



	Experiment title: Transport and reaction kinetics of sulfur species in silicate glasses	Experiment number: CH2653
Beamline: ID21	Date of experiment: from: 18/06/08, 8:00 to: 24/06/08, 8:00	Date of report: 19-Sep-08
Shifts: 18	Local contact(s): Jean Susini	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): * Max Wilke , (Chemistry of the Earth, GFZ Potsdam, Potsdam, Germany) * Harald Behrens , (Institut fuer Mineralogie, Hannover University, Hannover, Germany) * Jan Stelling , (Institut fuer Mineralogie, Hannover University, Hannover, Germany)		

We analyzed polished glass products from diffusion couple experiments [1]. Two types of experiments were conducted at pressures from 100 to 200 MPa, temperatures between 1050 and 1200°C and $p\text{H}_2 \sim 0.2$ bar in soda-lime silicate (NCS) glass melts. *Type (i) internal redox reaction experiments* contained a sulfate-doped and a sulfide-doped glass cylinder, and *type (ii) external redox reaction experiments* a H₂O-doped (~3wt%) and sulfide-doped glass cylinder. Sulfate was introduced as Na₂SO₄, sulfide as FeS or Na₂S. These experimental setups were used to obtain information on the transport and reaction kinetics of sulfur species and changes in speciation in silicate melts.

We used beam spots between 200 µm and 50 µm in diameter to record single S K-edge XANES spectra. Analyses with a beam focused to 0.8 µm diameter showed strong beam damage (photo-oxidation or photo-reduction), which was particularly high in the H₂O bearing samples. To keep the original sulfur species and minimize beam damage effects in the experimental glass products we recorded XRF line scans at fixed energies of 2467.0 eV, 2476.0 eV (sulfide) and 2482.5 eV (sulfate). Background and total sulfur were analyzed at 2460.0 and 2515.0 eV, respectively. We used beam sizes between 20 and 50 µm along the diffusion sample. These scans were suitable to obtain information on the diffusion of the diffusion sulfur species.

In type (i) experiments sulfate penetrates into the sulfide-bearing part, while sulfide diffuses into the sulfate-bearing part of the sample. Our XANES results on type (i) samples showed, that no intermediate sulfur species, i.e. sulfite [2], is formed during this redox exchange. The process can be described simply by a counter flux of sulfide and sulfate. Thus the species do not change their individual oxidation state (Fig. 1). Diffusion coefficients of sulfide and sulfate were calculated from fitted sulphur XANES XRF line scans, showing similar results for both sulphur species ($\log D = 13.4 \pm 0.1$ (D in m²/s) at 1100°C). This indicates that the kinetics of sulfur redox exchange is controlled by sulfate diffusion.

In type (ii) experiments water diffuses into the sulfide-bearing part of the diffusion couple. H₂O diffusion is orders of magnitude faster than sulfur diffusion [3,4] and, hence, H₂O penetrates into the sulfide-bearing part while sulfur is essentially immobile. XANES spectra show the formation of a sulfur pre peak at unexpected low energy, which is also detected in the XRF line scans (Fig. 2). Its intensity is related to the H₂O concentration measured by IR-microspectroscopy during CH2653. Additionally, the sulfide peak position shifts from 2474 to 2477 eV with increasing water concentration. However, no change in the redox state of sulfur occurs when the oxidizing agent H₂O diffuses into the sulfide-bearing glass. This might be explained by local buffering of the oxidation state of sulfur by hydrogen generated via the reaction:



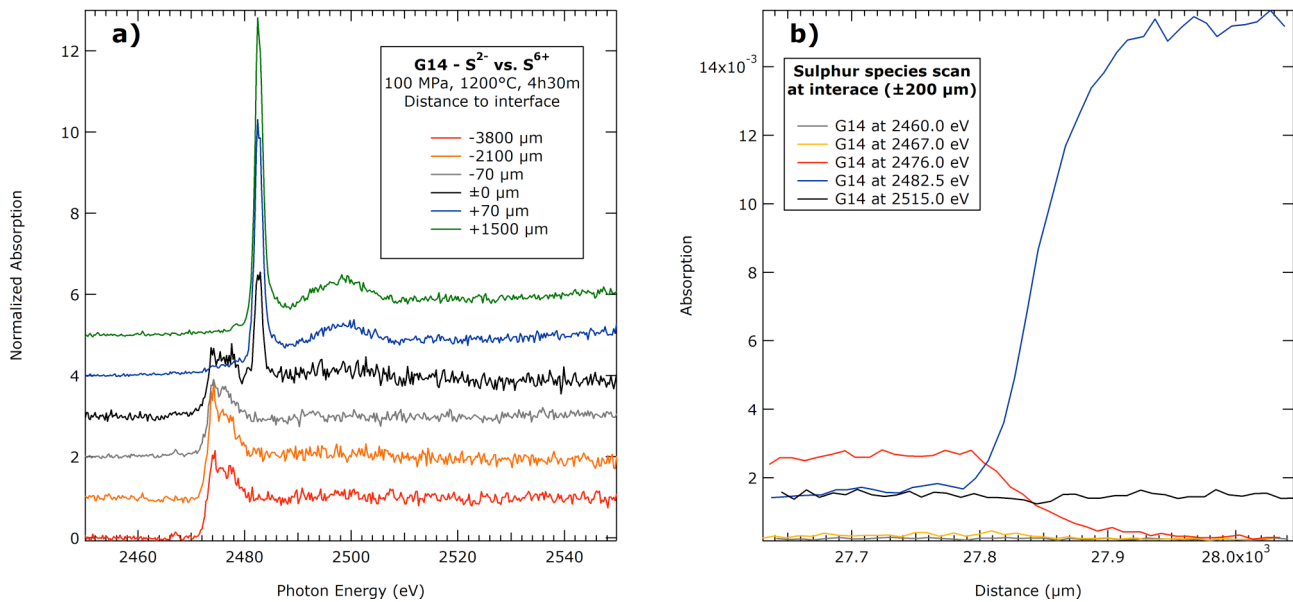


Fig.1 Type (i) glasses, **a)** S XANES spectra taken along the diffusion profile, **b)** XRF line scans along the diffusion profiles.

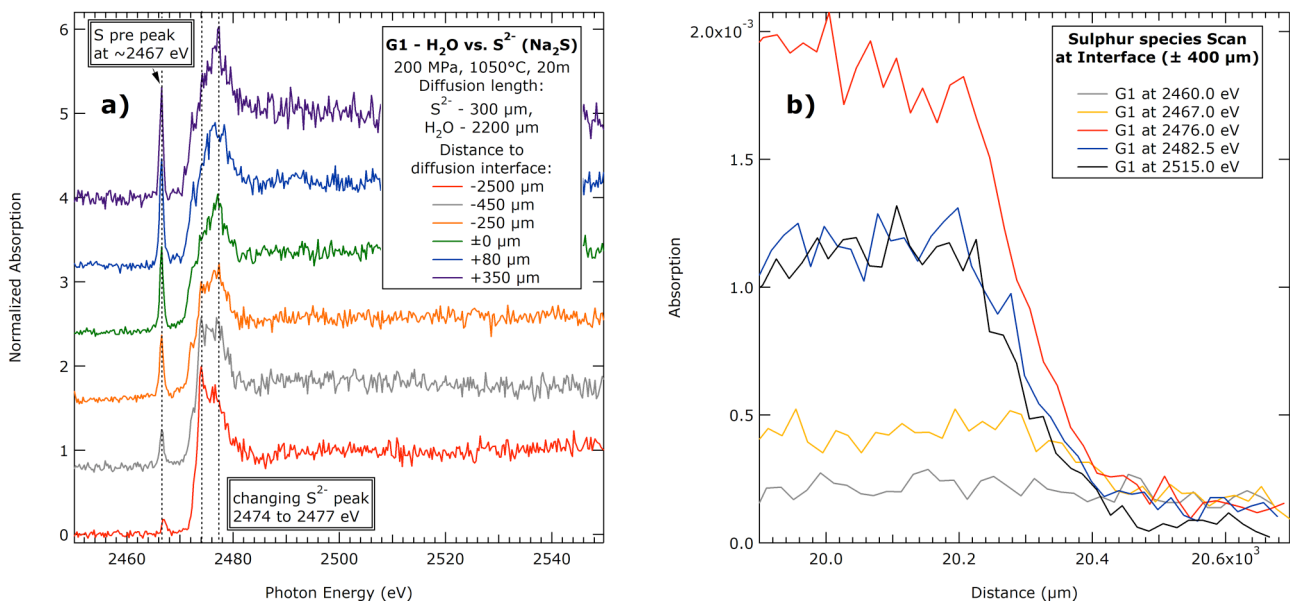


Fig.2 Type (ii) glasses, **a)** S XANES spectra along the water diffusion profile, increasing intensity of the sulphur pre peak is related to the H₂O concentration, **b)** XRF line scans along near the diffusion couple interface.

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- [2] N. Metrich, M. Bonnin-Mosbah, J. Susini, B. Menez, L. Galois (2002) *Geophys. Res. Lett.*, 33-1 - 33-4.
- [3] H. Behrens, Y. Zhang, and Z. Xu (2004) *Geochim. Cosmochim. Acta* 68, 5139-5150.
- [4] B. Watson (1994) *Rev. Mineral.* 30, 371-411.