TUNGSTEN ISOTOPIC COMPOSITIONS OF THE SNC METEORITES: FURTHER IMPLICATIONS FOR EARLY DIFFERENTIATION HISTORY OF MARS. C. N. Foley[1], M. Wadhwa[1], 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.

Introduction: The hafnium-tungsten (^{182}Hf-^{182}W) short-lived chronometer ($t_{1/2}$ ~9 Myr) has been used to date the timing of early metal-silicate differentiation events on the Earth, Moon, Mars (SNC parent body), and Vesta (eucrite parent body) [1-10]. Both hafnium and tungsten are highly refractory elements that are present in approximately chondritic relative abundances in bulk planets and planetesimals. However, during metal-silicate differentiation (or core formation), the lithophile Hf segregates into the silicate fraction while the siderophile W segregates into the metallic core. If this differentiation event occurs within ~5 half lives of ^{182}Hf, ~45 Myr, then its timing can be determined by measuring the excess of the daughter product, ^{182}W.

The Solar System initial ^{182}Hf/^{180}Hf ratio has recently been revised [7, 8, 9]. This has enabled new estimates for the timing of metal-silicate differentiation on the terrestrial planets and planetesimals. Core formation is now thought to have occurred within the first ~3 [7], ~13 [8], ~10-29 [7], and ~29 [7] Myr from the beginning of Solar System formation for Vesta, Mars, Earth and the Moon, respectively. These time scales are significantly shorter than those determined previously for each of these planetary bodies [1, 6, 10]. A previous estimate of the Solar System initial ^{182}Hf/^{180}Hf ratio was derived from the W isotopic analyses of carbonaceous chondrites by [1, 2], which indicated an ε^{182}W value ~2ε units higher than the value recently reported by [7, 8, 9]. Since the only reported W isotopic measurements for SNCs are from [6], this raises the question as to whether these values are reproducible. Accurate determination of the W isotopic compositions of the SNC meteorites will help to constrain the timing of core formation on Mars and the extent of heterogeneity in the martian mantle.

Previous measurements indicate that whole rock ε^{182}W values in the SNCs vary from ~0 to +3 ε units above terrestrial [6]. Moreover, these values appear to correlate with initial ε^{142}Nd values for the SNCs that have been analyzed [11], suggesting that core formation and silicate differentiation on Mars occurred very early in the history of Mars, and that subsequently, the martian mantle has remained poorly mixed. Since these data were reported, numerous new SNC meteorites have been recovered, and Nd isotopic data are available for several of these [12, and references therein]. Therefore, the goals of this study were to obtain new estimates of the range of ε^{182}W values in the SNC meteorites (by measuring the W isotopic compositions of not only those which were previously analyzed by [6] but also of new SNCs that have since been recovered) and to confirm the relationship between the ε^{182}W and initial ε^{142}Nd values. In this work, we report the W isotopic compositions of two basaltic shergottites, Zagami and Los Angeles, and one nakhlite, NWA 998. W isotopic analyses of additional SNCs are ongoing.

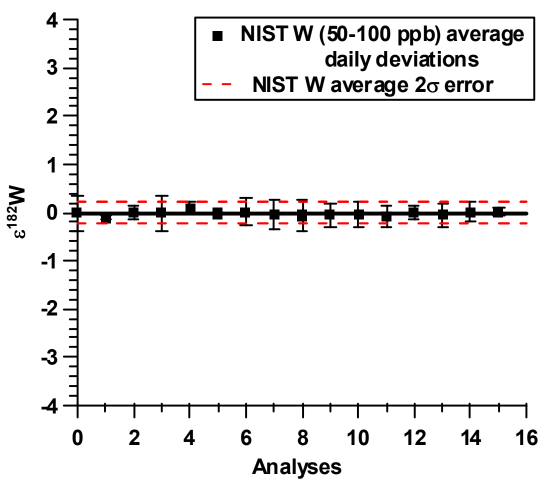
Methodology: The samples analyzed here were crushed with a clean agate mortar and pestle. Dissolution was performed by treatment with a 3:1 mixture of concentrated HF:HNO_3, followed by concentrated HNO_3, and samples were finally brought into solution in HCl. Isolation of W from samples was performed with column chromatography using AG-1X8 anion exchange resin (200-400 mesh). The chromatography procedure is similar to that used by [9, 13, 14]. Primary and secondary column chemistry was performed. The secondary column was necessary mostly to reduce the amount of Ti in the W-cut from the primary column. After the secondary clean-up column, the W-cut was evaporated and re-dissolved in 3% HNO_3-0.05 N HF for isotopic analysis.

W isotopic analyses were made using the Micromass IsoProbe multicollector ICPMS in the Isotope Geochemistry Laboratory at the Field Museum. The normalizing ratio used to correct the raw ^{182}W/^{183}W ratio for instrumental mass fractionation was ^{186}W/^{184}W = 0.927633 [3]. As a check, we also determined the fractionation corrected ^{182}W/^{183}W ratio by normalizing to a ^{184}W/^{183}W ratio of 2.139758 [15]. For all samples analyzed here, within 2σ errors, the ε^{182}W values for respective samples were the same using both normalization schemes. Sample solutions (typically with W concentrations of ~50-100 ppb) were introduced into the plasma using a CETAC Aridus MCN. The array of 9 Faraday collectors allowed simultaneous collection of all W isotopes. Each measurement was comprised of 40 cycles of 10 s integrations, and was preceded by a 10-minute washout and a 45 s integration of the background. Measurement of each sample was bracketed with multiple measurements of the NIST 3163 W standard. For each sample, at least 2 repeat measurements were performed interspersed with measurements of the NIST 3163 W standard. The $\varepsilon^{182}W$ value for each sample was the average of the calculated differences between each sample measurement and the average of repeated measurements of the NIST 3163 W standard bracketing that sample in epsilon (ε) units as shown below.

$$\varepsilon_{182W} = 10^4 \cdot \left(\frac{\left(\frac{^{182}W}{^{183}W}\right)_{Sample} - \left(\frac{^{182}W}{^{183}W}\right)_{NIST\ 3163\ Standard}}{\left(\frac{^{182}W}{^{183}W}\right)_{NIST\ 3163\ Standard}} \right)$$

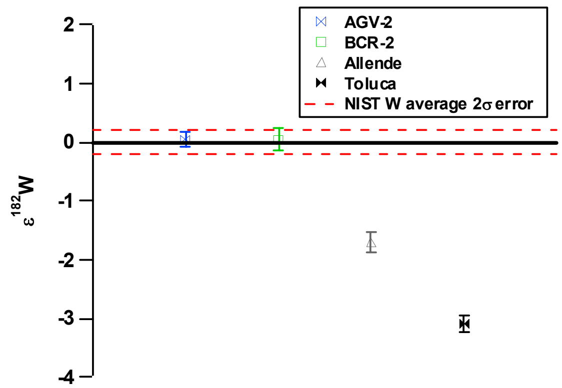
Results: Measurements of the W isotopic composition of the NIST 3163 standard were performed over the course of several months. Figure 1 shows the results of these analyses for the last ~2 months. Each data point consists of the average $\varepsilon^{182}W$ value obtained from repeat measurements of the NIST 3163 standard performed on a single day. As shown in the figure, the long term reproducibility (2σ) of our W isotopic measurements is ~0.2 ε.

Figure 1: *Long term reproducibility of W isotopic measurements of the NIST 3163 standard.*



W isotopic compositions of geostandards as well as previously analyzed meteorites were also measured to verify the accuracy of our experimental techniques. Terrestrial USGS andesite and basalt geostandards, AGV-2 and BCR-2 respectively, were first analyzed. As shown in Figure 2, the W isotopic compositions of AGV-2 and BCR-2 are, within errors, the same as those of the NIST 3163 standard represented by the solid line ± 2 σ (dashed lines). The $\varepsilon^{182}W$ values determined by us of the carbonaceous chondrite Allende and the iron meteorite Toluca (Figure 2) are similar, within errors, to values reported for these meteorites by [7, 8] (Table 1). In contrast, our results for Allende are not consistent with those acquired by [1,2].

Figure 2: *$\varepsilon^{182}W$ values for AGV-2, BCR-2, Allende, and Toluca relative to the terrestrial W standard NIST 3163 ± 2σ external errors.*

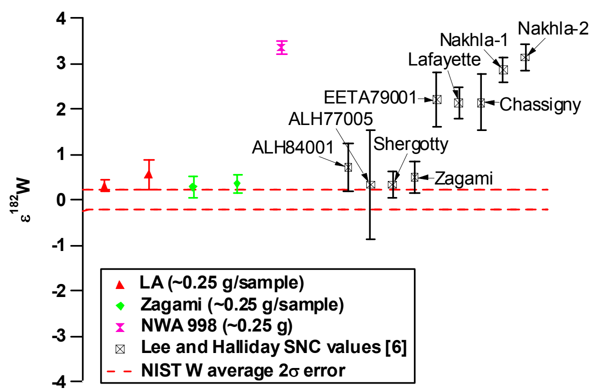


Our results for the SNC meteorites are similar to those acquired by [6], as illustrated in Figure 3. Specifically, the $\varepsilon^{182}W$ value of 0.32 ± 0.18 (2σ) determined by us for Zagami is, within error, the same as that reported for this meteorite by [6]. The basaltic shergottite Los Angeles, which has not been analyzed prior to this work, has an $\varepsilon^{182}W$ value of 0.43 ± 0.12 (2σ). This value is similar to that reported by [6] for other basaltic shergottites, Shergotty and Zagami, that have petrologic and geochemical similarities to Los Angeles. NWA 998, a nakhlite which also has not been analyzed prior to this work, has an $\varepsilon^{182}W$ value of 3.35 ± 0.14 (2σ), similar to that of Nakhla [6].

Table 1: *Average $\varepsilon^{182}W$ values ± 2σ.*

Sample	$\varepsilon^{182}W$ (this work)	2σ error	$\varepsilon^{182}W$ (previous work)	2σ error
NIST W	0.01	0.17		
AGV-2	0.04	0.13		
BCR-2	0.05	0.20		
Allende	-1.7	0.17	-1.9[7,8]	0.20[7,8]
Toluca	-3.09	0.13	-3.16[7]	0.15[7]
LA	0.43	0.12		
Zagami	0.32	0.18	0.50[6]	0.34[6]
NWA 998	3.35	0.14		

Figure 3: *ε^{182}W values for Los Angeles(LA), Zagami, and NWA 998 (this work) compared with the data of Lee and Halliday for various SNCs [6].*

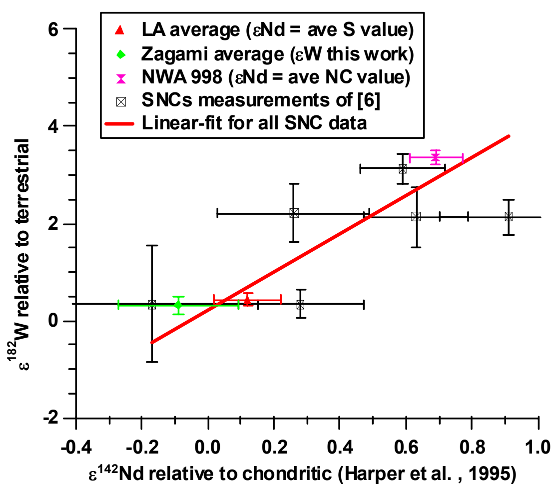


Discussion: Assuming an initial Solar System ^{182}Hf/^{180}Hf ratio of (1.09 ± 0.09) x 10^{-4} [7, 8], a Hf/W ratio for the martian mantle of ~5 [16, 17], and a simple two-stage model for differentiation on Mars, it is possible to estimate the timing of core formation (provided that the measured ^{182}W excesses in the SNC meteorites are solely the result of this process). Given the above assumptions, one may estimate ΔT_{CHUR} values (or timing of core formation relative to Solar System formation) of ~12-13 Ma from the W isotopic data for Zagami and Los Angeles and ~1.5 Ma from the data for NWA 998. However, it is significant to note that the W isotopic compositions of all the SNC meteorites are unlikely to be solely the result of core formation and may additionally be affected by silicate differentiation. This is suggested by the apparent correlation between the ε^{182}W and ε^{142}Nd values that was first noted by [6]. During core formation, Hf (lithophile) is fractionated from W (siderophile) whereas Sm and Nd (both lithophile) do not fractionate from each other. However, during crust-mantle differentiation, Hf/W ratios as well as Sm/Nd ratios are fractionated in the two silicate reservoirs. Therefore, if the correlation between ε^{142}Nd and ε^{182}W values in the SNCs can be further confirmed, it would indicate that on Mars, core formation and silicate differentiation both occurred when the short-lived radionuclides ^{182}Hf ($t_{1/2}$ ~ 9 Myr) and ^{146}Sm ($t_{1/2}$ ~ 103 Myr) were both extant.

Figure 4 shows a plot of ε^{182}W vs. ε^{142}Nd values in the SNC meteorites (including those analyzed by us). If we assume that the ^{142}Nd excesses in Los Angeles and in NWA 998 are similar to those in the basaltic shergottites (Shergotty and Zagami) and in the nakhlites, respectively, then the correlation between ε^{182}W and ε^{142}Nd noted earlier by [6] appears to be robust. Therefore, this provides further confirmation that core formation and silicate differentiation occurred very early in the history of Mars.

It is notable here that the SNCs with the least radiogenic W and near chondritic Nd isotopic compositions (i.e., the basaltic shergottites Shergotty, Zagami, and Los Angeles) have ^{182}W excesses that are still ~2.2 ε units above the revised chondritic value determined by [7, 8, 9]. This provides an upper limit on the timing of core formation on Mars of ~13 Myr and furthermore suggests that core formation preceded silicate differentiation.

Figure 4: *ε^{182}W vs. ε^{142}Nd in the SNC meteorites. ε^{182}W values are from this study and from [6], while ε^{142}Nd are from [15]. The ε^{142}Nd values shown here for LA and NWA 998 are average values, reported by [15], for shergottites (S) and nakhlites/chassignites (NC) respectively.*



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