



Experiment title: Double spectroscopy study of sulphur oxidation state and water in in magmas: implications for the sulphur transfer during ascent of arc magmas

ME-591

Beamline: ID 21	Date of experiment: from: 13/03/03 to: 18/03/03	Date of report: 21/07/03
Shifts: 15	Local contact(s): Jean Susini	<i>Received at ESRF:</i>

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We have recently proposed, on the basis of μ XANES-spectra at the sulfur K-edge 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].

We carried out experiments in May 2002 on olivine-hosted melt inclusions in the particular case of the July-August 2001 eruption of Mt Etna in Italy to follow the effect of the water degassing on sulphur speciation and on sulphide-bearing basaltic glass inclusions. However, because of instabilities of the beam source and almost permanent photon flux decrease, it was time consuming to get these series of XANES spectra and the spectra of sulphide-bearing glasses were very noisy and almost unusable. Working at low sulphur concentrations was impossible [see report ME397].

Based on these unsuccessful but informative previous experiments, the idea of the experiments performed in March 2003 [ME591] was to couple the sulphur and water microspectroscopy to study the transition from sulphate/sulphite (S^{VI}/S^{IV}) towards sulphide (S^{II}) species as a function of the water content prior to any immiscible sulphide liquid exsolution. It is of prime interest to know whether this transition is progressive with intermediate sulphur oxidation states (S^0 , S^{2+} or others) or not. The second objective was getting good spectra of sulphide-bearing glass inclusions.

During this new series of experiments, we extended our data set on reference compounds (particularly alkali sulphides) Na_2S , lapis-lazulite blue pigment, MgS (FeS) phase in meteorite, polished and unpolished CuS (covellite).

We got spectra on water-rich basaltic glass inclusions as planned, with an improved analytical procedure and “rapid” time acquisition, not available before. The μ XANES spectra at the S K-edge were acquired in 400s with a good statistic. With such analytical conditions and rapid time acquisition, we noted a progressive change of the redox state of sulphur with time which may

result in increasing the reduced species (Fig. 1). Since, the S^{IV}/S^{VI} ratio reaches a plateau after about 1500s, the beam-induced damages were not detectable during the previous experiments during which 5 spectra were successively acquired with 1350 s for each spectrum, although different tests were done to verify if the signal was stable through time.

The new series of data on water-rich glass inclusions were thus acquired taking into account the photo-reduction effect induced by X-ray.

We got a complete series of spectra on basaltic glasses from H_2O -oxidized to H_2O -poor, reduced basaltic glasses, with good statistics. However, the beam damaging effects precluded mapping of H_2O -rich inclusions as planned initially.

The figure 2 illustrates the sulphur speciation in glass inclusions trapped in primitive olivines, considered as representative of magma which partly degassed and lost water upon ascent. The sulphite (S^{IV}) species is superimposed to the sulphide signature identified with the low resonance peak at 2469.5 eV. However, the significance of the low energy edge features of the H_2O -poor, reduced basaltic glass inclusions are under progress and we are working on the μ XANES spectra of these glasses also to determine if S-S bond exists or not.

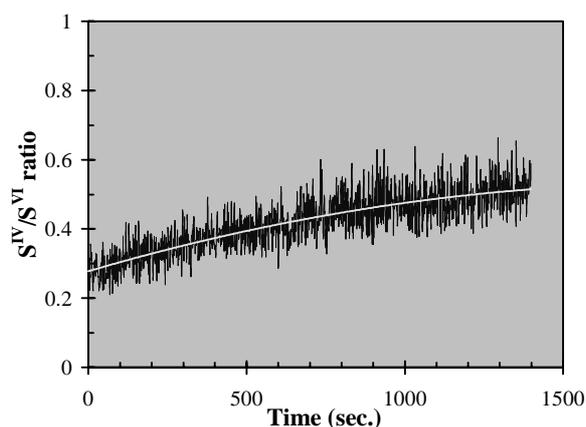


Fig. 1. Evolution of the S^{IV}/S^{VI} species ratio in glass inclusion containing 0.3 wt.% S and 3 wt.% H_2O , with radiation time and a 1 μ m beam spot

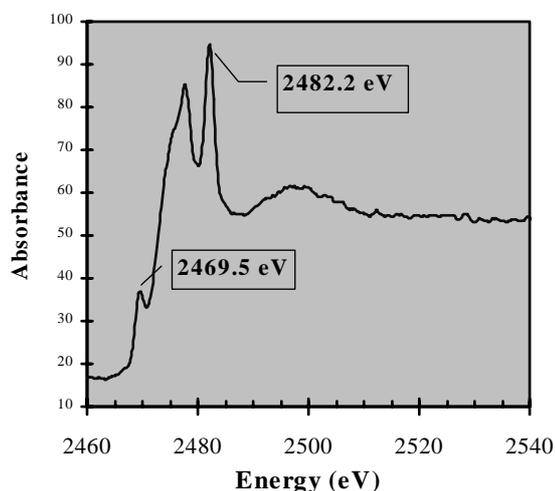


Fig. 2. μ XANES spectrum of glass inclusion (\sim 1 wt.% H_2O , 0.17 wt.% S) from Etna, 2001 eruption, after water degassing and sulphate species reduction.

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. (2003) *J. Phys. IV*, 104, 393-397.