IMPROVED CONTRAINTS ON THE RELATIVE TIMING OF METAL SEGREGATION IN THE EARLY SOLAR SYSTEM USING COUPLED W-Os ISOTOPES. R. J. Walker and M. Touboul, Department of Geology, University of Maryland, College Park, MD 20742, USA (rjwalker@umd.edu) .

Introduction: Over the past two decades, the short-lived ^{182}Hf-^{182}W chronometer ($T_{1/2}$= 8.9 Myr; [1]) has been widely used for dating early Solar System processes, due to the unique geochemical properties of the system. Tungsten is a siderophile (iron-loving) element, and as such, it is largely (but not completely) extracted from the silicate mantles of planetary bodies during segregation of metallic cores [2-5]. Hafnium, in contrast, is lithophile (silicate-loving) and is wholly retained in the silicate portion of planetary bodies. Therefore, determination of the abundance of the daughter nuclide, ^{182}W, relative to other stable, non-radiogenic W isotopes (e.g., ^{184}W) is of special interest for constraining the timing of planetary core formation, or other metal segregation processes. Indeed, prior studies have shown that the major magmatic iron meteorite groups formed within the first 1-3 Myr of Solar System formation [6-11]. The precision of the application of this system for the relative dating of the segregation of metal domains sampled by iron meteorites, however, has been somewhat hindered by changes in the isotopic abundance of W resulting from burnout and production effects, caused by long-term cosmic ray exposure (CRE). Successful attempts to measure changes to the isotopic composition of W resulting from CRE, and to correct for these effects have been made [11]. Yet, with the exception of [11], the lack of neutron fluence data for the same pieces of iron examined for W isotopes (CRE effects vary with depth in a meteorite) has limited the ability to correct for these effects and concurrently limited the precision by which W isotopes can be applied to the relative dating of iron groups.

Walker [12] recently reported that some isotopes of Os, especially ^{186}Os, ^{189}Os and ^{190}Os are also significantly affected by CRE. Nevertheless, that study showed that pieces of at least one member of each of the major iron meteorite groups has Os isotopic compositions that are not resolved from chondritic abundances, presumably reflecting negligible CRE to those specific pieces. This means that Os isotopic composition can be used as a relatively simple neutron fluence monitor, and irons from diverse groups (as well as ungrouped irons) can be selected for W isotopic analysis based on “normal” Os and the assumption of negligible modifications to W from CRE.

In addition, recent advances in W isotope measurement [13] mean that a 2σ SD for ^{182}W/^{184}W of <5 ppm is now possible. The new measurement capability, coupled with Os isotopic filtering of samples, should permit the resolution of metal-silicate segregation ages to <0.5 Myr.

Analytical Methods: As described by Walker [12] Os isotopes were measured by negative thermal ionization mass spectrometry using a *Thermo-Fisher Triton* at the UMd. For these measurements, Os isotope intensities were corrected for contributions from ^{17}O- and ^{18}O-substituted oxides. For our Os laboratory standard, interference corrected ^{186}Os/^{188}Os, ^{189}Os/^{188}Os and ^{190}Os/^{188}Os ratios were measured to 2σ external precisions of approximately ±40, ±10 and ±8 μ units (parts per million deviations from chondritic averages), respectively. Measurements for individual samples consisted of multiple measurements using the same filament loading, as well as at least two separate loadings of most samples and give comparable or better reproducibility, with 2σ of mean precisions as low as 3 ppm for repeated measurements of some ratios for some samples. Corrections for ingrowth of ^{186}Os from the decay of ^{190}Pt were made using Pt and Os concentration measurements made on adjoining pieces of each iron.

For W isotopic meaurments, we recently developed a new technique to measure ^{182}W/^{184}W to a 2σ precision of ±4.6 ppm, using negative thermal ionization mass spectrometry [13]. After chemical purification of W through a four-step ion exchange chromatographic separation, the W isotopic composition was measured as WO_3^- using the UMd *Triton*. Data were initially corrected for oxide interferences, assuming a predefined O isotope composition, and for mass fractionation, by normalization to ^{186}W/^{184}W or ^{186}W/^{183}W, using an exponential law. A small second-order effect, likely reflecting a mass dependent change of O isotope composition in the measured W oxides, is corrected by normalization to ^{183}W/^{184}W using a linear law. Repeated analysis of both standard solutions and rocks demonstrate external reproducibility of ^{182}W/^{184}W within ±4.6 ppm (2σ SD).

Results: Walker [12] showed that irons from groups IIAB, IIIAB, IVA and IVB, as well as two main group pallasites (PMG), show well-resolved anomalies in μ^{190}Os, μ^{189}Os and μ^{186}Os$_i$ (corrected for ingrowth from ^{190}Pt decay). These anomalies differ from the nucleosynthetic anomalies observed in components extracted from chondrites, and are attributed to variable, long-term exposure of the irons to cosmic rays. Of the five iron groups examined, however, there is at least one meteorite from each group that is not resolved, beyond analytical uncertainties, from bulk chondritic/terrestrial compositions. The meteorites with normal Os for the IAB, IIAB, IIIAB, IVA and IVB iron groups are Canyon Diablo, Negrillos (& Bennett County), Costilla Peak, Charlotte and Hoba, respectively. Krasnojarsk of the PMG, Eagle Station of the Eagle Station pallasite grouplet, and the ungrouped iron Nedagolla also all have normal Os isotopic compositions.

As of this writing we have analyzed three IIAB irons, Negrillos, Bennett County, and Filamena (for which we do not yet have Os data) for W isotopic composition. These irons have $\mu^{182}W$ values that are identical, within uncertainties, and average -348 (**Table 1**). This value is generally consistent with results of prior studies, albeit more precise [e.g., 9]. We also analyzed the IVA irons Gibeon and Jamestown for W. Gibeon has Os isotopic compositions well within uncertainties of chondrites, so the assumption we make is that this piece of Gibeon experienced a neutron fluence that did not significantly modify Os or W isotopic compositions. In contrast, Jamestown is depleted in ^{189}Os, and enriched in ^{186}Os and ^{190}Os, consistent with long-term CRE. The $\mu^{182}W$ value for Jamestown is 27.5 ppm lower than for Gibeon (**Table 1**), also consistent with CRE.

The iron with the largest Os isotopic anomalies is the IVB Tlacotepec, which has a μ ^{189}Os value of -55. This meteorite has a correspondingly low $\mu^{182}W$ of -425. This level of depletion is consistent with numerous prior W isotopic measurements [e.g., 7-9, 15].

Discussion: Although our database is currently limited, correlations between W and Os isotopes appear to be consistent with the effects of CRE. Whether or not both elements are affected in a predictable way that will allow accurate corrections to be made on W isotopic compositions using Os isotopes remains to be demonstrated.

Our new results show remarkable agreement in the W isotopic composition of the three IIAB irons analyzed, with a 2σ SD of only 7.2 ppm. Using the difference in the μ values between the average of the IIAB irons and the value for the IVA Gibeon, gives an age difference of 1.9 Myr. The older relative age of the IIAB irons is consistent with cooling rate data that suggest the IVA group may sample a much larger parent body [14]. Caveats must be applied to this calculation for the time being. Some studies have shown small isotopic heterogeneities among non-radiogenic isotopes of W, presumably resulting from diverse nucleosynthetic heterogeneities present in the respective parent bodies [10, 15], although those studies did not show resolved effects in other W isotopes for IIAB or IVA irons. We are in the process of refining our ability to detect and quantify heterogeneities among other W isotopes which would complicate the age comparisons.

References: [1] Vockenhuber C. and others (2004) *Phys. Rev. Lett.*, 93 (2004) 172501. [2] Palme H. & Rammensee W. (1981) *Proc. Lunar Planet. Sci.*, 12B, 949-964. [3] Newsom H.E. & Palme H. (1984) *Earth Planet. Sci. Lett*., 69, 354-364. [4] Sims K. W. W. and others (1990) in: H. E. Newsom and J. H. Jones (eds.), *Origin of the Earth*, Oxford University Press, 1990, pp. 291-317. [5] Walter M.J. and others (2000) in: R.M. Canup and K. Righter (eds.), *Origin of the Earth and Moon*, Lunar and Planetary Institute, Houston, 2000. [6] Harper C. & Jacobsen S. B. (1996) *GCA*, 60, 1131-1153. [7] Horan M. F. and others (1998) *GCA*, 62, 545-554. [8] Kleine T. et al. (2005) *GCA*, 69, 5805-5818. [9] Schérsten A. and others (2006) *Earth Planet. Sci. Lett.*, 241, 530-542. [10] Qin L. and others (2008) *Astrophys. J.*, 674, 1234-1241. [11] Markowski A. and others (2006) *Earth Planet. Sci. Lett.*, 250, 104-115. [12] Walker R. J. *Earth Planet. Sci. Lett*., in review. [13] Touboul M. & Walker R. J. (2011) *Int. J. Mass. Spectrom.*, 309, 109-117. [14] Yang J. and others (2011) *MAPS*, 46, 1227-1252. [15] Qin L. and others (2008) *Earth Planet. Sci. Lett*., 273, 94-104.

Table 1. Tungsten and Os isotopic data for group IIAB, IVA and IVB iron meteorites.

	$\mu^{182}W$	2σ	$\mu^{189}Os$	2σ
IIAB				
Bennett County	-345.1	6.6	-3.1	15.2
Duplicate	-349.3	10.8		
Duplicate	-346.1	8.3		
Negrillos	-344.4	13.2	0.3	8.0
Filomena	-350.1	6.2		
re-run	-354.0	6.6		
IVA				
Gibeon	-329.4	7.2	0.1	7.5
Jamestown	-356.9	8.8	-16.2	9.1
IVB				
Tlacotepec	-425.4	4.9	-54.9	3.9

μ units are ppm deviations from either terrestrial standards (W) or chondrites (Os). Re-run means a second analysis of the same filament loading. Duplicates represent additional digestions and processing of separate pieces of the meteorite.

This work was supported by NASA grant NNX10AG94G to RJW, which is gratefully acknowledged.