

Sulfur speciation in dacitic melts using X-ray absorption near-edge structure spectroscopy of the S *K*-edge (S-XANES): Consideration of radiation-induced changes and the implications for sulfur in natural arc systems

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ABSTRACT

The synchrotron technique of micro X-ray absorption near-edge structure spectroscopy at the sulfur *K*-edge (S-XANES) provides a unique opportunity to measure the proportion of different oxidation states of sulfur (S) in silicate glasses. Although applied extensively in the analysis of basaltic silicate glasses, few S-XANES studies have investigated variations in S oxidation states with f_{O_2} in felsic silicate glasses. In addition, no study has systematically compared the S-XANES results obtained from the same samples at different photon flux densities to quantify the relationship between exposure time and changes in S speciation in silicate glass, as has been done for Fe and V. This study evaluates observed differences in S speciation measured in experimentally produced H₂O-saturated dacitic glasses over a range of reducing to oxidizing conditions (from $\log f_{O_2} = \Delta\text{FMQ}-0.7$ to $\Delta\text{FMQ}+3.3$; FMQ is the fayalite-magnetite-quartz mineral redox buffer) and equilibrated at 1000 °C and 300 MPa.

S-XANES spectra were collected at three different photon flux densities using three microspectroscopy beamlines. As is observed in S-XANES analyses of basaltic silicate glasses, beam-induced changes to the S⁶⁺/ΣS are observed as a function of photon flux density and beam exposure time. Our results demonstrate that silicate glasses of dacitic composition undergo beam-induced photo-reduction in samples equilibrated at $\Delta\text{FMQ} > +1.75$ and photo-oxidation if equilibrated at $\Delta\text{FMQ} < +1$. The time required to observe beam-induced changes in the spectra varies as a function of flux density, and our study establishes an upper photon density limit at $\sim 1.0 \times 10^{12}$ photons/μm². The S⁶⁺/ΣS calculated from spectra collected below this absorbed photon limit at intermediate flux densities ($\sim 1-4 \times 10^9$ photons/s per μm²) are affected by beam damage, as no conditions were found to be completely free of beam-induced changes. However, the S⁶⁺/ΣS ratios calculated below the limit at intermediate flux densities are consistent with thermodynamic constraints, demonstrating that S⁶⁺/ΣS ratios calculated from S-XANES spectra can be considered reliable for estimating the oxygen fugacity.

Our results carry important implications for the S budget of felsic magmas and dissolution mechanisms in evolved melts. While our results from all three flux densities show the presence of S⁴⁺ dissolved in relatively oxidized ($\Delta\text{FMQ} > +1.75$) dacitic glass, even in the spectra exposed to the lowest photon densities, we are unable to rule out the possibility that the S⁴⁺ signal is the result of instantaneous X-ray irradiation induced beam damage using S-XANES alone. When our spectra are compared to S-XANES spectra from basaltic silicate glasses, important differences exist in the solubility of S²⁻ and S⁶⁺ between dacitic silicate melts, pointing to differences in solubility mechanisms as melt composition changes. This study highlights the need for further investigation into beam damage systematics, presence of S⁴⁺, and the solubility mechanisms of different oxidation states of S as silicate melt composition changes.

Keywords: Sulfur, S-XANES, oxidation states, sulfate, sulfide, beam damage