



	<u>Experiment title:</u> <b>Looking at sulfur in high-pressure aqueous fluids through X-ray diamond glasses</b>	<b>Experiment number:</b> MI-1190
<b>Beamline:</b> ID12	<b>Date of experiment:</b> from: 18 February 2015 to: 24 February 2015	<b>Date of report:</b> 26 February 2018
<b>Shifts:</b> 15	<b>Local contact(s):</b> Fabrice Wilhelm, ID12	<i>Received at ESRF:</i>
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## Report:

**Experimental:** The aim of this first methodological investigation was to verify the feasibility of collecting K-edge S XANES spectra from solids and solutions in a new perforated diamond anvil cell designed at ID12 [1], to prepare the necessary background for future in-situ measurements on S-bearing fluids and melts at high temperature and pressure. XANES spectra at the S K-edge (2.47 keV) have been recorded on model solid and aqueous S-bearing samples at ambient *T-P* conditions and in a perforated diamond anvil cell recently developed at this beamline (Fig. 1) and equipped with an iron gasket (150  $\mu\text{m}$  orifice diameter). The beam energy was selected using a Si(111) monochromator allowing an energy resolution of  $\sim 0.2$  eV at the S K-edge. The beam was further focused using Be parabolic refractive lenses to 4  $\mu\text{m}$  (V)  $\times$  40  $\mu\text{m}$  (H) (FWHM) to pass through the diamond windows of the cell. The total fluorescence yield signal was collected from the cell using a Si drift detector (Sirius detector from SGX sensortech). The attenuation of X-ray by the cell, equipped with a 30  $\mu\text{m}$  diamond plate, has already been measured [1], and was found to be low enough to enable a decent fluorescence signal for samples with several wt% sulfur contents.

**Results from measurements of reference solids and solutions at ambient T-P:** These measurements were performed using standard aluminum sample holders with 3 mm diameter grooves into which a finely ground powder or an aqueous solution was placed and covered with a Kapton film. It was found that most acidic and alkaline solutions reacted with the Al sample holder. *It is thus envisaged for future measurements at ambient conditions on chemically aggressive aqueous solutions to use gold-coated Al holders with holes of 2-3 mm in diameter in which the solution is placed and covered with Kapton films from both sides. This would also allow avoiding unwanted fluorescence from the holder bottom. As for solids, it is strongly recommended to finely ground them before loading into the holder to avoid eventual diffraction peaks.*

XANES spectra recorded with an unfocused beam (400x400  $\mu\text{m}$ ) with 8  $\mu\text{m}$  Al attenuator on aqueous 1 molal solutions of sulfate and thiosulfate showed no beam damage after several hours of acquisition. In contrast, with focused beam (4x40  $\mu\text{m}$ ), thiosulfate solutions showed detectable beam damage yielding formation of sulfate as evidenced by growth of the 2481 eV feature. Other, mono-valence, sulfur-bearing compounds (e.g., native S, Na<sub>2</sub>S) did not show detectable beam-induced changes with time of exposure, but presented some not-fully-understood differences in spectra between scans using unfocused or focused beam. Furthermore, subsequent scans with focused beam showed poorer reproducibility and presence of glitches/steps/diffraction peaks at different energies as compared to scans with the larger (unfocused) beam. *A possible explanation is inhomogeneity of solid samples, to which a smaller beam is much more sensitive. A far better homogeneity of powder samples would thus be necessary for future experiments (e.g., fine grinding and pelleting).*

### **Results from measurements in the perforated DAC under pressure:**

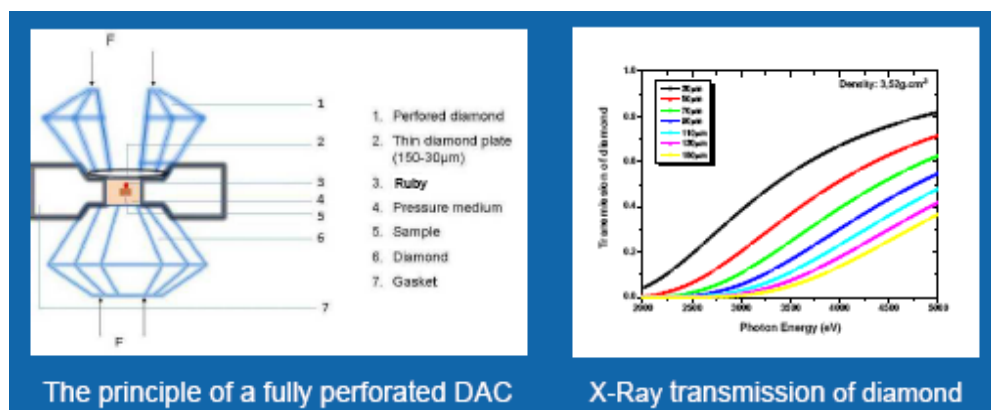
All attempts to load aqueous solutions into the perforated DAC with a 30  $\mu\text{m}$  diamond plate failed. Because of the strong wetting properties, the aqueous solution penetrated in between the gasket and the plate and expanded all over the diamond plate, resulting in a strong contribution to the S fluorescence signal from the solution outside the cell. It was thus envisaged for future experiments to directly glue the plate to the upper

perforated diamond to enable a rapid and accurate closure of the cell by quickly pressing the upper diamond onto the gasket after loading the solution into the gasket hole. A technological solution for glued diamond anvils is currently in progress.

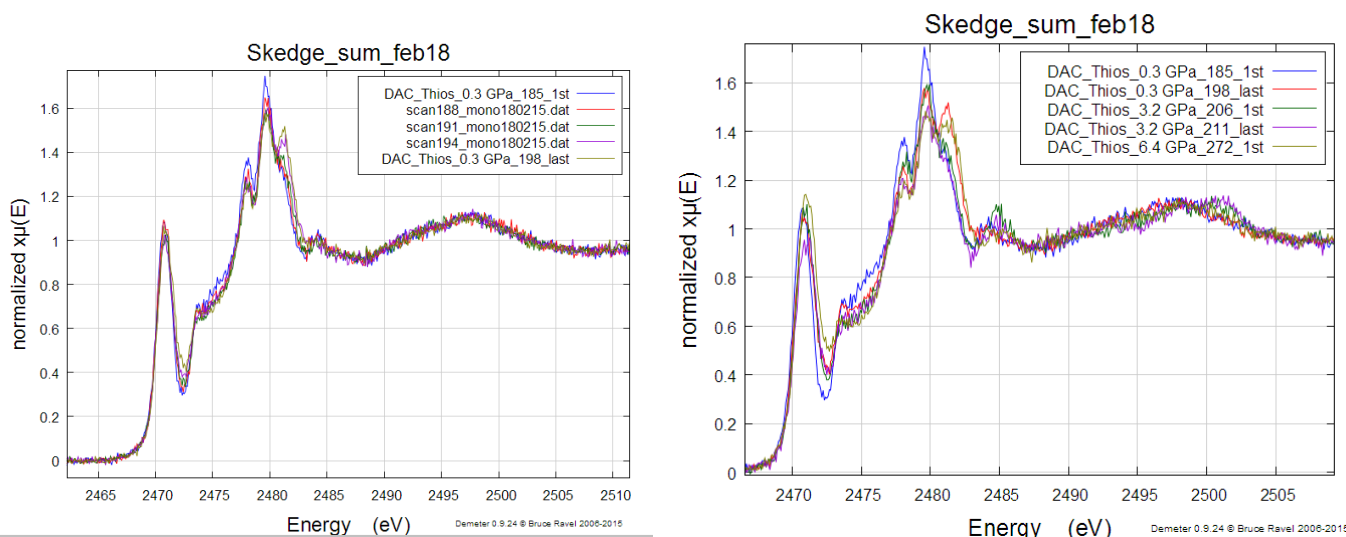
Thus, in the present experiment, we could only examine a sodium thiosulfate crystalline solid ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) in the actual DAC as a function of pressure (to 6.4 GPa) at ambient temperature. A few grains were loaded into the cell, which was pressurized with He. The obtained XANES spectra were of good quality (in terms of the signal-to-noise ratio), thus demonstrating the efficiency of the design for measurements of solid samples. Three pressure points were examined (0.3, 3.2, and 6.4 GPa) as a function of time in multiple scans. At a given pressure, subsequent scans reveal a minor beam-induced degradation of the sample expressed in growth of the sulfate feature (2481 eV) accompanied by a decrease of the feature of the sulfonate group ( $-\text{SO}_3$ ) of thiosulfate (2480 eV) (Fig.2 left). At higher pressures the rate of these spectral changes seems to slow down. When corrected for the temporal evolution, the net pressure effect was found to be negligible within the data noise (Fig. 2 right).

**Conclusions & perspectives:** This exploratory experiment allowed us to demonstrate, for the first time, the efficiency of the new DAC design for measuring XANES spectra at S K-edge on S-bearing solid phases. This experiment also revealed several technical issues of sample preparation (homogeneity) and confinement (sample holder for liquids) that will significantly be improved in future experiments. One of the important issues identified here and which may affect some specific sulfur compounds with multiple S valences is eventual beam-induced degradation. Thus, care will be taken in future experiments to attenuate the focused beam and to reduce the duration of beam exposure on the sample.

**References cited:** [1] Wilhelm et al. 2016, *HPR* 36, 445.



**Fig. 1.** A scheme of the new perforated DAC (left) and X-ray transmittance as a function of energy and diamond plate thickness. Our measurements were performed with 30-micron plates.



**Fig. 2.** Evolution of the XANES spectra of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}(s)$  in the perforated DAC as a function of time at 0.3 GPa (left), and as a function of pressure from 0.3 to 6.4 GPa (right).