



Sulfur speciation in minerals and glasses by high resolution X-ray emission spectroscopy

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Sulfur is characteristically heterovalent, exhibiting by far the greatest range in oxidation state (from 2- to 6+) of the geochemically abundant elements. It readily forms chemical bonds with both more electropositive and more electronegative elements, hence forming a wide range of minerals.

X-ray absorption spectroscopy, and more specifically XANES probes the unoccupied density of states and thus provides information on the oxidation state and local structure of S. However, the XANES spectrum is influenced by numerous effects, such as bond distances, bond angles and ligand type, making the analysis difficult. It is thus desirable to combine XANES with alternative spectroscopic techniques.

We use S $K\alpha$ and S $K\beta$ X-ray emission spectroscopy (XES) to investigate the chemical state and local environment of sulfur in different model mineral compounds, namely sulfides (S^{2-}), sulfites (S^{4+}), and sulfates (S^{6+}). The $K\alpha$ lines arise from 2p to 1s transitions and are expected to be mostly free from chemical bond effects, except for small energy shifts that reflect the valence orbital electron population via screening effects. The quasi-independence of the $K\alpha$ spectral shape on the oxidation state makes the analysis and energy shifts determination easier and more reliable as compared to XANES, and can thus be used to clearly determine the sulfur oxidation states in unknown or heterogeneous compounds. Alternatively, the $K\beta$ lines, close to the K-edge, directly yield the p-density of occupied valence states giving valuable information on the local coordination. We further performed ab initio quantum-chemical calculations by means of the StoBe code, based on the density functional theory (DFT) in order

to visualize the molecular orbitals and to infer how the chemical bonds are formed in these compounds.

The XES technique is now successfully applied to natural and synthetic silicate glasses. This allows us to accurately determine the sulfur oxidation states and to provide valuable information on the local chemistry, structure and thus on the geochemical role of S in these systems. More specifically we use the energy shift in the S $K\alpha$ lines to make quantitative analysis of the oxidation state of sulfur in heterogeneous systems and to determine whether S is present as sulfide or sulfate.