ESRF	Sulphur speciation in synthetic and natural quenched silicate melts	Experiment number: EC 1061
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Report:

The scope of the study is understanding the sulphur speciation by XANES at the S K-edge in synthetic and natural quenched silicate melts in order to better constrain the role of the sulphur oxidation state for the sulphur budget of natural magmas and the influence of sulphur oxidation state on degassing processes of basaltic volcanoes and to what extent degassing changes the oxidation state of natural magmas.

For the measurements at the S K-edge, a Si (111) double-crystal fixed-exit monochromator was used. A collimated beam with diameters between 50 and 200 μ m was used to avoid beam damage that occurs for beam sizes below 1 μ m (Wilke et al. 2008). The fluorescence yield was collected using a Si drift-chamber detector with 80 mm² active area. The contribution to the X-ray fluorescence signal by Na, Al, and Si was reduced by covering the detector with an 8 μ m thick Kapton foil, which substantially reduces the deadtime of the detector. This setup allowed acquisition of S XANES down to S contents of ca. 20 ppm.

A batch of natural samples taken at 2 volcanoes in Central America, Masaya and Cerro Negro, and one volcano in East Africa. Measurements focused on comparing the sulfur speciation in melt inclusions entrapped at depth in olivine crystals to the one found in matrix glass, which was quenched after eruption. The matrix glass represents the sulfur content and species after dgassing and eruption. Shown in Fig. 1a are examples of S XANES spectra obtained on melt inclusions (named earmi*) to those obtained on matrix glass and a sample of glass from the mid-ocean ridge (morb392*). All spectra are dominated by contributions from S^{2^-} with a small contribution by S^{6^+} in most cases (peak at ca. 2482 eV). There is a small but significant variation in the S oxidation state. However, no correlation with S content was found. Samples from Masaya and Cerro Negro show spectra that are dominated by contributions from S^{6^+} (for further details see de Moor et al. 2013).

In another batch of synthetic samples, produced at controlled redox conditions, the effect of bulk composition on the S speciation was studied. Shown in Fig. 1b are samples synthesized at redox conditions close to the S²⁻ \rightarrow S⁶⁺ equilibrium (sam8* to sam15*), as well as samples synthesized at much more oxidizing conditions. The spectra of the latter only show contributions by S⁶⁺ and only subtle differences in the shape of the spectra. In contrast, the other spectra show considerable variations indicating varying proportions of S²⁻ and S⁶⁺, which are only related to the variation of the bulk composition of the melt, particularly the Fe content.

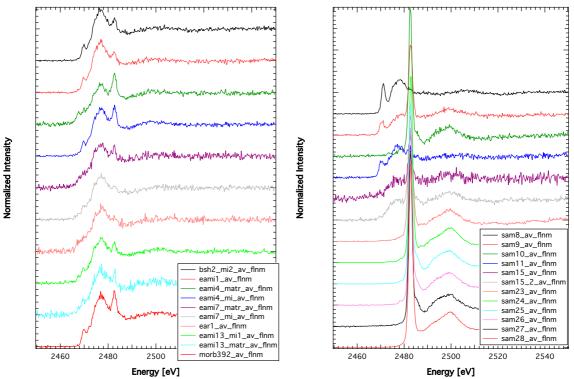


Figure 1: S K-edge XANES of selected samples. a) Spectra taken on melt inclusions in olivine and matrix glass. b) Spectra taken on glass samples synthesized at various redox conditions. See text for further details.

References:

Wilke M., Jugo P.J., Klimm K., Susini J., Botcharnikov R.E., Kohn S.C., Janousch M. (2008) The origin of S⁴⁺ detected in silicate glasses by XANES. American Mineralogist, 93, 235-240.

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