L-EDGE XANES MEASUREMENTS OF THE OXIDATION STATE OF TUNGSTEN IN IRON BEARING AND IRON FREE SILICATE GLASSES. L. R. Danielson[1,2], K. Righter[2], S. Sutton[3], M. Newville[3], L. Le[1,2], [1]Jacobs Sverdrup Co., Houston, TX 77058 United States (lisa.r.danielson@nasa.gov), [2]NASA JSC, 2101 NASA Road One, Houston, TX 77058 United States, [3]GSECARS University of Chicago, 9700 South Cass Avenue, Bldg. 434A, Argonne, IL 60439 United States.

Introduction: Tungsten is important in constraining core formation of the Earth because this element is a moderately siderophile element (depleted ~ 10 relative to chondrites) and, as a member of the Hf-W isotopic system, it is useful in constraining the timing of core formation. A number of previous experimental studies have been carried out to determine the silicate solubility and metal-silicate partitioning behavior of W, including its concomitant oxidation state. However, results of previous studies (Fig. 1) are inconsistent on whether W occurs as W^{4+} or W^{6+}.

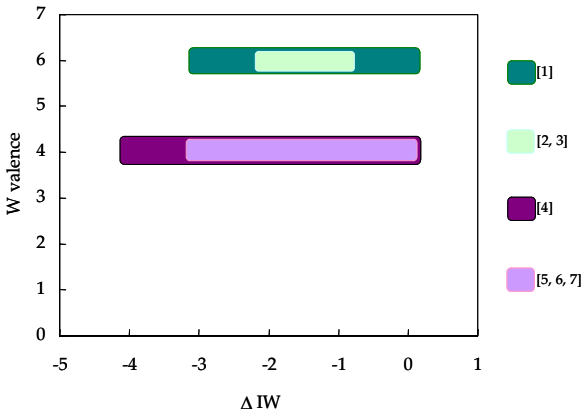

Figure 1. Comparison of W valence from previous results.

It is assumed that W^{4+} is the cation valence relevant to core formation [8]. Given the sensitivity to silicate composition of high valence cations [8], knowledge of the oxidation state of W over a wide range of fO_2 is critical to understanding the oxidation state of the mantle and core formation processes. This study seeks to measure the W valence and change in valence state over the range of fO_2 most relevant to core formation, around IW-2.

Experiments: Two compositions were used to determine the effects of iron content. Initial experiments, reported in [9] were conducted at 1300 °C, for durations of 24 to 96 hours and air or water quenched. One series was conducted using the An-Di eutectic, from QFM to IW-5 (log fO_2 -7.25 to -16. Experiments using an ankaramite starting composition were conducted from IW-1 to IW-5 (log fO_2 -11.75 to -16). Experiments were doped with 1wt% of WO_3. For both starting compositions, at IW-1, one set of experiments was doped with 1wt% of WO_2. Experiments at IW-2 and above were conducted using a Re wire loop technique, while experiments below IW-2 were conducted in sealed silica tubes as in Fig. 2.

The most recent experiments reported herein expanded the fO_2 range, from in air to IW-10 (ankaramite runs up to log fO_2 -0.4, CMAS runs down to log fO_2 -20) of the data set, and were designed to in an attempt to improve success with analyzable runs at low fO_2. Run duration was increased to 120 hours and all experiments were water quenched. Because the solubility of W decreases to ~100 ppmw [4] at the low fO_2 conditions of these experiments, amount of W as WO_3 added was below 1000 ppmw.

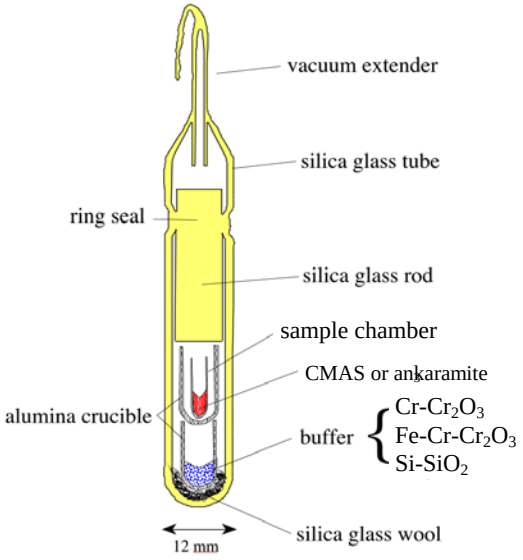

Figure 2. Schematic of sealed silica tube experiments conducted at lowest fO_2, below IW-2.

Analytical: A monochromatic X-ray beam from a Si(111) double crystal monochromator was focused onto the sample and the fluorescent X-ray yield was plotted as a function of incident X-ray energy (more detail can be found in [10]). The oxidation state of tungsten was inferred from the energy of the first peak in the LIII-edge derivative spectrum. WO_2, WO_3, $FeWO_4$, $CaWO_4$, were used as standards.

Results: Results (Fig. 3 and 4) for both the iron-bearing and iron-free starting materials suggest that only W^{6+} is present from the most oxidized conditions to IW (log fO_2 -10.75). At IW, tungsten starts to exhibit mixed valence but is still dominated by W^{6+} for

ankaramite. At IW-2, W^{4+} becomes more abundant for ankaramite, but a definitive transition to W^{4+} below IW-2 has not been observed. CMAS has a lower W valence than ankaramite below IW, with the most reduced state observed being W^{4+}. These results suggest that W^{4+} would be dominant below IW-2.

Even with improved experimental technique focused on reducing the "nugget effect," at IW-2 and below, metal exsolved from the silicate, complicating the analyses. Analyses in nugget free regions of the silicate portion of the experiments cluster around W^{5+}, while analyses in nugget-rich regions cluster around W^{2+}.

Four CMAS run products from Ertel [4] were also analyzed and shown for comparison in Fig. 4. These samples were reported as W^{4+}, from the slope of the W concentration vs. log fO_2 line. The Ertel run products are in good agreement with our CMAS run products, showing decreasing W valence with decreasing fO_2, but appear to be mixed W^{6+} and W^{4+} valence.

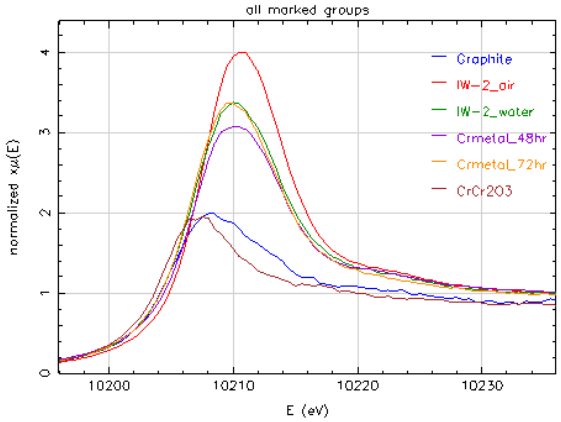

Figure 3. A sampling of results from some CMAS ru product analyses (figure 4), showing range of W valence, from W^{6+} (IW+1 air quench, red line) to around W^{2+} (IW-5, using Cr-Cr_2O_3 buffer, brick line). Data show differences between air (red line) and water quench (green line) at IW-2, with a 0.5+ reduction in W valence observed for a water quench. Other lines indicate a run in a graphite capsule, and runs using only Cr metal as a buffer.

Discussion and Conclusions: Both CMAS and ankaramite glasses show W^{6+} above IW and mixed valence below IW. The transition to W^{4+} only, appear to happen at or below IW-2 for iron free systems, but probably below IW-3 for iron bearing systems. Analyses of run products from previous experiments [4], support the observation the iron free transition to only W4+ occurs at or below IW-2.

The mixed states below IW-2 may result from analyses in which both silicate glass and exsolved W-bearing metal are present in the analytical volume in varying proportions. This suggests if all W were dissolved in the silicate in a nugget free condition, W valence would be less than W^{5+} at lowest fO_2.

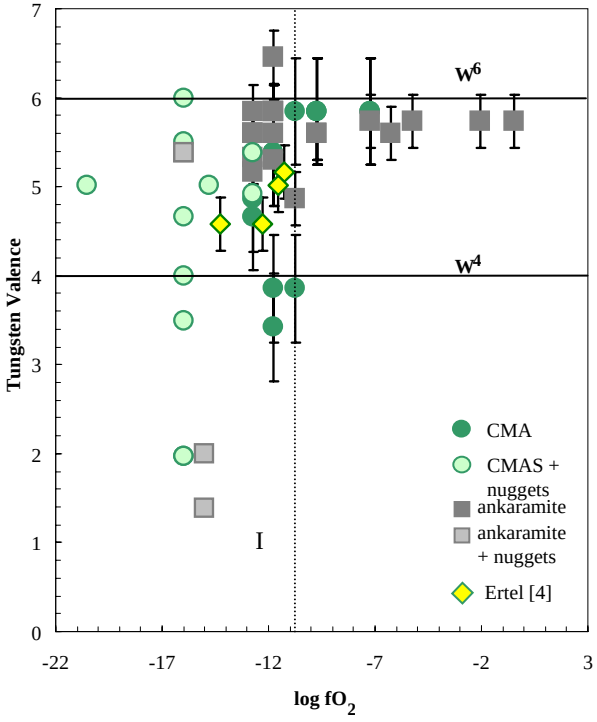

Figure 4. Summary of valence results inferred from the energy of the first peak in the LIII-edge derivative spectrum.

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