

Molecular Investigation of Sulfate Complexation in Solution and on Fe-Oxide Surfaces

Sulfate is a common anion in aquatic and soil systems, and influence ion adsorption and surface chemistry of mineral oxides [1]. In addition, it plays a major role in elemental cycles in acid mine drainage, alkaline, and marine environments, in which the concentration of aqueous sulfate often exceeds 10 mM [2]. Several researchers have examined the sorption of sulfate on Fe-oxides using macroscopic and vibrational spectroscopy measurements [3-8]. Based on ionic-strength dependent sorption, and diffuse-reflectance FTIR spectroscopic studies of sulfate adsorption on Fe-oxides, researchers predicted that sulfate forms outer-sphere complexes [8]. Although, some of the recent *in-situ* vibrational spectroscopy observations suggested that sulfate forms inner-sphere complexes on Fe-oxide surfaces, sulfate coordination on Fe-oxide surfaces is widely debated [3-7]. To identify sulfate complexes on Fe-oxides, we conducted a detailed investigation of sulfate coordination in different minerals using X-ray absorption spectroscopy and vibrational spectroscopy.

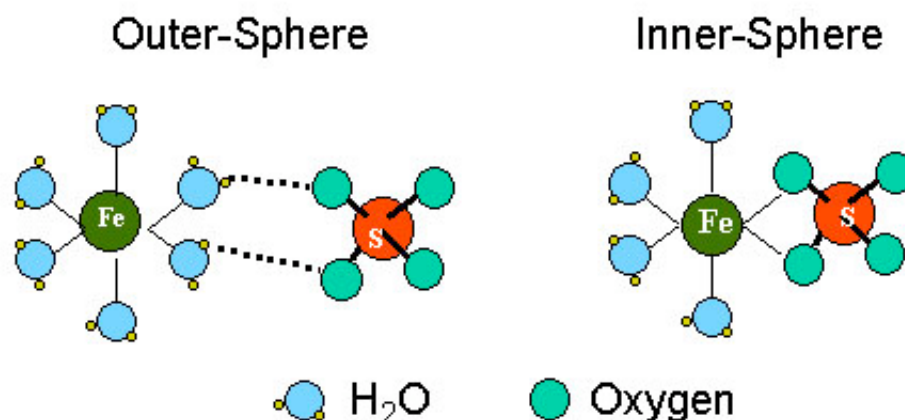


Figure 1: Schematic diagram illustrating the outer- and inner-sphere Fe-sulfate complexes in water. One of the possible structures for each type is shown above.

The soft X-ray spectroscopy (NEXAFS, EXAFS) studies were conducted at the Stanford Synchrotron Radiation Laboratory and the Advanced Light Source (Lawrence Berkeley Laboratory). The S-NEXAFS spectra of model compounds and sulfate reacted Fe-oxides (goethite, ferrihydrite, hematite) have been obtained on beamline 6-2 (SSRL) using a Si(111) double crystal monochromator. A Ni-coated mirror was used to reject the higher order harmonics. The slits in the beamline were adjusted until the spectral features of sodium thiosulfate were well resolved. Under these experimental conditions, the spectrometer has an energy resolution better than 0.6 eV. All of the NEXAFS spectra were collected in fluorescence mode (using a Lytle Detector) with a 0.1 eV step size at the absorption edge. Concentrated samples were mounted as thin smears on kapton tape to avoid self-absorption. These samples were also examined in transmission mode at the ALS (BL 9.3.1) for comparison and to examine self-absorption affects. To examine reproducibility and to obtain cleaner spectra, two to three scans were collected for the concentrated samples, and several scans (10-35) were obtained for dilute samples. Special cells were

designed using X-ray clean polypropylene film for examining the liquid samples at different pHs. All the spectra were calibrated against the peak corresponding to the $1s \rightarrow a_1^*$ transitions of the terminal S in thiosulfate at 2469.2 eV. S EXAFS studies were performed at beamline 2-3 (SSRL) for model compounds. For these measurements, the beamline is detuned over 80% below the S-absorption edge to remove higher order harmonics.

Our results indicate that the sulfur $1s$ -corehole transitions are dependent on coordination environment, and change significantly when sulfate protonates or forms complexes with mineral surfaces [9,10]. This is primarily caused by changes in the symmetry of sulfate from T_d to C_{3v} and other low symmetry forms. Metal complexation of sulfate also affected the energy position and shape (caused by different transitions) of the S absorption edge. In addition, the d-orbital interactions of Fe^{3+} with the unoccupied molecular orbitals of sulfate in $Fe-OSO_3$ complexes produce electronic transitions below the main absorption edge of S, which appear as pre-edges in front of the main S absorption edge. The sulfato complexes of other transition metals also showed similar pre-edge features, but at different energies. Using these spectral variations, we predicted the molecular structure of sulfate in aqueous solutions and on Fe-oxide surfaces. We find that sulfate primarily sorbs as outer-sphere and H-bonded complexes on goethite surfaces at $pH > 3.0$. Below this pH, a significant amount of sulfate sorbs as inner-sphere complexes. Although these complexes are identified as the dominant forms, the presence of other types of complexes can not be ruled out. Ferrihydrite also shows the same behavior. Although sulfate adsorption on hematite primarily shows the same features, inner-sphere sulfate complexes are also found in significant concentrations above pH 3.0. Sample drying and wetting also caused significant changes in the sulfate coordination environment. The sulfate ions bound as outer-sphere complexes, or H-bonded complexes on Fe-oxide surfaces cannot be replaced with other anions, such as Cl^- . Theoretical investigations of sulfato complexes using molecular dynamics and Density Functional Theory are in progress. A detailed discussion of experimental and theoretical studies will be presented.

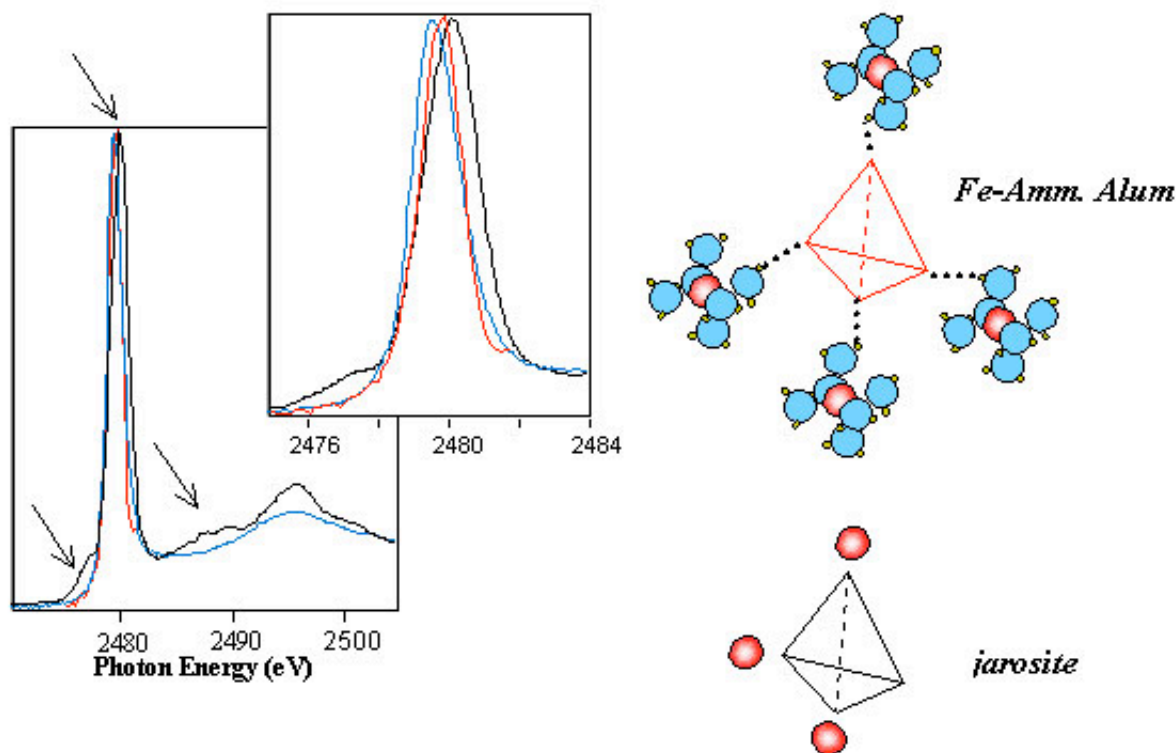


Figure 2: S X-ray absorption spectra of aqueous sulfate (blue), ferric ammonium alum (red), and jarosite (black). The local coordination environment of sulfate in these solids is shown on the right. The red, blue, and yellow spheres correspond to the Fe^{3+} , and oxygen and hydrogen atoms of water, respectively. The arrows point to the spectral differences.

Sulfur and Iron Speciation in Acid Mine Drainage Waters

We investigated speciation of Fe(II), Fe(III), and SO_4 in acid waters by Fourier-transform infrared and X-ray absorption spectroscopy. Acid waters in the form of acid mine drainage (AMD) pollute streams, underground water reservoirs, soils, and sediments at innumerable locations around the world. They usually originate by weathering of pyrite (FeS_2) and are rich in Fe and sulfate. The molalities of sulfate (15 mM) and iron (10, 20, 50 mM), and pH (1, 2, 3), used in our study, mimic the concentration of ions in AMD waters (Figure 3). Sulfate, and very likely also Fe(II), exist as monomers in acidic Fe(II)- SO_4 solutions. In contrast, sulfate interacts strongly with Fe(III). The predominating species in Fe(III)- SO_4 solutions are hydrogen-bonded complexes; inner-sphere complexes account only for 10% of the total sulfate. This finding complements thermodynamic data which suggest that most sulfate (~90%) is associated with Fe(III). However, the thermodynamic results provide no further details about the association between sulfate and Fe(III). Our results show that the mode of interaction between Fe(III) and sulfate is similar in aqueous phase and in nanocrystalline precipitate schwertmannite ($\sim\text{FeO}(\text{OH})_{3/4}(\text{SO}_4)_{1/8}$). Because of this similarity, schwertmannite should be the phase that controls solubility and availability of Fe(III), SO_4 , and indirectly also other components in the AMD solutions.

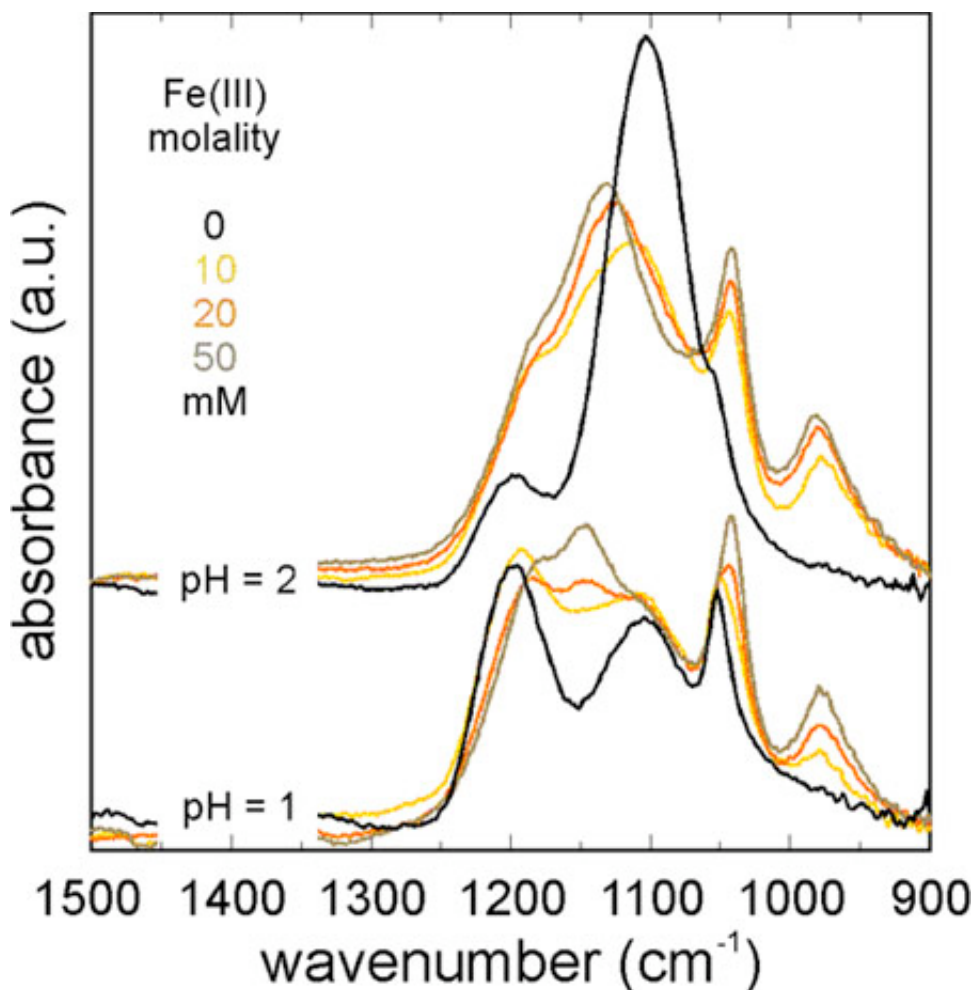


Figure 3: ATR-FTIR spectra of SO_4 in the presence of varying concentrations of Fe(III) . The observed spectral changes are consistent with distortion of the sulfate / bisulfate tetrahedron on interaction with Fe(III) .

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