ESRF	**Probing the oxidation states of sulphur and iron in basaltic magmas evolving under defined redox conditions. Applications to melt inclusion studies**	**EC-149**
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Report

Sulfur K-edge X-ray absorption near edge structure (XANES) spectra were recorded for experimental glasses of various compositions prepared at different oxygen fugacities (fO_2) in one-atmosphere gas-mixing experiments at 1400ºC. This sample preparation method only results in measurable S concentrations under either relatively reduced ($\log fO_2 < -9$) or oxidised ($\log fO_2 > -2$) conditions. The XANES spectra of the reduced samples are characterised by an absorption edge crest at 2476.4 eV, typical of S^{2-} (see Figure below). In addition, spectra of Fe-bearing compositions exhibit a pronounced absorption edge shoulder. Spectra for all the Fe-free samples are essentially identical, as are the spectra for the Fe-bearing compositions, despite significant compositional variability within each group. The presence of a sulfide phase, such as might exsolve on cooling, can be inferred from a pre-edge feature at 2470.5 eV.

The XANES spectra of the oxidised samples are characterised by an intense transition at 2482.1 eV, typical of the sulfate anion SO_4^{2-}. Sulfite (SO_3^{2-}) has negligible solubility in silicate melts at low pressures (see Figure below). The previous identification of sulfite species in natural glass samples is attributed to an artifact of the analysis (photoreduction of S^{6+}). S^{4+} does, however, occur unambiguously with S^{6+} in Fe-free and Fe-poor compositions prepared in equilibrium with $CaSO_4$ at 4-16 kbar, and when buffered with Re/ReO_2 at 10 kbar. Solubility of S^{4+} thus requires partial pressures of SO_2 considerably in excess of 1 bar. A number of experiments were undertaken in an attempt to access intermediate fO_2s more applicable to terrestrial volcanism. Although these were largely unsuccessful, S^{2-} and S^{6+} were found to coexist (see Figure below) in some samples that were not in equilibrium with the imposed fO_2.

The XANES spectra of natural olivine-hosted melt inclusions and submarine glasses representative of basalts at, or close to, sulfide saturation show mainly dissolved S^{2-}, but with minor sulfate, and additionally a peak at 2469.5 eV, which, although presumably due to immiscible sulfide, is 1 eV lower than that typical of FeS. The sulfate-related peak and the FeS(?)-related peak disappear with homogenization of the inclusions by heating to 1200 °C followed by rapid quenching, suggesting that both these features are a result of cooling under natural conditions. The presence of small amounts of sulfate in otherwise reduced basaltic magmas may be explained by the electron exchange reaction: $S^{2-} + 8Fe^{3+} = S^{6+} + 8Fe^{2+}$, which is expected to proceed strongly to the right with decreasing temperature. This reaction would explain why S^{2-} and S^{6+} are frequently found together despite the very limited fO_2 range over which they are thermodynamically predicted to coexist. The S XANES spectra of water-rich, highly oxidised, basaltic inclusions hosted in olivine from Etna and Stromboli confirm that nearly all S is dissolved as sulfate, explaining their relatively high S contents.

Reference

Métrich N., A. J. Berry, H. St. C O'Neill & J. Susini. (2009) Oxidation state of sulphur in synthetic and natural glasses determined by X-ray absorption spectroscopy. *Geochim. Cosmochim. Acta.*73, 2382-2399. doi:10.1016/j.gca.2009.01.025.

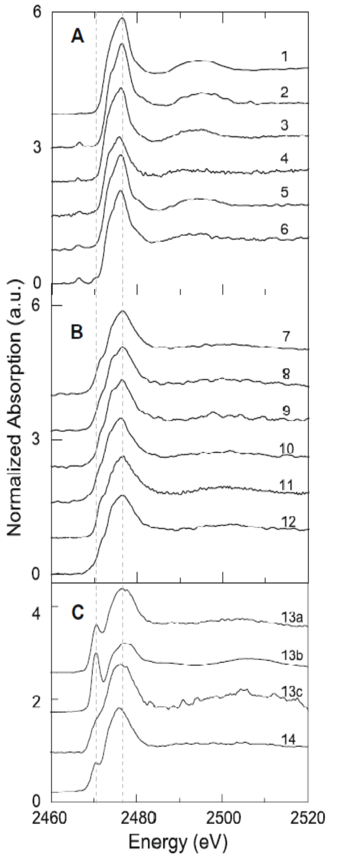

Fig. 3. S K-edge XANES spectra of samples prepared under reduced conditions. The numbers associated with each spectrum refer to the samples given in Table 1. (A) Fe-free, CAS/CMAS/NCMAS glasses, (B) Fe-bearing glasses, and (C) glass containing exsolved Fe-sulfide; 13a was acquired using a large (100 μm) beam, while 13b and 13c are microbeam (1 μm) spectra of the Fe-sulfide and glass components, respectively. The dashed lines are at 2470.5 and 2476.4 eV (S^{2-}).

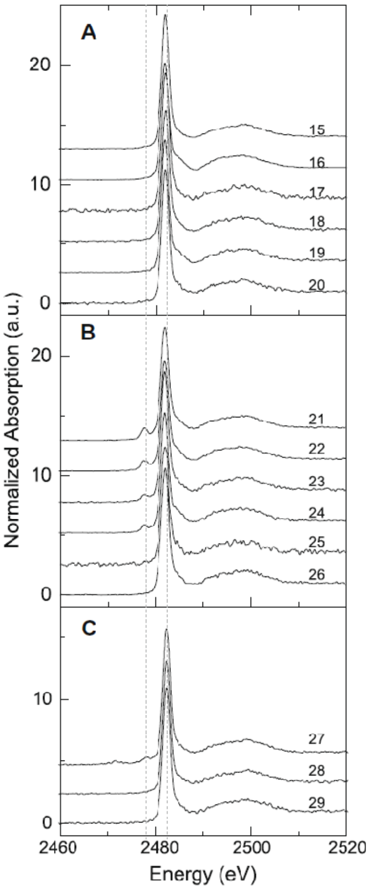

Fig. 4. S K-edge XANES spectra of samples prepared under oxidised conditions. The numbers associated with each spectrum refer to the samples given in Table 1. (A) Fe-free and Fe-bearing glasses, (B) anhydrite saturated glasses with no (21, 22) and variable FeO (23–26) contents, and (C) a CMAS–Fe glass buffered with Re/ReO$_2$ (27), Ru/RuO$_2$ (28), and PtO$_2$ (29). The dashed lines are at 2478.0 (S^{4+}) and 2482.1 (S^{6+}) eV.

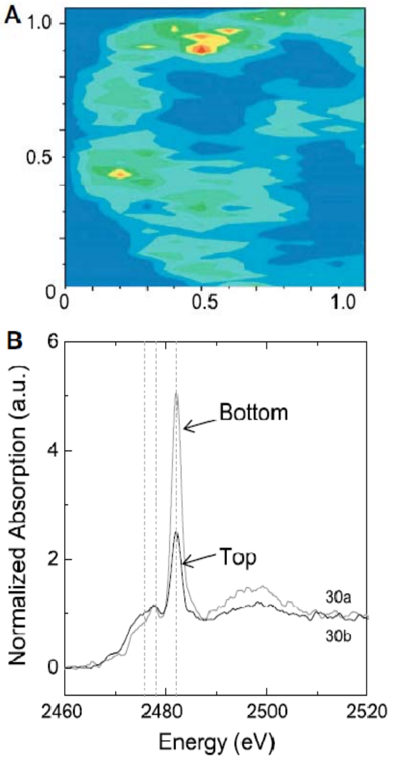

Fig. 6. (A) S^{6+} distribution map (1.1 × 1.1 mm) for part of a two glass re-equilibration sample (30), and (B) S K-edge XANES spectra from two points in this sample. The dashed lines are at 2476.4 (S^{2-}), 2478.0 (S^{4+}), and 2482.1 (S^{6+}) eV.

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