TUNGSTEN AND HAFNIUM DISTRIBUTION IN CALCIUM-ALUMINUM INCLUSIONS (CAIs) FROM ALLENDE AND EFREMOVKA. M. Humayun[1], S. B. Simon[2] and L. Grossman[2], [1]National High Magnetic Field Laboratory and Dept. of Geological Sciences, Florida State University, 1800 E. Paul Dirac Drive, Tallahassee, FL 32310 (humayun@magnet.fsu.edu), [2]Dept. of the Geophysical Sciences, University of Chicago, Chicago, IL 60637.

Introduction: A widely accepted paradigm for the origin of chondrites maintains that chondrites represent the earliest planetesimals to form from the solar nebula and that differentiated bodies formed by the subsequent melting of chondrites. A challenge to this paradigm comes from physical models of accretion that require rapid accretion of ~10 km planetesimals that are then melted by the heat released by ^{26}Al, followed by impact disruption of these bodies to form chondrules [1, 2]. Support for such models has been provided by recent ^{182}Hf-^{182}W chronology of CAIs and chondrule metals that imply that iron meteorites may have formed contemporaneously with, or even earlier than, metal from CAIs and chondrules [3]. Tungsten isotope compositions represent initial ^{182}W/^{184}W at the time of metal segregation. A relative chronology of iron meteorites has been possible from ε^{182}W measurements for iron meteorites [3, 4, and references therein]. Kleine et al. [3] have reported ε^{182}W= –3.47±0.20 from an Allende CAI isochron that included a magnetic separate (ε^{182}W= –3.17±0.70). These numbers are smaller than, or comparable to, the most negative ε^{182}W reported from iron meteorites. Cosmic-ray induced neutron burn-out of ^{182}W can produce negative effects that have been estimated to be no more than ε^{182}W~-0.3 [3]. This led Kleine et al. [3] to support the hypothesis that at least some iron meteorites represent an earlier generation of molten planetesimals that preceded chondrites.

Since ^{182}W is the daughter product of the decay of ^{182}Hf ($t_{1/2}$~9 Ma), a fundamental assumption in [3] is that metal (the W host) in Allende refractory inclusions last equilibrated W isotopically with its surrounding silicates (the Hf host) at the time of formation of the refractory inclusion. This assumption must be made by any study that attempts to relate the relative chronology of ^{182}Hf-^{182}W with an absolute chronology such as U-Pb so that a test of the robustness of this assumption is required. Unlike iron meteorites where the separation of Hf and W occurred on length-scales (L) of >1 metre (m), the physical separation of Hf and W in CAIs is generally $L<10^{-4}$ m, within the possible length-scale of diffusive exchange. Microanalysis of CAI metal from Efremovka showed that W had been redistributed in the solid state [5]. The same study found that W had been mobile in Allende CAIs, being present in sulfide veins [5]. Tungsten mobility is cause for concern, but is not sufficient evidence against the Kleine et al. [3] interpretation. In this contribution, we examine the distribution of Hf and W in metal, fassaite and melilite of CAIs from Allende (oxidized CV3) and Efremovka (reduced CV3) to constrain the possible effects of W disturbance after CAI metal formation.

Samples and Analytical Methodology: Section GBS of the Allende inclusion Golfball, an unusual Type B inclusion [6], contains a prominent spinel palisade body, which has a higher level of refractory metal grains than the remainder of GBS. Campbell et al. [5] described the metal composition in Ef2, a compact Type A, in detail. In both inclusions, melilite, fassaite and spinel are the dominant minerals with abundant refractory element-enriched metal grains or opaque assemblages.

All measurements reported here were performed on a New Wave UP213 laser ablation system coupled to a Finnigan Element™ ICP-MS at the NHMFL Plasma Analytical Facility. The UP213 is a frequency-quintupled Nd-YAG laser (213 nm UV) with a power output of 4 mJ, an aperture-controlled spot size (4-100 μm), and computer-controlled movable X-Y-Z stage with submicron spatial resolution. Measurements were performed with 12, 15 or 25 μm beam diameters. Aerosol is transported from the ablation cell by a flow of He (800 ml/min) with additional Ar (~1000 ml/min) make-up gas. Measurements included determination of the peaks ^{7}Li, ^{25}Mg, ^{27}Al, ^{29}Si, ^{34}S, ^{43}Ca, ^{49}Ti, ^{53}Cr, ^{57}Fe, ^{60}Ni, ^{180}Hf, ^{181}Ta, ^{182}W, ^{183}W, ^{193}Ir, ^{195}Pt and ^{197}Au in low resolution (R=300). Standards used included the NIST SRM 612 (Hf, Ta, W, Pt, and Au), the MPI-DING glasses, KL2-G, ML3B-G, GOR128-G (major elements), and the iron meteorites Filomena and Hoba [5]. Major element compositions were obtained by using sensitivity factors derived from averages of the three MPI-DING glasses. The abundances of Hf, W and Pt were calibrated against NIST SRM 612 glass. Detection limits were calculated as 3σ standard deviation of the blanks. Data points below detection limits were replaced by the detection limit values. Monitoring the W/Pt ratio identified lithophile behavior of W, which was then corroborated by examining Fe, Ni, S and Ir abundances. Lithophile W refers to W not accompanied by Ni, Ir and Pt.

Results: In Ef2, Hf was found to be strongly concentrated in fassaite (~12-22 ppm). Melilite had lower Hf (range= 0.02-0.2 ppm). Tungsten was concentrated in small inclusions of CAI metal, which was traced by simultaneous determination of Pt and Ir. In both fassaite and melilite, W ranged from the detection limit of 0.01 ppm to 0.3 ppm, with an average of 0.1 ppm, and was correlated with Pt abundance. Thus, most of the W appears to be in tiny metal inclusions within the silicate minerals, and not hosted in their crystal lattices. Two metal inclusions in melilite, both smaller than the beam diameter (25 µm), were encountered. One had a chondritic W/Pt ratio, while the other had $(W/Pt)_{CI}<0.01$. Both metal grains had detectable Hf, and the rim of the low-W metal had a Hf/W>1. No silicate analysis was found with lithophile W, i.e. $(W/Pt)_{CI}>1$.

A traverse across the spinel palisade body in GBS is shown in Figure 1. The traverse began outside the palisade body in melilite (A), encountered a fassaite grain by the boundary (B), crossed the spinel palisade (C) where it encounter Pt-rich metal, then passed through a large fassaite (D), and melilite (between E and F). Fassaite had ~10 ppm Hf; melilite <0.01 ppm Hf (with a few 0.1 ppm spikes), and there is a prominent Hf spike in the Pt-rich metal grain at the end of the traverse (F).

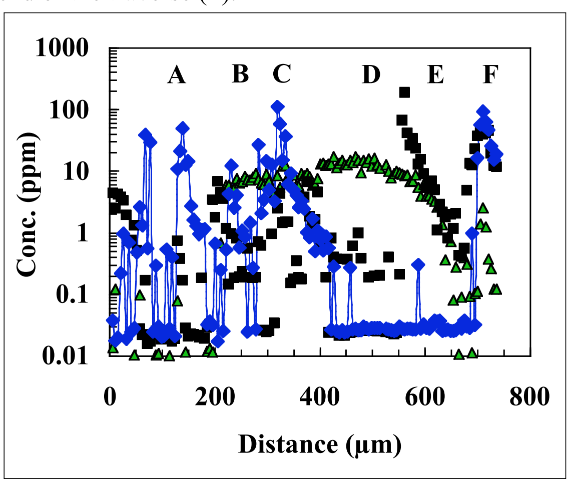

Figure 1: Traverse (12 µm beam diameter, 4 µm/s) across the palisade body in GBS from Allende (Hf: green triangles, W: black squares, Pt: blue diamond).

The Hf spikes (~0.1 ppm) in the melilite (A) may be associated with Pt-rich alloys. Tungsten is below detection limits (0.02-0.03 ppm) in both melilite (A) and fassaite (B and D), except for frequent spikes that are generally displaced from spikes in Pt. A notable exception is the metal grain (F), where Pt and W are correlated. A large peak of lithophile W (E) is noteworthy in the fassaite grain (D) inside the palisade body. The region (E) exhibits high Fe and W, while Pt is below detection limits (0.03 ppm). This is the largest lithophile W anomaly that we have found in GBS. Other lithophile W anomalies occur at the beginning of the traverse (A), and at the edge of the fassaite grain (B).

Discussion: Tungsten oxidizes close to the IW buffer [7] at high temperatures (>1200 K), but below the IW buffer at lower temperatures. At the extremely low redox states of CAI formation (where Ti+3 becomes stable), W is expected to be entirely in metal where it would be associated with Ir, Pt and other noble metals [5]. Oxidation or sulfurization of CAI metal to form the opaque assemblages has been shown to mobilize W [5]. The low levels of Hf present in melilite (<0.1 ppm), and the abundance of refractory metal particles enclosed by melilite implies that oxidation and mobilization of W during parent-body processes will have limited impact on the W isotope composition of CAI metal. Thus, isotope exchange must be sought at fassaite-metal boundaries. Such contacts are rare in Ef2, but a prominent set of metal particles in Allende GBS occur together with large peaks of lithophile W. From the absence of lithophile W, we identify Efremovka (and probably other reduced CV3 chondrites) as a more reliable source of CAI metal for analysis of the solar system initial $^{182}W/^{184}W$ ratio. Results on Allende CAIs (exemplified by Golfball) indicate that oxidized W may have entered fassaite from surrounding refractory metal grains. Thus, W isotope exchange may have occurred between fassaite, the host for radiogenic ^{182}W, and Allende opaque assemblages, the leaky hosts of unradiogenic W. Since this exchange must have occurred after the formation of Allende inclusions as refractory condensates, the process may contribute towards a shallower slope of the ^{182}Hf-^{182}W isochron on Allende CAIs determined by Kleine et al. [3].

The presence of Hf in CAI metal grains is inconsistent with the usual expectation that Hf is entirely hosted in silicates. The differential transport of Hf and W during alteration of Allende opaque assemblages needs to be better studied.

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