THE OXIDATION STATE OF TUNGSTEN IN IRON BEARING AND IRON FREE SILICATE GLASSES: RESULTS FROM W L-EDGE XANES MEASUREMENTS.

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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 W^{4+} or W^{6+}.
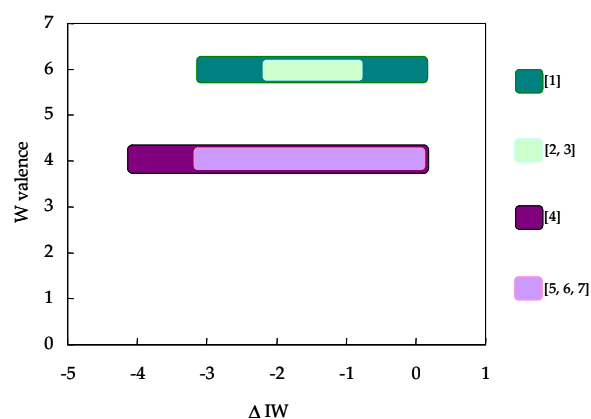

Figure 1. Comparison of W valence from previous results.

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. 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. 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

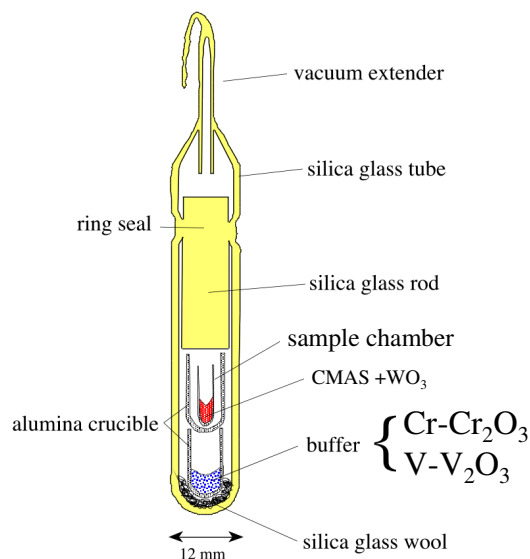1wt% of WO_2, and at IW+1, one set of experiments was quenched in water.

Figure 2. Scematic 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 (figures 3 and 4) for the CMAS starting materials suggest that only W^{6+} 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^{6+}. At IW-2, W^{4+} becomes more abundant, with the most reduced state observed being equal proportions of W^{4+} and W^{6+}. These preliminary results suggest that W^{6+} is still present, even below IW-5. At IW-2 and below, metal exsolves from the silicate, complicating the analyses. For ankaramite, only W^{6+} is present down to IW-1, with mixed valence beginning at IW-2, i.e., qualitatively similar behavior to the Fe-free samples.
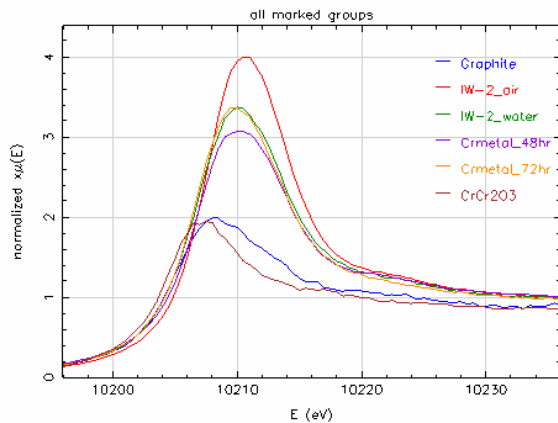
Figure 2. A sampling of results from 30 analyses (figure 4), showing range of W valence, from W^{6+} (red line) to around W^{2+} (blue line).
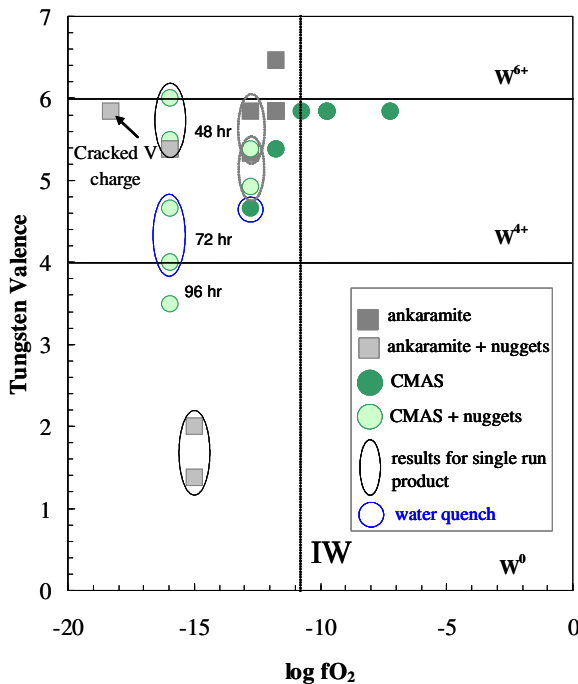

Figure 3. Summary of valence results inferred from the energy of the first peak in the LIII-edge derivative spectrum.

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 fO₂, 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-Cr₂O₃ buffer, suggest a time series is needed to determine the effects of longer run times at low fO₂.

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