratios.

4.2.2. Implications of ^{182}W-^{142}Nd systematics in the nakhlites

As is evident in Fig. 2, the ^{182}W-^{142}Nd systematics in the nakhlites are quite distinct from those of the shergottites. The ε^{182}W reported so far in the nakhlites is the most radiogenic among all the SNCs (this work; Lee and Halliday, 1997). The individual ε^{182}W values determined for the three nakhlites analyzed here are uniform, within analytical uncertainties, and give an average of 3.07 ± 0.14. If the data for Nakhla (ε^{182}W = 3.00 ± 0.20; Lee and Halliday, 1997) are included, the average ε^{182}W in all nakhlites measured so far is 3.05 ± 0.12. The ε^{142}Nd values previously reported for the nakhlites (Harper et al., 1995; Carlson and Irving, 2004) are also uniform, within errors, and have an average of 0.72 ± 0.09. The highly positive ε^{182}W and ε^{142}Nd in the nakhlites indicate that the nakhlite source was established early, while both ^{146}Sm and ^{182}Hf were extant, and was characterized by a high degree of fractionation of the Hf/W and Sm/Nd ratios. The combined ε^{182}W-ε^{142}Nd systematics in these samples may be utilized to infer the timing and nature of the differentiation event that established the nakhlite source.

We have modeled the evolution of ε^{182}W and ε^{142}Nd in the martian mantle to account for the ε^{182}W-ε^{142}Nd systematics in the nakhlites. As in the previous section, we assume that the absolute age of solar system formation with respect to the present is T_1 = 4567 Ma. We further assume that the initial evolution of ^{182}Hf-^{182}W and ^{146}Sm-^{142}Nd systematics on Mars occurs in a chondritic uniform reservoir (CHUR) and thus, during this stage of evolution, the ε^{182}W and ε^{142}Nd remained chondritic by definition. For the purpose of these calculations, we assume that metal segregation on Mars occurred as a single core formation event at T_2 = 4556 Ma (since $T_1 - T_2$ = 11 Myr; see previous section). Since Hf is lithophile and W is siderophile, core formation results in the elevation of the Hf/W ratio in the PMM from the chondritic value of ~1.16 (Anders and Grevesse, 1989; Palme and Beer, 1993) to ~5.1, but does not affect the Sm/Nd ratio in PMM (since both Sm and Nd are lithophile). Since there is no fractionation of Sm/Nd in the PMM during core formation, ε^{142}Nd remains chondritic but ε^{182}W evolves from the time of core formation T_2 to the time $T_{3''}$, when major silicate differentiation results in the formation of the nakhlite source (which has fractionated Hf/W and Sm/Nd ratios). The present-day ε^{182}W and ε^{142}Nd in this fractionated nakhlite source reservoir (i.e., ε^{182}W$_{NSR}$ and ε^{142}Nd$_{NSR}$, respectively) are then given by:

$$\varepsilon^{182}W_{NSR} = 0.37 - Q_{182}\left(f_{PMM}^{Hf/W} - f_{NSR}^{Hf/W} \right)\left(\frac{^{182}Hf}{^{180}Hf} \right)_{T_1} \left(e^{-\lambda_{182}(T_1 - T_{3''})} \right) \quad (5)$$

$$\varepsilon^{142}Nd_{NSR} = Q_{142} f_{NSR}^{Sm/Nd} \left(\frac{^{146}Sm}{^{144}Sm}\right)_{T_1} \left(e^{-\lambda_{146}(T_1 - T_{3''})}\right) \tag{6}$$

where $Q_{182} = 10^4\left(^{180}Hf/^{182}W\right)_{CHUR}$ = 15,500; $f_{PMM}^{Hf/W}$ is the Hf/W fractionation factor in the PMM and is given by $\left(\left(^{180}Hf/^{183}W\right)_{PMM}/\left(^{180}Hf/^{183}W\right)_{CHUR} - 1\right)$ = 3.4; $f_{NSR}^{Hf/W}$ is the Hf/W fractionation factor in the nakhlite source reservoir and is calculated in a similar fashion; $\left(^{182}Hf/^{180}Hf\right)_{T_1}$ ~1 × 10^{-4} (Kleine et al., 2002; Yin et al., 2002); λ_{182} = 0.077 Myr^{-1}; $Q_{142} = 10^4\left(^{144}Sm/^{142}Nd\right)_{CHUR}$ = 354 (Jacobsen and Wasserburg, 1984); $f_{NSR}^{Sm/Nd}$ is the Sm/Nd fractionation factor in the nakhlite source reservoir and is given by $\left(\left(^{147}Sm/^{144}Nd\right)_{NSR}/\left(^{147}Sm/^{144}Nd\right)_{CHUR} - 1\right)$; $\left(^{146}Sm/^{144}Sm\right)_{T_1}$ ~0.008 (e.g., Lugmair and Galer 1992; Prinzhofer et al., 1992; Nyquist et al., 1994; Stewart et al., 1994); λ_{146} = 6.73 Gyr^{-1}.

To model the ε^{182}W-ε^{142}Nd systematics in the nakhlite source reservoir, we have assumed two possible source compositions, each characterized by distinct Hf/W and Sm/Nd ratios, which are considered to have been formed at different times $T_{3''}$, such that the time interval ($T_1 - T_{3''}$) ranges up to 100 Myr. One of these is an extremely depleted martian mantle composition which has an Hf/W ratio of ~50 (^{180}Hf/^{183}W ~126) and ^{147}Sm/^{144}Nd ratio of ~0.303, and corresponds to a majorite-bearing deep mantle (MDM) source on Mars (Borg ad Draper, 2003; Righter and Shearer, 2003). Although it is unlikely that the nakhlites originated from a deep mantle source characterized by this degree of Hf/W and Sm/Nd fractionation, it may be viewed as the extreme end-member in terms of the degree of fractionation that may be expected in a mantle source on Mars. Another composition modeled here corresponds to a more plausible shallow mantle (GSM) source for the nakhlites characterized by an Hf/W ratio of ~17 (^{180}Hf/^{183}W ~43) and

$^{147}Sm/^{144}Nd$ ratio of ~0.266 (Righter and Shearer, 2003 and Harper et al., 1995, respectively). For comparison, we have also made calculations for the three depleted mantle source compositions modeled by Kleine et al. (2004).

Modeling results are shown in Fig. 5, where the black curves are results of calculations for the MDM (upper curve) and GSM (lower curve) source compositions, and the gray curves are the three depleted mantle source compositions modeled previously by Kleine et al. (2004). As can be seen in this figure, average composition of the nakhlites (solid diamond in Fig. 5) is best matched by the formation of a source with either (1) the GSM composition ($^{147}Sm/^{144}Nd$ ~0.266; $^{180}Hf/^{183}W$ ~43) at ~25 Myr, or (2) a depleted mantle with a less fractionated composition ($^{147}Sm/^{144}Nd$ ~0.255; $^{180}Hf/^{183}W$ ~22) at <10 Myr after solar system formation. The latter seems implausible given that metal segregation on Mars must have preceded silicate differentiation and we have established that the earliest time at which core formation was completed was ~11 Myr after solar system formation. Nevertheless, given the uncertainties in the individual nakhlite data plotted in Fig. 5 as well as in the estimation of an appropriate mantle source of the nakhlites, the results of our modeling calculations suggest that the timing of major silicate differentiation resulting in the establishment of a nakhlite source occurred *within* ~25 Myr after solar system formation (i.e., before 4542 Ma).

Our modeling results favor a fractionated GSM-like source (i.e., shallow mantle source having an $^{147}Sm/^{144}Nd$ ratio of ~0.266 and an $^{180}Hf/^{183}W$ ratio of ~43) for the nakhlites. Although the $^{147}Sm/^{144}Nd$ ratio of ~0.266 does not necessitate the presence of garnet in such a source, the extremely fractionated $^{180}Hf/^{183}W$ ratio of ~43 appears to require it (Righter and Shearer, 2003). However, the LREE-enrichment inferred in the nakhlite source (Wadhwa and Crozaz, 1995; Wadhwa et al., 2004) is in conflict with the presence of significant amounts of garnet. It is possible that the REE abundances in the nakhlite source have been affected by secondary metasomatic processes following its initial establishment (Harper et al., 1995; Borg et al., 2003; Wadhwa et al., 2004), which did not affect the Hf-W systematics. Although such a scenario would require a more complicated model for the evolution in the nakhlite mantle source, it still requires its early establishment (i.e., within ~25 Myr of solar system formation) so as to produce the large ε^{182}W and ε^{142}Nd anomalies observed in the nakhlites.

4.2.3. Further implications for Mars

Previous workers have suggested multiple distinct source reservoirs for the SNCs (Jones, 1989; Jagoutz, 1991; Borg et al., 1997, 2003; Brandon et al., 2000; Kleine et al., 2004). In Table 3, we have proposed the geochemical and isotopic characteristics, as well as the formation times of silicate reservoirs on Mars sampled by the SNC meteorites. It clear that at least three distinct silicate reservoirs are required to account for the ^{182}W-^{142}Nd systematics in the SNC meteorites. As discussed earlier in section 4.2.1., the depleted and enriched end-member shergottite source reservoirs were established at 4525^{+19}_{-21} Ma. The depleted end-member shergottite reservoir is characterized by $\varepsilon^{182}W \geq 0.6$ and $\varepsilon^{142}Nd \geq 0.9$, corresponding to an $^{180}Hf/^{183}W \geq 24$ (or $Hf/W \geq 9.5$) and $^{147}Sm/^{144}Nd \geq 0.285$, respectively. The enriched end-member shergottite reservoir had $\varepsilon^{182}W \leq 0.3$ and $\varepsilon^{142}Nd \leq -0.2$, corresponding to an $^{180}Hf/^{183}W \leq 11$ (or $Hf/W \leq 4.5$) and $^{147}Sm/^{144}Nd \leq 0.182$, respectively. In section 4.2.2., we showed that the depleted source reservoir of the nakhlites was most likely characterized by ^{180}Hf/^{183}W and ^{147}Sm/^{144}Nd ratios of up to ~43 and ~0.266, respectively, and was established within ~25 Myr of solar system formation.

In addition to the Sm-Nd and Hf-W characteristics of these reservoirs, another parameter that differentiates the source characteristics of the SNCs is the redox state (Table 3). Recent work suggests that while the depleted end-member shergottite reservoir is characterized by a redox state close to ~IW, the enriched end-member shergottite reservoir is significantly more oxidized (>~IW+2), possibly as a result of hydrous alteration (Wadhwa, 2001; Herd et al., 2002). Unlike the depleted end-member shergottite reservoir, the depleted nakhlite source reservoir appears to be rather oxidized (~IW+3.5; Wadhwa and Grove, 2002; Wadhwa et al., 2004). It has been suggested that the oxidation of the nakhlite source may be the result of metasomatism by an oxidizing fluid (which may also be responsible for the LREE-enrichment inferred in the nakhlite parent melts) (Borg et al., 2003; Wadhwa et al., 2004).

Although it seems likely that the depleted (reduced) end-member shergottite reservoir and depleted (oxidized) nakhlite source reservoir reside in the martian mantle, there is some ambiguity regarding whether the enriched (oxidized) end-member shergottite reservoir resides in the crust or the mantle of Mars. While this reservoir could indeed be crustal, recent modeling of an early magma ocean on Mars suggests that an enriched, oxidized component could be formed in the mantle (from the residual melt resulting from the crystallization of this magma ocean) and would have major and trace element characteristics and isotope systematics similar to those expected in this reservoir (Borg and Draper, 2003).

The requirement of at least three distinct source reservoirs on Mars to account for the W and Nd isotope characteristics in the SNCs has also been suggested by Kleine et al. (2004). However, the formation times and isotope characteristics of two of the three source reservoirs estimated by us are quite different from those determined by these authors. Specifically, our results, which indicate the early contemporaneous formation of the depleted and enriched end-member shergottite source reservoirs, are in contrast to the findings of Kleine et al. (2004). These authors have suggested that the depleted shergottite source reservoir (as sampled by DaG 476 and SaU 051) has an ε^{182}W and an ε^{142}Nd of –0.3-0.8 and 0.5-0.7, respectively, and was established at ~50-150 Myr after solar system formation. In contrast, the enriched shergottite source reservoir (as sampled by Shergotty and Zagami) was suggested by these authors to have an ε^{182}W and an ε^{142}Nd of 0.2-0.6 and –0.2-0.3, respectively, and to have been established significantly earlier (i.e., ~7-15 after solar system formation). The formation time and isotope characteristics determined by us for the nakhlite source reservoir broadly agree with the results of Kleine et al. (2004), who estimated that this reservoir was established ~10-20 Myr after solar system formation.

The results presented here (specifically, Figs. 3 and 4) support previous suggestions that the shergottites were formed by different degrees of mixing between components derived from depleted and enriched end-member source reservoirs that formed contemporaneously (e.g., Shih et al., 1982; Jones, 1989; Borg et al., 1997; Borg and Draper, 2003), and are thus petrogenetically related. However, the distinct ε^{182}W-ε^{142}Nd systematics in the shergottites, on the one hand, and the nakhlites, on the other, suggest that these two SNC groups cannot be petrogenetically related. Nevertheless, within the uncertainties afforded by the ^{182}Hf-^{182}W and ^{146}Sm-^{142}Nd chronometers, it is possible that the distinctive source reservoirs of the shergottites and the nakhlites were indeed formed almost contemporaneously (with the nakhlite source reservoir possibly being established somewhat earlier than the shergottite reservoirs), prior to ~4.5 Ga. This may be expected if these source reservoirs were established by the crystallization of a magma ocean on early Mars. In fact, as indicated earlier, it has recently been suggested that the major and trace element abundances and isotope systematics in the SNCs may be best explained by this means (Borg and Draper, 2003).

Finally, the fact that distinctive ^{182}W-^{142}Nd systematics are preserved in samples with relatively young crystallization ages (≤1.3 Ga; Nyquist et al., 2001, and references therein) shows that the source reservoirs for these samples have remained isolated from each other since they were established prior to ~4.5 Ga and that the martian mantle has not experienced global homogenization since that time (as also suggested previously; e.g., Shih et al., 1982; Harper et al., 1995; Borg et al., 1997). This, furthermore, implies that there were no giant impacts on Mars since the SNC source reservoirs were established and, additionally, that there was lack of whole-mantle convection on Mars through most of its history.

5. CONCLUSIONS

We have determined ε^{182}W values in a variety of SNC meteorites, including the basaltic shergottites (Shergotty, Zagami, EETA, EETB, DaG 476 and SaU 008), a lherzolitic shergottite (ALHA7005), nakhlites (GV, Lafayette and NWA 998) and the orthopyroxenite ALH84001. We additionally determined ε^{142}Nd values in several shergottites (Shergotty, Zagami, EETA, DaG 476, SaU 008 and ALHA77005). The combined ^{182}W-^{142}Nd systematics in the SNC meteorites offer powerful means of constraining the early differentiation history of Mars. The following are the main conclusions based on the work presented here:

1) New ε^{142}Nd values presented here require revision of previously reported ε^{142}Nd values for several shergottites (specifically, for ALHA77005, Shergotty, DaG 476, and SaU 008). Using these new ε^{142}Nd values, all shergottites for which Nd isotopic data is

available now fall along a single isochron in a plot of ε^{143}Nd versus ε^{142}Nd, which defines a precise model age of planetary differentiation (when the depleted and enriched en-member shergottite source reservoirs were established) of 4525^{+19}_{-21} Ma.

2) While ε^{182}W in the shergottites shows only a small range (from ~0.3 to ~0.7), ε^{142}Nd shows significant variation (from ~–0.2 to ~0.9). In a plot of ε^{142}Nd versus ε^{182}W, the shergottites define a linear trend from which the Hf/W ratios in the end-member depleted (Hf/W $\geq$ 9.5) and enriched (Hf/W $\leq$ 3.8) shergottite source reservoirs have been constrained. Moreover, from this linear trend we estimate an ε^{182}W of 0.37 ± 0.07 for the primitive martian mantle (PMM) following core formation. From this ε^{182}W value for the PMM it is possible to estimate a two-stage model age of core formation on Mars of 10.9 ± 0.4 Myr after solar system formation.
3) ^{182}W-^{142}Nd systematics in the nakhlites suggest that the major silicate differentiation event that formed the nakhlite mantle source on Mars occurred early (most likely within ~25 Myr after solar system formation) and resulted in significant fractionation of the Hf/W and Sm/Nd ratios in the nakhlite source.
4) Within the uncertainties afforded by the ^{182}Hf-^{182}W and ^{146}Sm-^{142}Nd chronometers, it is possible that the silicate differentiation events that established the source reservoirs of the shergottite and nakhlites, and possibly also ALH84001, occurred almost contemporaneously in the early history of Mars (with the nakhlite source reservoir possibly forming somewhat earlier than the shergottite source reservoirs). However, the distinct ε^{182}W-ε^{142}Nd systematics in the shergottites and the nakhlites require their origination from distinct source reservoirs. The preservation of such distinct ^{182}W-^{142}Nd systematics in rocks with relatively young ages ($\leq$1.3 Ga) indicates isolation of their

source reservoirs since they were established early in Mars' history. This further implies that the martian mantle has not been homogenized by giant impacts or global mantle convection since the SNC source reservoirs were established.

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Figure Captions

Figure 1. Long-term reproducibility (over the period of several months during which the sample analyses were made) of W and Nd isotopic measurements reported as ε^{182}W and ε^{142}Nd, respectively, of (a) the NIST 3163 W standard solution with a concentration of 10-50 ppb and (b) the Geological Survey of Japan JNDi-1 Nd standard solution with a concentration of 35-50 ppb. Each data point is the average of 5 to 10 brackets of repeat measurements of the standard performed on a single day.

Figure 2: ε^{182}W versus ε^{142}Nd in LREE-enriched basaltic shergottites (S = Shergotty; Z = Zagami; LA = Los Angeles), LREE-depleted basaltic shergottites (EETA = EETA79001 Lithology A; EETB = EETA79001 Lithology B; DaG 476 = Dar al Gani 476; SaU 008 = Sayh al Uhaymir 008), a lherzolitic shergottite (ALH = ALHA77005), and nakhlites (GV = Governador Valadares; Lafayette; NWA 998 = Northwest Africa 998). ALH84001 (ε^{182}W=0.49 ± 0.33) is not plotted here since its ε^{142}Nd value is undetermined. Solid squares indicate that both W and Nd isotopic compositions are from this work; open squares indicate that while W isotopic compositions are from this work, the Nd isotopic compositions are from previous studies (Harper et al., 1995; Carlson and Irving, 2004). The ε^{142}Nd value for LA is taken to be the average of the values for Shergotty and Zagami (taken from this work). Dashed gray lines show the chondritic W and Nd isotopic compositions.

Figure 3: ε^{142}Nd versus initial ε^{143}Nd at 175 Ma for the shergottites. In a two-stage model of Nd isotope evolution (after Fig. 5 of Borg et al., 2003), dashed lines show the various times at which

Sm-Nd fractionation may have occurred to establish silicate source reservoirs on Mars. The initial ε^{143}Nd values are from Borg et al. (2003) and references therein. Solid squares indicate ε^{142}Nd values from this work (S = Shergotty; Z = Zagami; EETA = EETA79001 Lithology A; DaG = Dar al Gani 476; ALH = ALHA77005); open squares indicate ε^{142}Nd values for EETA79001 Lithology B (EETB) and QUE94201 (QUE) from Harper et al. (1995) and Borg et al. (1997), respectively. The slope of the correlation line for the shergottite data indicates that mantle sources of the shergottites were established at 4525^{+19}_{-21} Ma.

Figure 4: ε^{142}Nd versus ε^{182}W in the basaltic shergottites. Symbols are as indicated in Fig. 2. Solid black line is the best-fit line to the data (calculated using the linear regression method of Williamson, 1968) with a slope of 0.28 ± 0.14. The intercept of 0.37 ± 0.07 is the ε^{182}W value inferred for the primitive martian mantle (PMM), which is significantly more radiogenic compared to the bulk chondritic value of –1.9 (average of values reported by Kleine et al., 2002, 2004; Schoenberg et al., 2002; Yin et al., 2002) and results from the elevated Hf/W ratio in the bulk mantle following core formation. Assuming an initial solar system ^{182}Hf/^{180}Hf ratio of $\sim 1 \times 10^{-4}$ and an Hf/W ratio of ~5.1 in the PMM, an ε^{182}W of 0.37 ± 0.07 yields a two-stage model age of core formation of 10.9 ± 0.4 Myr after the beginning of the solar system.

Figure 5: ε^{182}W versus ε^{142}Nd in the nakhlites plotted with the results of modeling calculations (shown as the black and gray curves, and discussed in more detail in the text). The solid diamond indicates the average composition of the three nakhlites, GV, Lafayette and NWA 998, plotted here (open squares). Each plotted open circle on the curves represents the present-day ε^{182}W and ε^{142}Nd attained in a source region (characterized by unique Sm/Nd and Hf/W ratios for each

curve) established at a particular time $T_{3''}$ such that the time interval ($T_1 - T_{3''}$), where T_1 is the time of solar system formation, ranges up to 100 Myr. The upper black curve shows the results for a majorite-bearing deep mantle (MDM) source, characterized by a ^{147}Sm/^{144}Nd ratio of ~0.303 and a ^{180}Hf/^{183}W ratio of ~126. The lower black curve shows the results for a garnet-bearing shallow mantle (GSM) source with a ^{147}Sm/^{144}Nd of ~0.266 and a ^{180}Hf/^{183}W of ~43. The gray curves are results of calculations for three depleted mantle source compositions modeled by Kleine et al. (2004), the ^{147}Sm/^{144}Nd-^{180}Hf/^{183}W pairs for which are (0.231, 18), (0.255, 22), and (0.281, 27). Comparison of the average nakhlite composition with results of model calculations shown here indicates that the nakhlite source is likely to have been established *within* ~25 Myr after the beginning of the solar system.

Table 1. Column chemistry for separation of W.

Step	Volume (ml)	Solution
Procedure for silicate samples (3 ml 200-400 mesh Bio-Rad AG 1 × 8 resin in 10 ml column)		
Clean resin	6	Ultrapure (18mΩ/cm) water
Clean resin	6	0.5 N HCl-0.5 N HF
Clean resin	20	7 N HCl-1 N HF
Clean resin	6	Ultrapure (18mΩ/cm) water
Equilibrate resin	6	0.5 N HCl-0.5 N HF
Load sample	3.75	1 N HCl-0.5 N HF
Rinse	7.5	0.5 N HCl-0.5 N HF
Rinse	6	0.5 mM HCl-0.5 mM HF
Elute Ti	7.5-45	9 N HCl-0.01 N HF
Rinse	2	7 N HCl-1 N HF
Elute W	18	7 N HCl-1 N HF
Rinse	6	Ultrapure (18mΩ/cm) water
Procedure for metal-rich samples (3 ml 200-400 mesh Bio-Rad AG 1 × 8 resin in 10 ml column)		
Clean resin	6	Ultrapure (18mΩ/cm) water
Clean resin	6	0.5 N HCl-1 N HF
Clean resin	20	9 N HCl-1 N HF
Clean resin	6	Ultrapure (18mΩ/cm) water
Equilibrate resin	6	0.5 N HCl-1 N HF
Load sample	3.75	0.5 N HCl-1 N HF
Rinse	15	0.5 N HCl-1 N HF
Rinse	2	9 N HCl-1 N HF
Elute W	18	9 N HCl-1 N HF
Rinse	6	Ultrapure (18mΩ/cm) water

Table 2. W and Nd isotopic data for terrestrial and meteoritic samples.[a]

Sample	Sample type	Wt. (g)[b]	ε^{182}W (this work)	ε^{182}W (previous work)	Wt. (g)[c]	ε^{142}Nd (this work)	ε^{142}Nd (previous work)
Terrestrial samples							
NIST 3163	W standard		0.01 ± 0.17				
JNdi-1[d]	Nd standard					0.00 ± 0.11	
BCR2	Basalt		0.04 ± 0.13				
AGV2	Andesite		0.05 ± 0.20				
Meteoritic samples (other than SNCs)							
Allende Average	CV3 chondrite		–1.86 ± 0.08	–1.90 ± 0.20[e]			
Allende #1		1.0	–1.92 ± 0.12				
Allende #2		1.0	–1.81 ± 0.12				
Toluca Average	IA iron meteorite		–2.85 ± 0.28	–3.18 ± 0.30[f]			
Toluca #1		0.4	–2.70 ± 0.40				
Toluca #2		0.4	–3.00 ± 0.40				
SNC samples							
Shergotty	Basaltic shergottite	0.20	0.27 ± 0.13	0.34 ± 0.28[g]	0.07	–0.22 ± 0.13	0.28 ± 0.19[i]
Zagami Average	Basaltic shergottite		0.32 ± 0.12	0.50 ± 0.34[g]		–0.16 ± 0.10	–0.09 ± 0.18[i]
Zagami #1		0.20	0.28 ± 0.16		0.10	–0.15 ± 0.15	
Zagami #2		0.30	0.35 ± 0.19		0.11	–0.17 ± 0.12	
Los Angeles Average	Basaltic shergottite		0.44 ± 0.21				
Los Angeles #1		0.25	0.31 ± 0.18				
Los Angeles #2		0.23	0.56 ± 0.39				
EETA79001	Basaltic shergottite			2.21 ± 0.60[g] 0.4 ± 0.4[h]			
Lithology A		1.0	0.65 ± 0.29		0.13	0.36 ± 0.10	0.26 ± 0.23[i]
Lithology B		0.60	0.35 ± 0.21				0.30 ± 0.29[i]
DaG 476 Average	Basaltic shergottite		0.66 ± 0.11	–0.3 ± 0.6[h]		0.81 ± 0.26	0.40 ± 0.26[j]
DaG 476 #1		2.78	0.57 ± 0.15		0.12		
DaG 476 #2		2.11	0.75 ± 0.15		0.13		
SaU 008 Average	Basaltic shergottite		0.40 ± 0.20	0.8 ± 0.5[h]		0.91 ± 0.31	0.22 ± 0.16[j]
SaU 008 #1		1.51	0.29 ± 0.38		0.13		
SaU 008 #2		2.00	0.51 ± 0.15		0.12		
ALHA77005	Lherzolitic shergottite	1.10	0.91 ± 0.32	0.34 ± 1.2[g]	0.18	0.29 ± 0.10	–0.17 ± 0.32[i]
Governador Valadares	Nakhlite (clinopyroxenite)	0.42	2.99 ± 0.12				0.79 ± 0.19[i]
Lafayette	Nakhlite (clinopyroxenite)	0.42	2.87 ± 0.12	2.14 ± 0.36[g]			0.91 ± 0.21[i]
Northwest Africa 998	Nakhlite (clinopyroxenite)	0.57	3.35 ± 0.40				0.60 ± 0.20[k]
ALH84001	Orthopyroxenite	0.42	0.49 ± 0.33	0.72 ± 0.52[g]			

[a] W isotopic data are reported as $\varepsilon^{182}\mathrm{W} = (^{182}\mathrm{W}/^{183}\mathrm{W})_{\mathrm{Sample}}/(^{182}\mathrm{W}/^{183}\mathrm{W})_{\mathrm{Standard}} - 1] \times 10^4$. Nd isotopic data are reported as $\varepsilon^{142}\mathrm{Nd} = (^{142}\mathrm{Nd}/^{144}\mathrm{Nd})_{\mathrm{Sample}}/(^{142}\mathrm{Nd}/^{144}\mathrm{Nd})_{\mathrm{Standard}} - 1] \times 10^4$. For all samples except for the NIST 3163 and JNdi-1 standards, uncertainties are the either $\pm 2\sigma_m$ of repeat measurements of the samples or $\pm 2\sigma_m$ of repeat measurements of an equal number of standards analyzed along with the samples, whichever is greater; for the NIST 3163 and JNdi-1 standards, uncertainties are $\pm 2\sigma_p$. σ_m = standard deviation of the mean; σ_p = standard deviation of the population. [b] Weight in grams of the sample used for the W isotopic analyses (this work). [c] Weight in grams of the sample used for the Nd isotopic analyses (this work). [d] Geological Survey of Japan Nd standard. [e] Average of values reported by Kleine et al., 2002, 2004; Schoenberg et al., 2002; Yin et al., 2002. [f] Yin et al., 2002. [g] Lee and Halliday, 1997. [h] Kleine et al., 2004; the ε^{142}Nd value listed here for SaU 008 is the one that was reported for SaU 051 (paired with SaU 008). [i] Harper et al., 1995. [j] Jagoutz et al., 2003; these data for DaG 476 and SaU 005 (paired with SaU 008) are revised from an earlier report by Jagoutz et al. (2000) which had indicated ε^{142}Nd values of ~0.8 in these meteorites. [k] Carlson and Irving (2004).

Table 3. W-Nd isotope characteristics and redox states of silicate source reservoirs on Mars.

Silicate reservoir on Mars	SNCs sampling the reservoir	Redox state	ε^{182}W	ε^{142}Nd	^{180}Hf/^{183}W	^{147}Sm/^{144}Nd	Formation time
Depleted shergottite reservoir (in mantle)	LREE-depleted shergottites (e.g., QUE94201, DaG 476, SaU 008)	Reduced (~IW)	≥ 0.6	≥ 0.9	≥ 24	≥ 0.285	$4525^{+19}/_{-21}$ Ma
Enriched shergottite reservoir (in mantle or crust)	LREE-enriched shergottites (e.g., Shergotty, Zagami, LA)	Oxidized (>IW+2)	≤ 0.3	≤ -0.2	≤ 9.4	≤ 0.182	$4525^{+19}/_{-21}$ Ma
Depleted nakhlite reservoir (in mantle)	All nakhlites	Oxidized (~IW+3.5)	~3.1	~0.7	~43	~0.266	≥4542 Ma

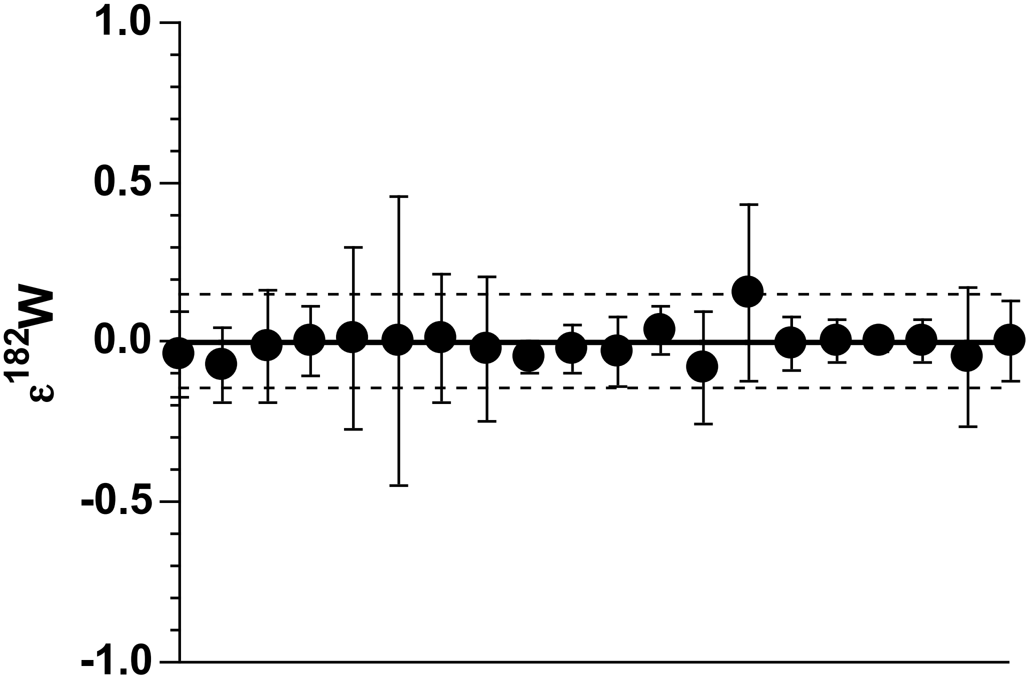

Figure 1a
Foley et al.

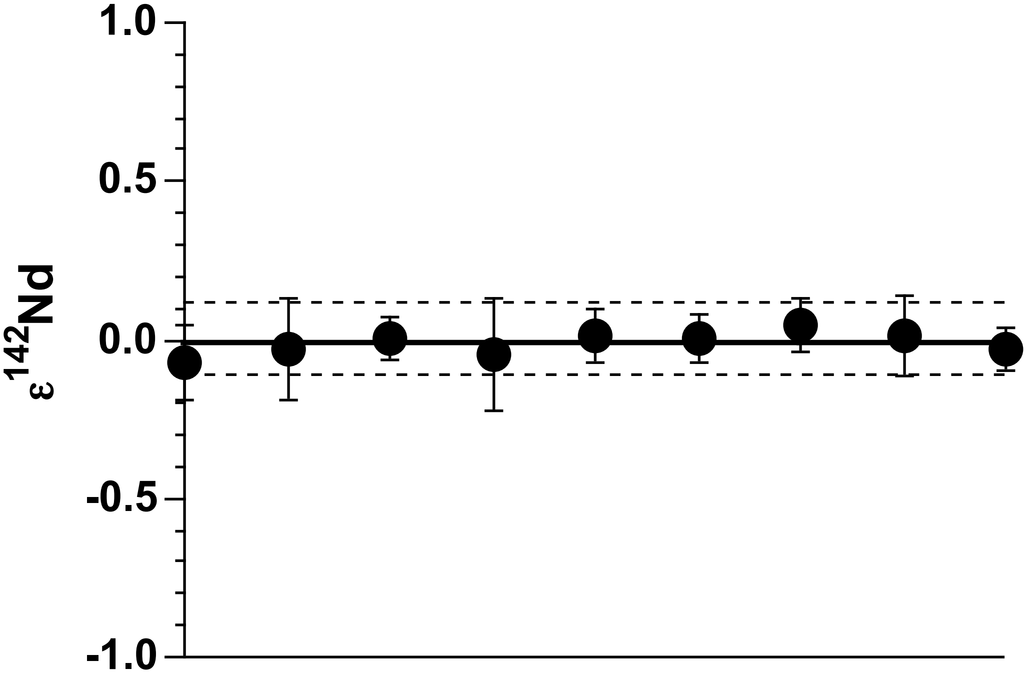

Figure 1b
Foley et al.

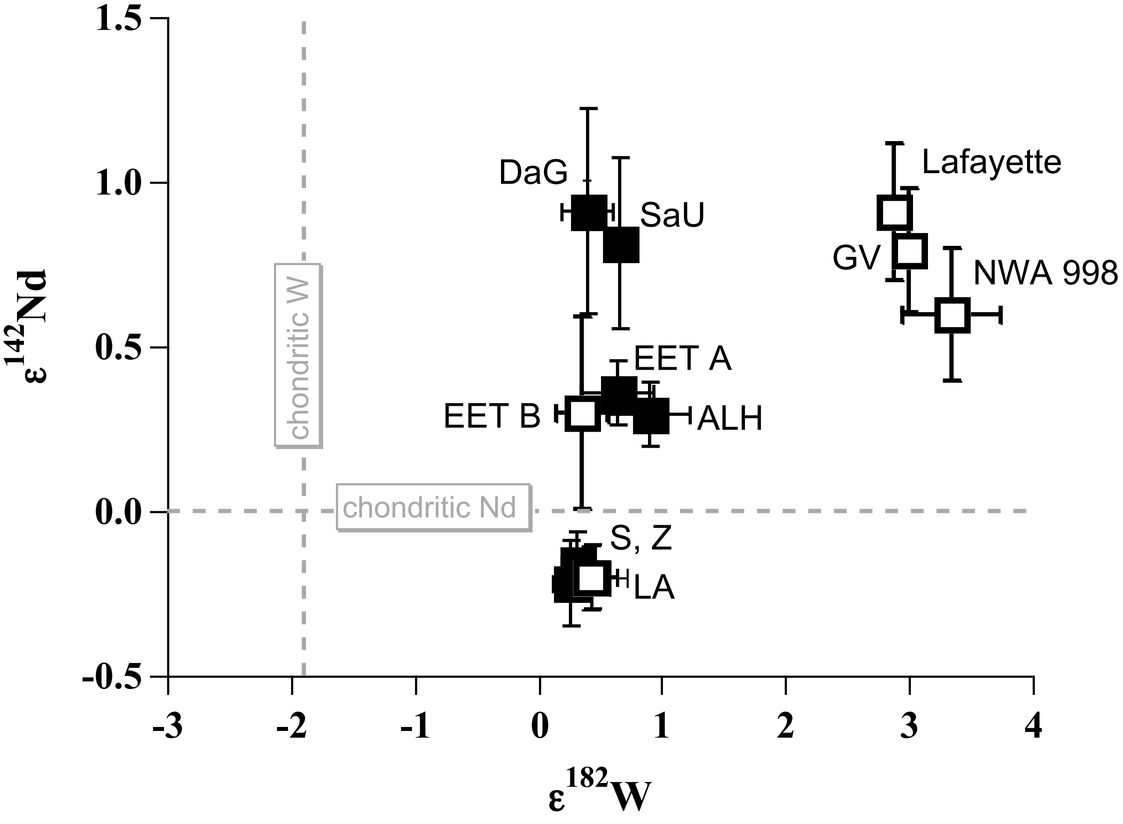

Figure 2
Foley et al.

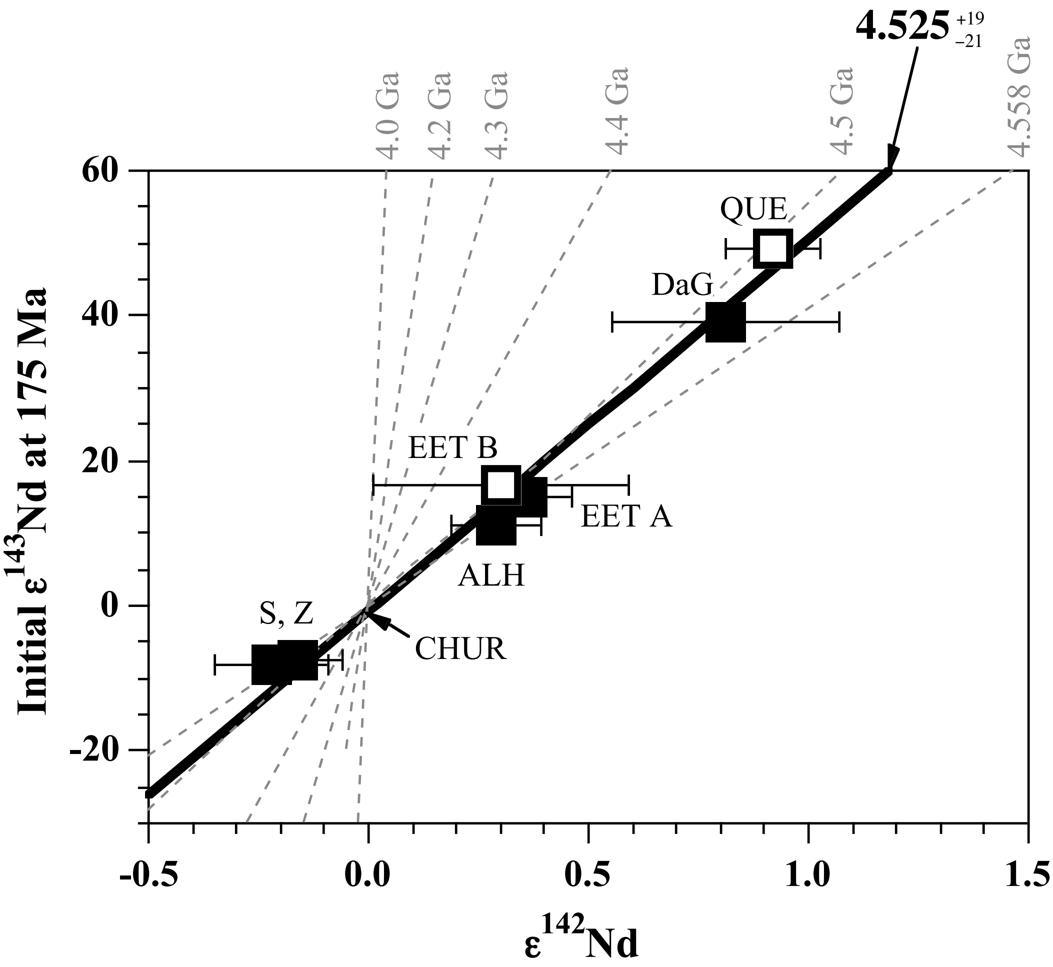

Figure 3
Foley et al.

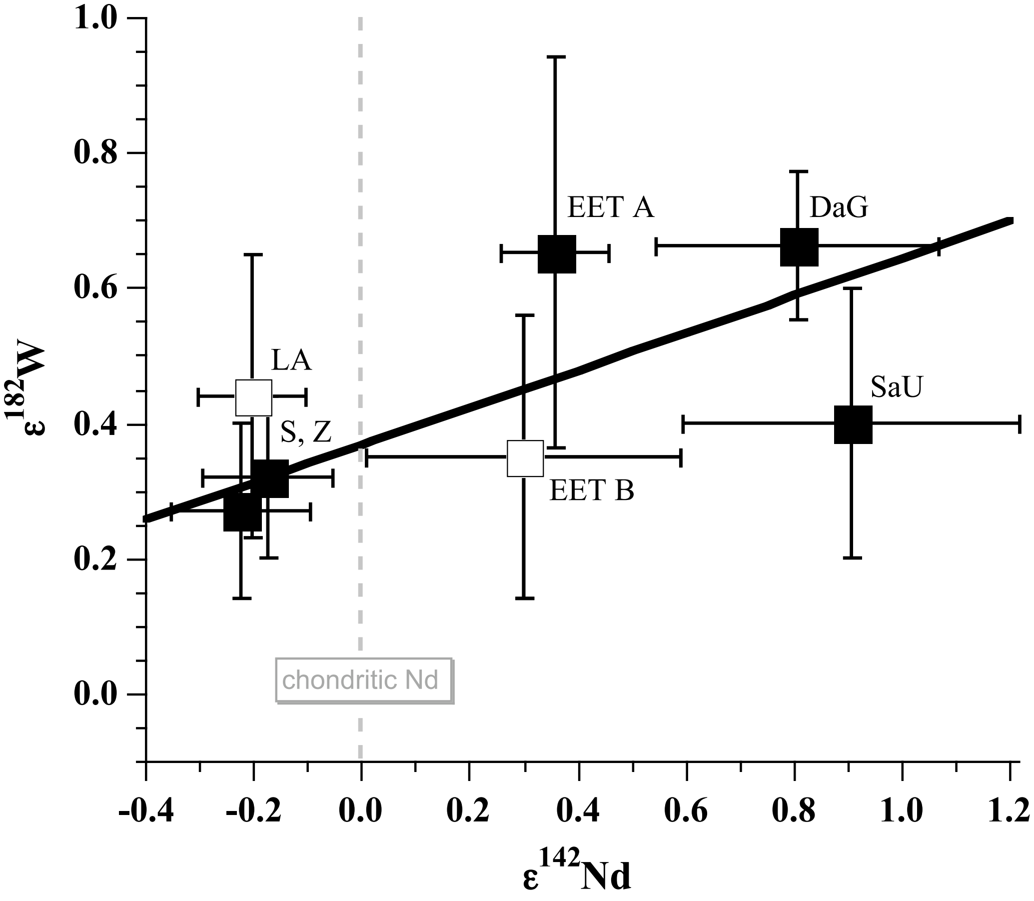

Figure 4
Foley et al.

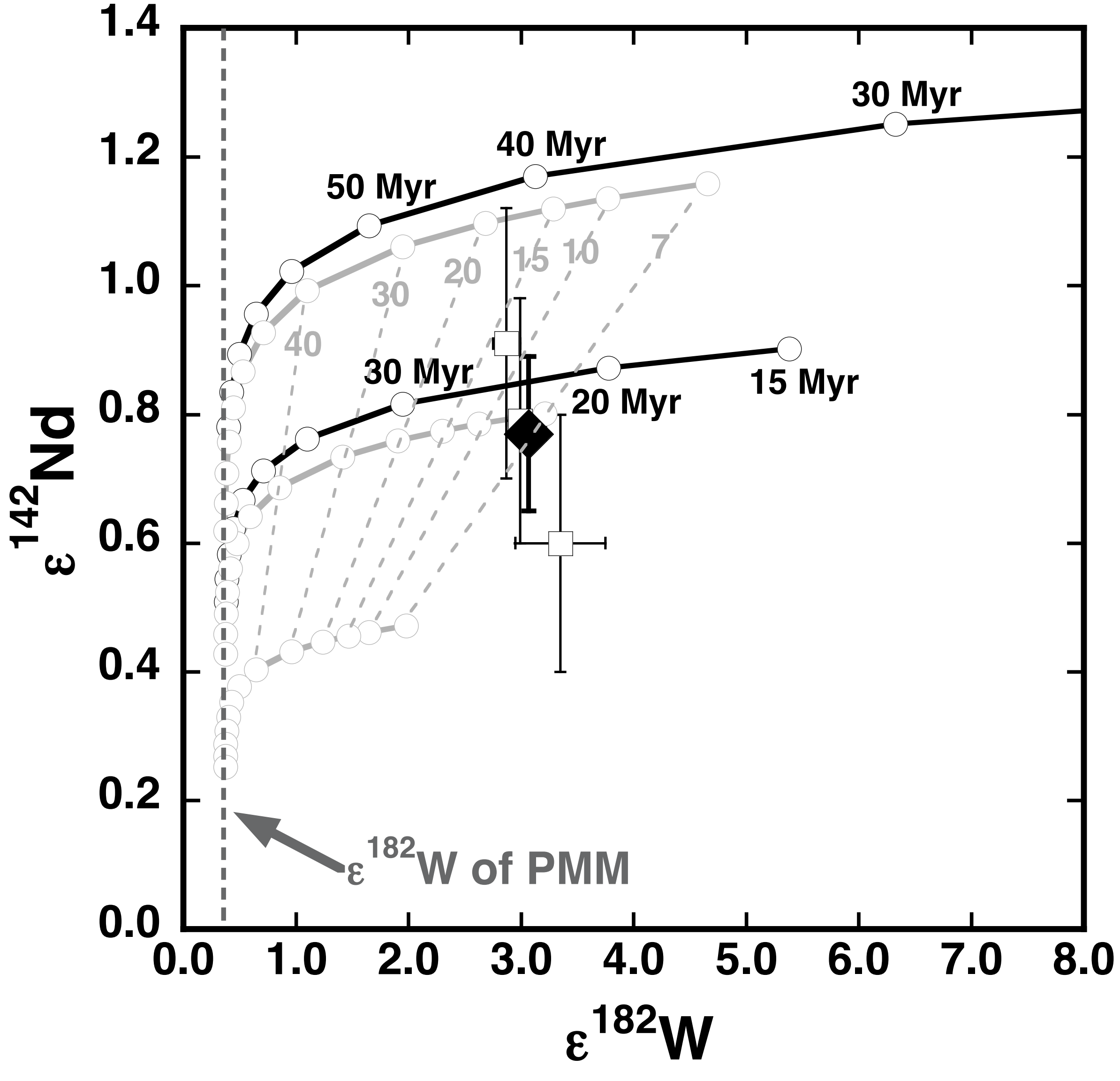

Figure 5
Foley et al.