

**REVISED TUNGSTEN ISOTOPE CHRONOLOGY OF IVB IRON METEORITES FROM W-Os SYSTEMATICS.** N. Wittig<sup>1</sup>, M. Humayun<sup>1</sup>, S. Huang<sup>2</sup> & A. D. Brandon<sup>3</sup>. <sup>1</sup>National High Magnetic Field Laboratory and Dept. of Earth, Ocean & Atmospheric Science, Florida State University, Tallahassee, FL 32310, USA ([wittig@magnet.fsu.edu](mailto:wittig@magnet.fsu.edu)), <sup>2</sup>Dept. of Earth & Planetary Sciences, Harvard University, Cambridge, MA 02138, USA, <sup>3</sup>Dept. of Earth & Atmospheric Sciences, University of Houston, Houston, TX 77204, USA.

**Introduction:** Any sensible model of early Solar System formation necessitates that condensation of refractory solids (CAI) precedes asteroidal parent-body accretion and magmatic differentiation into Fe-Ni cores and silicate mantles. However, the time difference between the formation of CAIs and iron meteorites must be established empirically. <sup>182</sup>Hf-<sup>182</sup>W dating of CAIs [1, 2] and iron meteorites [e.g., 3-6] implies condensation of refractory solids and differentiation of planetesimals within 1-2 m.y. [2]. An exception is group IVB irons which exhibit  $\epsilon^{182}\text{W}$  values that are apparently less radiogenic ( $\epsilon^{182}\text{W} -3.6\pm 0.1$ , [3-5]), than the CAI initial ( $\epsilon^{182}\text{W} -3.28\pm 0.12$  [1,2]). Such a result could imply that either the Allende CAI initial is too radiogenic due to parent-body metamorphism [7], or that corrections for galactic cosmic-ray (GCR) neutron capture and burn-out [2-5] are insufficient.

Previous attempts to correct the GCR impact on W isotopes relied on noble gases as a GCR exposure proxy [3] or on a 2-step process: 1) the samples with the lowest  $\epsilon^{182}\text{W}$  were corrected by the maximum possible calculated neutron dosage and the corrected values were taken as an upper bound; and 2) the samples with the highest  $\epsilon^{182}\text{W}$  were taken as a lower bound [5].

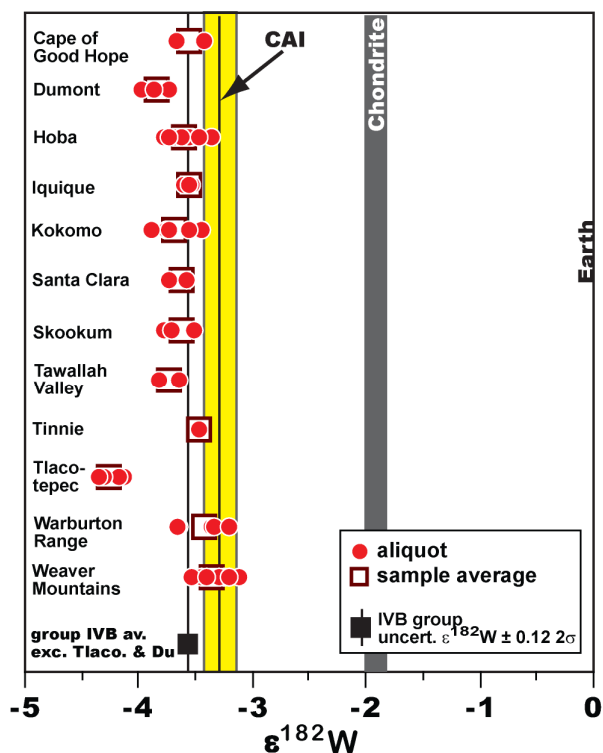
Huang and Humayun [8] showed that neutron capture on <sup>189</sup>Os creates measurable deficiencies in <sup>189</sup>Os/<sup>188</sup>Os (and correlated excesses in <sup>190</sup>Os/<sup>188</sup>Os) in IVB irons, and that stable Os isotope ratios could serve as a neutron dosimeter for W isotopes.

We present W isotope data from 12 of the 13 known IVB iron meteorites including 5 irons for which W isotope data have not been reported previously (Dumont, Iquique, Kokomo, Tinnie and Weaver Mountains). We couple this nearly complete characterization of group IVB  $\epsilon^{182}\text{W}$  to Os isotope data from the same samples. Coupling W and Os isotopes allows us to precisely determine the degree of GCR modification of <sup>182</sup>W and then to establish an accurate pre-irradiation  $\epsilon^{182}\text{W}$  from which relative chronology of irons relative to CAIs can be obtained.

**Analytical Methodology:** Approximately 0.5 g of each of the IVB irons were digested in inverse aqua regia (3:1 HNO<sub>3</sub>:HCl) in sealed carius tubes. Os was extracted by solvent extraction and W was purified by

a combination of cation and anion exchange procedures, generally following [4,9].

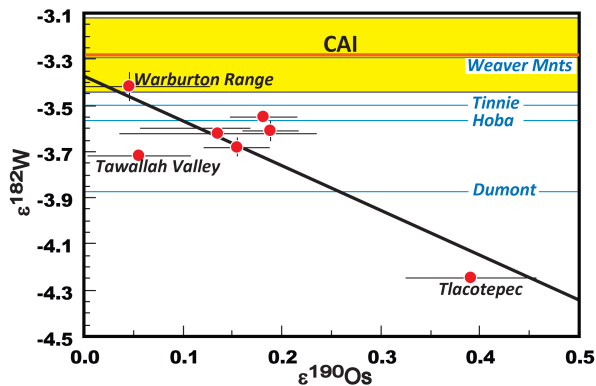
Tungsten isotope measurements were performed on a Thermo Neptune™ MC-ICP-MS on 10-25 ng aliquots using an ESI Apex™ introduction system and Thermo SuperJet8.3 Ni sampler and Spectron T1001Ni-X skimmer cones [10]. The data are reported against reference material NIST SRM 3163. Our current W isotope procedures allow determination from small aliquots with a long-term (12 months, SRM 3163 n = 200) reproducibility of  $\pm 0.18\epsilon$  (2 $\sigma$ ). Replicate measurements of IVB aliquots yield a reproducibility that is on the order of 0.10 to 0.24  $\epsilon$  (2 $\sigma$ ). Os isotope data were determined previously on a sub-set of IVB irons and are reported as  $\epsilon^{189}\text{Os}$  and  $\epsilon^{190}\text{Os}$  relative to a terrestrial Os standard solution (HPS) [8]. Precision of standard runs was 0.14 and 0.03  $\epsilon$  on  $\epsilon^{189}\text{Os}$  and  $\epsilon^{190}\text{Os}$ , respectively. Extending the Os isotope data with improved precision is our current focus.



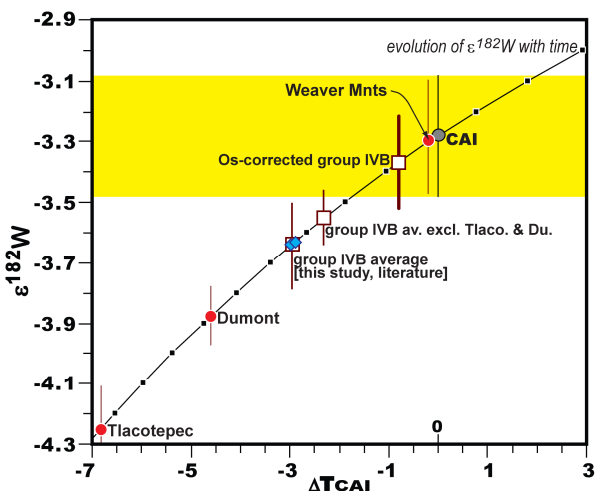
**Fig. 1.**  $\epsilon^{182}\text{W}$  of group IVB iron meteorites [this study], chondrites ([2, ref. therein] gray band) and CAI ([1,2] yellow band).

**Results:** Our  $\epsilon^{182}\text{W}$  data (Fig. 1) for samples previously characterized (Cape of Good Hope, Hoba, Santa Clara, Skookum, Tawallah Valley, Tlacotepec, Warburton Range) agree well with literature data [3-6]. The majority of group IVB iron meteorites define a mean value of  $\epsilon^{182}\text{W} -3.55 \pm 0.12$  ( $2\sigma$ ,  $n = 10$ , excluding Dumont, Tlacotepec). Among the newly characterized samples, Dumont exhibits lower  $\epsilon^{182}\text{W}$  ( $-3.88 \pm 0.14$  ( $2\sigma$ )) relative to the majority of IVBs, but is less extreme than Tlacotepec ( $\epsilon^{182}\text{W} -4.25 \pm 0.2$ ). Iquique and Kokomo have typical group IVB  $\epsilon^{182}\text{W}$  clustering around the average value of  $-3.6$ , whereas Weaver Mountains and Tinnie, together with Warburton Range have higher  $\epsilon^{182}\text{W}$  approaching the CAI value. Our Os data are in good agreement with those of [11]. Among the currently characterized group IVB iron meteorites, Tlacotepec shows distinct  $\epsilon^{189}\text{Os}$  deficit and  $\epsilon^{190}\text{Os}$  excess from GCR exposure [8]. Fig. 2 shows the correlation between  $\epsilon^{190}\text{Os}$  excesses and  $\epsilon^{182}\text{W}$  deficits for IVB irons.

**Discussion:** Our nearly complete W isotope characterization of IVB irons shows larger variability among the group than previously reported [3-6]. Fig. 2 shows that the  $\epsilon^{182}\text{W}$  variations in IVBs are anti-correlated with  $\epsilon^{190}\text{Os}$  excesses. For example, Tlacotepec shows the strongest GCR-signal with  $\epsilon^{182}\text{W}$ - $\epsilon^{189}\text{Os}$  deficits/ $\epsilon^{190}\text{Os}$  excesses. Warburton Range has a  $\epsilon^{182}\text{W}$  within error of the CAI value [1], and an  $\epsilon^{190}\text{Os}$  excess within error of the terrestrial value ( $\epsilon^{190}\text{Os} 0.05 \pm 0.08$   $2\sigma$ ), indicating essentially no GCR neutron burn-out on  $^{182}\text{W}$  or  $^{189}\text{Os}$ . We currently do not have Os isotope data for Weaver Mountains, but it has the highest  $\epsilon^{182}\text{W}$  ( $\epsilon^{182}\text{W} -3.29 \pm 0.23$ ,  $2\sigma$ ) among the measured IVB irons well within range of the CAI value ( $-3.28 \pm 0.12$ ,  $2\sigma$ , [1]). Thus, Warburton Range and Weaver Mountains set lower bounds on the pre-irradiation  $\epsilon^{182}\text{W}$  of the IVB irons. The intercept of the Os-W regression line projected to an  $\epsilon^{190}\text{Os}$  of 0 yields the pre-irradiation  $\epsilon^{182}\text{W}$  of  $-3.37 \pm 0.19$  ( $2\sigma$ ) for the IVB irons for which Os-W data are available (Fig. 2). An identical pre-irradiation  $\epsilon^{182}\text{W}$  of  $-3.36 \pm 0.16$  ( $2\sigma$ ) is derived from  $\epsilon^{189}\text{Os}$ . The error on the current Os-W regression is dominated by Tawallah Valley. Our previous pre-irradiation  $\epsilon^{182}\text{W}$  of  $-3.12 \pm 0.15$  ( $2\sigma$  [12]) resulted from a smaller sample set and utilized weighted regression parameters. Regardless of the mathematical treatment of IVB iron Os-W isotope correlation, the Os-corrected  $\epsilon^{182}\text{W}$  is within uncertainty of the CAI value and indicates that IVB iron meteorites, like other magmatic irons [2], formed within  $\sim 2$  Myr of the first solids (CAIs, Fig. 3), a time difference which is not resolvable.



**Fig. 2.**  $\epsilon^{182}\text{W}$ - $\epsilon^{190}\text{Os}$  of IVB iron meteorites (red circle,  $2\sigma$ ) indicate a pre-GCR irradiation  $\epsilon^{182}\text{W}$  of  $-3.37 \pm 0.19$  ( $2\sigma$ , black).  $\epsilon^{182}\text{W}$  of CAIs (red line, yellow band is  $\pm 2\sigma$  [1,2]) is given for comparison. Blue lines show  $\epsilon^{182}\text{W}$  for samples without Os isotope data.



**Fig. 3.**  $\epsilon^{182}\text{W}$ - $\Delta T_{\text{CAI}}$  of group IVB irons. Shown are the key samples Weaver Mountains, Dumont and Tlacotepec (red circle), group IVB averages (red square) using all samples (this study, literature {blue diamonds [3-5]}). Uncertainties are  $2\sigma$ , the Os corrected  $\epsilon^{182}\text{W}$  error is driven by the deviation of Tawallah Valley from the regression line (Fig. 2).

## References

- [1] Burkhardt, C. et al. (2008) *GCA*, **72**, 6177–6197. [2] Kleine, T. et al. (2009) *GCA*, **73**, 5150–5188. [3] Markowski, A. et al. (2006) *EPSL*, **250**, 104–115. [4] Markowski, A. et al. (2006) *EPSL*, **242**, 1–15. [5] Qin L. et al. (2008) *EPSL*, **273**, 94–104. [6] Schersten, A. et al. (2006) *EPSL*, **241**, 530–542. [7] Humayun, M. et al. (2007) *GCA*, **71**, 4609–4627. [8] Huang, S. and Humayun, M. (2008) *LPSC*, XXXIX, 1168. [9] Shirey, S. B. and Walker, R. J. (1995) *Anal. Chem.*, **67**, 2136–2141. [10] Shirai, N. and Humayun, M. (2011) *JAAS* **26**, 1414–1420. [11] Walker R. J. (2011) *Min. Mag.*, **75**, 2108. [12] Wittig N. and Humayun M. (2011) *Min. Mag.*, **75**, 2168.