

Speciation of sulfur and iron in silicate glasses of geological interest by micro-XANES. Inference on sulfur degassing during volcanic eruptions

Excess degassing of sulfur dioxide (SO₂) during eruptions has been evidenced at numerous volcanoes, particularly in subduction zones. There is a growing consensus on that sulfur gas species (SO₂, H₂S) can be transferred into the magmatic vapor phase prior to eruption during either gas accumulation in long-lived shallow reservoirs or continuous gas segregation in open-conduit systems. However, the actual degassing mechanism of basaltic magmas at the origin of large SO₂ release is not satisfactorily explained by most of the geochemical models involving the magmatic redox conditions. It is commonly accepted that sulfur is transported exclusively as sulfide (S^{II-}) or/and sulfate (S^{VI}) by mantle-derived melts, before being released as SO₂ and/or H₂S in volcanic emissions.

The experiments carried out (ME-314 together with MI-402) provide the first direct and quantitative determination of the oxidation state of sulfur in a selection of minute glass inclusions trapped in olivine crystals, using X-ray Absorption Near-Edge Structure (XANES) microspectroscopy at the sulfur K-edge. The inclusions are representative of the variety of basaltic magmas that have supplied the activity different active volcanic sites: Mid-Atlantic Ridge, Stromboli and Mt Vesuvius (Italy). The micro-XANES experiments at the sulfur K-edge (2472 eV) were carried out using the X-ray microscopy beam line, **ID21**. The synchrotron X-ray source was demagnified down to a micro-probe by using Fresnel zone plate lenses [1]. The spot size ranges from 0.5x0.5 to 2x2 μm². At the sulfur K-edge (2472 eV), energy scans were obtained by a fixed-exit Silicon (111) monochromator providing an energy resolution of 0.3 eV. The use of an X-ray fluorescence microprobe provides the required resolution in both energy and space together with an appropriate detection limit. The fluorescence signal was collected using a single-element energy-dispersive high purity Ge detector. Micro-XANES spectra at the K-edge of iron were also acquired in two of the glass inclusions. The [Fe³⁺/ΣFe] ratio in these inclusions was calculated on the basis of the pre-edge peaks against reference basaltic glasses [2].

Figure 1 illustrates the micro-XANES spectra of the glass inclusions ([1] to [6]), and of one sulfate-bearing silicate glass given for comparison. The spectra of inclusions indicate sulfur dissolved as sulfide (S^{II-}) in Mid-Atlantic Ridge basalts (Spectrum [1]). In contrast, they reveal the ubiquitous presence of sulfite (S^{IV}) species in addition to sulfate (S^{VI}) in inclusions representative of oxidized and water-rich basaltic magmas from subduction environment

(Spectra [2] to [5]). The first peaks related to sulfite (S^{IV}) and sulfate (S^{VI}) are unequivocally identified at 2477.9 and 2482.1 eV, respectively, in each of these inclusions.

The $[Fe^{3+}/\Sigma Fe]$ redox ratio in two inclusions from Mid-Atlantic Ridge and Stromboli is calculated to be 0.12 and 0.19, respectively, with a relative error of 10%. These independent estimates confirm much higher oxidizing conditions in arc basalts (e.g., Stromboli) relative to Mid-Atlantic Ridge-type basalts. Hence, sulfur is not only dissolved in oxidized basalts as sulfate, but it also coexists with significant amounts of sulfite (S^{IV}). Based on these results we propose a new model involving sulfite (S^{IV}) as the intermediate species yielding to highly efficient partitioning of sulfur into gas phase at the origin of excess SO_2 release in subduction zones. The results are presented in one article which is in press [3].

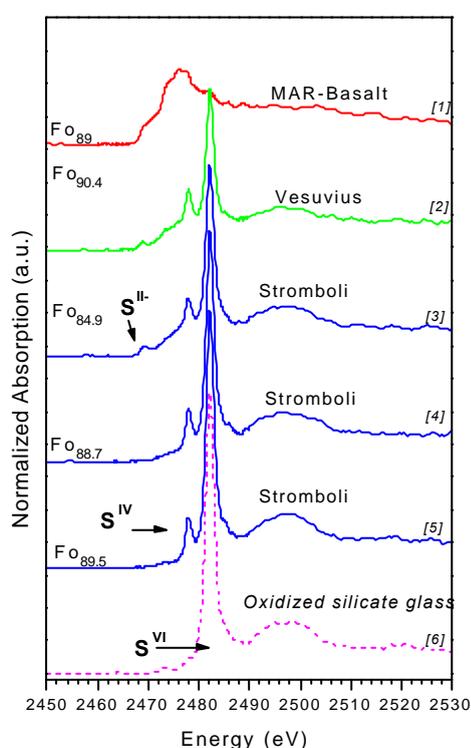


Fig. 1: Micro-X-ray Absorption Near-Edge Structure (XANES) spectra at sulfur K-edge of the glass inclusions [1] to [5] and of one sulfate-bearing reference silicate glass. The sulfur concentration ranges from 840 to 2950 ppm. Fo refers to the composition of the olivine crystal which contains the inclusion [e.g., Fo₈₉: $[Mg/(Fe+Mg)] = 0.89$].

References

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