

**THE OXIDATION STATE OF TUNGSTEN IN IRON BEARING AND IRON FREE SILICATE GLASSES: RESULTS FROM W L-EDGE XANES MEASUREMENTS.** L. R. Danielson<sup>1</sup>, K. Righter<sup>1</sup>, S. Sutton<sup>2</sup>, M. Newville<sup>2</sup>, L. Le<sup>1</sup>, <sup>1</sup>NASA JSC, 2101 NASA Road One, Houston, TX 77058 United States (lisa.r.danielson@nasa.gov), <sup>2</sup>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<sup>4+</sup> or W<sup>6+</sup>.

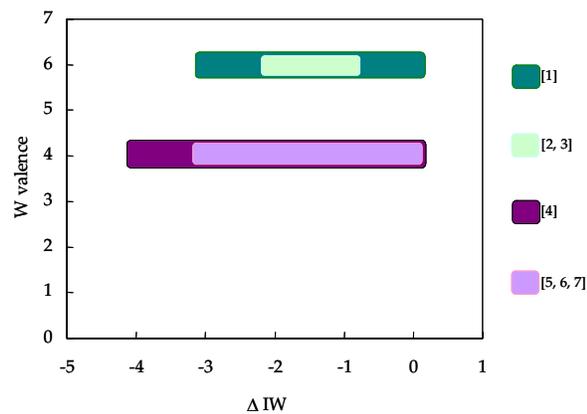


Figure 1. Comparison of W valence from previous results.

It is assumed that W<sup>4+</sup> 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. Experiments were conducted at 1300 °C, for durations of 24 to 96 hours and air quenched. One series was conducted using the An-Di eutectic, from  $\log fO_2$  -7.25 to -18 (Fig. 2). Experiments using an ankaramite starting composition were conducted from  $\log fO_2$  -1.65 to -18.3. Experiments were doped with 1wt% of  $WO_3$ . For both starting compositions, at IW-1, one set of experiments was

doped with 1wt% of  $WO_2$ , and at IW+1, one set of experiments was quenched in water.

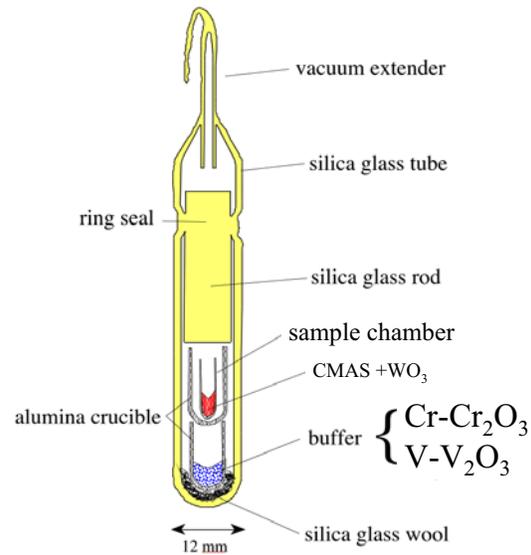


Figure 2. Schematic of sealed silica tube experiments conducted at lowest  $fO_2$ .

**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 [9]). 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 the CMAS starting materials suggest that only W<sup>6+</sup> is present from the most oxidized conditions to IW ( $\log fO_2$  -10.75). At IW-1, tungsten starts to exhibit mixed valence but is still dominated by W<sup>6+</sup>. At IW-2, W<sup>4+</sup> becomes more abundant, with the most reduced state observed being equal proportions of W<sup>4+</sup> and W<sup>6+</sup>. These preliminary results suggest that W<sup>6+</sup> is still present, even below IW-5. At IW-2 and below, metal exsolves from the silicate, complicating the analyses. For ankaramite, only W<sup>6+</sup> is present down to IW-1, with mixed valence beginning at IW-2, i.e., qualitatively similar behavior to the Fe-free samples.

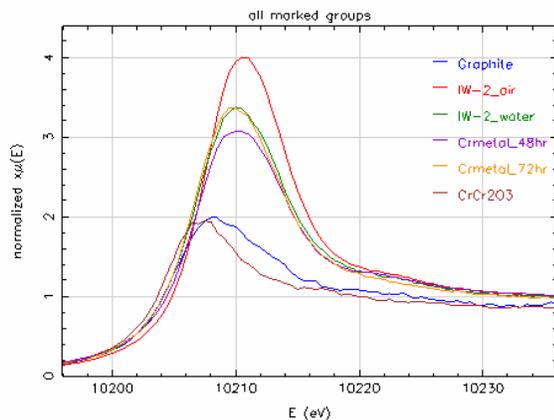


Figure 3. A sampling of results from 30 analyses (figure 4), showing range of W valence, from  $W^{6+}$  (red line) to around  $W^{2+}$  (blue line).

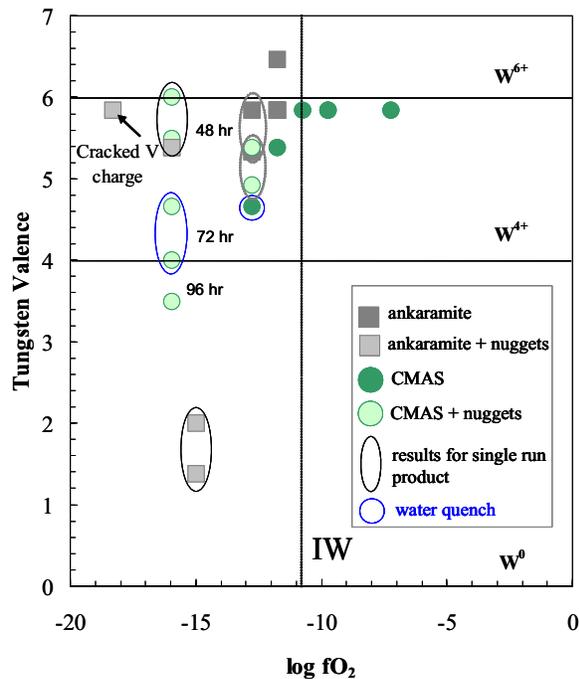


Figure 4. Summary of valence results inferred from the energy of the first peak in the LIII-edge derivative spectrum.

**Discussion and Conclusions:** Both CMAS and ankaramite glasses show  $W^{6+}$  above IW and mixed valence below IW. The mixed states may result from analyses in which both silicate glass and exsolved W-bearing metal are present in the analytical volume in varying proportions. This “nugget effect” is likely to impact the results below IW-2. Nonetheless, the results for nugget-free samples indicate that W is present in the  $W^{6+}$  state in systems more oxidized than ~IW-1

and that the transition between  $W^{4+}$  and  $W^{6+}$  occurs just below IW-1. Quench effects may be significant as indicated by the IW-2 CMAS water quenched run, in which W seems to still be dissolved.

Future experiments will focus on this oxidation state transitional range of  $fO_2$ , IW-1 and IW-4, and the nugget effect minimized by limiting W concentrations to the 100 ppm range, well below W solubility. The most reducing runs, at the Cr-Cr<sub>2</sub>O<sub>3</sub> buffer, suggest a time series is needed to determine the effects of longer run times at low  $fO_2$ .

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