



## **Sulfur and Iron Oxidation State in quenched Melts as a Function of Oxygen Fugacity**

**M. Wilke** (1), R. E. Botcharnikov (2) and P.J. Jugo (3)

(1) GeoForschungsZentrum Potsdam, 14473 Potsdam, Germany ([max@gfz-potsdam.de](mailto:max@gfz-potsdam.de)), (2) Leibniz Universität Hannover, 30167 Hannover, Germany, (3) Laurentian University Sudbury, ON P3E 2C6, Canada

Although Sulfur occurs only as a trace element in magmatic systems its behavior is directly related to a variety of important geological processes (e.g. formation of ore deposits, global cooling by S-rich explosive volcanism). The solubility of sulfur depends strongly on its oxidation state that may vary from  $S^{2-}$  to  $S^{6+}$ , and thus shows strong dependence on the oxygen fugacity in the system. XANES measurements at the S K-edge provide unique information on the sulfur species present. The fine structure at the S K-edge is dominated by localised 1s-2p transitions, which are strongly dependent on the electronic configuration of S [1]. Spectra were recorded at the ESRF, Grenoble, ID 21 micro-focus beamline using a combination of broad and focused beams (200  $\mu\text{m}$  and 0.8  $\mu\text{m}$  diameter). The pre-edge feature of the Fe K-edge XANES can be used to determine the Fe oxidation state [2]. Fe spectra were acquired at HASYLAB, DESY Hamburg, beamline L using a focused beam with ca. 20  $\mu\text{m}$  diameter. We report data on glasses of a variety of naturally occurring compositions synthesized at 1 GPa, 1100 to 1350 °C (dry conditions) and at 200 MPa and 1050°C (5 wt% total  $\text{H}_2\text{O}$ ). Our data shows that the occurrence of  $S^{4+}$  species can be related to beam damage occurring during the XANES analysis or even during electron probe analysis, which preceded the XANES analysis. We have used the intensities of the respective resonances for  $S^{2-}$  and  $S^{6+}$  in the XANES to determine the sulfur oxidation state in the glasses as a function of the redox conditions during synthesis. The S oxidation state of the hydrous glasses decreases as a function of increasing hydrogen fugacity. The Fe oxidation state of the glasses decreases likewise for high  $S^{6+}$ -contents (above 90%). At a hydrogen

fugacity of ca. 3 bar (ca. 80% S<sup>6+</sup>), the trend of the Fe oxidation state kinks towards higher values and drops down again at higher hydrogen fugacity. No clear correlation with the occurrence of other S-bearing phases is observed. However, the oxygen fugacity during these syntheses depends on the water activity and sulfur fugacity (only hydrogen fugacity is fixed externally). The former is close to one but not buffered, whereas the latter is unknown. Both might influence the redox equilibria in the melt.

[1] Fleet M.E. (2005) *Can. Mineral.* **43** 1811-1838

[2] Wilke M., Farges F., Petit P.E., Brown G.E. Jr., Martin F. (2001) *Am. Mineral.* **86**, 714-730.