



	Experiment title: Oxidation state of S in partially crystallized basaltic melts quenched from high-temperature and pressure	Experiment number: ME-1269
Beamline: ID21	Date of experiment: from: 4/11/05, 8:00 to: 14/11/05, 8:00	Date of report: 21-Feb-06
Shifts: 27	Local contact(s): Jean Susini	<i>Received at ESRF:</i>
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We used a combination of unfocused (200 μm diameter) and focused beam (0.8 μm diameter) measurements to obtain the S XANES spectra in a series of glasses of basaltic [1] and andesitic compositions quenched from experiments conducted at 1300 $^{\circ}\text{C}$ and 1 GPa, and some natural basaltic and basanitic glasses. During our experiments, the only significant problem was the accidental setup of the ROI of one of the detectors on the first shift. This was not recognized before the 15th shift and resulted in longer acquisition times than necessary and in the analysis of a smaller number of samples than initially planned. Despite this, we obtained significant results, which are summarized in figures 1 and 2. Fig. 1 shows a compilation of XANES spectra acquired with the unfocused (200 μm) beam. Three standards (pyrrhotite, Na-sulfite and hauyine) are shown as reference for the sulfide (S^{2-}), sulfite (S^{4+}) and sulfate (S^{6+}) peak positions. The pyrrhotite used for reference formed from an immiscible sulfide liquid during quenching of experimental basaltic glass. The Na-sulfite used as standard was heavily oxidized to sulfate, but still showed the peak position characteristic of sulfite. Hauyine is shown as reference for sulfate, although CaSO_4 was also measured several times to determine the peak position characteristic of sulfate. The spectra are roughly arranged from reduced to more oxidized upwards. Quenched experimental glasses coexisting with sulfides (e.g. PJ-004) showed a single broad “hump” centered at 2.4765 keV. However, natural basaltic glasses sometimes showed an additional (and sharper) peak around 2.4705 keV (as in the pyrrhotite reference) but with variable intensities (cf. Lau Basin 20-5-1 and Loihi Seamount KK-15-4). In some natural basaltic and basanitic glasses, both sulfide and sulfate species were detected (e.g. Loihi Seamount KK-19-21; Kilauea basanite 508-3-A7). In both cases, the “sharp” sulfide peak was present at ~ 2.4695 keV. The presence of sulfate species could be caused by sulfur oxidation in a reaction such as: $8\text{Fe}^{3+} + \text{S}^{2-} = 8\text{Fe}^{2+} + \text{S}^{6+}$ (1), as proposed by [2]. However, the lack of sulfate peaks in other Fe-bearing samples (e.g. PJ-004; Loihi KK-15-4) indicates that this reaction is not typical, and therefore, the spectra likely reflect: (a) true multiple speciation, or (b) particular $f\text{O}_2$ conditions (hence, $\text{Fe}^{3+}/\text{Fe}^{2+}$) that allow reaction (1) to occur upon

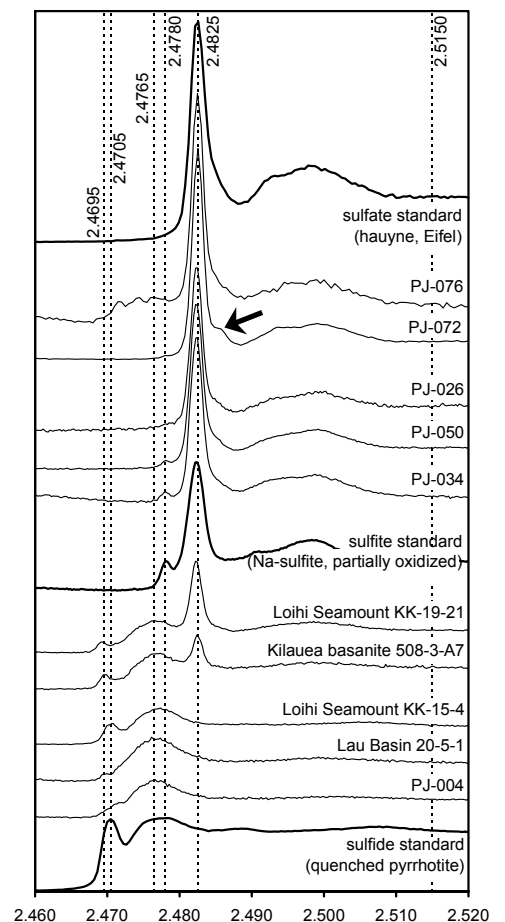


Figure 1. Highlight of S XANES results for ME-1269. Abscissa = energy in keV; ordinate scale is arbitrary.

quenching. The spectra for some experimental basalts with fO_2 close to FMQ+2 (e.g. PJ-034, PJ-050 [1]) show that sulfite species are present under some fO_2 conditions. The presence of only sulfate species in samples for which microprobe analysis (S K α shifts, [3]) assigned sulfate mole fractions $[X(S^{6+})]$ less than 1 (e.g. PJ-026) confirm that sulfur speciation estimates using microprobe analysis are not absolute, as suggested by [3]. Analysis of glasses of andesitic composition (e.g. PJ-072) show an additional shoulder at 2.4857 keV (arrow in Fig. 1) that was not observed for glasses of basaltic composition, and that may indicate differences in S behaviour with differences in melt polymerization or melt composition. Multiple speciation was detected in an experimental andesitic glass (PJ-076) for which fO_2 was set at \sim FMQ+1.6, halfway in the narrow band of fO_2 in which sulfur speciation is expected to change from sulfide to sulfate.

Experiments equilibrated in the narrow band of fO_2 between the stability of sulfide and sulfate are difficult to produce. As an alternative to study the transition between sulfide and sulfate speciation, we analyzed a disequilibrium experiment in which the progressive reduction of a sulfate-saturated andesitic melt was quenched. The reduction front was very narrow (less than 50 μ m in width, Fig. 2); therefore, tests with the unfocused beam could not resolve speciation changes along the profile. In addition, we verified the photoreduction effect with time of the focused synchrotron beam, as documented in [4]. To avoid these

limitations we did a series of scans at various energies moving the focused beam along the reduction profile. This provided detailed information about the changes in speciation along the reduction front, without causing photoreduction (due to the limited exposure time). Fig. 2A shows variations in intensity for energies corresponding to several characteristic sulfur features along the reduction front (the position set as $x = 0$ corresponds to a pyrrhotite grain). The intensity against distance profiles were obtained with a focused beam of 0.8 μ m diameter. The initial high counts were produced by the presence of pyrrhotite. We measured variations at energies corresponding to the two sulfide features, sulfite, sulfate, as well as the energy before the edge and after the edge (cf. reference lines in Fig. 1). The decrease in sulfate species (from right to left) and well as the increase in sulfide species is noticeable. Sulfite is never higher than the sulfide “hump” along the reduction profile, an indication that sulfite species were not present. Sulfite species in significant amounts would result in a “sulfite” curve above the sulfide “hump” curve, which is the case at $x > 60$ μ m. However, spectra acquired with the unfocused beam at $x > 60$ μ m showed that only sulfate species were present. Fig. 2B shows an approximate quantification of the dominant species along the reduction front. We used the spectra of sulfide-saturated and a sulfate-saturated glasses (PJ-004 and PJ-072 in Fig. 1) and the relative intensity of the sulfide and sulfate peaks relative to the energy step to define the respective speciation scales. The profile in Fig. 2B essentially shows a smooth transition from sulfide to sulfate along the reduction front.

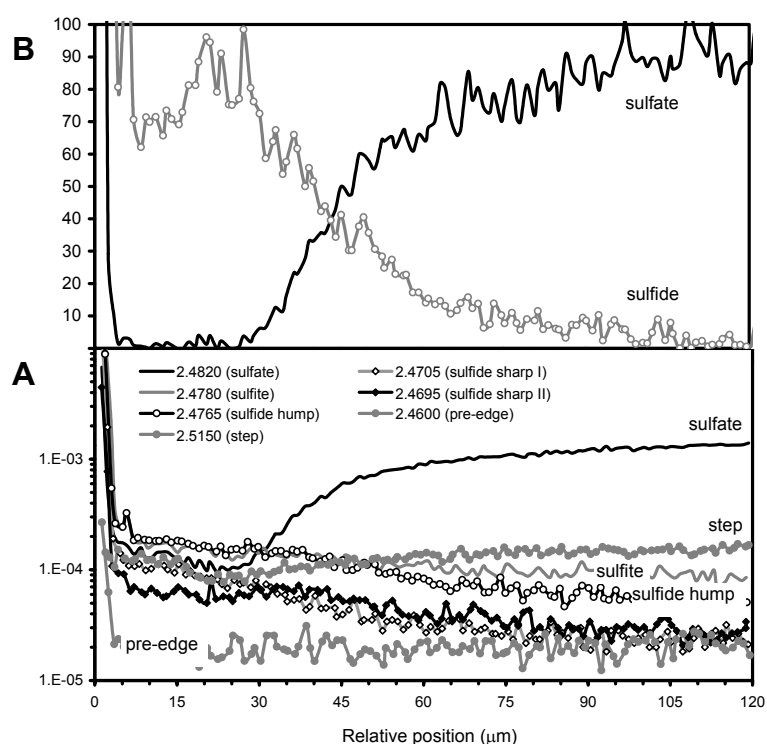


Figure 2. **2A** Variations in characteristic energies in a transect along a reduction front in an experimentally quenched andesitic glass (relative position measured respect to a sulfide grain). **2B** Intensities for sulfide and sulfate along the reduction front normalized to 100% (see text for details).

[1] Jugo, P.J., Luth, R.W. and Richards, J.P. (2005) *Journal of Petrology*, 46:783-798.

[2] Métrich, N., Berry, A., O'Neill, H. and Susini, J. (2005) ESRF User report 26797_A.

[3] Jugo, P.J., Luth, R.W. and Richards, J.P. (2005) *Geochimica et Cosmochimica Acta*, 69:497-503.

[4] Métrich, N., Susini, J., Galois, L., Calas, G. (2003) ESRF User report 25157_A.