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The early differentiation history of Mars from ^{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 isotopes in the SNC (Shergottite-Nakhlite-Chassignite (martian)) meteorites. We have determined that $\epsilon^{182}\text{W}$ values in the nakhlites are uniform within analytical uncertainties and have an average value of ~ 3 . Also, while $\epsilon^{182}\text{W}$ values in the shergottites have a limited range (from 0.3–0.7), their $\epsilon^{142}\text{Nd}$ values vary considerably (from -0.2 – 0.9). There appears to be no correlation between $\epsilon^{182}\text{W}$ and $\epsilon^{142}\text{Nd}$ in the nakhlites and shergottites. These results shed new light on early differentiation processes on Mars, particularly on the timing and nature of fractionation in silicate reservoirs. Assuming a two-stage model, the metallic core is estimated to have formed at ~ 12 Myr after the beginning of the solar system. Major silicate differentiation established the nakhlite source reservoir before ~ 4542 Ma and the shergottite source reservoirs at $4525 \begin{bmatrix} +19 \\ -21 \end{bmatrix}$ 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 nakhlites and shergottites may have occurred contemporaneously, possibly during crystallization of a global magma ocean. The distinct ^{182}W - ^{142}Nd isotope systematics in the nakhlites and the shergottites imply the presence of at least three isotopically distinct silicate reservoirs on Mars, two of which are depleted in incompatible lithophile elements relative to chondrites, and the third is enriched. The two depleted silicate reservoirs most likely reside in the Martian mantle, while the enriched reservoir could be either in the crust or the mantle. Therefore, the ^{182}W - ^{142}Nd isotope systematics indicate that the nakhlites and the shergottites originated from distinct source reservoirs and cannot be petrogenetically related. A further implication is that the source reservoirs of the nakhlites and shergottites on Mars have been isolated since their establishment before ~ 4.5 Ga. Therefore, there has been no giant impact or efficient global mantle convection to thoroughly homogenize the Martian mantle following the establishment of the SNC source reservoirs. Copyright © 2005 Elsevier Ltd

1. INTRODUCTION

The ^{182}Hf - ^{182}W extinct chronometer ($t_{1/2} \sim 9$ 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; Kleine et al., 2002; Yin et al., 2002; Kleine et al., 2004). Both Hf and W are highly refractory and are assumed to be present in approximate chondritic relative abundances in the terrestrial planets (i.e., $^{180}\text{Hf}/^{183}\text{W} \sim 2.8$; Harper and Jacobsen, 1996). During core formation, the lithophile Hf preferentially partitions into the silicate reservoir, whereas the siderophile W partitions into the metallic core. For Mars, Hf-W fractionation during core formation is expected to result in a $^{180}\text{Hf}/^{183}\text{W}$ ratio of ~ 13 in its bulk silicate reservoir (inferred from the La/W ratio estimated for the primitive Martian mantle and the chondritic La/Hf ratio; Palme and Beer, 1993; Kong et al., 1999). Moreover, silicate differentiation is expected to produce further Hf-W fractionation in crustal and mantle reservoirs on Mars, possibly producing $^{180}\text{Hf}/^{183}\text{W}$ ratios up to ~ 126 in garnet-bearing deep mantle reservoirs and up to ~ 43

in majorite-bearing shallow mantle reservoirs (Richter and Shearer, 2003). Therefore, if core formation and silicate differentiation events occurred within the first ~ 50 Myr of solar system history, they would result in the establishment of silicate reservoirs with highly variable ^{182}W excesses.

The ^{146}Sm - ^{142}Nd short-lived chronometer ($t_{1/2} \sim 103$ Myr) has also been applied towards understanding early silicate differentiation on Mars (e.g., Harper et al., 1995; Borg et al., 1997; Borg et al., 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, that is, $^{146}\text{Sm}/^{144}\text{Sm} \sim 0.008$ (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 $^{142}\text{Nd}/^{144}\text{Nd}$ ratio relative to chondrites is only on the order of ~ 1 ϵ -unit (one part in 10^4).

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The earliest reported W and Nd isotopic analyses of the SNCs showed that their whole rock $\epsilon^{182}\text{W}$ values (defined as deviations of the $^{182}\text{W}/^{183}\text{W}$ or $^{182}\text{W}/^{184}\text{W}$ ratio from the terrestrial standard value in parts per 10^4) vary from ~ 0 to ~ 3 (Lee and Halliday, 1997), while their $\epsilon^{142}\text{Nd}$ values (defined as deviations of $^{142}\text{Nd}/^{144}\text{Nd}$ 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 correlation between $\epsilon^{182}\text{W}$ and $\epsilon^{142}\text{Nd}$ in the SNC meteorites, from which it was inferred that core formation and silicate differentiation processes on Mars were “coeval and cogenetic” and occurred while both ^{182}Hf and ^{146}Sm were extant (Lee and Halliday, 1997). However, it has subsequently been shown that $\epsilon^{182}\text{W}$ in terrestrial samples is more radiogenic than in chondrites by ~ 2 ϵ units (Kleine et al., 2002; Schoenberg et al., 2002; Yin et al., 2002). Therefore, the $\epsilon^{182}\text{W}$ in the SNCs is clearly superchondritic. It has been suggested that the superchondritic $\epsilon^{182}\text{W}$ and the nearly chondritic $\epsilon^{142}\text{Nd}$ in some SNCs resulted from core formation preceding silicate differentiation and occurred within the first ~ 12 to 13 Myr of solar system formation (Kleine et al., 2002; Schoenberg et al., 2002; Yin et al., 2002). Nevertheless, the suggested correlation between $\epsilon^{182}\text{W}$ and $\epsilon^{142}\text{Nd}$ 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 $\epsilon^{182}\text{W}$ and $\epsilon^{142}\text{Nd}$ 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 isotope systematics in a greater variety of shergottite and nakhlite samples than those analyzed in previous such investigations. Specifically, we report here the $^{182}\text{W}/^{183}\text{W}$ 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 relatively light rare earth element (LREE) enriched basaltic shergottites (i.e., those with whole-rock chondrite-normalized La/Lu ratios of ~ 1) Shergotty, Zagami and Los Angeles (LA), and the LREE-depleted basaltic shergottites (i.e., those with chondrite-normalized La/Lu ratios of $\ll 1$) 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); three nakhlites: Governador Valadares (GV), Lafayette, and Northwest Africa 998 (NWA 998); and the orthopyroxenite ALH84001. We also report the $^{142}\text{Nd}/^{144}\text{Nd}$ isotopic compositions of six of the shergottites: ALHA77005, Shergotty, Zagami, EETA, DaG 476, and SaU 008 (REE data from Shih et al., 1982; Lødders,

1998 and references therein; Dreibus et al., 2000; Folco et al., 2000; Barrat et al., 2001). 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 m Ω /cm); both were in ultrasonic baths for ~ 10 to 15 min. 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:HNO₃, followed by concentrated HNO₃ and concentrated HCl. Dissolution of Toluca and Allende required the additional use of aqua regia and perchloric acid, respectively, to ensure complete dissolution of all phases in these samples.

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 1 N 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 to 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 the Ti, which 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. Approximately 0.2 g of Toluca was loaded on the column, and two passes through this column were performed to ensure effective separation of W from the rest of the elements in the sample matrix. The total sample yield of W for silicate and metal-rich samples using the procedures described above is 70 to 80% . 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

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

analyses. Before being used, the new beakers were boiled twice in 50% HNO₃ and then in ultrapure water (for a minimum of 6 h 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°C for a minimum of 3 h, followed by a thorough rinse with ultrapure water; this procedure was repeated twice for each beaker. The resin for W column chemistry was precleaned before 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 a cation exchange column with nitric acid as elutant; (2) purification of the REE cut using an RE-Spec resin and nitric acid; (3) separation of Nd from the other REE using cation exchange resin (NH₄ form) and methylactic acid (repeated twice for some samples); (4) removal of the methylactic acid from the Nd cut using a cation exchange cleanup column; and (5) removal of any remaining Ce and Sm from the Nd cut using a cleanup column (repeated twice) with Ln-spec resin and hydrochloric acid. This last Ln-Spec cleanup column procedure was similar to that de-

scribed by Pin and Zalduegui (1997). The total sample yield of Nd using the procedures described above is ~90%. Total procedural blanks were ~7 pg Nd and were negligible compared to the amount of Nd in the samples. The clean Nd cut was dried down and then brought into a solution of 0.5 N HNO₃ for isotopic analyses.

2.2. Mass Spectrometry

Tungsten and neodymium isotopic analyses were made using a Micromass IsoProbe multicollector inductively coupled plasma mass spectrometer (MC-ICPMS) in the Isotope Geochemistry Laboratory at the Field Museum. For W isotopic measurements, sample solutions, typically with a W concentration of 20 ppb, were introduced into the plasma using a CETAC Aridus microconcentric nebulizer (MCN), and resulted in an ion beam intensity of ~1.5 × 10⁻¹¹ A for ¹⁸²W. The array of 9 Faraday collectors allowed simultaneous collection of all W isotopes as well as ¹⁸⁸Os (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 fractionation-corrected (see below) ¹⁸²W/¹⁸³W ratio.

Each W isotope measurement of a standard or a sample solution was comprised of 20 to 40 cycles of 10 s integrations and was preceded by a 10-min washout and a 45-s integration of the background. Each sample measurement was bracketed on either side with multiple measurements of the NIST 3163 W standard. For each sample, at least two repeat measurements were performed interspersed with measurements of the NIST 3163 W standard. The W ion beam intensities for standards and samples were matched to within ± 15%. We corrected the measured ¹⁸²W/¹⁸³W ratio for instrumental mass fractionation by normalizing to ¹⁸⁶W/¹⁸⁴W = 0.927633 (Lee and Halliday, 1997) using the exponential law (Russell et al., 1978). As a check, we also determined the fractionation corrected ¹⁸²W/¹⁸³W ratio by normalizing to ¹⁸⁴W/¹⁸³W = 2.139758 (Harper and Jacobsen, 1996). For all samples, the corrected ¹⁸²W/¹⁸³W ratios were the same using either one of these normalization schemes within 2σ errors. All ¹⁸²W/¹⁸³W ratios measured in the samples are reported here relative to the terrestrial standard in parts per 10⁴, that is, as ε¹⁸²W values, defined as follows:

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

The measurement protocol for Nd isotopic analyses was similar to that used for W isotopic analyses. Sample solutions typically with a Nd concentration of ~50 ppb were introduced into the plasma using a CETAC Aridus MCN, resulting in an ion beam intensity of ~3 × 10⁻¹¹ A for ¹⁴²Nd. We measured all Nd isotopes except for ¹⁵⁰Nd. In addition to the Nd isotopes, ¹⁴⁰Ce and ¹⁴⁹Sm 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 ¹⁴²Nd/¹⁴⁴Nd ratios were negligible for all samples except for DaG 476 and SaU

008, for which the Sm correction was $\sim 0.2 \epsilon$ units.

Measurements of samples, with at least three repeats, were bracketed on either side with multiple measurements of the Geological Survey of Japan JNdi-1 Nd standard. As with the W analyses, the Nd ion beam intensities for standards and samples were matched to within $\pm 15\%$. The normalizing ratio used to correct the raw $^{142}\text{Nd}/^{144}\text{Nd}$ ratio for instrumental mass fractionation was the $^{146}\text{Nd}/^{144}\text{Nd}$ ratio in the terrestrial standard of 0.7219 (using the exponential law). All $^{142}\text{Nd}/^{144}\text{Nd}$ ratios measured in the samples are reported here relative to the terrestrial standard in parts per 10^4 , that is, as $\epsilon^{142}\text{Nd}$ values, defined as follows:

$$\epsilon^{142}\text{Nd} = \left(\frac{\left(\frac{^{142}\text{Nd}}{^{144}\text{Nd}} \right)_{\text{Sample}} - \left(\frac{^{142}\text{Nd}}{^{144}\text{Nd}} \right)_{\text{Standard}}}{\left(\frac{^{142}\text{Nd}}{^{144}\text{Nd}} \right)_{\text{Standard}}} \right) \cdot 10^4 \quad (2)$$

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. Figure 1a and b show the results of these analyses. Each data point is an average calculated from 5 to 10 repeat measurements of the standard (treated as an unknown sample) 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 $\pm 0.3 \epsilon$ units (2σ). The long-term reproducibility of W and Nd isotopic measurements is better than $\pm 0.1 \epsilon$ units (2σ) (shown as the dashed lines in Fig. 1; Table 2).

3. RESULTS

The results of our W and Nd isotopic analyses are given in Table 2 and illustrated in Figure 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 BCR-2 and AGV-2, the carbonaceous chondrite Allende, and the IA iron meteorite Toluca. As can be seen in Table 2, $\epsilon^{182}\text{W}$ in the terrestrial rock standards BCR-2 and AGV-2 is identical to that in the NIST W standard. The $\epsilon^{182}\text{W}$ values determined for Allende and Toluca are, within uncertainties, identical to those recently reported by several investigators (Kleine et al., 2002; Schoenberg et al., 2002; Yin et al., 2002; Kleine et al., 2004). The accuracy of our Nd isotopic analyses for mafic silicate samples is demonstrated by the results obtained for the terrestrial basaltic rock standard BCR-1. As can be seen in Table 2, $\epsilon^{142}\text{Nd}$ in BCR-1 is identical to that in the JNdi-1 Nd standard.

Tungsten isotopic compositions are reported here for several basaltic shergottites, that is, the LREE-enriched basalts Shergotty, Zagami, and LA, and the LREE-depleted basalts EETA, EETB, DaG 476, and SaU 008. The $\epsilon^{182}\text{W}$ 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 $\epsilon^{182}\text{W}$ 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 $\epsilon^{182}\text{W}$ value of 0.49 ± 0.33 , which falls within the range of $\epsilon^{182}\text{W}$ in the basaltic shergottites. The three nakhlites analyzed here (GV, Lafayette and NWA 998) have W isotopic compositions that are quite distinct from, and

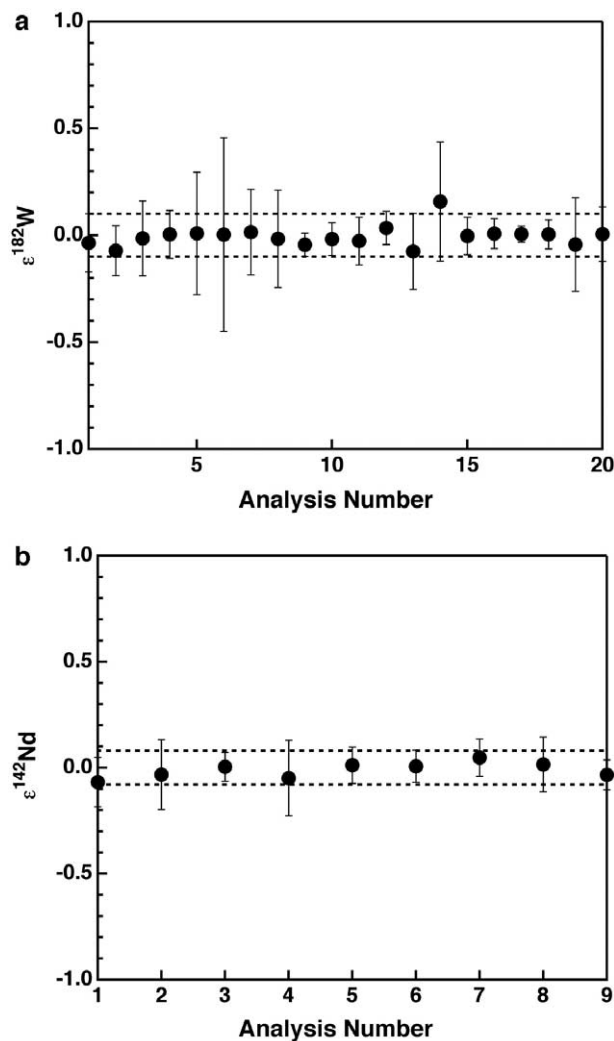


Fig. 1. Long-term reproducibility (over a period of several months during which the sample analyses were made) of W and Nd isotopic measurements reported as $\epsilon^{182}\text{W}$ and $\epsilon^{142}\text{Nd}$, respectively, of (a) the NIST 3163 W standard solution, and (b) the Geological Survey of Japan JNdi-1 Nd standard solution. Each data point is the average of 5 to 10 repeat measurements of the standard at a comparable concentration to that measured in the SNCs (described in text), treated as an unknown sample, performed on a single day.

significantly more radiogenic than, those of the shergottites and the orthopyroxenite ALH84001. Within uncertainties, all three nakhlites analyzed here have identical $\epsilon^{182}\text{W}$ values, with a weighted average of 2.95 ± 0.08 .

The $\epsilon^{142}\text{Nd}$ values we measured in six shergottites (five basaltic and one lherzolitic) show a range of $\sim 1 \epsilon$ unit. The LREE-enriched shergottites Shergotty and Zagami have the lowest $\epsilon^{142}\text{Nd}$ values that are identical, within errors, and have a weighted average of -0.18 ± 0.08 . The LREE-depleted shergottites DaG 476 and SaU 008 have the highest $\epsilon^{142}\text{Nd}$ values that are also identical, within errors, and have a weighted average of 0.85 ± 0.20 . The $\epsilon^{142}\text{Nd}$ values in the basaltic shergottite EETA (0.36 ± 0.10) and the lherzolitic shergottite ALHA77005 (0.29 ± 0.10) are intermediate be-

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

Sample	Sample type	W _t (g) ^b	$\epsilon^{182}\text{W}$ (this work)	$\epsilon^{183}\text{W}$ (previous work)	W _t (g) ^c	$\epsilon^{142}\text{Nd}$ (this work)	$\epsilon^{142}\text{Nd}$ (previous work)
Terrestrial samples							
NIST 3163	W standard		-0.01 ± 0.10				
JNdi-1 ^d	Nd standard					-0.01 ± 0.08	
BCR-1	Basalt					-0.01 ± 0.17	
BCR-2	Basalt		0.04 ± 0.13				
AGV-2	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		0.31 ± 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		0.35 ± 0.16				
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^i
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		0.48 ± 0.14	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 $\epsilon^{182}\text{W} = ({}^{182}\text{W}/{}^{183}\text{W})_{\text{Sample}} / ({}^{182}\text{W}/{}^{183}\text{W})_{\text{Standard}} - 1] \times 10^4$. Nd isotopic data are reported as $\epsilon^{142}\text{Nd} = ({}^{142}\text{Nd}/{}^{144}\text{Nd})_{\text{Sample}} / ({}^{142}\text{Nd}/{}^{144}\text{Nd})_{\text{Standard}} - 1] \times 10^4$. For all samples except for the NIST 3163 and JNdi-1 standards, uncertainties are 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 $\epsilon^{142}\text{Nd}$ 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 $\epsilon^{142}\text{Nd}$ values of ~ 0.8 in these meteorites.

^k Carlson and Irving (2004).

tween those of Shergotty and Zagami, on the one hand, and DaG 476 and SaU 008, on the other.

Figure 2 shows a plot of $\epsilon^{182}\text{W}$ versus $\epsilon^{142}\text{Nd}$ for the SNCs in which all the W isotopic data are from this work; while most of the Nd isotopic data (solid symbols) are from this study, some (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 $\epsilon^{182}\text{W}$ but wide-ranging $\epsilon^{142}\text{Nd}$, while nakhlites define a distinct compositional group with uniform $\epsilon^{182}\text{W}$ and $\epsilon^{142}\text{Nd}$ (within 2σ errors).

4. DISCUSSION

4.1. ${}^{182}\text{W}$ - ${}^{142}\text{Nd}$ Isotope Systematics in the SNCs: Comparison with Previous Results and Assessment of Potential Effects of Terrestrial Contamination

4.1.1. Tungsten isotopes

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

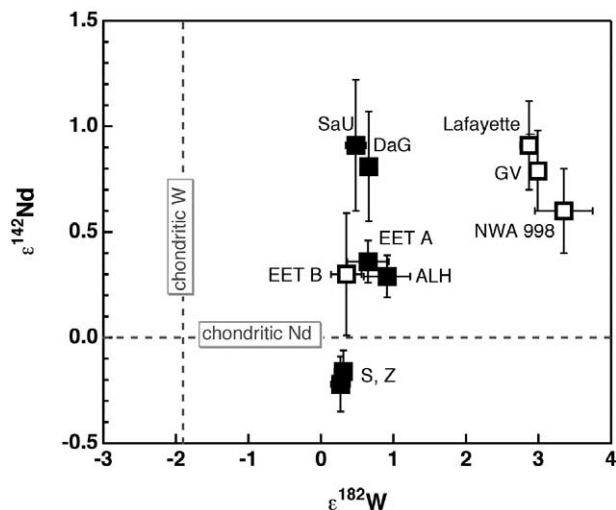


Fig. 2. $\epsilon^{182}\text{W}$ vs. $\epsilon^{142}\text{Nd}$ in LREE-enriched basaltic shergottites (S = Shergotty; Z = Zagami), LREE-depleted basaltic shergottites (EETA = EETA79001 Lithology A; EETB = EETA79001 Lithology B; DaG 476 = Dar al Gani 476; SaU 008 = Sayh al Uhaymir 008), a lherzolitic shergottite (ALH = ALHA77005), and nakhlites (GV = Governador Valadares; Lafayette; NWA 998 = Northwest Africa 998). ALH84001 ($\epsilon^{182}\text{W} = 0.49 \pm 0.33$) and LA ($\epsilon^{182}\text{W} = 0.35 \pm 0.16$) are not plotted here since their $\epsilon^{142}\text{Nd}$ values are 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). Dashed gray lines show the chondritic W and Nd isotopic compositions: the chondritic $\epsilon^{182}\text{W}$ value is less radiogenic than the terrestrial value by 1.9 ϵ units (Kleine et al., 2002; Schoenberg et al., 2002; Yin et al., 2002; this work); the chondritic $\epsilon^{142}\text{Nd}$ value is assumed to be identical to that of the terrestrial standard.

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 $\epsilon^{182}\text{W}$ for EETA79001 of 2.21 ± 0.60 . More recently, Kleine et al. (2004) reported a significantly lower $\epsilon^{182}\text{W}$ 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 $\epsilon^{182}\text{W}$ 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 those reported by Lee and Halliday (1997), but agree within uncertainties with those reported by Kleine et al. (2004).

The $\epsilon^{182}\text{W}$ 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). The reason for these discrepancies is not known. However, the addition of a terrestrial component may be responsible for the apparently lower $\epsilon^{182}\text{W}$ values previously reported for these two samples. In this con-

text, it is notable that the DaG 476 shergottite is petrologically and geochemically similar to SaU 008, and as such, both these shergottites may be expected to have identical $\epsilon^{182}\text{W}$ values. In fact, the $\epsilon^{182}\text{W}$ values reported by us for these two desert shergottites are indeed identical within errors, and (in contrast to the value for DaG 476 reported by Kleine et al. [2004]) are unambiguously higher than the terrestrial value (Table 2). This supports the lack of a terrestrial component in the bulk samples of these two desert shergottites analyzed here and hints at the possible presence of such a component in the sample of DaG 476 analyzed by Kleine et al. (2004). Similarly, the nakhlites are petrologically and geochemically similar to each other and, therefore, may also be expected to have identical $\epsilon^{182}\text{W}$ values. This is indeed the case for the three nakhlites (including Lafayette) analyzed here (Table 2). In contrast, the $\epsilon^{182}\text{W}$ value for Lafayette reported by Lee and Halliday (1997) is clearly lower than that for the other nakhlites (Table 2), possibly also hinting at the presence of a terrestrial component in the bulk sample of this meteorite analyzed by these authors.

Finally, Lee and Halliday (1997) presented $\epsilon^{182}\text{W}$ values for two SNCs that were not analyzed in this study. Specifically, these authors reported $\epsilon^{182}\text{W}$ for two splits of Nakhla (that give an average value of 2.99 ± 0.20), which agrees well with the values reported here for the three other nakhlites, GV, Lafayette, and NWA 998. They additionally reported $\epsilon^{182}\text{W}$ for the unique dunitic SNC meteorite, Chassigny (2.14 ± 0.62).

4.1.2. Neodymium isotopes

A wide range of $\epsilon^{142}\text{Nd}$ values has previously been reported in the shergottites (Harper et al., 1995; Borg et al., 1997; Jagoutz et al., 2000; Jagoutz et al., 2003). However, several of these $\epsilon^{142}\text{Nd}$ values (specifically, for ALHA77005, Shergotty, DaG 476, and SaU 008) are in question. The Nd isotopic compositions of ALHA77005 and Shergotty do not fall on the $\epsilon^{142}\text{Nd}$ - $\epsilon^{143}\text{Nd}$ 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 $\epsilon^{142}\text{Nd}$ 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 $\epsilon^{143}\text{Nd}$, the difference in the $\epsilon^{142}\text{Nd}$ between these two samples, coupled with the fact that the Shergotty data point falls off the $\epsilon^{142}\text{Nd}$ - $\epsilon^{143}\text{Nd}$ isochron, makes the previously determined $\epsilon^{142}\text{Nd}$ value for this meteorite questionable. Jagoutz et al. (2000) had initially reported an $\epsilon^{142}\text{Nd}$ of ~ 0.8 for DaG 476 and SaU 005. Subsequently, these authors revised their estimates of the $\epsilon^{142}\text{Nd}$ values for these two samples to the substantially lower ones shown in Table 2 (Jagoutz et al., 2003).

In this investigation we chose to determine the $\epsilon^{142}\text{Nd}$ values in ALHA77005, Shergotty, DaG 476, and SaU 008 not only because their previously reported values are questionable, but also because they represent the full range of petrologic and geochemical diversity among the shergottites. Specifically, Shergotty is a pyroxene-plagioclase basalt that is relatively LREE-enriched (chondrite-normalized La/Lu ~ 1), DaG 476 and SaU 008 are olivine-bearing basalts that are highly LREE-depleted (chondrite-normalized La/Lu ~ 0.1), and ALHA77005

is a lherzolite with an intermediate degree of LREE-depletion (chondrite-normalized La/Lu ~ 0.5) (Lodders, 1998). As an independent check of the accuracy of our analyses, we additionally determined the $\epsilon^{142}\text{Nd}$ values in two other shergottites (i.e., Zagami and EETA) for which the previously reported values are not in dispute.

For the two shergottites, Zagami and EETA, the $\epsilon^{142}\text{Nd}$ values determined by us agree with the values reported earlier by Harper et al. (1995) (Table 2). However, our $\epsilon^{142}\text{Nd}$ value for ALHA77005 is higher than that reported by these authors. Moreover, our $\epsilon^{142}\text{Nd}$ value for Shergotty is lower than that reported by these authors, although it is identical, within errors, to that for Zagami (this work; Harper et al., 1995). As discussed earlier, this is to be expected, given the petrologic and geochemical similarities between Shergotty and Zagami. Furthermore, the new $\epsilon^{142}\text{Nd}$ values reported here for ALHA77005 and Shergotty fall along the $\epsilon^{142}\text{Nd}$ - $\epsilon^{143}\text{Nd}$ isochron defined by other shergottites (see Fig. 3, implications of which are discussed in more detail in section 4.2.1.).

The $\epsilon^{142}\text{Nd}$ values presented here for DaG 476 and SaU 008 are systematically higher than those reported by Jagoutz et al. (2003), but are in agreement with the values previously reported by Jagoutz et al. (2000). The $\epsilon^{142}\text{Nd}$ values that we determined for these two LREE-depleted shergottites are consistent with those of the LREE-depleted shergottite QUE94201 ($\epsilon^{142}\text{Nd} = 0.92 \pm 0.11$; 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 contamination in the samples analyzed here (see section 2.1.), we believe it is likely that our samples of DaG 476 and SaU 008 contain an insignificant terrestrial component. Lack of a significant terrestrial component in the samples analyzed by us is further supported by the fact that all the $\epsilon^{142}\text{Nd}$ values reported here fall along a single well-defined linear array in Figure 3 (implications of which are discussed in more detail in section 4.2.1). Terrestrial contamination would have the effect of lowering the measured $\epsilon^{142}\text{Nd}$ values of the samples, and therefore may account for the apparent discrepancy between our data and that of Jagoutz et al. (2003).

In contrast to the shergottites which show a wide range in their $\epsilon^{142}\text{Nd}$ values, the $\epsilon^{142}\text{Nd}$ values reported previously for the nakhlites are identical within analytical errors (Harper et al., 1995; Carlson and Irving, 2004). This may be expected, since while the shergottites are quite diverse in their petrologic and geochemical characteristics, the nakhlites are rather similar to each other. Given this, it is reasonable to assume that the $\epsilon^{142}\text{Nd}$ values previously determined for the nakhlites are indeed robust. Therefore, in the following discussion, the previously reported $\epsilon^{142}\text{Nd}$ values for GV and Lafayette (Harper et al., 1995) and for NWA 998 (Carlson and Irving, 2004) are utilized along with the $\epsilon^{182}\text{W}$ values reported here to make inferences regarding the timing of nakhlite source formation.

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 isotope 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 Figure 2, the shergottites and nakhlites have distinct $\epsilon^{182}\text{W}$ - $\epsilon^{142}\text{Nd}$ 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) may not be valid in light of the ^{182}W - ^{142}Nd isotope systematics presented here. Implications of the $\epsilon^{182}\text{W}$ - $\epsilon^{142}\text{Nd}$ systematics in the SNC meteorites are discussed in more detail in the sections below.

4.2.1. Implications of ^{182}W - ^{142}Nd isotope 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. 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 ($t_{1/2} \sim 106$ Gyr) and the short-lived ^{146}Sm - ^{142}Nd ($t_{1/2} \sim 103$ Myr) chronometers in conjunction with each other to these shergottites to define the age of silicate differentiation (Borg et al., 1997; Borg et al., 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 $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of their source reservoir. Borg et al. (1997) applied this method for determining the time of source formation for the QUE94201 shergottite and 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 $\epsilon^{143}\text{Nd}$ of the samples at 175 Ma were plotted against their present-day $\epsilon^{142}\text{Nd}$ (Fig. 5 of Borg et al., 2003), and this $\epsilon^{142}\text{Nd}$ - $\epsilon^{143}\text{Nd}$ isochron yielded a model age of planetary differentiation of $4513 \left[\begin{array}{c} +19 \\ -21 \end{array} \right]$ Ma. However, as is evident from Figure 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 $\epsilon^{142}\text{Nd}$ values reported here for Shergotty, Zagami, EETA, DaG 476 and ALHA77005, including the

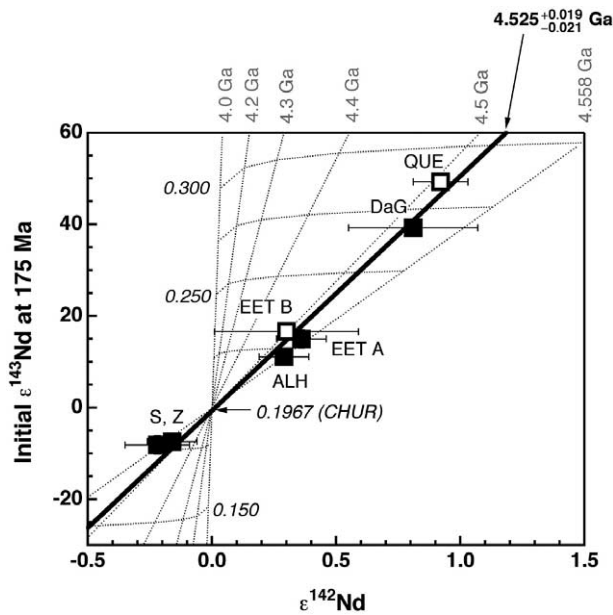


Fig. 3. Present-day $\epsilon^{142}\text{Nd}$ vs. initial $\epsilon^{143}\text{Nd}$ at 175 Ma for the shergottites. In a two-stage model of Nd isotope evolution (after Fig. 5 of Borg et al., 2003), dashed straight lines show the various times at which Sm-Nd fractionation may have occurred to establish silicate source reservoirs on Mars. Dashed (near-horizontal) curves represent constant $^{147}\text{Sm}/^{144}\text{Nd}$ ratios of the source reservoirs. The initial $\epsilon^{143}\text{Nd}$ values are from Borg et al. (2003) and references therein. Solid squares indicate $\epsilon^{142}\text{Nd}$ values from this work (S = Shergotty; Z = Zagami; EETA = EETA79001 Lithology A; DaG = Dar al Gani 476; ALH = ALHA77005); open squares indicate $\epsilon^{142}\text{Nd}$ values for EETA79001 Lithology B = EETB and QUE94201 = QUE from Harper et al. (1995) and Borg et al. (1997), respectively. Initial $\epsilon^{143}\text{Nd}$ values are taken from the literature (Borg et al., 2003 and references therein). The slope of the correlation line for the shergottite data indicates that mantle sources of the shergottites were established at $4525 \begin{matrix} +19 \\ -21 \end{matrix}$ Ma.

previously measured values for EETB (Harper et al., 1995) and QUE94201 (Borg et al., 1997), and using previously determined initial $\epsilon^{143}\text{Nd}$ values for all these samples (Borg et al., 2003 and references therein), we have replotted the $\epsilon^{142}\text{Nd}$ - $\epsilon^{143}\text{Nd}$ isochron for the shergottites (Fig. 3). As can be seen in Figure 3, all the shergottites for which both $\epsilon^{142}\text{Nd}$ and $\epsilon^{143}\text{Nd}$ are determined fall on a well-defined linear array that corresponds to a model age of planetary differentiation, when the shergottite source reservoirs were established, of $4525 \begin{matrix} +19 \\ -21 \end{matrix}$ 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. Furthermore, while this age is in agreement with that obtained by Borg et al. (2003), the new $\epsilon^{142}\text{Nd}$ values reported here demonstrate that the data for *all* shergottites whose Nd isotopic compositions have been determined fall along a single linear array in terms of their $\epsilon^{142}\text{Nd}$ - $\epsilon^{143}\text{Nd}$ systematics. This provides definitive support for a single major differentiation event on Mars that established the source reservoirs of all shergottites.

The $\epsilon^{142}\text{Nd}$ - $\epsilon^{143}\text{Nd}$ 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 Figure 3 the (0,0) point is characterized by a present-day chondritic $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of 0.1967. Shergottites plotting above this point were derived from LREE-depleted sources with superchondritic $^{147}\text{Sm}/^{144}\text{Nd}$ 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 $^{147}\text{Sm}/^{144}\text{Nd}$ 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 Figure 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 $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of ~ 0.285 , while the enriched end-member reservoir had a maximum $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of ~ 0.182 .

In addition to the more precise timing of shergottite source formation provided by the new $\epsilon^{142}\text{Nd}$ values reported here, the combined ^{182}W - ^{142}Nd isotope systematics in the shergottites provide information on the timing of core formation on Mars and the nature of their source reservoirs. The $\epsilon^{182}\text{W}$ value in the primitive Martian mantle (PMM) may be obtained from the intercept of the best-fit line to the shergottite data shown in Figure 4 (i.e., the $\epsilon^{182}\text{W}$ value corresponding to a chondritic $\epsilon^{142}\text{Nd}$) and is estimated to be 0.34 ± 0.07 . This value is similar to, but more precisely determined than, that estimated recently for the PMM by Kleine et al. (2004) (i.e., 0.4 ± 0.2). Therefore, using the $\epsilon^{182}\text{W}$ value of 0.34 ± 0.07 and a $^{180}\text{Hf}/^{183}\text{W}$ ratio of 13 for the PMM (assuming a Hf/W ratio of ~ 5 for the PMM, derived 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 $^{182}\text{Hf}/^{180}\text{Hf}$ 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 11.6 ± 0.4 Myr (uncertainty based only on errors on the W isotopic composition of the PMM) after solar system formation. This two-stage model age is in agreement with those calculated by Kleine et al. (2002) and Yin et al. (2002). A higher initial $^{182}\text{Hf}/^{180}\text{Hf}$ ratio of 1.6×10^{-4} proposed recently by Quitté and Birk (2004) would imply a somewhat younger two-stage core formation model age. However, this higher initial value is based on the tungsten isotopic composition of a single iron meteorite (Tlacotepec), and it is possible that burnout of W isotopes by cosmic rays could be at least partly responsible for the lower $\epsilon^{182}\text{W}$ values in some irons, like Tlacotepec, with long exposure ages (Masarik, 1997; Leya et al., 2000; Leya et al., 2003; Markowski et al., 2005). Given this, in the following sections we will assume an initial $^{182}\text{Hf}/^{180}\text{Hf}$ ratio of $\sim 1 \times 10^{-4}$ proposed by Kleine et al. (2002) and Yin et al. (2002).

It is noted that 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

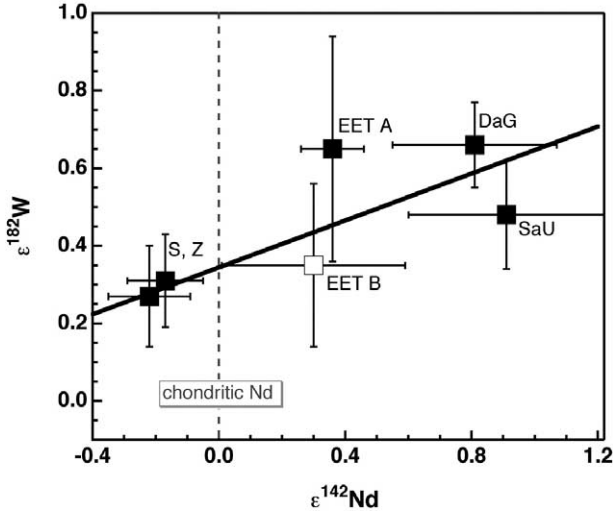


Fig. 4. $\epsilon^{142}\text{Nd}$ vs. $\epsilon^{182}\text{W}$ in the basaltic shergottites. Solid black line is the best-fit line to the data (calculated using the linear regression method of Williamson [1968] with a slope of 0.30 ± 0.14). The intercept of 0.34 ± 0.07 is the $\epsilon^{182}\text{W}$ 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; Schoenberg et al., 2002; Yin et al., 2002; Kleine et al., 2004) and results from the elevated Hf/W ratio in the bulk mantle following core formation. Assuming an initial solar system $^{182}\text{Hf}/^{180}\text{Hf}$ ratio of $\sim 1 \times 10^{-4}$ and an $^{180}\text{Hf}/^{183}\text{W}$ ratio of ~ 13 in the PMM, an $\epsilon^{182}\text{W}$ of 0.34 ± 0.07 yields a two-stage model age of core formation of 11.6 ± 0.4 Myr after the beginning of the solar system. Symbols are as indicated in the caption of Figure 2.

continuous and likely extend over millions of years (e.g., Jacobsen and Harper, 1996; Harper and Jacobsen, 1996; Halliday and Lee, 1999; Halliday, 2000; Halliday et al., 2003). If one assumes that the accretion histories of the terrestrial planets were approximated by an exponentially decreasing rate of accretion (Wetherill, 1986) and that during this accretion history core formation occurs continuously (with equilibration between metal and silicates), the two-stage model age then provides an upper limit on the time between solar system formation and the completion of accretion and core formation (Jacobsen, 2005 and references therein).

From the relationship between $\epsilon^{182}\text{W}$ and $\epsilon^{142}\text{Nd}$ 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 Figure 4, we determine that an $\epsilon^{142}\text{Nd}$ of ~ -0.2 (in the LREE-enriched shergottites such as Shergotty and Zagami) corresponds to an $\epsilon^{182}\text{W}$ of ~ 0.3 , while an $\epsilon^{142}\text{Nd}$ of ~ 0.9 (in the LREE-depleted shergottites such as DaG 476 and SaU 008) corresponds to an $\epsilon^{182}\text{W}$ of ~ 0.6 . As discussed earlier, the Nd isotopic systematics in the shergottites (specifically, the $\epsilon^{142}\text{Nd}$ - $\epsilon^{143}\text{Nd}$ isochron shown in Fig. 3) have been used to obtain a model age of planetary differentiation of $4525 \begin{bmatrix} +19 \\ -21 \end{bmatrix}$ Ma and estimates of the minimum and maximum $^{147}\text{Sm}/^{144}\text{Nd}$ ratios for the depleted and enriched end-member shergottite source reservoirs of ~ 0.285 and ~ 0.182 , respectively. The range of $\epsilon^{182}\text{W}$ in the shergottites can then be used to deter-

mine the Hf/W ratios in their end-member (depleted and enriched) source reservoirs as follows:

$$\begin{aligned} \epsilon^{182}\text{W}_{\text{SSR}} = & Q_{182} f_{\text{PMM}}^{\text{Hf/W}} \left(\frac{^{182}\text{Hf}}{^{180}\text{Hf}} \right)_{T_1} \left(e^{-\lambda_{182}(T_1-T_2)} - e^{-\lambda_{182}(T_1-T_3)} \right) \\ & + Q_{182} f_{\text{SSR}}^{\text{Hf/W}} \left(\frac{^{182}\text{Hf}}{^{180}\text{Hf}} \right)_{T_1} e^{-\lambda_{182}(T_1-T_3)} - 1.9 \quad (3) \end{aligned}$$

such that $\epsilon^{182}\text{W}_{\text{SSR}}$ is the present-day $\epsilon^{182}\text{W}$ 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 ~ 12 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, $(T_1 - T_2) = 12$ Myr and $(T_1 - T_3) = 42$ Myr; $[Q_{182}] = [10^4(^{180}\text{Hf}/^{182}\text{W})_{\text{CHUR}}] = 15,500$, where $[(^{180}\text{Hf}/^{182}\text{W})_{\text{CHUR}}]$ is the ratio in the present-day chondritic uniform reservoir (CHUR) (Harper and Jacobsen, 1996); $[f_{\text{PMM}}^{\text{Hf/W}}]$ is the Hf/W fractionation factor in the PMM and is given by $[(^{180}\text{Hf}/^{183}\text{W})_{\text{PMM}}(^{180}\text{Hf}/^{183}\text{W})_{\text{CHUR}} - 1] = 3.4$; $[f_{\text{SSR}}^{\text{Hf/W}}]$ is the Hf/W fractionation factor in the shergottite source reservoir and is calculated in a similar fashion; and $[(^{182}\text{Hf}/^{180}\text{Hf})_{T_1}] \sim 1 \times 10^{-4}$ (Kleine et al., 2002; Yin et al., 2002); $\lambda_{182} = 0.077 \text{ Myr}^{-1}$. The term “ -1.9 ” on the right side of Eqn. 3 accounts for the fact that the $\epsilon^{182}\text{W}_{\text{SSR}}$ value is given, by definition as per Eqn. 1 relative to the bulk silicate earth (BSE), which is more radiogenic than chondrites by 1.9ϵ units (Kleine et al., 2002; Schoenberg et al., 2002; Yin et al., 2002; this work). Since $\epsilon^{182}\text{W}$ in the PMM is estimated to be 0.34 , Eqn. 3 may be simplified to:

$$\epsilon^{182}\text{W}_{\text{SSR}} = 0.34 - Q_{182} (f_{\text{PMM}}^{\text{Hf/W}} - f_{\text{SSR}}^{\text{Hf/W}}) \left(\frac{^{182}\text{Hf}}{^{180}\text{Hf}} \right)_{T_1} \left(e^{-\lambda_{182}(T_1-T_3)} \right) \quad (4)$$

From the above equation, we estimate that the depleted shergottite end-member source reservoir characterized by an $\epsilon^{182}\text{W}_{\text{SSR}}$ of ≥ 0.6 (and with a minimum $^{147}\text{Sm}/^{144}\text{Nd} \sim 0.285$, based on the $^{147,146}\text{Sm}$ - $^{143,142}\text{Nd}$ systematics in the LREE-depleted shergottites such as QUE94201 and DaG 476; Borg et al., 2003) has an $^{180}\text{Hf}/^{183}\text{W} \geq 25$. The enriched shergottite end-member source reservoir characterized by an $\epsilon^{182}\text{W}_{\text{SSR}}$ of ≤ 0.3 (and with a maximum $^{147}\text{Sm}/^{144}\text{Nd} \sim 0.182$, based on the $^{147,146}\text{Sm}$ - $^{143,142}\text{Nd}$ systematics in the LREE-enriched shergottites such as Shergotty and Zagami) has an $^{180}\text{Hf}/^{183}\text{W} \leq 11$. 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 $^{180}\text{Hf}/^{183}\text{W}$ ratio of ~ 13 . 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 ~ 4.5 Ga Sm-Nd age of the orthopyroxenite ALH84001 (Jagoutz et al., 1994; Nyquist et al., 1995) implies that its mantle source reservoir was established before this time when

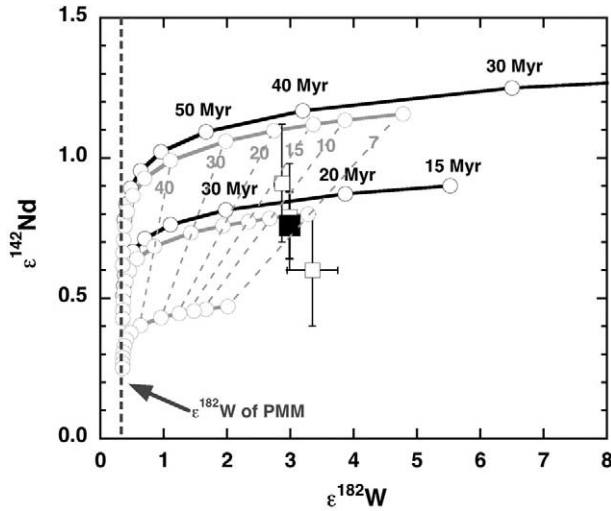


Fig. 5. $\epsilon^{182}\text{W}$ vs. $\epsilon^{142}\text{Nd}$ in the nakhrites plotted with the results of modeling calculations (shown as the black and gray curves, and discussed in more detail in the text). The solid square indicates the average composition of the three nakhrites, GV, Lafayette, and NWA 998, plotted here (open squares). Each plotted open circle on the curves represents the present-day $\epsilon^{182}\text{W}$ and $\epsilon^{142}\text{Nd}$ 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 $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of ~ 0.303 and a $^{180}\text{Hf}/^{183}\text{W}$ ratio of ~ 126 . The lower black curve shows the results for a garnet-bearing shallow mantle (GSM) source with a $^{147}\text{Sm}/^{144}\text{Nd}$ of ~ 0.266 and a $^{180}\text{Hf}/^{183}\text{W}$ of ~ 43 . The gray curves are results of calculations for three depleted mantle source compositions modeled by Kleine et al. (2004), the $^{147}\text{Sm}/^{144}\text{Nd}$ - $^{180}\text{Hf}/^{183}\text{W}$ pairs for which are (0.231, 18), (0.255, 22), and (0.281, 27). Comparison of the average nakhrite composition with results of model calculations shown here indicates that the nakhrite source was established within ~ 25 Myr after the beginning of the solar system and was likely characterized by $^{180}\text{Hf}/^{183}\text{W} \sim 22\text{--}43$ and $^{147}\text{Sm}/^{144}\text{Nd} \sim 0.255\text{--}0.266$.

^{146}Sm and ^{182}Hf are likely to have been extant. Therefore, the fact that $\epsilon^{182}\text{W}$ in ALH84001 (0.49 ± 0.33) is, within errors, similar to the $\epsilon^{182}\text{W}$ estimated for the PMM (0.34 ± 0.07) indicates that the Hf/W ratio of the mantle source reservoir of ALH84001 did not fractionate significantly relative to that of the PMM. If one assumes that the mantle source for this orthopyroxenite was established contemporaneously with the

shergottite source reservoirs (i.e., at $4525 \begin{bmatrix} +19 \\ -21 \end{bmatrix}$ Ma), its $\epsilon^{182}\text{W}$ of ~ 0.49 indicates that the $^{180}\text{Hf}/^{183}\text{W}$ ratio in its source was ~ 19 , somewhat higher than the Hf/W ratio in the PMM. This is generally consistent with its Sm-Nd isotopic systematics, which give an ancient age (~ 4.5 Ga) and a slightly positive initial $\epsilon^{143}\text{Nd}$ at this time (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 to only a modest degree relative to chondrites.

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

As is evident in Figure 2, the ^{182}W - ^{142}Nd isotope systematics in the nakhrites are quite distinct from those of the shergot-

ites. The $\epsilon^{182}\text{W}$ reported so far in the nakhrites is the most radiogenic among all the SNCs (this work; Lee and Halliday, 1997). The individual $\epsilon^{182}\text{W}$ values determined for the three nakhrites analyzed here are uniform, within analytical uncertainties, and give a weighted average of 2.95 ± 0.08 . If the data for Nakhla ($\epsilon^{182}\text{W} = 2.99 \pm 0.20$; Lee and Halliday, 1997) are included, the weighted average $\epsilon^{182}\text{W}$ for all nakhrites measured so far is still 2.95 ± 0.08 . The $\epsilon^{142}\text{Nd}$ values previously reported for the nakhrites (Harper et al., 1995; Carlson and Irving, 2004) are also uniform, within errors, and give a weighted average of 0.69 ± 0.09 . The highly positive $\epsilon^{182}\text{W}$ and $\epsilon^{142}\text{Nd}$ in the nakhrites indicate that the nakhrite source was established early while both ^{146}Sm and ^{182}Hf were extant and was characterized by a substantial degree of fractionation of the Hf/W and Sm/Nd ratios. The combined $\epsilon^{182}\text{W}$ - $\epsilon^{142}\text{Nd}$ systematics in these samples may be utilized to infer the timing and nature of the differentiation event that established the nakhrite source.

We have modeled the evolution of $\epsilon^{182}\text{W}$ and $\epsilon^{142}\text{Nd}$ in the Martian mantle to account for the $\epsilon^{182}\text{W}$ - $\epsilon^{142}\text{Nd}$ systematics in the nakhrites. 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 $\epsilon^{182}\text{W}$ and $\epsilon^{142}\text{Nd}$ 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 $T_2 = 4555$ Ma (since $T_1 - T_2 = 12$ Myr; see previous section). Since Hf is lithophile and W is siderophile, core formation results in the elevation of the $^{180}\text{Hf}/^{183}\text{W}$ ratio in the PMM from the chondritic value of 2.8 (Anders and Grevesse, 1989; Palme and Beer, 1993) to ~ 13 but does not affect the Sm/Nd ratio in PMM (since both Sm and Nd are lithophile). Since there is no fractionation of the Sm/Nd ratio in the PMM relative to chondrites during core formation, $\epsilon^{142}\text{Nd}$ remains chondritic, but $\epsilon^{182}\text{W}$ evolves from the time of core formation T_2 to the time T_3' when major silicate differentiation results in the formation of the nakhrite source (which has fractionated Hf/W and Sm/Nd ratios relative to chondrites). The present-day $\epsilon^{182}\text{W}$ and $\epsilon^{142}\text{Nd}$ in this fractionated nakhrite source reservoir (i.e., $\epsilon^{182}\text{W}_{\text{NSR}}$ and $\epsilon^{142}\text{Nd}_{\text{NSR}}$, respectively) are then given by:

$$\epsilon^{182}\text{W}_{\text{NSR}} = 0.34 - Q_{182} \left(f_{\text{PMM}}^{\text{Hf/W}} - f_{\text{NSR}}^{\text{Hf/W}} \right) \left(\frac{^{182}\text{Hf}}{^{180}\text{Hf}} \right)_{T_1} \left(e^{-\lambda_{182}(T_1 - T_3')} \right) \quad (5)$$

$$\epsilon^{142}\text{Nd}_{\text{NSR}} = Q_{142} f_{\text{NSR}}^{\text{Sm/Nd}} \left(\frac{^{146}\text{Sm}}{^{144}\text{Sm}} \right)_{T_1} \left(e^{-\lambda_{146}(T_1 - T_3')} \right) \quad (6)$$

such that $[f_{\text{NSR}}^{\text{Hf/W}}]$ is the Hf/W fractionation factor in the nakhrite source reservoir; $[Q_{142}] = [10^4 (\text{Sm}^{142}\text{Nd})_{\text{CHUR}}] = 354$ (Jacobsen and Wasserburg, 1980); $[f_{\text{NSR}}^{\text{Sm/Nd}}]$ is the Sm/Nd fractionation factor in the nakhrite source reservoir and is given by $[(^{147}\text{Sm}^{144}\text{Nd})_{\text{NSR}} / (^{147}\text{Sm}^{144}\text{Nd})_{\text{CHUR}} - 1]$; and $[(^{146}\text{Sm}^{144}\text{Sm})_{T_1}] \sim 0.008$ (e.g., Lugmair and Galer 1992; Prinzhofer et al., 1992; Nyquist et al., 1994; Stewart et al., 1994); $\lambda_{146} = 6.73 \text{ Gyr}^{-1}$. All other variables are as given for Eqn. 3

To model the $\epsilon^{182}\text{W}$ - $\epsilon^{142}\text{Nd}$ systematics in the nakhlite source reservoir, we have assumed two possible source compositions, each characterized by distinct Hf/W and Sm/Nd ratios. These 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 that has a $^{180}\text{Hf}/^{183}\text{W} \sim 126$ and a $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of ~ 0.303 (Borg and Draper, 2003; Righter and Shearer, 2003, respectively), and corresponds to a majorite-bearing deep mantle (MDM) source on Mars. 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 possible in a mantle source on Mars. Another composition modeled here corresponds to a garnet-bearing shallow mantle (GSM) source for the nakhlites characterized by a $^{180}\text{Hf}/^{183}\text{W} \sim 43$ and $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of ~ 0.266 (Harper et al., 1995; Righter and Shearer, 2003, 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 Figure 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, the average composition of the nakhlites (solid square in Fig. 5) is best matched by the formation of a source with either (1) the GSM composition ($^{180}\text{Hf}/^{183}\text{W} \sim 43$; $^{147}\text{Sm}/^{144}\text{Nd} \sim 0.266$) at ~ 25 Myr, or (2) a depleted mantle with a less fractionated composition ($^{180}\text{Hf}/^{183}\text{W} \sim 22$; $^{147}\text{Sm}/^{144}\text{Nd} \sim 0.255$) at ~ 8 Myr after solar system formation. The nakhlite source formation age in the latter scenario is only slightly older than the two-stage model age of core formation (i.e., ~ 12 Myr after solar system formation). As such, instead of assuming a simple two-stage model, if one assumes that the accretionary history of Mars involved an exponential decrease in its accretion rate along with continuous core formation, the latter scenario would indicate that the processes of accretion, core formation, and silicate differentiation were essentially coeval.

Therefore, our modeling results suggest that a fractionated shallow mantle source for the nakhlites was established *within* ~ 25 Myr after solar system formation (i.e., before 4542 Ma) and had a $^{180}\text{Hf}/^{183}\text{W}$ ratio of ~ 22 to 43 and a $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of ~ 0.255 to 0.266. Although $^{147}\text{Sm}/^{144}\text{Nd}$ ratios in the range of ~ 0.255 to ~ 0.266 do not necessitate the presence of garnet in such a source, $^{180}\text{Hf}/^{183}\text{W}$ ratios as high as ~ 43 would require it (Righter and Shearer, 2003). However, the LREE-enrichment inferred in the nakhlite source (Wadhwa and Crozaz, 1995; Wadhwa et al., 2004) is inconsistent with the presence of significant amounts of garnet. These characteristics may be reconciled if the depleted nakhlite source was affected by secondary metasomatism by a LREE-enriched fluid following its initial establishment (Harper et al., 1995; Borg et al., 2003; Wadhwa et al., 2004). 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 $\epsilon^{182}\text{W}$ and $\epsilon^{142}\text{Nd}$ 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; Brandon et al., 2000; Borg et al., 2003; 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. The timing of the major differentiation events on Mars as recorded in the SNC meteorites is additionally summarized in Figure 6. Table 3 illustrates that at least three distinct silicate reservoirs are required to account for the ^{182}W - ^{142}Nd isotope 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 $\epsilon^{182}\text{W} \geq 0.6$ and $\epsilon^{142}\text{Nd} \geq 0.9$, corresponding to an $^{180}\text{Hf}/^{183}\text{W} \geq 25$ and $^{147}\text{Sm}/^{144}\text{Nd} \geq 0.285$, respectively. The enriched end-member shergottite reservoir had $\epsilon^{182}\text{W} \leq 0.3$ and $\epsilon^{142}\text{Nd} \leq -0.2$, corresponding to an $^{180}\text{Hf}/^{183}\text{W} \leq 11$ and $^{147}\text{Sm}/^{144}\text{Nd} \leq 0.182$, respectively. In section 4.2.2., we showed that the depleted source reservoir of the nakhlites was most likely characterized by $^{180}\text{Hf}/^{183}\text{W}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ ratios of ~ 22 to 43 and ~ 0.255 to 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 condition close to the iron-wüstite (IW) buffer, 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 ($\sim IW + 3.5$; 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. As per their Table 4,

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	$\epsilon^{182}\text{W}$	$\epsilon^{142}\text{Nd}$	$^{180}\text{Hf}/^{183}\text{W}$	$^{147}\text{Sm}/^{144}\text{Nd}$	Formation time
Depleted shergottite reservoir (in mantle)	LREE-depleted shergottites (e.g., QUE94201, DaG 476, SaU 008)	Reduced ($\sim\text{IW}$)	≥ 0.6	≥ -0.9	≥ 25	≥ 0.285	4525^{+10}_{-21} Ma
Enriched shergottite reservoir (in mantle or crust)	LREE-enriched shergottites (e.g., Shergotty, Zagami, LA)	Oxidized ($> \text{IW} + 2$)	≤ 0.3	≤ -0.2	≤ 11	≤ 0.182	4525^{+10}_{-21} Ma
Depleted nakhlite reservoir (in mantle)	All nakhlites	Oxidized ($\sim\text{IW} + 3.5$)	~ -3	~ -0.7	$\sim 22-43$	$\sim -0.255-0.266$	≥ 4542 Ma

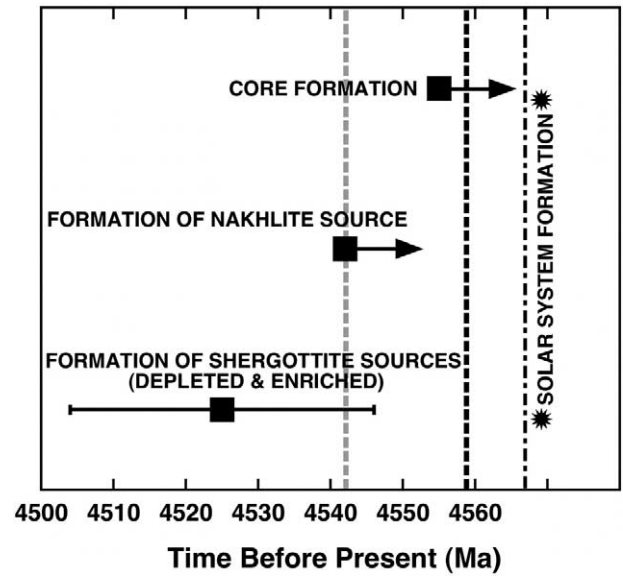


Fig. 6. The timing of major differentiation events on Mars based on ^{182}W - ^{142}Nd isotope systematics in the SNC meteorites. For a simple two-stage model, core formation is estimated to occur ~ 12 Myr after solar system formation, that is, at 4555 Ma, assuming the time of solar system formation to be 4567 Ma (dash-dotted line); however, this more likely represents an upper limit on the time between solar system formation and the completion of accretion and core formation (see text for details). The nakhlite source was established before ~ 4542 Ma, while the two end-member (depleted and enriched) shergottite source reservoirs were established at 4525^{+19}_{-21} Ma. Dashed lines indicate the two most likely possibilities for the time of nakhlite source formation: (1) If the nakhlite source was characterized by a moderate degree of fractionation (i.e., $^{180}\text{Hf}/^{183}\text{W} \sim 22$ and $^{147}\text{Sm}/^{144}\text{Nd} \sim 0.255$), it had to be established ~ 8 Myr after solar system formation (dashed black line). In this case, the silicate differentiation event that established the nakhlite source would have been coeval with the process of continuous accretion and core formation on Mars. (2) If the nakhlite source was characterized by a more significant degree of fractionation (i.e., $^{180}\text{Hf}/^{183}\text{W} \sim 43$ and $^{147}\text{Sm}/^{144}\text{Nd} \sim 0.266$), then it would have been established later (~ 25 Myr after solar system formation) following the completion of core formation (dashed gray line). In this case, the nakhlite and shergottite source reservoirs could have formed contemporaneously.

these authors suggest that the depleted shergottite source reservoir (as sampled by DaG 476 and SaU 051) has an $\epsilon^{182}\text{W}$ between -0.9 and 0.3 with an $\epsilon^{142}\text{Nd}$ between 0.5 and 0.7 and was established at 50 to 150 Myr after solar system formation. The enriched shergottite source reservoir (as sampled from Shergotty and Zagami) is suggested by these authors to have an $\epsilon^{182}\text{W}$ between 0.2 to 0.6 with an $\epsilon^{142}\text{Nd}$ between -0.2 and 0.3 and to have been established significantly earlier (i.e., 7–15 Myr after solar system formation). In contrast, as discussed earlier, we have demonstrated that the depleted shergottite source reservoir is characterized by an $\epsilon^{182}\text{W} \geq 0.6$ with an $\epsilon^{142}\text{Nd} \geq 0.9$, while the enriched shergottite source reservoir is characterized by an $\epsilon^{182}\text{W} \leq 0.3$ with an $\epsilon^{142}\text{Nd} \leq -0.2$, and both these end-member reservoirs were established *contemporaneously* (at 4525^{+19}_{-21} Ma). 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 to 20 Myr after solar system formation. Therefore, although Kleine et al. (2004) require three different silicate differentiation events occurring at different times to establish the source reservoirs of the shergottites and the nakhlites, our results demonstrate that the two end-member (depleted and enriched) shergottite reservoirs were established during a single global silicate differentiation event that occurred at 4525^{+19}_{-21} Ma and that the nakhlite source reservoir is likely to have been established before ~ 4542 Ma, such that the possibility exists that all three sources were established approximately contemporaneously (Fig. 6, dashed gray line).

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 $\epsilon^{182}\text{W}$ - $\epsilon^{142}\text{Nd}$ 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, as discussed above, 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), before ~ 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). Alternatively, the early establishment of the source reservoirs of the shergottites and nakhlites on Mars may have been facilitated by extensive hydrous melting processes analogous to those proposed for the establishment of Archean cratonic reservoirs on the early Earth (Saltzer et al., 2001). In such a scenario, the nakhlite reservoir may have been a depleted shallow mantle source established early by this H_2O -fluxed melting event and was subsequently enriched by melts and degassed volatiles from the deep Martian mantle (thereby accounting for its LREE-enriched, oxidized nature). As this early differentiation event waned, melting processes would have resulted in the degassing and reduction of depleted shallow mantle source reservoirs (sampled by shergottites such as DaG 476, SaU 008, and QUE94201) along with the establishment of complementary enriched lithospheric mantle or crustal reservoirs (sampled by shergottites such as Shergotty, Zagami, and Los Angeles).

Finally, the fact that distinctive ^{182}W - ^{142}Nd isotope 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 before ~ 4.5 Ga and that the Martian mantle has not experienced thorough 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 that convective processes on Mars have been inefficient through most of its history, thereby allowing for the preservation of ancient mantle reservoirs.

5. CONCLUSIONS

We have determined $\epsilon^{182}\text{W}$ values in a variety of SNC meteorites, including the basaltic shergottites (Shergotty, Zagami, EETA, EETB, DaG 476, and SaU 008), a lherzolithic shergottite (ALHA77005), nakhlites (GV, Lafayette and NWA 998), and the orthopyroxenite ALH84001. We additionally determined $\epsilon^{142}\text{Nd}$ values in several shergottites (Shergotty, Zagami, EETA, DaG 476, SaU 008, and ALHA77005). The combined ^{182}W - ^{142}Nd isotope 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 $\epsilon^{142}\text{Nd}$ values presented here require revision of previously reported $\epsilon^{142}\text{Nd}$ values for several shergottites (specifically, for ALHA77005, Shergotty, DaG 476, and SaU 008). Using these new $\epsilon^{142}\text{Nd}$ values, all shergottites for which Nd isotopic data are available now fall along a single isochron in a plot of $\epsilon^{143}\text{Nd}$ versus $\epsilon^{142}\text{Nd}$, which defines a precise model age of planetary differentiation (when the depleted and enriched end-member shergottite source reservoirs were established) of 4525^{+19}_{-21} Ma.
2. While $\epsilon^{182}\text{W}$ in the shergottites shows only a small range (from 0.3 to 0.7), $\epsilon^{142}\text{Nd}$ shows significant variation (from -0.2 to 0.9). In a plot of $\epsilon^{142}\text{Nd}$ versus $\epsilon^{182}\text{W}$, the shergottites define a linear trend from which the Hf/W ratios in the end member depleted ($^{180}\text{Hf}/^{183}\text{W} \geq 25$) and enriched ($^{180}\text{Hf}/^{183}\text{W} \leq 11$) shergottite source reservoirs have been determined. Moreover, from this linear trend we estimate an $\epsilon^{182}\text{W}$ of 0.34 ± 0.07 for the primitive Martian mantle (PMM) following core formation. From this $\epsilon^{182}\text{W}$ value for the PMM it is possible to estimate a two-stage model age of core formation on Mars of 11.6 ± 0.4 Myr after solar system formation.
3. ^{182}W - ^{142}Nd isotope systematics in the nakhlites suggest that the major silicate differentiation event that formed the nakhlite mantle source on Mars occurred early (within ~ 25 Myr after solar system formation) and resulted in moderate (i.e., $^{180}\text{Hf}/^{183}\text{W} \sim 22$ and $^{147}\text{Sm}/^{144}\text{Nd} \sim 0.255$) to significant (i.e., $^{180}\text{Hf}/^{183}\text{W} \sim 43$ and $^{147}\text{Sm}/^{144}\text{Nd} \sim 0.266$) fractionation of the Hf-W and Sm-Nd systems in the nakhlite source.
4. If the nakhlite source was characterized by a moderate degree of fractionation (i.e., $^{180}\text{Hf}/^{183}\text{W} \sim 22$ and $^{147}\text{Sm}/^{144}\text{Nd} \sim 0.255$), it had to be established ~ 8 Myr after solar system formation. This age is only slightly older than the two-stage model age of core formation for Mars. As such, assuming an accretionary history involving an exponential decrease in its accretion rate along with continuous core formation, this would indicate that the processes of accretion, core formation, and silicate differentiation were essentially coeval. However, if the nakhlite source was charac-

terized by a significant degree of fractionation (i.e., $^{180}\text{Hf}/^{183}\text{W} \sim 43$ and $^{147}\text{Sm}/^{144}\text{Nd} \sim 0.266$), then it would have been established later (~ 25 Myr after solar system formation) following the completion of core formation. In this case, silicate differentiation events that established the source reservoirs of the shergottites, nakhlites, and possibly also ALH84001 may have occurred almost contemporaneously in the early history of Mars.

5. The distinct $\epsilon^{182}\text{W}$ - $\epsilon^{142}\text{Nd}$ systematics in the shergottites and the nakhlites require their origination from distinct source reservoirs. The preservation of such distinct ^{182}W - ^{142}Nd isotope systematics in rocks with relatively young ages (≤ 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 efficient global mantle convection since the SNC source reservoirs were established.

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