ESRF	**Experiment title:** **Speciation of light elements (C, N, S) in micro-glasses of geological interest using micro-XANES**	**Experiment number**: **MI-402**
Beamline: ID 21	**Date of experiment**: from: 06/02/00 to: 10/02/00	**Date of report**: 29/02/00
Shifts: **9** +3 (set-up)	**Local contact(s)**: Jean Susini	*Received at ESRF:*

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Report: This is a preliminary report because the experiments have been carried out just 3 weeks before and 12 other shifts will occur in April.

Experimental conditions

The energy was scanned from 2.45 to 2.53 keV around the sulphur K-edge in order to acquire the XANES spectrum of this element in different matrices of interest. The beam spot size was optimized at 0.4×0.4 μm^2 with a measured flux about of 10^8 photons/s. The XANES spectra were recorded in fluorescence mode with a Ge detector. The focussing set up was under secondary vacuum in order to minimise air absorption. The scans were recorded by dividing the near edge in three regions for which the step scanning was adapted as a function of our precision request. In other words, in the edge, special structures need a good resolution to be detected, as it is less important above the edge where EXAFS structures appear.

Samples

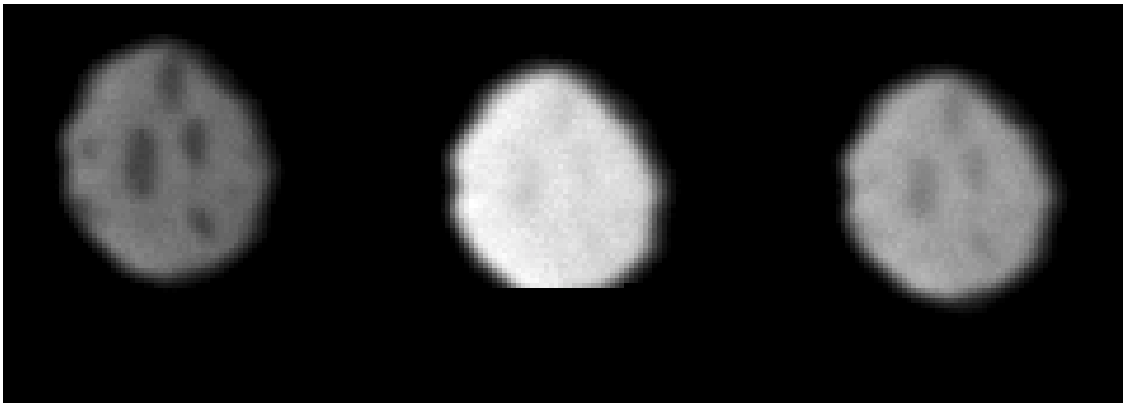
Glass inclusions in olivines from three active volcanic zones were investigated, covering a range of compositions with variable oxidation conditions from mid-ocean ridge basalts (Famous zone with reduced sulphur) to subduction setting (Stromboli). An intermediate glass composition was analysed (reference, Piton de la Fournaise, Pf). Only few information is known about sulphur speciation, and particularly in glasses. For this reason, we acquired XANES spectra of reference samples of metallic sulfides, di-sulfides and sulphates and also glass references containing a known concentration of sulphur. With a particular convolution of these references, the interpretation of the complete XANES spectra is therefore possible.

Important results

One glass inclusion from Piton de la Fournaise contains a particularly sulphur-rich phase, with a very regular spherical shape (diameter of 10 µm). Three maps of this phase were recorded at three energies corresponding to specific structures in the XANES spectrum of sulphur. These maps are presented on figure 1.

Figure 1: Maps acquired with incident X-rays of 2.472, 2.477 and 2.482 keV

These maps highlight **heterogeneities at the micron scale**, this case has to be studied thoroughly before interpretation. Out of the regions of heterogeneity, we obtained the **XANES spectrum of FeS**, never reported before, and preserved as immiscible liquid associated in a quench glass inclusion. Figure 2 presents the XANES spectra of FeS and FeS_2.



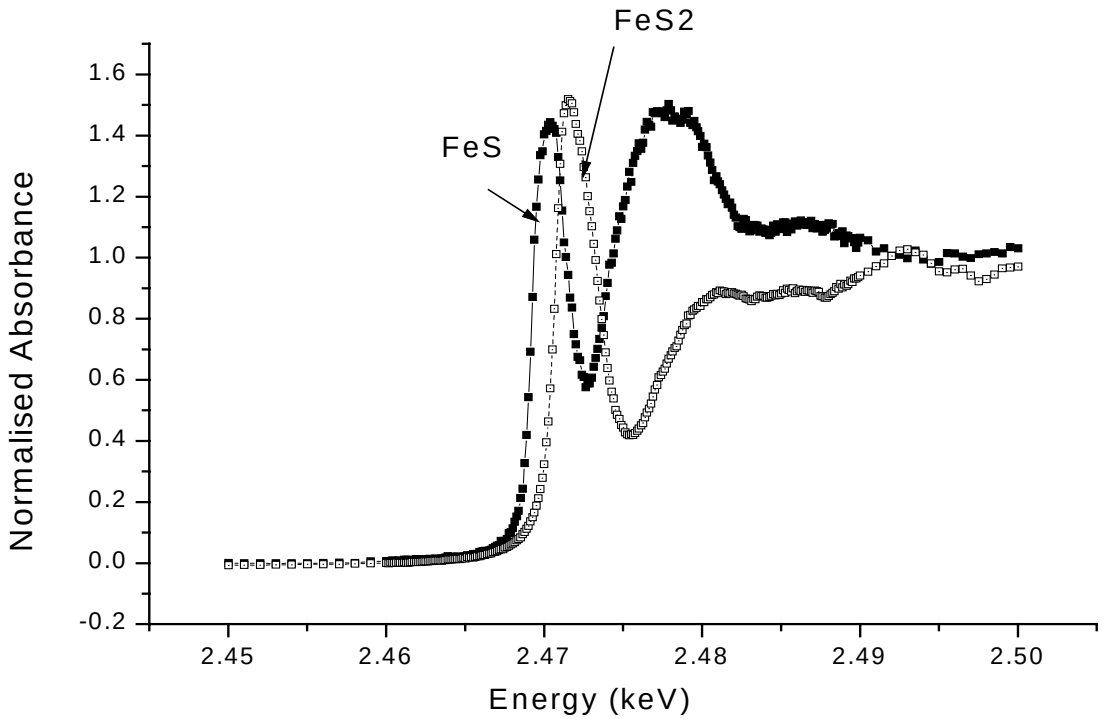
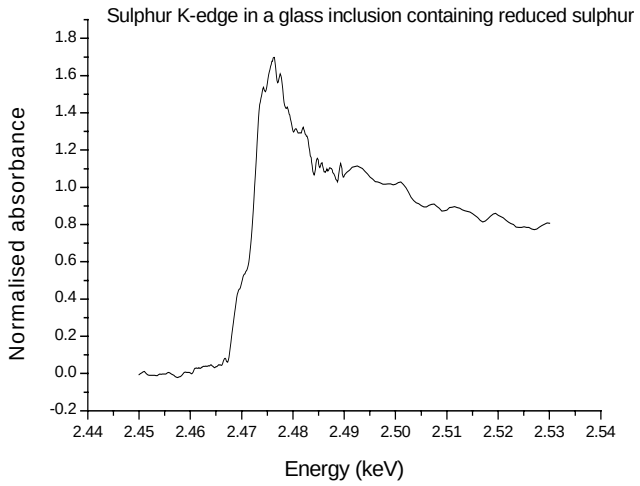


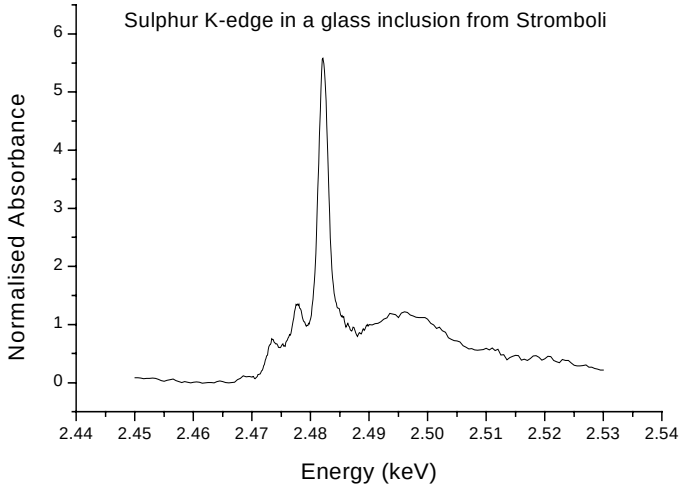
Figure 2: XANES spectra of FeS and FeS_2 in the same experimental conditions

The white line of the sulphur in these two phases is shifted by 1.5 eV. As known, the sulphur valence is –2 in FeS, for this reason, the energy of the white line is lower than for the valence –1 in FeS_2.

Most of beam time was dedicated to the acquisition of XANES spectra on 5 glass inclusions. A full analysis of each sample needed near five hours and more when an heterogeneity was found. The low sulphur content of the glass inclusions (around 1000 ppm) is the main reason. The determination of the speciation of sulphur at this level of concentration is a real challenge.

The two figures presented here below show the differences in the sulphur K-edge in two glass inclusions of extreme compositions: the reduced glass inclusion and the oxidised glass inclusion. On the right figure, the strong peak at 2.482 keV is characteristic of sulphur at valence +6 (the sulphate SO_4^{2-}), the other structures have to be identified with the references. The left figure highlights a sulphur oxidation state and a local environment completely different than on the right one. These data have been predicted in the past, it is not completely new in the mind but it was not demonstrated experimentally. A glass inclusion of an intermediate composition has been studied, the XANES spectrum evidences also an intermediate structure.


Sulphur K-edge in a glass inclusion containing reduced sulphur
Normalised absorbance
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
2.44
2.45
2.46
2.47
2.48
2.49
2.50
2.51
2.52
2.53
2.54
Energy (keV)


Sulphur K-edge in a glass inclusion from Stromboli
Normalised Absorbance
6
5
4
3
2
1
0
2.44
2.45
2.46
2.47
2.48
2.49
2.50
2.51
2.52
2.53
2.54
Energy (keV)