	Experiment title: Behavior of hafnium and tungsten in silicate melts:	Experiment number:
Beamline: BM23	Date of experiment: from: 12/02/2014 to: 18/02/2014	Date of report: 17/07/2014
Shifts: 18	Local contact(s): Olivier Mathon (mathon@esrf.fr)	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Benjamin Cochain, SUPA, CSEC, Univ. of Edinburgh Charlotte de Grouchy, SUPA, CSEC, Univ. of Edinburgh		

Abstract:

Short-lived radiogenic isotopes such as ^{182}Hf ($^{182}\text{Hf} \Rightarrow ^{182}\text{W}$) potentially record accretional processes and an array of planetary specific differentiation mechanisms [1,2]. A basic understanding of how these elements partition between mineral/metal and silicate melt is thus critical to interpreting early planetary differentiation events [3]. It has, however, been shown that extensive variables such as chemical composition, temperature, pressure and oxygen fugacity have an effect on mineral/metal–silicate partitioning of W [4,5]. In addition, there is nowadays a debate on whether W changes oxidation state from 6+ to 4+ around 6 GPa with increasing pressure [4,5,6]. Because previous experiments have been done on quenched systems, we investigated the speciation and local structure of W in tungsten bearing silicate melts using in-situ high pressure and temperature XANES and EXAFS at the W L_3 edge.

Experimental conditions:

High P-T conditions up to 4 GPa-1600 K, have been generated by the Paris-Edinburgh press that we regularly use for X-ray diffraction on melts at ESRF. The experimental cell-assembly consisted of a boron-epoxy gasket (7 mm diameter), a graphite heater, and a diamond capsule capped by Pt-Rh discs to preserve the chemical integrity of the sample. We used nanocrystalline diamond capsules (from T. Irifune) as the glitches from either a single or even polycrystalline crystal would have prevented a proper collection of the EXAFS signal. Pyrex powder was packed on the external sides of the Pt-Rh caps (i.e. away from the sample) to control the oxygen fugacity. The intensity of the beam before and after the sample was measured by ion

chambers in order to collect the EXAFS signal. P was measured from the X-ray diffraction signal of a Pt foil inserted on the side of the diamond capsule. The X-ray diffraction signal was collected from a MAR CCD detector. T was read from the power curve, as we now have a good database for this cell assembly.

The sample was a hydrous synthetic basalt containing ~5wt % of WO_3 . EXAFS spectra were collected above the liquidus at the W L_3 -edge (10.2 KeV), at three different P steps (150, 200, 300 bars) and on the quenched sample back to room conditions. We also recorded spectra on W oxide standards (WO_2 , WO_3 , CaWO_4) in order to identify W speciation by comparison.

Results:

Absorption from the cell assembly

In our previous work at the Br K-edge (13.6 KeV), 5 EXAFS spectra were recorded for a given P/T condition to obtain a good signal to noise ratio [6]. In this work, 5 EXAFS spectra were enough to get a good signal to noise ratio for the ambient pressure conditions. However, we noticed a deterioration of the quality of the data under pressure (see figure 1). It was due to the absorption of the cell assembly that expands under pressure. Because of this problem, we decided to record only the XANES part of the XAS data.

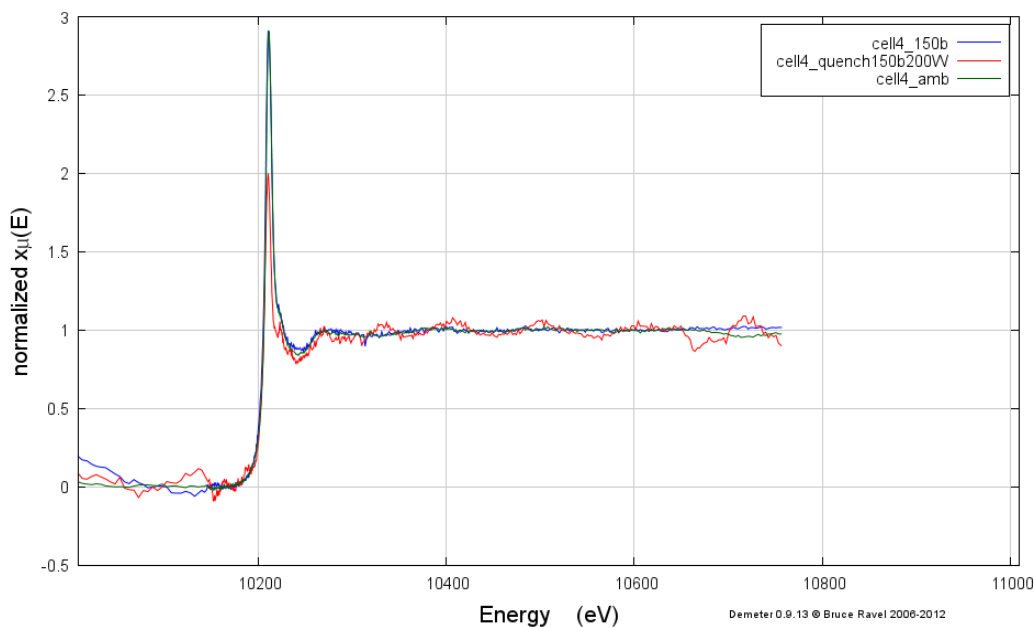


Figure 1: EXAFS spectra at the W L_3 edge of W-bearing synthetic basalt in the cell assembly at different P-T conditions

W oxidation states

We determined the oxidation state of W at different P-T conditions from the position of the inflexion point, E_0 , of the white line (maximum of the first derivative on figure 2).

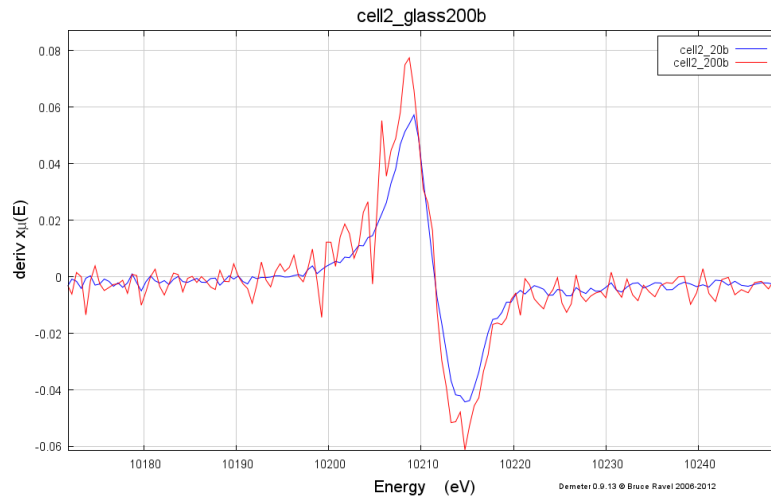


Figure 2: First derivative of the XANES spectra at the $W L_3$ edge of W -bearing synthetic basalt in the cell assembly at different P - T conditions

The results show an influence of the pressure on the position of the inflexion point of the XANES white line. This suggests that the oxidation state of W in silicate melt varies with the pressure (from $6+$ to $4+$). However, we need more data than the 3 pressure points we currently have to confirm the influence of pressure on the oxidation state of W , especially given the error bars introduced by the high signal to noise ratio of the data. We also need to check the oxidation state of Fe at the same time in order to indentify if there is any interactions with other redox variable elements, in particular during the quench. The present results show indeed that W regains its $6+$ valence during the quench while it was $4+$ in the melt.

- 1) Harper and Jacobsen, *Geochim. Cosmochim. Acta*, 60, 1131–1153, 1996.
- 2) Lee et al., *Science*, 278, 1098–1133, 1997.
- 3) Shearer and Righter, *Geophys. Research Letters*, 30, 2003
- 4) Cottrell et al., *Earth and Planetary Science Letters* 281 (2009) 275–287
- 5) Wade et al., *Geochimica et Cosmochimica Acta* 85 (2012) 58–74
- 6) Cochain et al., submitted.