

Influence of ion coprecipitation and adsorption on iron (hydr)oxide structure and aggregate morphology

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Introduction

Due to their ubiquity in the environment, high surface area, and affinity for both inorganic and organic molecules, iron oxides and hydroxides (FeOx) play an important role in mediating contaminant mobility. Coprecipitation and adsorption of ions influence the reactivity and long-term stability of FeOx minerals by altering their crystal structure, grain size and morphology, and extent of particle aggregation. Al, Si, phosphate, and organic matter, for example, may coprecipitate at stoichiometric ratios up to 50%. These ions, along with heavy metals and other less common elements, may produce changes in reactivity and structure even at significantly lower concentrations. While numerous lab-based studies have parameterized the influence of individual variables, the difficulty inherent in characterizing naturally-precipitated FeOx minerals in a complicated matrix has limited the extrapolation of results to field systems.

Methods

We analyze natural samples collected from the Pb-, Zn-, and Cd-contaminated Tar Creek Superfund Site through a combination of sequential chemical extractions targeting iron phases and Mössbauer spectroscopy to monitor how heavy metal speciation varies during reactive transport and whether FeOx structural parameters obtained via Mössbauer correlate with sample bulk chemistry. We also show results of small angle X-ray scattering (SAXS) on synthetic ferrihydrite samples to investigate how ion coprecipitation and sorption affect aggregate morphology.

Results

Si and organic matter content covary most significantly with Mössbauer parameters, although extraction of P and Al by the sequential extraction steps targeting more crystalline FeOx phases suggests that they may also be an important determinant. Of the ions tested, phosphate produced the largest effect on aggregate structure, increasing mean particle radius and aggregate fractal dimension. This combination of techniques ultimately provides insight into how the matrix may alter iron reactivity and thus control contaminant speciation.

Probing the interactions between glutamic acid and diopside

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Abstract

The manner in which organic molecules adsorb onto the mineral/water interface may hold implications for the origin of life. Chiral amino acids may have selectively adsorbed onto the chiral growth faces of silicate minerals by three or more non-colinear points of attachment, which may have led to the evolution of homochirality. Diopside is a common clinopyroxene mineral with the chiral growth faces (110) and (1-10), which are also the principal cleavage planes prominent in powdered samples. We demonstrated with batch adsorption experiments that up to 30% of L-glutamic acid (initially 20 μ M) adsorbs onto crushed natural diopside at pH=10. We investigated the enantioselective potential of diopside by probing the interactions between glutamic acid and the chiral growth faces (110) and (1-10) with vibrational sum frequency generation (SFG) spectroscopy. Prior to our experiment, we prepared two 0.63 mm thick (1-10) diopside sections of approximately 500 mm², which were cleaned with a plasma cleaner. One diopside section was submerged in 100 μ M L-glutamic acid for 2h and dried under nitrogen, whereas the other section served as a blank. The SFG spectra we collected for the diopside section with L-glutamic acid significantly differed from those of the blank. As a preliminary analysis, we assigned asymmetric and symmetric stretching modes for the β -methylene group and a symmetric stretching mode for the γ -methylene group of L-glutamic acid. We obtained SFG spectra of adsorbed L-glutamic acid under two experimental mutually perpendicular polarization combinations. In principle, spectra such as these can establish the configuration of the adsorbed molecule. A comparison of the ratio of SFG signal intensity for the methylene vibrational modes between the two polarization combinations will determine the dipole orientation of the methylene stretches relative to the diopside surface. This technique may be useful for establishing an enantioselective trend in glutamic acid adsorption.