ESRF	**Tracking the effects of composition, oxygen fugacity, pressure and cooling on sulfur speciation in quenched silicate melts by µXANES at the sulfur K-edge**	
Beamline: ID 21	**Date of experiment**: from: 12/11/03 to: 18/11/03	**Date of report**: 3/08/05
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Sulfur dissolves in silicate melts in at least two and possibly three oxidation states: S^{2-}, SO_4^{2-} and possibly SO_3^{2-} [1,2,3]. The solubility of S in magmas is directly related to its oxidation state, and is important for understanding geological processes such as the origin of magmatic sulfide ores, sulfur degassing from volcanic eruptions and hence global climate change, and the geochemical behavior of the chalcophile trace elements (Re-Os, PGE). We have already done different series of XANES experiments on natural glass/melt inclusions and sulfide compounds [2,3, see also report ME591]. The XANES spectra of glass inclusions, representative of basaltic magmas saturated with respect to the immiscible FeS sulfide liquid, showed the coexistence of different sulfur species (sulfate, sulfide, even sulfite, S^V..), difficult to interpret in terms of redox conditions (fO_2, fS_2), only.

The aim of this work was to determine the oxidation state of S in experimental, silicate melts (i.e., glasses) that were very rapidly quenched and prepared under carefully controlled conditions of temperature (T), pressure (P), oxygen fugacity (fO_2), and sulfur fugacity (fS_2) for a large range of melt compositions. This builds on previous S K-edge XANES studies of natural volcanic glasses [3]. Almost 1000 synthetic glasses have been prepared as part of a study on the solubility of S in silicate melts as a function of the variables listed above. This work was published for reduced conditions [4], where S^{2-} is the dominant sulfur species. These synthetic glasses provided an ideal set of references for S XANES experiments to detail the effects of the different parameters (compositions, fO_2, fS_2, T, P) on sulfur speciation. Importantly, the synthetic samples allow spectra for both S^{2-} and SO_4^{2-} to be recorded for the same composition for many different melt types.

XANES experiments (ME709) were performed, in November 2003, using the X-ray microscopy beamline, ID21. Complementary XANES spectra were also acquired on Na-rich experimental quenched melts, in March 2004 [see report ME822]. All these experiments were successful.

Glasses ranging from typical MORB-type basalts to Ca-(Na, Mg) rich compositions were synthesized under reducing conditions (log fO_2 –8.79 to – 10.92; log fS_2 –1.91) at 1200-1400°C and 1 bar. The XANES spectra of all glasses show a main peak at 2476.3 eV (S^{2-}), while those of the Fe-bearing glasses also contain a shoulder on the absorption edge (2471.7 eV) and differ in their structure after the edge. All these XANES spectra are clearly different in the energy position of the first peak and the structure after the main edge from those recorded on sulfide-bearing minerals. High-pressure experiments saturated with FeS display a low energy peak at 2470.5 eV, indicating a contribution from sulfide microglobules that can be easily assessed by combining the XANES spectrum of the glass anf that of the sulfide globule.

For glasses synthesized under oxidizing conditions (log fO_2 –0.49 to – 0.30; log fS_2 –0.18 to – 0.31; log fSO_2 –1.47 to –2.06) at 1200-1400°C and 1 bar, all spectra are essentially identical, with a main peak at 2482 eV (Sulfate) despite large variations in composition.

The modeling of the site geometry of sulfur dissolved as sulfide and sulfate in some selected basaltic glasses is in progress.

We show also that sulfite (S^{4+}) species may co-exist with sulfate (S^{6+}) in Fe-free glasses under some oxidizing conditions. S^{2+} and S^{6+} were not found to coexist in the experimental glasses. The spectra of these samples differ significantly from those of basaltic melt inclusions in which the main peak occurs at 2476.5 eV (S^{2-}), in addition to the S^{6+} peak at 2482.2 eV, and an unassigned peak at 2469.4 eV. The presence of both S^{2-} and S^{6+} may reflect intermediate redox conditions, although this is unlikely given the very narrow fO_2 range over which the two oxidation states are expected to coexist. An alternative explanation is post-entrapment oxidation. For example, all natural silicate glasses contain Fe both as Fe^{2+} and Fe^{3+}, permitting the possibility of the electron exchange reaction: $S^{2-} + 4\ Fe^{3+} + 2\ O^{2-} = 4\ Fe^{2+} + SO_4^{2-}$.

Since such a reaction essentially involves only a redistribution of electrons, it should proceed extremely rapidly, and may either be unquenchable, or perhaps occur during quenching.

These results were presented at the Goldschmidt conference (Session 05: Advances in in-situ microanalysis of trace elements), in May 2005 [5]. A manuscript is aso in preparation.

References

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