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The pressure-induced local structural change around tungsten in silicate glass

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Supplementary Information

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Experimental Methods

A tungsten-doped basaltic glass was synthesised for EXAFS measurements. Basalt powder was prepared originally from gel, mixed with 0.8 wt. % WO_3 powder, and melted at 1473 K for 30 min in a furnace under reduced H_2-CO_2 gas atmosphere (two log units below the wüstite-magnetite buffer). Under this condition, tungsten exists in a silicate melt almost exclusively as W^{6+} (Wade *et al.,* 2013). It was then quenched to a glass by being dropped into water. The chemical composition and homogeneity of the basaltic glass were examined with an electron probe micro-analyser equipped with a field-emission source (FE-EPMA, JEOL JXA-8530F) (Table S-1).

At 1 bar, the EXAFS spectrum of the basaltic glass sample was collected at beamline BL01B1 at the SPring-8 synchrotron facility. High-pressure EXAFS measurements were carried out at beamline BL4A, Photon Factory, KEK with a beam focused to 5 μm × 5 μm area on a sample by using a KB mirror system. In this study, we calibrated the energy based on the white line peak of $Na_2WO_4 \cdot 2H_2O$ at 10.198 keV by following Kashiwabara *et al.* (2013). The sample was compressed to high pressures in a DAC using diamond anvils with 300 μm culet size. The basalt glass was loaded into a sample chamber at the centre of an X-ray transparent gasket that was composed of an outer Kapton ring and an inner boron (+ epoxy) disk (Merkel and Yagi, 2005). Before compression, the sample chamber was about 80 μm across and 50–100 μm thick. At high pressure, first we searched for a sample position in a DAC by a micro-X-ray mapping technique. An X-ray fluorescence (XRF) map for tungsten was collected based on its L_α line of tungsten (Fig. S-1). Subsequently high-pressure EXAFS measurements were

performed near the L_{III} absorption edge of tungsten in the fluorescence mode because of its relatively low concentration in the sample. The sample was irradiated from a direction perpendicular to the compression axis through the X-ray transparent gasket in order to avoid absorption of X-rays by diamond (anvils). The energy range for the EXAFS scans was 10.145–10.566 keV. Pressure was measured based on a Raman shift of a diamond anvil (Akahama and Kawamura, 2004). No pressure change was observed before and after the EXAFS measurement.

These EXAFS data were reduced using a REX2000 software (*Rigaku Co. Ltd.*) with a parameter generated by the FEFF 7.0 code (Zabinsky *et al.*, 1995). The k^3-weighted EXAFS oscillation was extracted from each spectrum in the range of 2.3–8.2 $Å^{-1}$ except for two data points (Table 1). The Fourier transformation (FT) of the k^3-weighted oscillation was performed, and the radial structural function was obtained. In order to extract information on the nearest neighbours of tungsten atoms from the radial structural function, the first-neighbour shell EXAFS was filtered out from high frequency noise and outer shells using Hanning window function. The filtered FT-EXAFS spectra were back-transformed to k-space using parameters extracted from the crystal structure of $CaWO_4$ scheelite by the FEFF 7.0. Curve fitting analysis was performed for the first shell (W-O).

Supplementary Table

Table S-1 The chemical composition of the basaltic glass sample.

	wt. %
SiO_2	46.16(25)
TiO_2	9.79(13)
Al_2O_3	13.84(6)
FeO	8.76(23)
MgO	7.78(10)
CaO	9.31(2)
Na_2O	4.46(13)
K_2O	0.13(1)
WO_3	0.78(8)
Total	101.01

Supplementary Figure

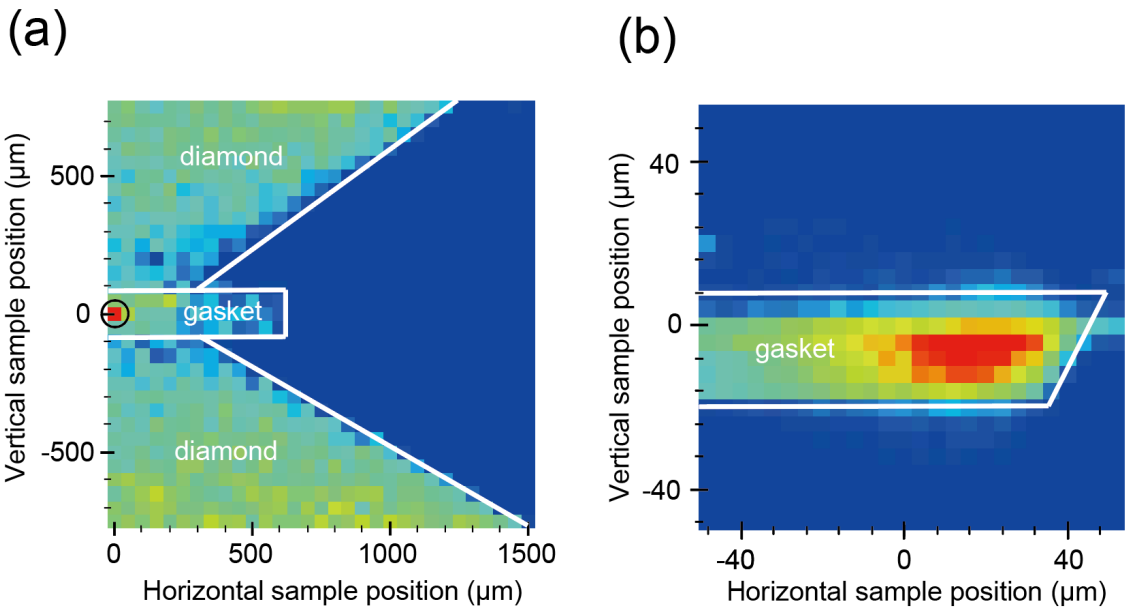

Figure S-1 Micro-XRF maps of tungsten in a basaltic glass sample at 48 GPa for searching sample position in a DAC. Incident X-ray with 10.5 keV was used to obtain the W *Lα* map. Maps were obtained for **(a)** 1500 μm × 1500 μm area by 31 × 31 steps and then **(b)** 100 μm × 100 μm area by 26 × 26 steps by moving the sample with respect to the X-ray beam. The black circle in **(a)** indicates the area shown in **(b)**.

Supplementary Information References

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