



	<b>Experiment title:</b> Oxidation state of S in terrestrial magmas: S XANES studies on the transition from sulfide to sulfate speciation in silicate melts using nat...	<b>Experiment number:</b> EC-97
<b>Beamline:</b> ID21	<b>Date of experiment:</b> from: 21/02/07, 8:00 to: 26/02/07, 8:00	<b>Date of report:</b> 31-Aug-07
<b>Shifts:</b> 15	<b>Local contact(s):</b> Jean Susini	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b> * <b>Max Wilke</b> , (Institut fuer Geowissenschaften, Potsdam University, Potsdam, Germany) * <b>Pedro Jugo</b> , (Institut fuer Mineralogie, Frankfurt University, Frankfurt a.M., Germany) * <b>Roman Botcharnikov</b> , (Institut fuer Mineralogie, Hannover University, Hannover, Germany)		

We used a combination of unfocused (200  $\mu\text{m}$  diameter) and focused beam (0.8  $\mu\text{m}$  diameter) measurements to obtain the S K-edge XANES spectra in a series of glasses of basaltic [1] and andesitic compositions quenched from experiments conducted at 1300 °C and 1 GPa, and synthetic hydrous glasses quenched from 200 MPa and 1050°C, covering a wide variety of natural compositions. These measurements represent a continuation of experiment ME-1269. In the previous experiment, the spectra for some basaltic glasses with  $f\text{O}_2$  close to FMQ+2 (e.g. PJ-034, PJ-050 [1]) show that sulfite species are present (Fig. 1a, small peak at 2478 eV, peak 2482 eV denotes sulfate). As these samples had been used for electron microprobe analysis, we checked whether there is a relation of this analysis to the presence of sulfite species. For this purpose, the samples were re-polished providing a pristine surface for analysis. As shown in Fig. 1b no indication for sulfite species is left, indicating that the sulfite species was formed by the electron beam. As reported for ME-1269 formation of sulfite can be a severe problem also during XANES measurements if a focused beam is used. Repetitive measurements on hydrous glasses have shown that in some cases sulfite is formed even during measurements with the unfocused beam. [2].

XANES measurements on a series of hydrous glasses synthesized at 200 MPa, 1050°C and various redox conditions were used to determine the relationship of S oxidation state to this parameter. The S oxidation state was approximated using the intensity at the energy position of the peak for sulfate and sulfide in glass, respectively (see Fig. 2a). The intensity at either position was determined by using the integral in the energy windows indicated by the frames in the figure. The integral of sulfate was normalized to the sum of the two integrals and used as a figure of merit for the S oxidation state. Using the two end-member spectra shown in Fig. 2a, the dependence of this ratio on the S oxidation state was calibrated.

The peak ratio was determined on spectra of the series of hydrous glasses. The resulting S oxidation state is plotted as a function of the hydrogen partial pressure in Fig. 2b. Higher hydrogen pressures correspond to more reducing conditions. The sulfate content decreases with increasing hydrogen pressure. The decrease of the sulfate content is rather similar for basaltic and andesitic compositions. The trend of the data for the rhyodacite is shifted, showing lower sulfate content at a given hydrogen pressure. This difference might be attributed to a compositional effect on the sulfur redox equilibrium or, more likely, to a difference in the prevailing oxygen fugacity in the sample container during the synthesis.

In addition, natural glass samples of ocean floor basalts and melt inclusions of arc-related magmas were analyzed. Samples of ocean floor basalts indicate low sulfate contents, with mostly sulfide species being present. Arc-related magmas, in contrast, show only sulfate species. These findings are in good agreement with earlier results. e.g. [3], [4].

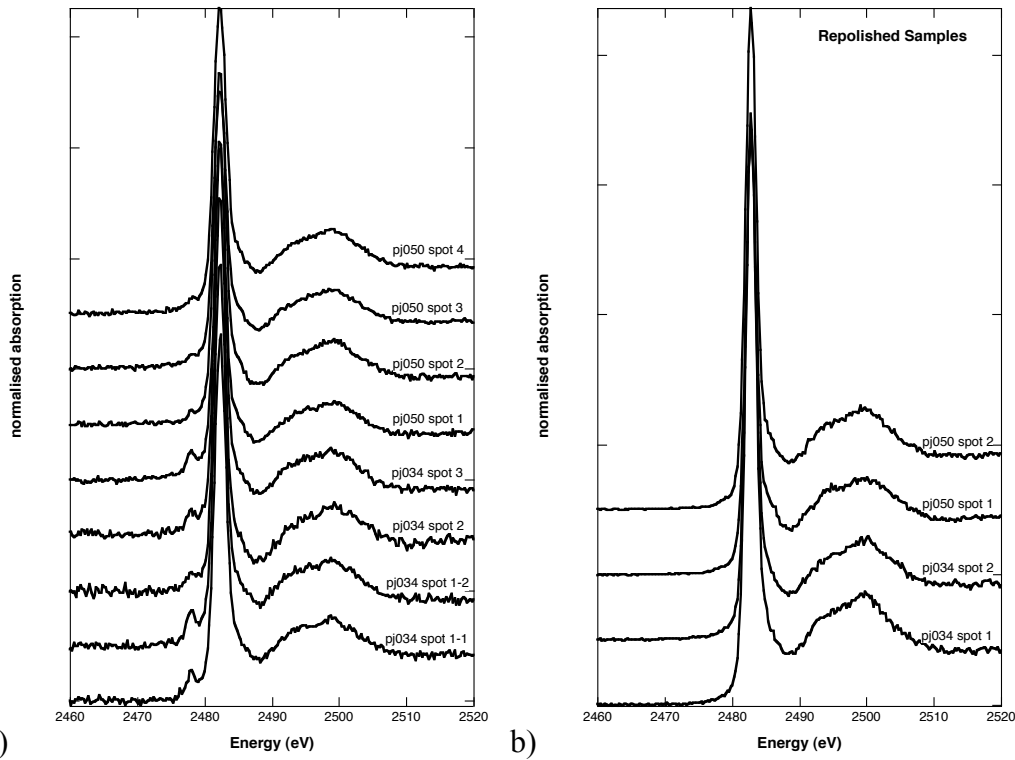


Fig. 1: a) S XANES spectra of basaltic glasses taken on various spots as indicated. Samples had been previously analyzed by electron microprobe. b) The same samples measured after repolishing of the surface.

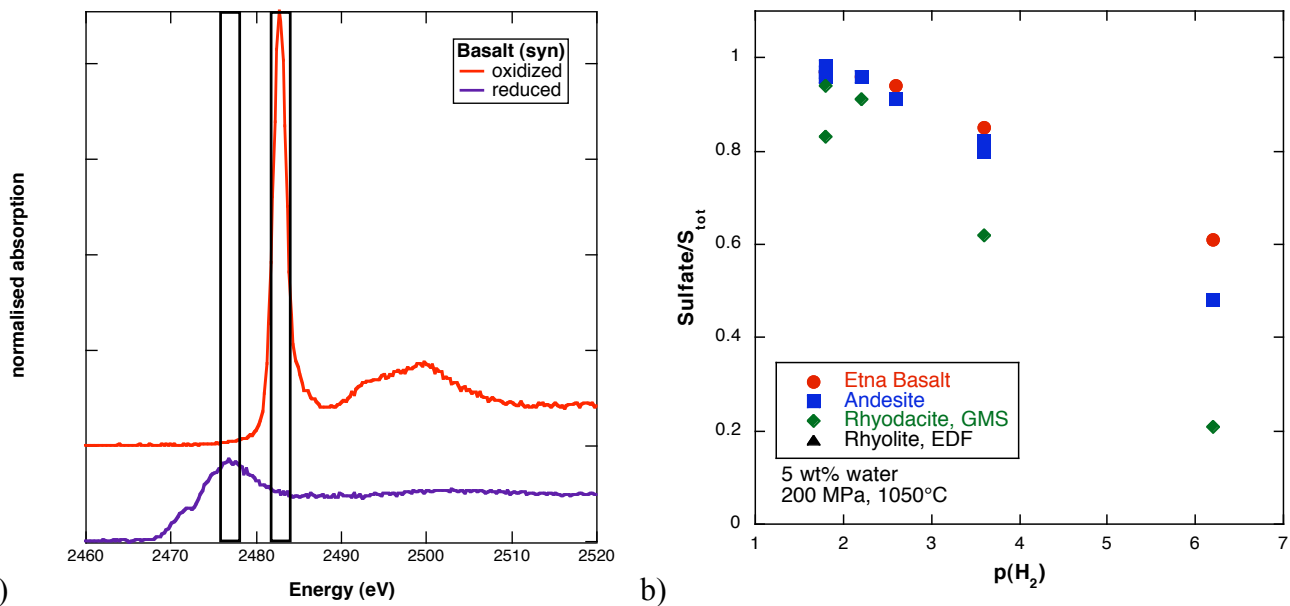


Fig. 2: a) S XANES of an oxidized and reduced basaltic glass as indicated. Frames indicate energy windows that were used to determine the intensity at the two energy positions for sulfide and sulfate, respectively. b) Sulfate content of a series of synthetic hydrous glasses covering a wide range of natural compositions plotted as a function of the hydrogen pressure during synthesis.

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 [3] Wallace P. J. and Carmichael I. S. E. (1994) *American Mineralogist*, 79, 161–167.  
 [4] De Hoog J.C.M., Hattori K.H., and Hoblitt R.P. (2004) *Contributions to Mineralogy and Petrology*, 146, 750–761.