TUNGSTEN ISOTOPIC COMPOSITION OF THE SNC METEORITE LOS ANGELES: 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 radionuclide system (half life ~9 Myr) has been used to date early solar system differentiation events for the Earth, Moon, Mars (SNC parent body), and Vesta (eucrite parent body)[1-10]. During planetary differentiation, the lithophile Hf segregates into the silicate fraction (crust and/or mantle) while the siderophile W segregates into the metallic core. If this differentiation occurs within the life-time of ^{182}Hf, ~45 Myr, then its timing can be determined by measuring the excess of the daughter product, ^{182}W.

The recently revised estimates of Solar System initial ^{182}Hf/^{180}Hf ratio based on new W isotopic data for chondritic meteorites have enabled new assessments of the timing of planetary differentiation for the Vesta, Earth, Mars, and the Moon [7,8,9]. Planetary differentiation is now thought to have occurred within the first ~3 [7], ~13 [8], ~10-29 [7], and ~29 [7] Myr from Solar System formation for Vesta, Mars, Earth and the Moon, respectively. These values differ significantly from previous estimates of ~11 [10], ~30 [6], ~62 [1], and >62 Myr [1] from Solar System formation for each of these planetary bodies, respectively. The previous estimate of the Solar System initial ^{182}Hf/^{180}Hf ratio was based primarily on W isotopic analyses of Allende by Lee and Halliday [1,2] (which indicated an ε_{182W} 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 also raises the question as to whether or not these SNC values are reproducible. Verification of the SNC W isotopic composition will determine the time of planetary differentiation and the extent of heterogeneity in the martian mantle.

Previous measurements show that whole rock ε_{182W} values in the SNCs vary from ~0 to +3 ε units above terrestrial [6]. Moreover, these values appear to correlate with initial ^{142}Nd values for each of the SNCs that has been analyzed [11], suggesting that core formation and silicate differentiation on Mars occurred very early in the history of Mars, and that subsequenstly, 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_{182W} in the SNC meteorites (by reassessing ε_{182W} values of those which were previously analyzed and obtaining new ones for those that were not) and to confirm the relationship between the ε_{182W} and ε_{142Nd}. We report here preliminary data for the W isotopic composition of the Los Angeles basaltic shergottite. W isotopic analyses of additional SNCs are ongoing.

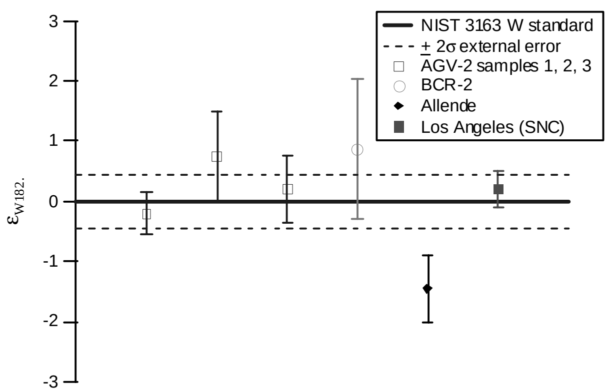
Methodology: The samples analyzed here were crushed with a clean agate mortar and pestle. Dissolution was performed by treatment with a 3:1 mixture of concentrated HF:HNO_3, followed by concentrated HNO_3, and samples were finally brought into solution in HCl. Isolation of W from samples was performed using column chromatography using AG-1X8 anion exchange resin (200-400 mesh). The chromatography procedure is similar to that used by [9] and [13].This procedure relies chiefly on the principle that the binding affinity of W on this resin is high with low normality HF and HCl, but greatly decreases with 7 N HCl-1 N HF [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 redissolved in 3% HNO_3-0.05 N HF for isotopic analysis.

Measurements of ^{182}W, relative to the stable isotope ^{183}W, have been acquired using the Micromass Iso-Probe multicollector ICPMS at the Field Museum. The normalizing ratio used to correct the ^{182}W/^{183}W for intrumental mass fractionation was ^{184}W/^{183}W = 2.139758 [15]. Sample solutions (typically with W concentrations of ~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 comprised of 40 cycles of 10 s integrations, and was preceded by a 10 minute wash-out and a 45 s integration of the background. Measurements of each sample were bracketed with multiple measurements of the NIST 3163 W standard. The ε_{182W} composition of the sample was determined by calculating the difference between the average of 40 ratios for a sample and the average of repeated measurements (comprising 40 ratios each) of the NIST 3163 W standard in epsilon (ε) units as shown on the following page.

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

Results and Discussion: Terrestrial USGS andesite and basalt geostandards, AGV-2 and BCR-2 respectively, were first analyzed to verify the experimental techniques. As shown in Figure 1 analyses of AGV-2 and BCR-2 are, within error, isotopically the same as the NIST 3163 W standard, represented by the solid line ± 2 σ (dashed lines).

Figure 1: ε_{182W} of AGV-2 (3 separately processed ~0.5 g samples), BCR-2 (~0.5 g), Allende (~1 g sample), and Los Angeles (SNC meteorite 0.5 g sample) relative to the terrestrial standard NIST 3163 $\pm$ 2σ external errors.



After verification that our experimental techniques work with terrestrial samples, the W composition of Allende was measured. As shown (Figure 1) our preliminary result of ε_{182W} = -1.46 $\pm$ 0.66 (2σ) is the same within error of the values reported by [7, 8, and 9] of -1.93 $\pm$ 0.28, –1.9 $\pm$ 0.4, and –2.24 $\pm$ 0.29 respectively. In contrast, it is not consistent with the ε_{182W} value for Allende acquired by [2] of –0.10 $\pm$ 0.56.

The preliminary result for the ε_{182W} measurement of a ~500 mg sample of the Los Angeles (LA) basaltic shergottite is also shown in Figure 1. Like the other basaltic shergottites measured by [6] that are petrologically similar to LA (i.e., Shergotty and Zagami), LA has an ε_{182W} value which is approximately equivalent to terrestrial, 0.2 $\pm$ 0.33 (2σ). The measured LA ε_{182W} value is ~2.1 ε units above the revised chondritic value from [7, 8, 9]. As discussed by [7, 8] this evidence for the presence of radiogenic ^{182}W in the shergottite source can be attributed to core formation on Mars ~11-13 Myr after the beginning of the Solar System.

Further verification of these results will be done by processing a separate 500 mg sample of LA, as well as analyzing additional SNC meteorites. Also, the correlation of ε_{182W} with Nd and Sr isotopic systematics will be examined to determine if there is evidence for mixing of a crustal-like component with a mantle component. Verification of such a trend is pertinent to understanding the Martian differentiation history.

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