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. New-
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Introduction: Tungsten is important in constrain-
ing core formation of the Earth because this element is
a moderately siderophile element (depleted ~ 10 rela-
tive to chondrites) and, as a member of the Hf-W iso-
topic 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⁺.

<table>
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<th>W valence</th>
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<td>1</td>
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<tr>
<td>-5</td>
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Figure 1. Comparison of W valence from previous re-
sults.

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 man-
tle 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 de-
termine 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 con-
ducted from log fO₂ -1.65 to -18.3. Experiments were
doped with 1wt% of WO₃. For both starting com-
positions, at IW-1, one set of experiments was doped with
1wt% of WO₂, and at IW+1, one set of experiments
was quenched in water.

Figure 2. Schematic of sealed silica tube experimen-
t 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 tung-
sten was inferred from the energy of the first peak in
the LIII-edge derivative spectrum. WO₂, WO₃, 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.
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$_2$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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