THE OXIDATION STATE OF TUNGSTEN IN IRON BEARING AND IRON FREE SILICATE GLASSES: RESULTS FROM W L-EDGE XANES MEASUREMENTS. L. R. Danielson¹, K. Righter¹, S. Sutton², M. Newville², L. Le¹, NASA JSC, 2101 NASA Road One, Houston, TX 77058 United States (lisa.r.danielson@nasa.gov), 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 (figure 1) are inconsistent on whether W occurs as W⁴⁺ or W⁶⁺.

![Figure 1](https://ntrs.nasa.gov/search.jsp?R=20070008221)

Figure 1. Comparison of W valence from previous results.

It is assumed that W⁴⁺ 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 fO₂ 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 fO₂ 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 fO₂ -7.25 to -18. Experiments using an ankaramite starting composition were conducted from log fO₂ -1.65 to -18.3. Experiments were doped with 1wt% of WO₃, and at IW+1, one set of experiments was quenched in water.

![Figure 2](https://ntrs.nasa.gov/search.jsp?R=20070008221)

Figure 2. Schematic of sealed silica tube experiments conducted at lowest fO₂.

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. WO₃, WO₄, FeWO₄, CaWO₄, were used as standards.

Results: Results (figures 3 and 4) for the CMAS starting materials suggest that only W⁶⁺ is present from the most oxidized conditions to IW (log fO₂ -10.75). At IW-1, tungsten starts to exhibit mixed valence but is still dominated by W⁶⁺. At IW-2, W⁴⁺ becomes more abundant, with the most reduced state observed being equal proportions of W⁴⁺ and W⁶⁺. These preliminary results suggest that W⁶⁺ is still present, even below IW-5. At IW-2 and below, metal exsolves from the silicate, complicating the analyses. For ankaramite, only W⁶⁺ is present down to IW-1, with mixed valence beginning at IW-2, i.e., qualitatively similar behavior to the Fe-free samples.
that the transition between W\(^{6+}\) 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\(_2\)O\(_3\) buffer, suggest a time series is needed to determine the effects of longer run times at low fO\(_2\).

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