THE DIFFERENTIATION HISTORY OF MANTLE RESERVOIRS ON MARS FROM W AND ND ISOTOPIC COMPOSITIONS OF SNC METEORITES. C. N. Foley[1], M. Wadhwa[1], L. Borg[2], and P. E. Janney[1], [1] Isotope Geochemistry Laboratory, Department of Geology, The Field Museum, 1400 S. Lake Shore Dr., Chicago, IL 60605 (nfoley@fmnh.org), [2]Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131.

Introduction: The ^{182}Hf-^{182}W short-lived chronometer ($t_{1/2}$ ~9 Ma) has previously been used to estimate the timing of metal-silicate differentiation on Mars (e.g., [1-3]). Hf and W are highly refractory and assumed to be present in approximately chondritic relative abundances on 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 (within ~50 Ma of solar system formation), the bulk silicate reservoir will have an excess of ^{182}W relative to chondritic meteorites. Moreover, silicate differentiation occurring within the first ~50 Ma of the solar system may result in further Hf-W fractionation, and produce silicate reservoirs characterized by different ε^{182}W values [4].

The ^{146}Sm-^{142}Nd short-lived chronometer ($t_{1/2}$ ~ 103 Ma) has also been used to place limits on the timing of planetary accretion and differentiation on Mars (e.g., [5, 6]). Since Sm and Nd are refractory lithophiles, it is assumed that they were acquired in the terrestrial planets in chondritic proportions and that core formation as well as volatile loss did not fractionate them. While both elements are incompatible, 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 a range of ^{142}Nd excesses and deficits relative to chondrites.

Previous measurements of ε^{182}W values in the SNC whole-rocks reveal a range from ~0 to +3 ε-units relative to terrestrial [1]. These ε^{182}W values appeared to correlate with the ε^{142}Nd values of [5], leading to the suggestion that both ^{182}Hf and ^{146}Sm were extant during major differentiation of the Martian mantle, and were fractionated by similar processes (i.e., silicate differentiation) [1,7]. Furthermore, supra-chondritic ε^{182}W for whole-rock samples having near-chondritic ε^{142}Nd suggested that core formation occurred early in the history of Mars (within ~13 Ma after solar system formation, assuming $(^{182}\text{Hf}/^{180}\text{Hf})_0$ $\sim 1\times10^{-4}$) [2,3,8,9].

The goal of the present study is to rigorously evaluate the relationship between ε^{182}W and ε^{142}Nd in the martian meteorites, since this has important implications for the timing of differentiation of Martian mantle reservoirs. Last year we reported the results of new W isotopic measurements of the shergottites Zagami and Los Angeles (LA), and the nakhlite NWA 998 [9,10]. Here we report ε^{182}W values for the shergottites DaG 476, SaU 008, EETA79001A, EETA79001B, and ALH77005, and the orthopyroxenite ALH84001. We also report ε^{142}Nd values for three shergottites: Zagami, DaG 476, and SaU 008. W and Nd isotopic analyses of additional meteorites are in progress.

Methodology: To minimize terrestrial weathering effects, interior chips showing the least evidence of alteration were selected for W and Nd analyses.

Tungsten. Sample preparation and chemical separation techniques for W are summarized in [9,10]. Isotopic analyses of W were made using the GV Instruments IsoProbe multicollector ICPMS in the Isotope Geochemistry Laboratory at the Field Museum. Sample solutions of ~30-50 ppb W were introduced into the plasma using a CETAC Aridus MCN. The array of 9 Faraday collectors allowed simultaneous collection of all W isotopes, as well as ^{188}Os. 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 NIST 3163 W. The normalizing ratio used to correct the raw ^{182}W/^{183}W ratio for instrumental mass fractionation was $^{186}\text{W}/^{184}\text{W} = 0.927633$ [1].

Neodymium. Whole-rock samples were ultrasonicated for ~30 minutes in ultra-pure (18mΩ/cm) water, prior to being dried, crushed and dissolved in $HF:HNO_3$. Column chemistry for Nd separation was performed at the University of New Mexico using procedures similar to those described in [11], with each sample being put through the α-HIBA separation procedure twice to ensure good separation of Ce from Nd. Isotopic measurements of Nd were made using the multicollector ICPMS at the Field Museum. Measurement protocol was similar to that for W isotopic analyses. Sample solutions of ~35-50 ppb Nd were introduced into the plasma using a CETAC Aridus MCN. The array of 9 Faraday collectors allowed simultaneous collection of all Nd isotopes (except ^{150}Nd), as well as ^{140}Ce and ^{149}Sm. Measurements of samples, with at least 3 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 $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$.

Results and Discussion: The reproducibilities of repeat measurements of $^{182}W/^{183}W$ and $^{142}Nd/^{144}Nd$ ratios in the NIST 3163 and the JNdi-1 standards, respectively, on any given measurement day are typically $\leq \pm 0.3$ ε (2σ). We previously reported W isotopic analyses of terrestrial andesite (AGV-2), terrestrial basalt (BCR-2), Allende, and Toluca [9,10], which are in agreement with the results of [2,3,8].

Figure 1 shows the W and Nd isotopic compositions of the martian meteorites that we have studied so far; note that the Nd isotopic compositions of Zagami, DAG 476, and SaU 008, and all W isotopic compositions are from this work. Our W data are generally in agreement with previous values [1,12], with the exception of EETA79001 (for which an $\varepsilon^{182}W$ value of 2.21±0.60 was initially reported by [1]). The most significant result from this study is that the $\varepsilon^{182}W$ values of all the basaltic shergottites and the orthopyroxenite ALH84001 are similar, having an average value of 0.46±0.10, whereas the lherzolitic shergottite ALH77005 has only a slightly higher value. The nakhlite NWA 998 has the highest $\varepsilon^{182}W$ of all the measured samples, consistent with values determined for the other nakhlites [1].

The $\varepsilon^{142}Nd$ values measured so far show a range of ~1 ε-unit, with the lowest (near-chondritic value) for Zagami and the highest for SaU 008 (Fig. 1). While our $\varepsilon^{142}Nd$ value for Zagami is consistent with a previous report [5], those for DaG 476 and SaU 008 are systematically higher than the $\varepsilon^{142}Nd$ values reported for these meteorites by [13]. Our higher $\varepsilon^{142}Nd$ values are consistent with that for QUE 94201 ($\varepsilon^{142}Nd$ of 0.92±0.11, [11]), which is considered similar to these meteorites in other geochemical and isotopic characteristics. Our samples of DaG 476 and SaU 008 may contain a smaller terrestrial weathering component than the samples analyzed by [13], accounting for this discrepancy.

These new data reveal no simple linear relationship between the martian meteorite $\varepsilon^{182}W$ and $\varepsilon^{142}Nd$ values (Fig. 1), as initially suggested by [1]. The variation of $\varepsilon^{142}Nd$ with fairly constant $\varepsilon^{182}W$ in the basaltic shergottites implies continuation of silicate differentiation while ^{146}Sm was extant but after ^{182}Hf had fully decayed (~50 Ma after solar system formation). More specifically, the W isotopic systematics presented here indicate that differentiation and establishment of the shergottite source region on Mars occurred no earlier than ~4516 Ma, assuming solar system formation at ~4566 Ma. This is consistent with previously determined $\varepsilon^{142}Nd$ and $\varepsilon^{143}Nd$ systematics that suggest that martian silicate differentiation occurred at 4513 (+33/-27) Ma [6].

The large positive $\varepsilon^{182}W$ and $\varepsilon^{142}Nd$ anomalies observed in the nakhlites (represented here by the NWA 998) are consistent with early isolation of the nakhlite mantle source [1,5]. These systematics also suggest that the nakhlites are derived from a fundamentaly different source reservoir than the shergottites.

Thus, our results imply the following major phases of Martian differentiation: 1) early core formation, within ~13 Ma of solar system formation, and following this, 2) continuation of major silicate differentiation resulting in the final establishment of the shergottite source around 4.513 Ga (i.e. while ^{146}Sm was still extant, but ^{182}Hf was extinct). The nakhlite mantle source may have its unique $\varepsilon^{182}W$ and $\varepsilon^{142}Nd$ as a result of coupled Sm/Nd and Hf/W fractionation while both ^{146}Sm and ^{182}Hf were extant (i.e., earlier than the shergottite mantle source). Alternatively, Sm-Nd and Hf-W were decoupled in the nakhlite source; this would require that Hf/W were fractionated early (by a process not yet understood) and that Sm/Nd fractionation occurred (during silicate differentiation) independently of this earlier event after ^{182}Hf was extinct, but ^{146}Sm was still extant.

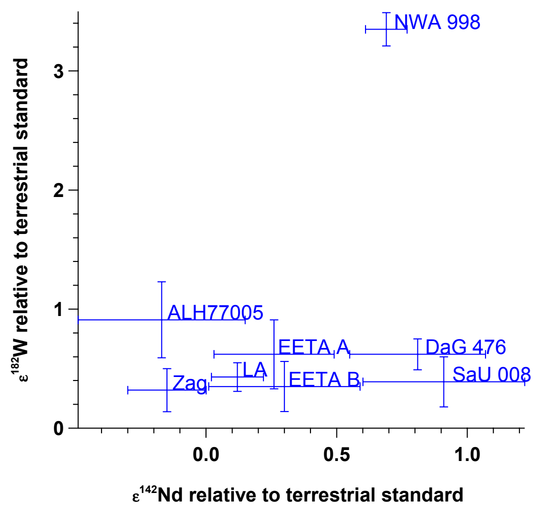

Figure 1: $\varepsilon^{182}W$ versus $\varepsilon^{142}Nd$ for SNC meteorites. Nd isotopic compositions for Zagami, DAG 476, and SaU 008, and all W isotopic compositions are from this work. Nd isotopic compositions of ALH77005, EETA79001A, EETA79001B from [5]; those for LA and NWA 998 assumed to be similar to average values for shergottites and NC meteorites, respectively [5]. ALH84001 ($\varepsilon^{182}W$ = 0.49±0.34) is not shown here (since $\varepsilon^{142}Nd$ is undetermined).

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