



**Experiment title:**  
**High-resolution emission spectroscopy of Sulfur in geological relevant materials**

**Experiment number:**  
 EC 244

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<b>Shifts:</b> 18	<b>Local contact(s):</b> Sigrid Eeckhout	

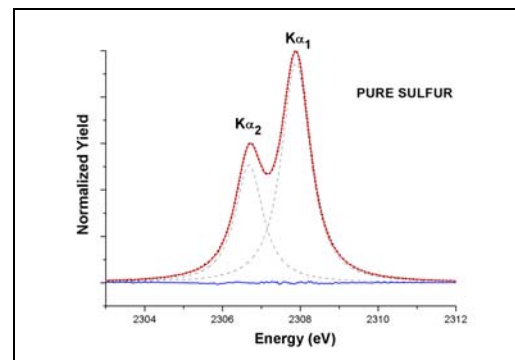
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**Preliminary Report:**

We investigated via X-ray emission spectroscopy, the chemical state and local environment of sulfur in a set of representative sulfur rich mineral compounds and three mid ocean ridge basaltic glasses (MORB). These glasses were sampled during the Deep Sea Drilling project (ODP leg 168) at different distances from the Juan de Fuca ridge. We recorded with success  $K\alpha$  and  $K\beta$  fluorescence lines with the help of a wavelength dispersive x-ray emission spectrometer based on Rowland geometry with Johansson type crystals. This setup provided sufficient resolution to resolve the  $K\alpha_1$  and  $K\alpha_2$  fluorescence lines (figure 1). Furthermore, count rates are sufficient

to measure glasses with S concentrations below 1000 ppm in a few hours.



**FIGURE 1: Sulfur  $K\alpha$  line convoluted with voigt functions**

Figure 2 reports the  $K\alpha$  spectra recorded with this setup for four selected samples with different formal oxidation state state. The Sulfur  $K\alpha$  emission spectrum arises from transitions between the 2p and 1s shells. Figure 3 shows the S  $K\alpha_1$  maximum energy position, fitted with voigt functions, and we observe a strong shift of the edge position with the formal oxidation state, i.e. the valence band electron occupation caused by a change in electron density around the S atom.

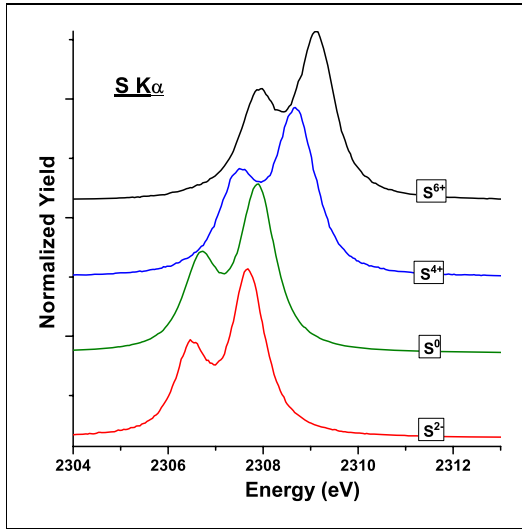


FIGURE 2: S  $K\alpha$  spectra of several sulfur compounds

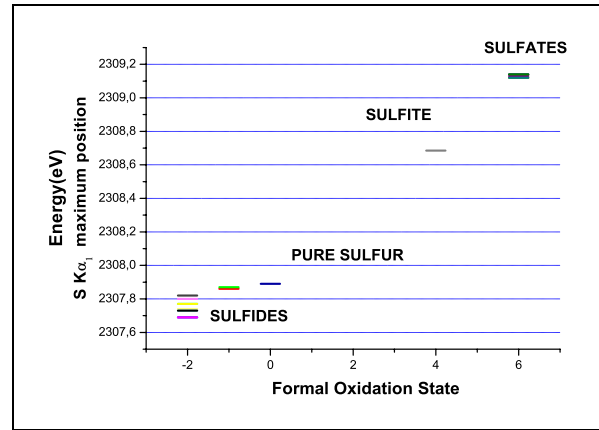


FIGURE 3: S  $K\alpha_1$  maximum energy position for some minerals in correlation with the formal oxidation state

The little dependence on the chemical environment of the  $K\alpha$  line allows to easily make a quantitative analysis in mixed-valence systems. Evaluation of the relative amount of S present as sulfide ( $S^{2-}$ ) and sulfate ( $S^{6+}$ ), are shown in figure 4. The results were extracted by fitting the spectra with a linear combination of the two expected sulfur species. To explain the changes in the sulfate concentration further analysis on the composition of the sample are in progress.

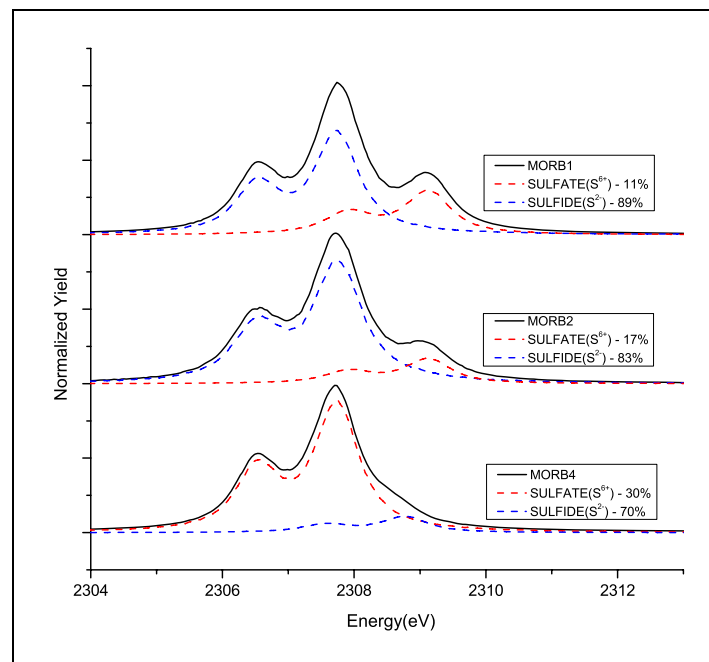
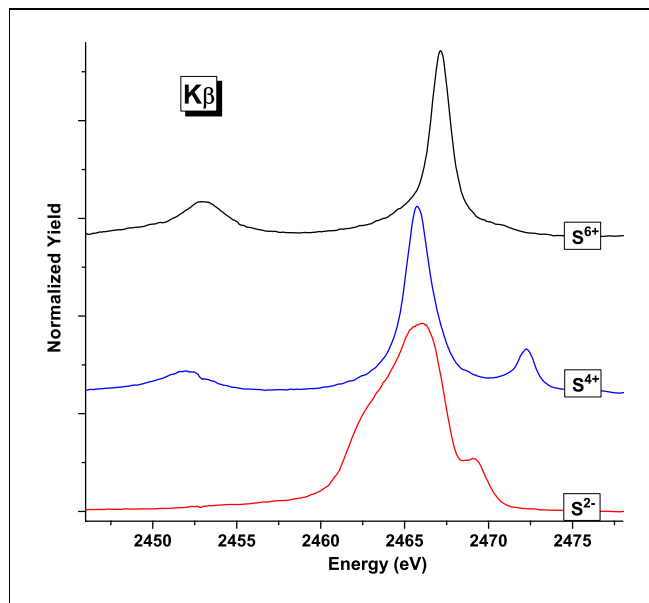


FIGURE 4: S  $K\alpha$  spectra of three basaltic glasses from the Juan the Fuca ridge fitted with a linear combination of sulfate and sulfide minerals

We also report in figure 5 the K $\beta$  emission spectra of different sulfur rich mineral compounds. K $\beta$  lines, close to the K-edge, directly yield the p-density of occupied valence states giving valuable information on the local coordination around S. Due to the electron configuration of the sulfur atom, which includes a 3p valence state, its K $\beta$  emission spectrum reflects the chemical environment of sulfur with high sensitivity.



**FIGURE 5: S K $\beta$  spectra of three sulfur compounds**