ARE NON-RADIOGENIC W ISOTOPE ANOMALIES IN IRON METEORITES ANALYTICAL ARTIFACTS? J. C. Holst[1], C. Paton[1] and M. Bizzarro[1], [1]Centre for Star and Planet Formation, Natural History Museum of Denmark, University of Copenhagen, Øster Voldgade 5-7, DK-1350 Denmark (jcholst@snm.ku.dk).

Introduction: The short-lived radionuclide ^{182}Hf decays to stable ^{182}W via double β-decay with a half-life of 8.9 ± 0.09 Myr [1]. The presence of ^{182}Hf at the time of solar system formation has been thoroughly documented in the past two decades as widespread variations in the abundance of daughter isotope ^{182}W in early formed solids. However, the accuracy of any short-lived radionuclide chronometer relies on the assumption of isotopic homogeneity in establishing an accurate timescale for the formation of solids in the early solar system.

Recent high-precision W isotope measurements of iron meteorites, however, suggest the presence of resolvable anomalies in ε^{184}W and ε^{180}W [2, 3], implying that the assumption of homogeneity may not be justified. ^{184}W is produced by the so-called *s-,* and *r-processes* of stellar nucleosynthesis, whereas ^{180}W is produced by the *p-process*. The documented anomalies have been interpreted as resulting from injection and insufficient mixing of different stellar sources into the nascent solar system [2, 3]. Heterogeneity in W isotopes can potentially have a significant impact on the use of the Hf-W decay system, compromising its use as an accurate early solar system chronometer. As such, the discovery of W isotope heterogeneity requires confirmation.

The presence of isobaric interferences resulting from organic species on the W mass array ($C_{13}H_{24}^+$, $C_{14}H_{12}^+$, C_{15}^+, $C_{13}H_{27}^+$, $C_{15}H_3^+$, $C_{14}H_{15}^+$) could in principle generate the isotope anomalies reported for ε^{180}W and ε^{184}W. In detail, we note that a ~500 count per second (cps) interference on ^{180}W would generate epsilon-level anomalies, whereas a ~2500 cps interference on mass 183 would result in apparent deficits in ε^{184}W of ~0.1 to 0.2. Thus, to evaluate the accuracy of previously reported non-radiogenic W isotope anomalies, we have developed analytical protocols for the high-precision measurement of W isotopes by high-resolution multi-collector inductively coupled plasma mass spectrometry (HR-MC-ICPMS). These methods allow us to resolve all potential isobaric interferences on the W mass array that are related to organic species. Here, we report the W isotope composition of three iron meteorites using these techniques.

Samples and methods: We processed 0.3-1.2 g pieces of the iron meteorites Tlacotepec, Skookum (IVBs), and Cape York (IIIAB). Samples were chosen in order to compare W isotopic results with previous investigations and because they have contrasting Ni isotope compositions, namely excesses in ^{62,64}Ni for IVBs and deficits in ^{62,64}Ni for IIIABs [4, 5]. Samples were cut and abraded using W-free abrasives and successively cleaned for 10-20 minutes in ethanol and 0.02M HNO_3 in an ultrasonic bath. They were then digested in 6M HCl – 0.06M HF prior to W purification using a three-step anion separation consisting of: an initial matrix elution in 1M HF – 0.1M HNO_3 [6]; a matrix clean up, primarily removing residual Fe and high field-strength elements; and a third column to separate any remaining Hf that can cause a direct isobaric interference on ^{180}W. Total procedural blanks for tungsten, including digestion, are ~100 pg and therefore negligible to the present study. W isotopes were measured on the Neptune Plus MC-ICPMS in Copenhagen using a standard-sample bracketing technique, acquiring data in low-, medium- and high-resolution modes. The sensitivity of the instrument for W in low-, medium- and high-resolution mode was 3000, 500, and 250 V/ppm, respectively. Measurements conducted in medium- and high-resolution mode were performed on the low-mass side of the W peak, at a position allowing for an effective mass resolving power (M/ΔM) of ~2000 and ~4000, respectively [7]. Importantly, measurements in high-resolution mode are expected to fully resolve all organic species. The ^{180}Hf interference on ^{180}W was monitored on mass ^{178}Hf, using a Faraday detector connected to an amplifier with a 10^{12} Ω feedback resistor. Similarly, the ^{180}W beam was measured with a Faraday detector connected to an amplifier with a 10^{12} Ω feedback resistor, whereas all other W and Os masses were collected in Faraday detectors connected to amplifiers with 10^{11} Ω feedback resistors. Samples and standards were analyzed with signal intensities matched to better than 10%, with a typical intensity of 40mV on ^{180}W. Interferences from ^{184,186}Os on the W mass array were monitored at mass ^{188}Os, and were negligible in all cases. For both samples and standards, the typical intensity of ^{178}Hf was ~2500 cps. The accurary of the Hf interference correction was investigated by doping pure W solutions with variable amounts of Hf, and found to be accurate within the typical uncertainty of the ^{180}W measurements. Each analysis comprised a total of 1678 s of baseline measurements (obtained on peak) and 839 s of data acquisition (100 scans integrated over 8.39 s). Sample analyses were interspaced by analyses of the NIST 3163 W standard to monitor instrumental mass fractionation. All data reduction was conducted off-line using the freely distributed Iolite data reduction package which runs within Igor Pro [8]. Background intensities were interpolated using a smoothed cubic spline, as were changes in mass bias with time. Iolite's Smooth spline auto choice was used in all cases, which determines a theoretically optimal degree of smoothing based on variability in the reference standard throughout an analytical session, which corresponds typically to 24 h of continuous measurement without adjusting the instrument's tuning parameters. For each analysis the mean and standard error of the measured ratios were calculated, using a 3 sd threshold to reject outliers. Sample analyses were combined to produce an average weighted by the propagated uncertainties of individual analyses. W isotope data are reported in the epsilon notation (per 10^4 deviation from NIST 3163). W isotope ratios were internally normalized to $^{186}W/^{184}W$= 0.92767 and $^{186}W/^{183}W$= 1.98594 [9] using the exponential law.

Results: W isotope results are summarized in Table 1. Low resolution measurements were made for Cape York and Skookum and yielded excesses in $\varepsilon^{180}W$ of ~1.00 ± 0.17 and 2.36 ± 0.42, combined with deviations of -0.16 and 0.08 ± 0.03 in $\varepsilon^{184}W$ relative to NIST 3163. In medium resolution mode, excesses in $\varepsilon^{180}W$ ranging 0.95 ± 0.19 to 4.67 ± 0.67 were still apparent for all three samples analyzed. We note that the excess in $\varepsilon^{180}W$ present in Tlacotepec is significantly greater than that observed in Skookum. This observation is not in keeping with a nucleosynthetic origin for the $\varepsilon^{180}W$ excesses, if these two IVB iron meteorites are derived from the same parent body. $\varepsilon^{184}W$ deviations display a narrower range from -0.07 to 0.07 and are only marginally resolved from the standard. In high resolution mode, Cape York has no resolvable anomaly in $\varepsilon^{180}W$. However, additional work is required to constrain the $\varepsilon^{184}W$ composition, given that this sample has only been analyzed once. $\varepsilon^{182}W$ values are within uncertainty regardless of the applied resolution mode and are in good agreement with previously reported data [2], [10].

Table 1. . Preliminary results for $\varepsilon^{180}W$, $\varepsilon^{182}W$ and $\varepsilon^{184}W$ in iron meteorites. $\varepsilon^{18x}W = [(^{18x}W/^{18x}W)_{sample}/(^{18x}W/^{18x}W)_{std} - 1] \times 10^4$. Errors are 2 S.E.

Resolution	*Sample*	$\varepsilon^{180}W$	$\varepsilon^{182}W$	$\varepsilon^{184}W$	*n*
Low resolution					
	Cape York	**1.00 ±0.17**	**-3.45 ± 0.02**	**0.08 ± 0.03**	**4**
	Skookum	**2.36 ± 0.42**	**-3.29 ± 0.04**	**-0.16 ± 0.03**	**10**
Medium resolution					
	Cape York	**0.95 ± 0.19**	**-3.45 ± 0.02**	**0.07 ± 0.02**	**6**
	Skookum	**3.07 ± 0.61**	**-3.29 ± 0.08**	**-0.02 ± 0.04**	**6**
	Tlacotepec	**4.67 ± 0.67**	**-3.78 ± 0.05**	**-0.07 ± 0.02**	**8**
High resolution					
	Cape York	**-0.21 ± 0.8**	**-3.44 ± 0.07**	**0.12 ± 0.05**	**1**

Discussion: Our new W isotope data obtained in low- and medium-resolution show variable excesses in $\varepsilon^{180}W$ for three iron meteorites, which is in agreement with an earlier study [3]. However, when analyzed in high-resolution, Cape York did not show a resolvable excess in $\varepsilon^{180}W$. This suggests that previously observed $\varepsilon^{180}W$ excesses may be the result of an unresolved isobaric interference on ^{180}W. Potential interfering organic species are $C_{13}H_{24}^+$, $C_{14}H_{12}^+$, C_{15}^+, and $C_{13}NH_{10}^+$. Apart from C_{15}^+, all other organic species should in principle be effectively resolved in medium-resolution mode, namely with a mass resolving power of ~2000. In contrast, C_{15}^+ requires a mass resolving power of at least 3500 and therefore, we suggest that this species is responsible for the apparent $\varepsilon^{180}W$ excesses observed in low- and medium-resolution mode, which correspond to an interference of ~500 cps.

Previous studies have documented $\varepsilon^{184}W$ deficits of approximately 0.1ε in IVB iron meteorites [2]. Our low-resolution data also have apparent deficits for Skookum (-0.16 ± 0.03). However, when analyzed in medium-resolution mode, there is no resolvable deficit. Thus, we infer that anomalies observed in low-resolution are caused by an organic interference that is mostly resolved when measuring in medium-resolution mode. The presence of a small $\varepsilon^{184}W$ deficit in Tlacotepec in medium-resolution suggests that the interfering species may be only partly resolved for this sample. Deficits in $\varepsilon^{184}W$ can result from interferences on ^{183}W and possible organic interferences are $C_{13}H_{27}^+$, $C_{15}H_3^+$, $C_{14}H_{15}^+$. $C_{15}H_3^+$ requires the highest effective mass resolving power of ~2500 and is most likely to be causing the interference. This stresses the need to reduce the levels of organics by thorough oxidation [11].

Conclusions: The results presented here show that reported anomalies in stable, non-radiogenic, non-cosmogenic W isotopes may not be due to heterogeneity arising from insufficient mixing of various nucleosynthetic sources. In contrast, the anomalies most likely represent analytical artifacts resulting from molecular interferences that can only be resolved using high-resolution MC-ICPMS with a mass resolving power >3500. Moreover, we have shown that in low-resolution mode, deficits in $\varepsilon^{184}W$ most likely arise from an organic interference on ^{183}W which is fully resolved for Skookum in medium-resolution.

References: [1] Vockenhuber C. et al. (2004) *Phys. Rev. Let. 93,* 172501-1. [2] Qin L. et al. (2008) *ApJ 674*, 1234. [3] Shulz T. & Münker C. (2010) *73rd Met. Soc.,* #5116. [4] Regelous M. et al. (2008) *EPSL 272,* 330. [5] Bizzarro M. et al. (2010) *Met. Soc.,* #5161. [6] Kleine T. et al. (2008) *LPS XXXIX*, #2367. [7] Bizzarro M. et al. (2011) *JAAS 26,* 565. [8] Hellstrom J. et al. (2008) *Min. Ass. Canada short course series 40,* 343. [9] Völkening J. et al. (1991) *Int. Journ. Mass Spec. Ion Proc. 107,* 361. [10] Kruijer T. et al. (2010) *73rd Met. Soc.,* #5102. [11] Burkhardt C. et al. (2008) *GCA 72,* 6177.