

Report for the experiment ES238

The scope of this study was to determine S and Fe valence states in quenched natural and synthetic melts (i.e. glasses). The results are used to elucidate the oxidation mechanism in subduction zones and the redox relationship between Fe and S which are of great importance for the understanding of subduction related magmatism and the concomitant cycling of volatiles and gases. Natural samples comprise melt inclusions (MIs) trapped in spinels from the mantle wedge brought up to the surface by magmas of Avacha and Ritter volcano in the Kamchatka (Russia) and West Bismarck Arc (Papua New Guinea), respectively, as well as MIs in primitive olivines from Kluchevskoy Volcano, Kamchatka. The experimentally synthesised glasses represent slab melt or volcanic lava compositions and were synthesised under controlled redox conditions (fO₂) with systematically varied Fe/S ratios. For the measurements at the S K-edge, a Si (111) double-crystal fixed-exit monochromator was used. A focused beam (<1 μm) was used to enhance spatial resolution for the MIs and samples containing crystalline phases in addition to glass. The MIs in the minerals were located by S Kα X-ray fluorescence mapping. To minimize beam damage with the focused beam, an Al-foil attenuator (6 μm) was placed before the sample. The thickness of the attenuator was chosen according to test measurements at fixed excitation energy of sulfite peak (ca. 2.478 keV) produced by beam damage (Wilke et al., 2008). Large crystal-free glass mounts were measured with a defocused beam (200 μm pinhole) to minimize beam damage. The fluorescence yield was collected using a Si drift-chamber detector with 80 mm² active area. The contribution to the X-ray fluorescence signal by Na, Al, and Si was reduced by covering the detector with an 8 μm thick Kapton foil, which substantially reduces the deadtime of the detector. This setup allowed acquisition of S XANES down to S contents of ca. 20 ppm.

Fe speciation was measured at the Fe K-edge using a Si (220) double-crystal fixed-exit monochromator. The fluorescence yield was collected using a Si drift-chamber detector with 80 mm² active area. Focused beam (<1 μm) was applied in transmission and fluorescence modes. Transmission mode measurements were possible on double-polished (~200 μm thick) glass samples providing spectra with higher intensity and lower noise than those obtained in fluorescence mode. Beam damage was observed in both modes indicating that beam-induced redox reactions occur not only on the surface but also within the entire volume excited by the beam. Beam damage was minimized by placing a 150 μm Al-foil attenuator before the samples. The Fe-XANES spectra were collected for the whole XANES range as well as for the pre-edge range (with higher energy resolution). Variations of the pre-edge peak intensities were used to determine Fe speciation in the samples.

First results and interpretations

We have measured 18 experimental samples for both S and Fe to determine the effect of melt composition and redox state on the interplay between S and Fe speciation (see Fig.1). We have also re-analysed 8 experimental samples from our previous XANES experiments for both S and Fe to validate our experimental approaches and check for reproducibility. The results show good agreement between sessions. The obtained results indicate that the Fe/S ratio of the melt has a control on the S speciation at given redox conditions as illustrated in Fig.1. Study of experimental samples at the sulfide/sulfate redox equilibrium demonstrates that the increase in FeO content from 0 to 18 wt% can change the proportion of S species by 90% which may have crucial constraints for the interpretation of redox conditions based on S speciation.

Five experimental samples have been investigated to evaluate the effect of redox gradient and S diffusion on the speciation of S and Fe in water-bearing basaltic melts. S K-edge XANES profiles at fixed excitation energies (2.455, 2.478, 2.483 and 2.520 keV for S) have been measured across the

interface of each diffusion couple (400 to 1100 points over 1000-1200 μm distance) to determine peak and background intensity values (see Fig.2).

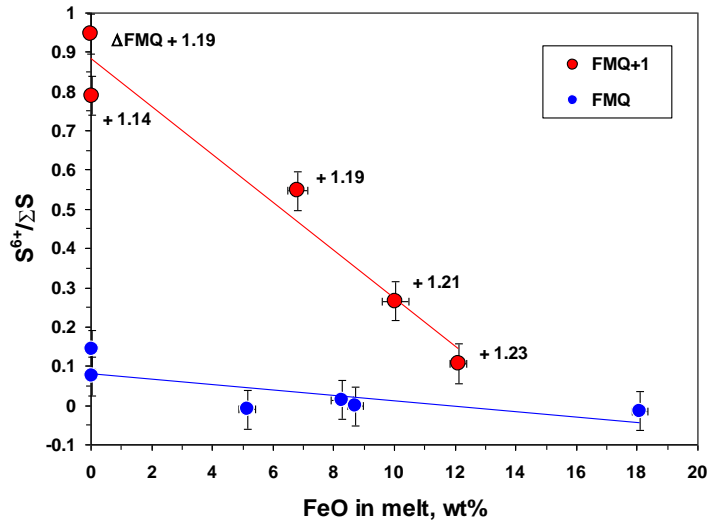


Fig.1. The effect of FeO content on the speciation of S in pseudo-andesitic melts at $\log f\text{O}_2$ fixed at $\sim\text{FMQ}-0.1$ (blue points) and $\text{FMQ}+1.2$ (red points). The data indicate significant compositional effect of the melt on the speciation of S at given redox conditions.

In addition, at five to six points along each profile, the whole S K-edge XANES energy range (2.44 to 2.56 keV) was measured to prove the fixed-energy data. For Fe, several points along the same profile have been measured in transmission or fluorescence (or both)

modes focusing on the entire Fe XANES energy range and on the pre-edge energy range to improve resolution. The results show detectable decoupling in S and Fe speciation induced by kinetic processes. Iron speciation is rapidly adjusted to the prevailing redox conditions, whereas S speciation is significantly affected by diffusion and redox change.

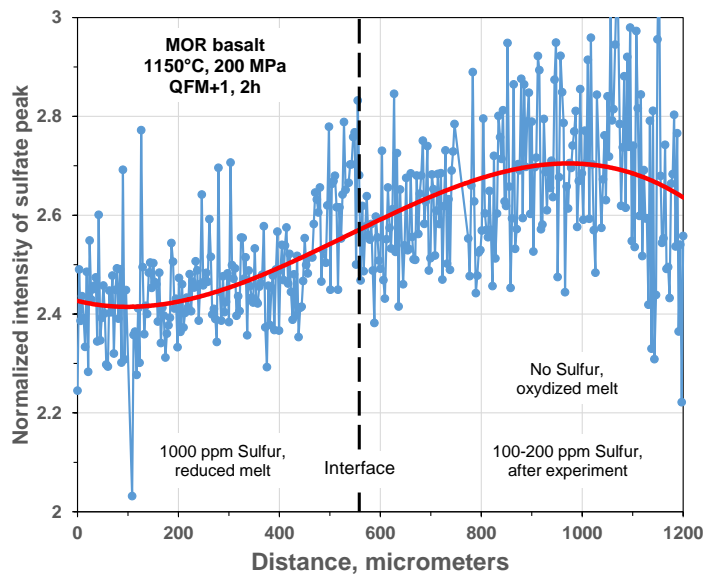


Fig.2. Normalized intensity of sulfate peak at 2.483 keV as a function of distance across the interface between S-bearing reduced and S-free oxidized basaltic glasses/melts. This diffusion couple was obtained in the experiment at 200 MPa, 1150°C and redox conditions corresponding to $\log f\text{O}_2+1$ relative to QFM oxygen buffer. The profile shows continuous increase in the proportion of sulfate species with S diffusion. On the contrast, the analysis of Fe redox speciation indicated identical redox state of Fe (not shown for simplicity) along the same profile pointing to redox decoupling of S and Fe in kinetic processes.

Another set of investigated samples was represented by natural melt inclusions and matrix glasses from volcanoes in Kamchatka, experimentally re-equilibrated to recover initial concentrations of H_2O and CO_2 by re-hydration of melt inclusions at relevant magmatic T, P and $f\text{O}_2$ (for details see Mironov et al. 2015). The XANES data will be used to evaluate changes in S and Fe speciation by melt inclusion re-hydration imposing variations in melt composition and in redox conditions. The analyses of S speciation in melt inclusions were successful indicating close correspondence with imposed redox conditions, whereas the XANES data for Fe are not reliable due to contamination of Fe fluorescence signal from melt inclusions by the signal from underlying host olivine. These results indicate that either double-polished samples must be used or that a novel analytical approach should be developed to analyse melt inclusions.

Next study was focused on natural mantle-derived spinel harzburgites brought to the surface by recent volcanic activity at Avacha and Ritter volcanoes located in Kamchatka (Russia) and the West

Bismarck Arc (Papua New Guinea), respectively. The spinels within the xenoliths contain melt inclusions (MI) trapping primary arc picrite and high-Ca boninite melts (HT inclusions) and evolved dacite melts (LT inclusions) compositionally similar to fractionated arc picrite and high-Ca boninite.

All MIs contain S^{6+} as documented by a peak at 2482.8 eV in XANES spectra (Fig. 3). The S^{6+} is contained as sulfate within the glass structure and/or as anhydrite, which precipitated from the melt upon saturation. In addition to dissolved S^{6+} , all HT inclusions contain S^{2-} that is heterogeneously distributed as sulfides (as indicated by a peak at 2472.5 eV, Fig. 3a), and thus yield variable $S^{6+}/\Sigma S$ values ranging from 0.24 to 0.88 for each HT inclusion depending on the contribution of sulfide to the overall XANES measurement. The LT inclusions almost solely contain sulfate (Fig. 3b), and anhydrite crystals are very abundant within these inclusions. The $S^{6+}/\Sigma S$ ratios for LT are always close or equal to 1. The melt pockets (MP) contain a homogenous mixture of S^{6+} and S^{2-} within the glass, with lower $S^{6+}/\Sigma S$ (~ 0.57 , Fig. 2b) compared to HT and LT glasses.

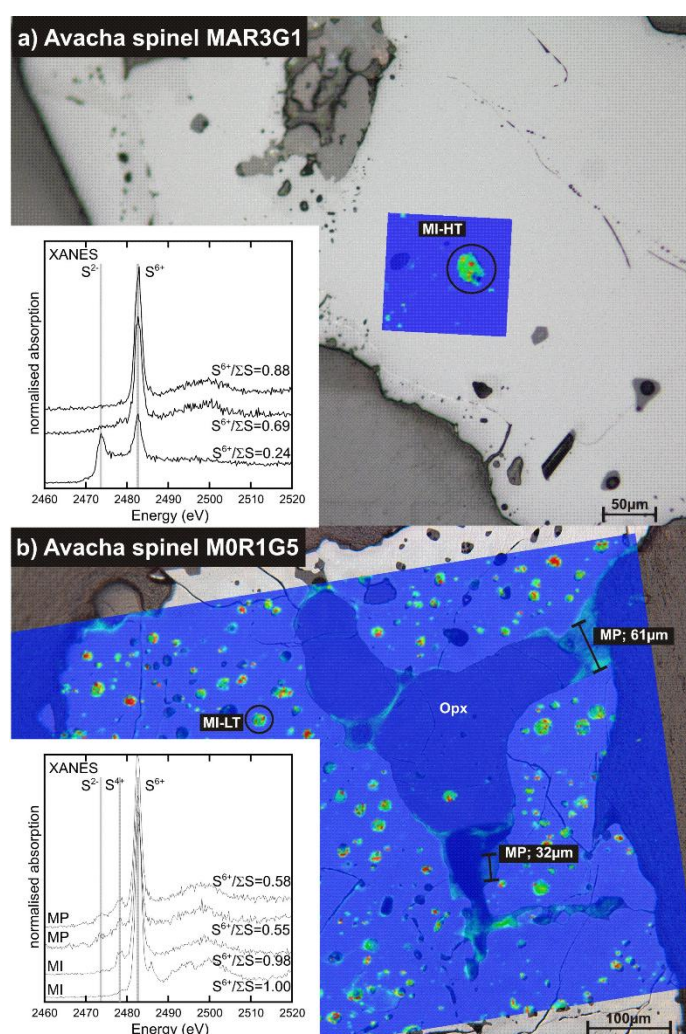


Fig.3. Sulfur distribution and speciation in spinel-hosted melt inclusions (MI). Reflected light images of Avacha spinel grains and representative S K-edge XANES spectra of MI. Coloured inlays show the abundance of S in the spinel and enclosing MI determined by S K α X-ray imaging (heat map; red = high S concentration; blue = low S concentration). a) Avacha spinel containing high-temperature (HT), picrite and high-Ca boninite inclusions characterised by an heterogeneous distribution of S. The glass (green color) contains mostly S^{6+} with $S^{6+}/\Sigma S$ up to 0.88 (top spectrum in inlet). The high S concentrations (red colours) are due to the presence of a sulfide minerals as evidenced by a sulfide peak at 2472.5 eV in the XANES spectrum (bottom spectrum in inlet). b) Avacha spinel containing many low temperature (LT) inclusions and melt pockets (MP). The LT inclusions only contain S^{6+} either in the glass (green colours; 2nd spectrum from the bottom in inlet) or in anhydrite (red colors; bottom spectrum in inlet). The MP have a homogenous S distribution in the glass and contain more reduced S with $S^{6+}/\Sigma S$ of 0.55 to 0.58 (top two spectra). Due to the use of a micro-focused beam during XANES measurements some minor S^{4+} was generated in the glass (peak at 2478 eV in top 3 spectra).

The melt inclusions containing sulfate and sulfide species formed during percolation of primary arc liquids in the mantle and their host spinel exhibits elevated ferric iron contents (analyzed by EPMA), recording an oxidation process. These observations indicate that: (i) sulfate quantities liberated from the slab are high enough to reach the source of primary arc melts; and (ii), interaction of sulfate with ferrous iron-rich arc mantle rocks or melts causes a reduction of sulfate to sulfide and the concomitant oxidation of ferrous to ferric iron. Such a sulfur-iron redox coupling could have made an important contribution to the oxygenation of the Earth's atmosphere during the "Great Oxidation

Event" ~2.45 Ga ago, where a major modification in the net sulfur cycle has been deduced in relation to changes in the composition of slab-derived liquids (Klimm et al., *Nature*, *under review*).

References

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