



Sulfur K-edge XANES analysis of natural and synthetic basaltic glasses: Implications for S speciation and S content as function of oxygen fugacity

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XANES analyses at the sulfur K-edge were used to determine the oxidation state of S in natural and synthetic basaltic glasses and to constrain the fO_2 conditions for the transition from sulfide (S^{2-}) to sulfate (S^{6+}) in silicate melts. XANES spectra of basaltic samples from the Galapagos spreading center, the Juan de Fuca ridge and the Lau Basin showed a dominant broad peak at 2476.8 eV, similar to the spectra obtained from synthetic sulfide-saturated basalts and pyrrhotite. An additional sharp peak at 2469.8 eV, similar to that of crystalline sulfides, was present in synthetic glasses quenched from hydrous melts but absent in anhydrous glasses and may indicate differences in sulfide species with hydration or presence of minute sulfide inclusions exsolved during quenching. The XANES spectra of a basalt from the 1991 eruption of Mount Pinatubo, Philippines, and absarokitic basalts from the Cascades Range, Oregon, U.S.A., showed a sharp peak at 2482.8 eV, characteristic of synthetic sulfate-saturated basaltic glasses and crystalline sulfate-bearing minerals such as haüyne. Basaltic samples from the Lamont Seamount, the early submarine phase of Kilauea volcano and the Loihi Seamount showed unequivocal evidence of the coexistence of S^{2-} and S^{6+} species, emphasizing the relevance of S^{6+} to these systems. XANES spectra of basaltic glasses synthesized in internally-heated pressure vessels and equilibrated at fO_2 ranging from FMQ-1.7 to FMQ+2.7 showed systematic changes in the features related to S^{2-} and S^{6+} with changes in fO_2 . No significant features related to sulfite (S^{4+}) species were observed. These results were used to construct a function that allows estimates of $S^{6+}/\Sigma S$ from XANES data. Theoretical considerations and comparison of compiled $S^{6+}/\Sigma S$ data obtained by SK α shifts estimated with electron probe microanalysis (EPMA) and $S^{6+}/\Sigma S$ obtained from XANES spectra show that data obtained from EPMA measurements underestimate $S^{6+}/\Sigma S$ in samples that are sulfate-dominated (most likely because of photo-reduction effects during analysis) whereas $S^{6+}/\Sigma S$ data from XANES provide a close match to the expected theoretical values. The XANES-derived relationship for $S^{6+}/\Sigma S$ as a function of fO_2 indicates that the transition from S^{2-} to S^{6+} with increasing fO_2 occurs over a narrower interval than what is predicted by the EPMA-derived relationship. The implications for natural systems is that small variation of fO_2 above FMQ+1 will have a large effect on S behavior in basaltic systems, in particular regarding the amount of S that can be transported by basaltic melts before sulfide saturation can occur.