



	<b>Experiment title:</b> Transport and reaction of sulphur species in silicate melts	<b>Experiment number:</b> CH2844
<b>Beamline:</b> ID21	<b>Date of experiment:</b> from: 15.04.09, 08:00 to: 21.04.09, 08:00	<b>Date of report:</b> 19-Sep-09
<b>Shifts:</b> 15	<b>Local contact(s):</b> Emilie Chalmin, Jean Susini, Margaret Rak	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b> *Max Wilke, (GFZ Potsdam, Potsdam, Germany) *Jan Stelling, Harald Behrens, (Institut fuer Mineralogie, Hannover University, Hannover, Germany) *Linda Backnaes, (Institut fuer Nichtmetallische Werkstoffe, TU Claustal, Clausthal-Zellerfeld, Germany)		

We analyzed polished glass products from diffusion couple experiments [1]. Samples of soda-lime silicate (NCS) and sodium-trisilicate (NS3) glass melts were synthesized at total Ar pressures of 200 MPa, temperatures between 1050 and 1200°C and  $p\text{H}_2 \sim 0.2$  bar. The measurements performed during this session complete data that were collected during a previous experiment (CH2653).

We used beam spots between 200  $\mu\text{m}$  and 50  $\mu\text{m}$  in diameter to record single S K-edge XANES spectra. Analyses with a focused beam using the KB-mirror showed strong beam damage (photo-oxidation or photo-reduction). Due to the high photon dose achieved by the mirror optics this effect is immediate and could not be avoided by any protocols. In addition, XRF line scans were performed at fixed energies of 2466.5 eV (pre-edge feature), 2474.0 eV (sulphide I), 2477.0 eV (sulphide II) and 2482.5 eV (sulphate). Background and total sulphur were analyzed at 2460.0 and 2515.0 eV, respectively. By this, beam damage effects are minimized and the original sulphur species is preserved. Using the KB-mirror optics a beam size of 0.60 x 0.88  $\mu\text{m}$  has been achieved for scans along the diffusion profile. Total length of the profiles was 2000  $\mu\text{m}$  with a step size of 10  $\mu\text{m}$ . We avoided beam damage by counting 2 sec/step and shifting by 10  $\mu\text{m}$  laterally between the line scans. These scans were suitable to obtain information on the diffusion of the diffusing sulphur species.

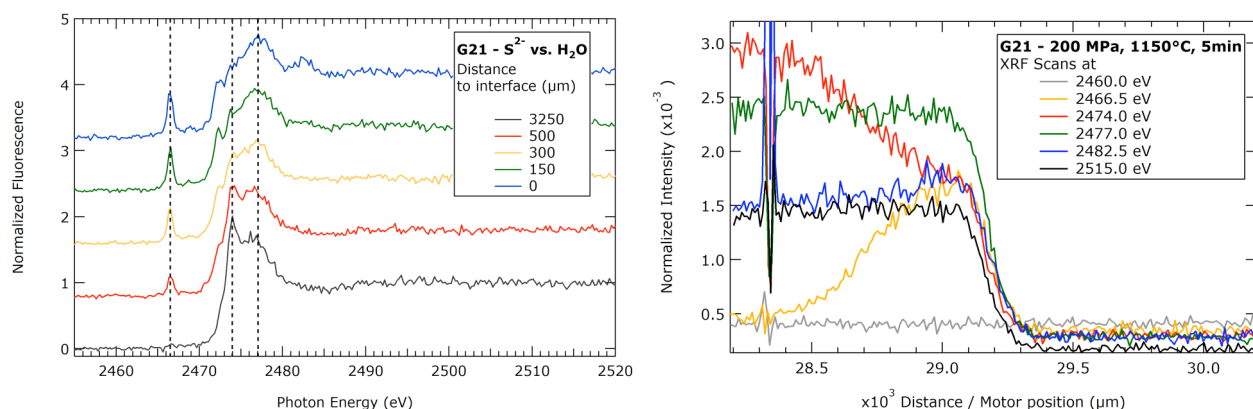
A large variety of samples was analyzed that covered various synthesis conditions and synthesis durations. Here we show only two representative examples. In Figure 1 data are shown for the case of water diffusion into the sulphide-bearing part of the diffusion couple.  $\text{H}_2\text{O}$  diffusion is orders of magnitude faster than sulphur diffusion [2,3]. Thus,  $\text{H}_2\text{O}$  penetrates as a fast-diffusing oxidizing agent into the sulphide-bearing part while sulphur is essentially immobile. XANES spectra show the formation of a sulfur pre-edge feature at unexpected low energy, which is also detected in the XRF line scans. As the intensity of the pre-edge feature increases, the intensity of the sulphide I peak drops whereas the sulphide II peak remains stable. At a photon energy of 2472.5 eV another peak at 2474 emerges slightly. The intensity of the changes in the sulphur K edge is related to the  $\text{H}_2\text{O}$  concentration measured by IR-microspectroscopy during CH2844 (and CH2653).

However, no change in the redox state of sulphur occurs when the oxidizing agent  $\text{H}_2\text{O}$  diffuses into the sulphide-bearing glass. This might be explained by local buffering of the oxidation state of sulphur by hydrogen generated via the reaction

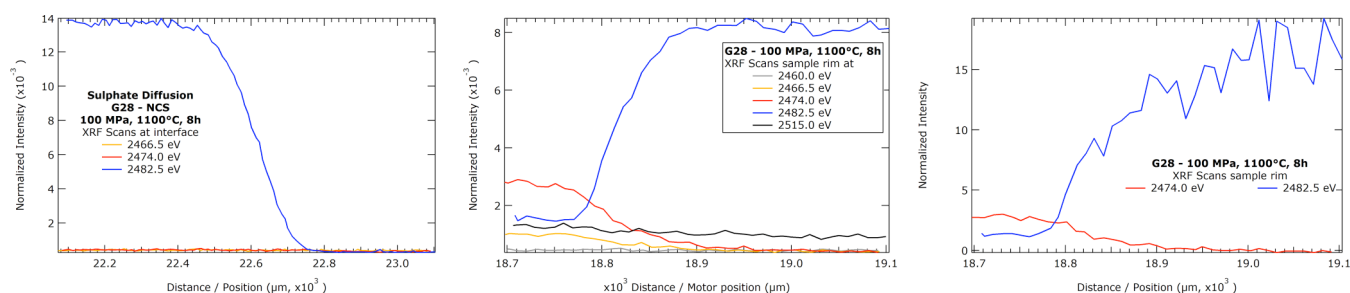


Figure 2 shows data obtained for sulphate diffusion between a sulphate-bearing and a sulphur-free glass cylinder. At the diffusion interface only diffusion of the sulphate species is observed with no indication for conversion of  $\text{S}^{6+}$  to  $\text{S}^{2-}$ . At the rim of the diffusion couple sample a reaction front is also visible by eye. In this case a clear signal of sulphide can be detected, which decreases towards the centre of the sample. The signal of sulphate shows exactly opposite behaviour. This can be explained by permeation of hydrogen through the metal of the sample container during the synthesis, which causes a reduction front to move

towards the centre of the sample. Due to the low solubility of the hydrogen in the silicate melt [4], the reduction front penetrates by only up to 200  $\mu\text{m}$  into the glass sample. Thus, the diffusion process of sulphate in the middle part of the diffusion couple is not affected.



**Fig.1** Diffusion of  $\text{S}^{2-}$  vs.  $\text{H}_2\text{O}$  in NCS glass, **a)** S K XANES spectra taken along the diffusion profile, **b)** XRF line scans along the diffusion profiles.



**Fig.2** Diffusion of sulphate in NCS glass, **a)** XRF line scans across the diffusion couple interface, **b)** XRF line scans at the rim of the sample, **c)** same data as b) signals indicated were corrected for background (2460 eV) and normalized to total sulphur signal (2515 eV).

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