EVIDENCE OF CORRELATED COSMOGENIC EFFECTS IN IRON METEORITES: IMPLICATIONS FOR THE TIMING OF METAL-SILICATE DIFFERENTIATION IN ASTEROIDS. L. Qin[1,2,4,5], N. Dauphas[1,2,3,4,5], M. Wadhwa[2,4,5], P. E. Janney[4,5], A. M. Davis[2,3,4,5], and J. Mazarik[6]. [1]Origins Laboratory, [2]Department of the Geophysical Sciences, [3]Enrico Fermi Institute, [4]Chicago Center for Cosmochemistry, The University of Chicago, Chicago IL 60637, USA. [5]Department of Geology, The Field Museum, Chicago IL 60605, USA. [6]Department of Nuclear Physics, Komensky University, SK-842 48 Bratislava, Slovakia. (E-mail: qinlp@uchicago.edu)

Introduction: The ^{182}Hf–^{182}W decay system ($t_{1/2}$=9 My) provides a useful chronometer of early solar system processes, notably metal-silicate differentiation [1-8]. Hf-W systematics of refractory inclusions indicate that these objects formed with an initial ^{182}Hf/^{180}Hf ratio of ~1×10^{-4} and an initial ε^{182}W of –3.47 ± 0.20 [6]. Some iron meteorites have ε^{182}W more negative than the initial CAI value [3, 5-8]. Taken at face value, this would indicate that core formation in the parent bodies of these meteorites predated CAI formation. Recently, Markowski et al. [8] measured the W isotopic compositions along a depth profile in Grant, a IIIB iron meteorite. They showed that this iron meteorite is affected by cosmogenic effects corresponding to a decrease of ε^{182}W by neutron-capture burnout of W isotopes. One major challenge in establishing the ^{182}Hf-^{182}W system as a reliable chronometer is to find a way to accurately correct for these cosmogenic effects [9, 12]. Knowledge of exposure ages alone is not sufficient because the cosmic irradiation is also modulated by the depth of burial in the parent-body. A robust way of estimating cosmic-ray effects would be to identify correlated cosmogenic effects in the other W isotopes besides ^{182}W. We recently began an investigation to identify such correlated cosmogenic effects [10]. We report here our latest results, which have implications for the timing of core formation on the parent bodies of iron meteorites.

Methods: *Chemical separation of W.* Previous studies relied on anion-exchange columns to remove matrix and interfering elements (Os) and were limited to small sample sizes (typically < 700 mg). In this study, an improved two-step procedure for chemical separation of W was developed which allows us to recover high-purity W with high-yields (typically better than 85%) from large sample sizes (up to 2 g). In the first step of this procedure, most of the transition metals (Fe, Ni, Co) are removed from the sample solution using a cation-exchange column. In this step, the concentrations of matrix elements are reduced by 2 orders of magnitude. Further purification of W is achieved in the second step using anion-exchange columns. The Os/W ratio after purification is ~10^{-5}, corresponding to a negligible correction of <0.01 ε unit on ε^{182}W.

MC-ICPMS analysis. The W isotopic compositions were analyzed by MC-ICPMS (Micromass Isoprobe) at the Field Museum. We have developed the methods for the precise and accurate determination of ε^{182}W and ε^{184}W. The NIST W standard was used as the reference material. The measured ^{182}W/^{183}W and ^{184}W/^{183}W ratios were mass bias corrected by normalizing to a ^{183}W/^{186}W ratio of 0.501800. The ε values of the samples were calculated relative to the average of the bracketing standards. We found that mismatch of W concentration between the standard and samples can significantly affect the accuracy of the ε^{184}W measurements, although ε^{182}W is not affected outside of the analytical precision. Therefore, all the measurements reported here were obtained with concentration matching of better than 3% between standards and samples. Using these methods, the precision was better than ±0.1 for ε^{182}W and ±0.07 for ε^{184}W ($2\sigma_{mean}$; obtained with 10–20 replicates).

Results: Iron meteorites with low exposure ages (Gibeon, IVA, and Cedartown, IIAB) and high exposure ages (Deep Springs, ungrouped, and Tlacotepec, IVB) were studied. Except for Cedartown, more than two aliquots of each meteorite were separately processed and analyzed for evaluating the external reproducibility. All samples were extensively leached in acids (resulting in a 10% mass loss) prior to dissolution to avoid contamination by terrestrial W. Some samples were also analyzed by both soft and hard extraction (two modes of ion extraction available on the Micromass Isoprobe; see [11] for details). Finally, NIST W solutions alone or mixed with matrix elements recovered from Tlacotepec elutions ("TLP matrix + NIST W" in Fig. 1) were also processed to evaluate the accuracy of our methods; these have ε^{182}W and ε^{184}W values that are zero within errors (Fig. 1).

As shown in Fig. 1, Gibeon and Cedartown have ε^{182}W values similar to or in excess of the initial CAI value (i.e., –3.47±0.20; [6]). This indicates that metal-silicate differentiation on the parent bodies of these irons was contemporaneous with or slightly postdated CAI formation. ε^{184}W is normal within uncertainties for both Gibeon and Cedartown. Analyses of two different aliquots of Deep Springs yielded identical ε^{182}W values of –3.80±0.07 and –3.77±0.07, and a resolvable depletion in ε^{184}W (–0.18±0.06 and –0.15±0.07). Tlacotepec samples (obtained from different museum sources) showed a range of ε^{182}W from –4.01±0.08 to –4.19±0.07, consistent with previous work [3, 5-8]. The ε^{184}W values for Tlacotepec ranged from –0.14±0.06 to –0.06 ±0.05 (with an average of –0.08±0.02). Thus, the two iron meteorites with long exposure ages (2268 My for

Deep Springs and 982 My for Tlacotepec) show resolvable depletions in ε^{184}W.

Discussion: *Accuracy of the measurements*. We carefully evaluated analytical artifacts that could affect the accuracy of the measurements and could potentially account for the nonzero ε^{184}W for Deep Springs and Tlacotepec. Mass scans obtained on purified samples show that the separation protocol provides very clean W solutions. Hard extraction and soft extraction (use of negative and positive extraction voltages in measurements) give identical results, which makes it doubtful that any molecular interferences are the source of the observed variations among samples, because such interferences are typically more prominent in hard versus soft extraction modes. The interference from Os is negligible (Os/W <0.001%). NIST W doped with Tlacotepec matrix and subsequently processed through our chemical procedures for W separation shows no anomaly in ε^{184}W. A number of different laws for correction of instrumental mass fractionation were used in the data reduction of the Deep Springs analyses. All such calculations yielded ε^{182}W and ε^{184}W values that were identical within errors. We finally examined the possible effect of mass-dependent fractionation during column chemistry and found that samples (Gibeon and Cedartown) that were processed at the same time as Deep Springs or Tlacotepec had similar fractionation factors (~0.15‰/amu), but showed no depletion in ε^{184}W.

The effect of GCR. As discussed above, after a critical evaluation of all potential analytical artifacts that could affect the W isotope measurements of Deep Springs and Tlacotepec, we conclude that the observed ε^{184}W depletions in these samples must be real. ^{184}W is a stable isotope of W and thus any variations in its abundance in iron meteorites must result from burnout caused by GCR exposure. To a first approximation, the ε^{184}W depletions reported here for Deep Springs and Tlacotepec are correlated with their respective exposure ages. According to simulations of thermal neutron capture in iron meteorites [12], the change in ε^{182}W due to GCR exposure should be approximately linearly correlated with ε^{184}W, although the model predicts an enrichment in ε^{184}W rather than a depletion. But since the effect is small compared to current uncertainties in the neutron capture cross-sections of W isotopes, the negative variations that we observe are within the permissible range of model predictions (± 0.20 ε in ^{184}W/^{183}W for a depletion in ^{182}W/^{183}W of 0.5 ε resulting from GCR exposure).

Conclusions: Iron meteorites with low exposure ages show no effect of exposure to GCR in ε^{184}W and their ε^{182}W values indicate that metal segregation in their parent asteroids was contemporaneous with or occurred shortly after the formation of CAIs. We report the first evidence for correlated cosmogenic effects in W isotopes for the high exposure age iron meteorites Deep Springs and Tlacotepec. The low ε^{182}W (compared to the CAI initial) measured in these meteorites must reflect the effects of GCR irradiation and it is likely that metal-silicate differentition in the parent bodies of these meteorites occurred after CAI formation. ε^{184}W can potentially be used to correct for cosmogenic effects, but ε^{180}W may actually be a better proxy [10].

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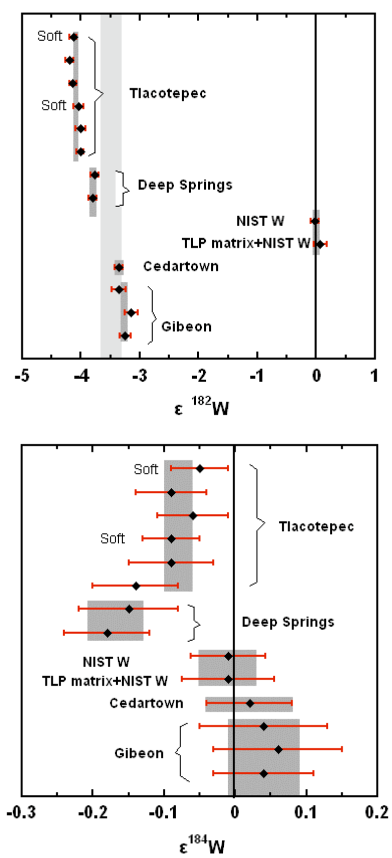

Figure 1. ε^{182}W and ε^{184}W in Iron meteorites and NIST W. The light grey band indicates the initial CAI ε^{182}W; the dark grey bands indicate the average ε^{182}W and ε^{184}W compositions of each meteorite.