



	<b>Experiment title: Influence of the sulphur speciation in silicate glasses and glass inclusions on bubble nucleation in magmas and volcanic degassing processes</b>	<b>Experiment number:</b> <b>ME-397</b>
<b>Beamline:</b> <b>ID 21</b>	<b>Date of experiment:</b> from: 01/05/02 to: 06/05/02	<b>Date of report:</b> 29/08/02
<b>Shifts:</b> <b>12</b>	<b>Local contact(s):</b> Jean Susini	<i>Received at ESRF:</i>
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We have recently proposed, on the basis of  $\mu$ XANES-spectra performed on ID21 beam line, that sulphur is mainly transported as sulphite ( $S^{IV}$ ) and sulphate ( $S^{VI}$ ) by  $H_2O$ -mantle-derived melts before being released as  $SO_2$  and/or  $H_2S$  in volcanic emissions [1,2]. The model involves sulphite ( $S^{IV}$ ) as the intermediate species yielding to highly efficient partitioning of sulphur between the silicate melts (magmas) and the volcanic gas phase at the origin of excess  $SO_2$  release at subduction zone volcanoes.

We have carried out new experiments on melt inclusions well preserved in olivine grains in the particular case of the July-August 2001 eruption of Mt Etna (Italy). This volcano is well known to produce  $H_2O$  and S-rich magmas [3] and a large  $SO_2$  flux during permanent degassing [4] in a complex tectonic setting implying the possible contribution of slab-derived fluids as recently discussed in Nature [5]. A selection of glass inclusions and glass fragments was also studied to detail to sulphur speciation as sulphide ( $S^{II-}$ ) in samples from active volcanic zones (Iceland, Mid-Atlantic Ridge and one lateral strombolian cone (P. Vincenzo) of Piton de la Fournaise volcano in Reunion island).

About 15 samples were examined and we have acquired at least 5 spectra per sample and some images at 2482eV. In order to improve the data set on reference compounds, we have got new XANES spectra on sulphides (PbS, NiS,  $FeS_2$ ), sulphates in various matrices (all together  $BaSO_4$ , scapolite containing 2.3 wt% S and a sulphate-bearing silicate glass with 970ppmS), sodium sulphite ( $Na_2SO_3$ ) and sodium thiosulphate ( $Na_2S_2O_3$ ) for which

we confirmed that sulphur is dissolved as  $S^{I-}$  and  $S^{5+}$  according to [6]. Because of instabilities of the beam source and almost permanent photon flux decrease, it has been time consuming to get our series of XANES spectra. It also excluded working on extensively degassed glasses with good statistics.

The energy scans at the sulphur K-edge were obtained using a fixed-exit Silicon (111) monochromator providing an energy resolution of 0.3 eV. The synchrotron X-ray source was demagnified down to a micro-probe ( $0.5 \times 0.5 \mu\text{m}$ ) by using Fresnel zone plate lenses [7]. The fluorescence signal was collected using a single-element energy-dispersive high purity Ge detector and the experiments done under secondary vacuum in order to minimise the air absorption.

Two main results arise from these experiments. It seems that sulphite ( $S^{IV}$ ) and sulphate ( $S^{VI}$ ) are dominant in the glass inclusions representative of the most primitive melts that refilled the 2001 activity of Mt Etna (Figure). These melts are water-rich (3.2 wt%  $\text{H}_2\text{O}$ ) and not saturated with respect to any S-condensed phase (either sulphide or anhydrite) that implies that sulphur dissolved in the melts is controlled by the vapour phase. It is worth noting that Etna magmas display high total iron content compared with Stromboli  $\text{H}_2\text{O}$ -rich primary melts [2] with 10 wt% vs 6.5 wt%  $\text{FeO}_{\text{total}}$ , respectively.

Indeed, sulphite is one of the key species in the transfer of sulfur in  $\text{H}_2\text{O}$ -rich-magmas. Only, XANES spectroscopy unambiguously evidences its occurrence. As a preliminary conclusion, we also suggest that water may have a predominant effect on the redox state and speciation of sulphur.

During magma ascent and  $\text{H}_2\text{O}$  and  $\text{CO}_2$  release, the immiscible sulphide globule appears and the speciation of the remaining sulphur in melts shifts towards sulphide ( $S^{II-}$ ). The  $\mu\text{XANES}$  spectra of these glass inclusions are closely similar to some of the  $\mu\text{XANES}$  spectra acquired in  $\text{H}_2\text{O}$ -poor magmas from diverse environments from Mid-Atlantic Ridge to Iceland (Figure).

We also provide a first and complete series of  $\mu\text{XANES}$  spectra of sulphur in natural volcanic glasses from reduced samples (mainly  $S^{II-}$ ) for which spectra significantly differ from those of crystallised  $\text{FeS}$  or  $\text{FeS}_2$  phases to the most oxidised terms representative of primary  $\text{H}_2\text{O}$ -rich magmas.

## References

[1] Bonnin-Mosbah et al. (2001) *Spectr. Chim. Acta* **57**, 711; [2] Métrich et al. (2002) *Geophys. Res. Lett.* **29**, 33-1; [3] Métrich et al., (1993) *J. Volcanol. Geoth. Res.* **59**, 131; [4] Allard (1997) *Geoph. Res. Lett.*, **24**, 2219; [5] Schiano et al., (2001) *Nature* **412**, 900; [6] Li et al. (1995) *Can. Mineral.* **33**, 949; [7] David et al., (2000) *Appl. Phys. Letters*, **77**, 3851.