ESRF	**Experiment title:** The effect of degassing on the oxidation state of sulfur in volcanic glasses	**Experiment number**: ES-48
Beamline: ID21	**Date of experiment**: from: 03/07/13 to: 09/07/13	**Date of report**:
Shifts: 18	**Local contact(s)**: Camille Rivard	*Received at ESRF:*

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Report:

The aim of this experiment was to determine the effect of degassing on the redox relations of volcanic magma. Such data are needed to model sulfur emissions from volcanoes. The experiment was enabled by a set of samples erupted by Kilauea volcano, Hawaii. The magma was quenched on eruption to form a glass, which also contained crystals of the mineral olivine ($Mg_{1.8}Fe_{0.2}SiO_4$) that had crystallised before eruption. These crystals contain small inclusions of the magma (typically 50-100 μm; see Fig.1) that were trapped during crystal growth, and are therefore protected from the degassing. A comparison of the inclusions with the unprotected, external (or host) glass will thus enable the effect of degassing to be determined.

S and Fe K-edge XANES spectra were recorded for a large number of inclusions and host glasses. The preparation of the samples as thin sections with the inclusion exposed on both the top and bottom surfaces and the capabilities of the beamline were both ideal. Systematic and coupled differences in the oxidation states of both S (Fig. 2) and Fe were observed. These correlate with the S content and hence degree of degassing (loss of S as SO_2) that was determined prior to the beamtime by electron microprobe analysis (at Iowa State University). Since the beamtime we have been undertaking extensive sample characterisation using destructive and/or potentially damaging methods, which must be done after the XANES. These include determining the water content by SIMS (at Arizona State University) and FTIR (at the Australian National University), which involves removing the thin sections from the glass and the risk of the samples fragmenting, and laser ablation ICP-MS (also at the Australian National University) to determine differences in the trace element content of the melts and olivine. The final technique to be applied to these samples is the measurement of S isotopic ratios using a SHRIMP (sensitive high resolution ion micro-probe), which are expected to vary systematically with the degree of degassing. This will be the first time that such an extensive range of analytical methods will have been applied to a melt inclusions study.

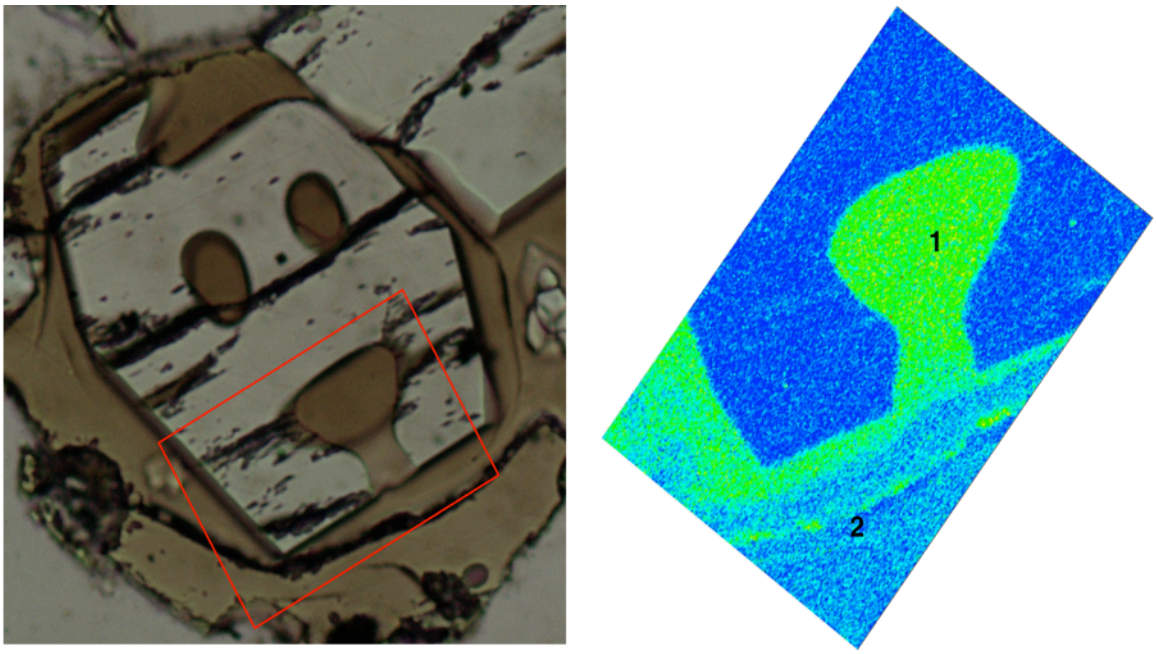

Figure 1: Optical image (left) of an olivine crystal, surrounded by glass, containing two circular melt inclusions ("eyes") and an open inclusion ("mouth"). The S X-ray fluorescence map of the area approximated by the red box (long edge ~ 1 mm) is shown on the right. The S content is high in the inclusion (1) but decreases rapidly with distance in the connected bulk glass (2) as a result of degassing.

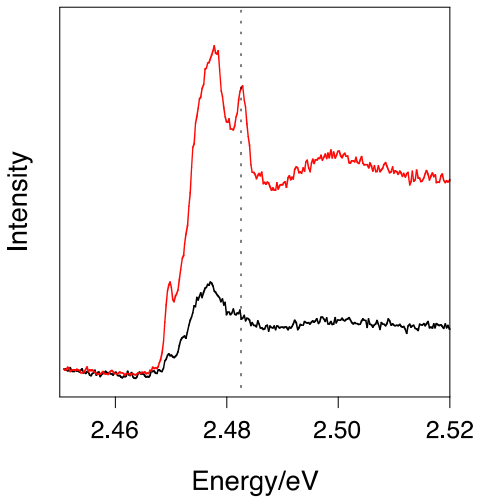

Figure 2: S K-edge XANES spectra of an inclusion (red; point 1 in Fig. 1) and host glass (black; point 2 in Fig. 1). The dotted line at 2.482 eV corresponds to S^{6+} i.e. oxidation. The difference in intensities of the two spectra reflect the different S concentrations due to degassing.

The experiment has been successful in all regards, and indeed exceeds our original expectations, because we were also able to measure inclusions breaking out of their host olivine crystals and "caught in the act" of degassing (e.g., as in Fig. 1). These inclusions show gradients in S, H_2O and accompanying changes in S^{2-}/S^{6+} and Fe^{2+}/Fe^{3+} ratios. A major discovery is that S loss during degassing is limited by the decrease in $p(SO_2)$ caused by changing Fe^{2+}/Fe^{3+}. We expect to prepare a manuscript for submission to Nature or Science aimed at a wide audience, followed by a publication detailing all aspects of the experiments in a prestigious geosciences journal like Geochimica et Cosmochimica Acta.