ESRF	**Experiment title: An XANES study on sulphur speciations in vitreous rocks (lava flows and dikes) from Boavista Island, Cape Verde Archipelago**	**Experiment number**: CH-1457
Beamline: ID 21	**Date of experiment**: from: March 5, 2003 to: March 11, 2003	**Date of report**: 2003.08.29
Shifts: 18 #	**Local contact(s)**: Dr. Jean Susini, Dr. Barbara Fayard	*Received at ESRF:*

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Beam time shared by two projects: CH-1457 and ME-589

Report:

Together with water vapour and carbon gases, sulphur is an abundant volatile constituent of magmas, either reduced as $S^{=}$ or oxidized as S^{6+} or S^{4+}. Temperature, pressure, H_2O content and bulk composition plus oxidation state of the melt are relevant factors for understanding the liquid immiscibility of sulphide and the incorporation of SO_2 and/or H_2S during degassing from an active volcano, in parallel with the strong emission of elemental sulphur accompanying volcanic eruptions.

Natural glasses are therefore potential testimonies of the chemical evolution of sulphur and X-ray near-edge absorption structure at the S *K*-edge plays a crucial role in providing direct evidence on S-speciation. Glass inclusions hosted by olivine crystals were recently studied by micro-XANES with success, providing evidence for the presence of S^{4+} [1].

The XANES experiments performed at line ID-21 were focused on vitreous rocks (pliocenic age) from Boavista Island (Cape Verde Archipelago) occurring either as dikes and veins or as extended lava layers and displaying S-contents up to 3000 ppm [2]. Eight glass samples free from crystalline phases – previously studied by XRD and analysed by μ-SRXRF at the LURE – were selected for this first XANES experiment, along with sulphur and two lava flows collected during the last eruption of Fogo volcano (Cape Verde) in April 1995. Haüyne – a mineral containing isolated $SO_4^{=}$ tetrahedra surrounded by Na^{+}/Ca^{2+} cations within cages of a cubic aluminosilicate framework – was chosen as adequate model for sulphate in a natural glass.

A total of 1300 scans between 2.45 and 2.53 KeV were performed to collect S *K*-edge XANES spectra of enough quality (about 80 scans for each spectrum). The samples were irradiated at various points to ascertain the homogeneity of the glassy material.

Various speciation states could be identified, despite some still uninterpreted spectra details: oxidized (S^{6+} and S^{4+}), reduced ($S^{=}$ and sulphur dimmers, $[S_2]^{-}$) and possibly chain concatenation as in S^0, as illustrated by the spectra reproduced in figures 1 & 2. A preliminary notice on these results was delivered in June at the 6th National Geology Congress [3].

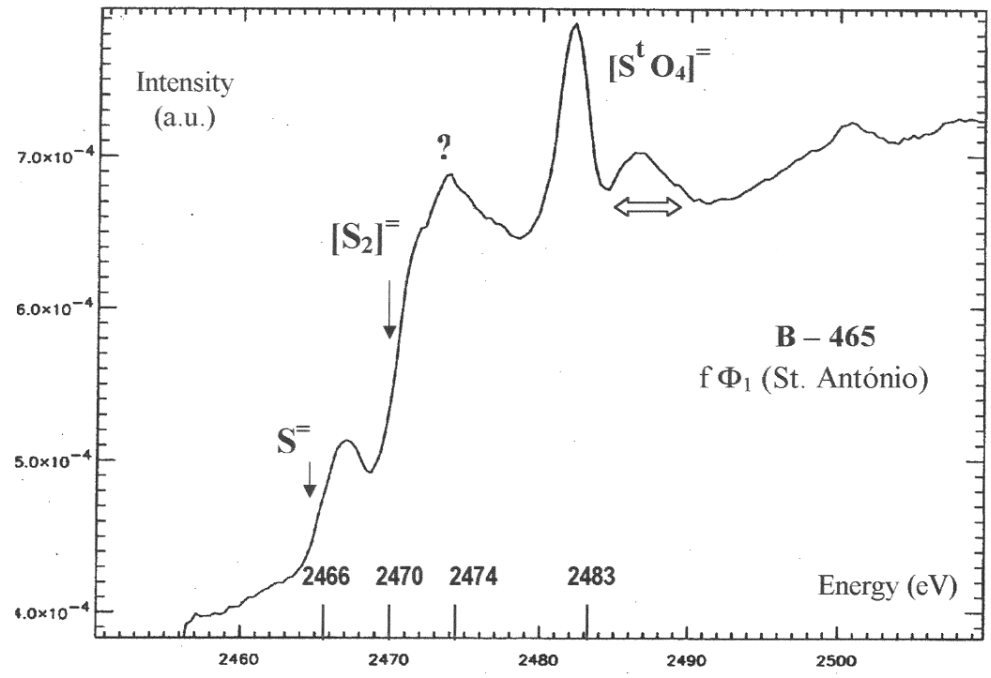

Fig. 1

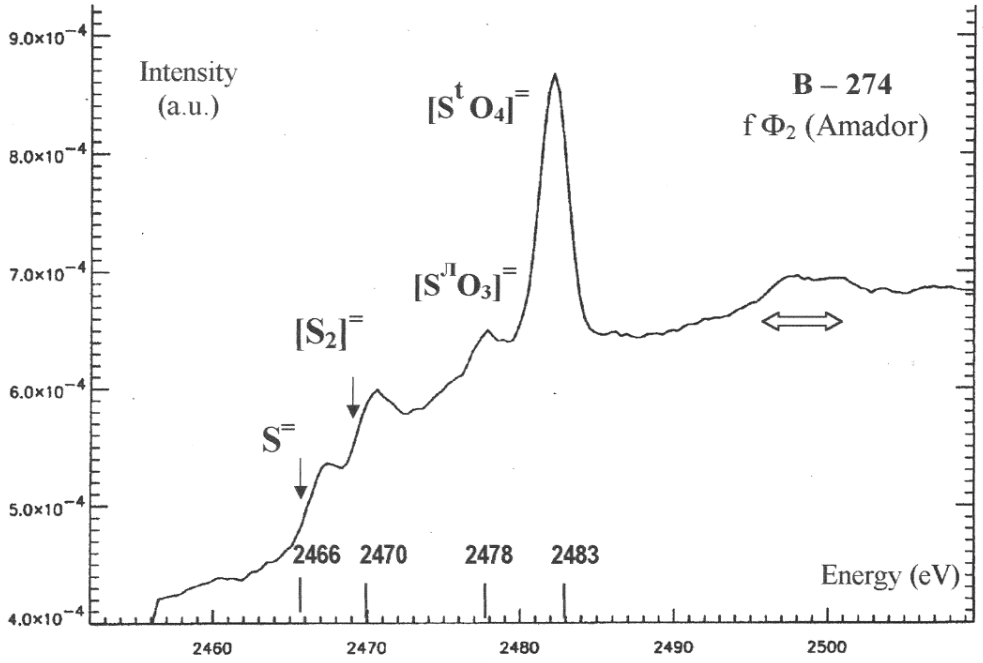

Fig. 2

Theoretical calculations and spectra modelling with FEFF8.10 program [4] are now in progress.

[1] N. METRICH *et al.* (2002) *J. Geophys. Res.* 29, 33-1 to 33-4.

[2] M.O. FIGUEIREDO *et al.* (2003) *J. Non-Crystalline Solids* 323 78-83.

[3] M.O. FIGUEIREDO *et al.* (2003) *Ciências da Terra* (UNL), Lisboa, spec. vol. V, CD-ROM, B32-35.

[4] A. ANKUDINOV, B. RAVEL & J. REHR (2000) Manual of FEFF8.10 program. The FEFF Project. Dept. Phys., Univ. Washington, Seattle, USA, 62 p.