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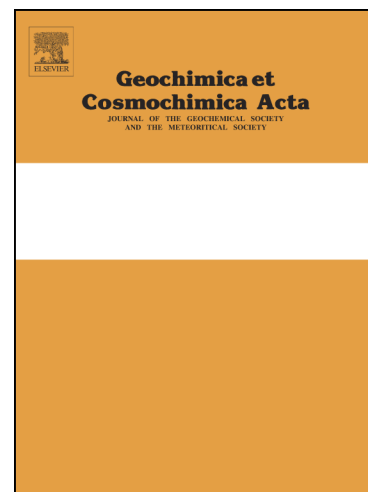
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Structure and reactivity of oxalate surface complexes on lepidocrocite derived from infrared spectroscopy, DFT-calculations, adsorption, dissolution and photochemical experiments

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Abstract

Oxalate, together with other ligands, plays an important role in the dissolution of iron(hydr)oxides and the bio-availability of iron. The formation and properties of oxalate surface complexes on lepidocrocite were studied with a combination of infrared spectroscopy (IR), density functional theory (DFT) calculations, dissolution, and photochemical experiments. IR spectra measured as a function of time, concentration, and pH (50-200 μ M oxalate, pH 3-7) showed that several surface complexes are formed at different rates and in different proportions. Measured spectra could be separated into three contributions described by Gaussian line shapes, with frequencies that agreed well with the theoretical frequencies of three different surface complexes: an outer-sphere complex (OS), an inner-sphere monodentate mononuclear complex (MM), and a bidentate mononuclear complex (BM) involving one O atom from each carboxylate group. At pH 6, OS was formed at the highest rate. The contribution of BM increased with decreasing pH. In dissolution experiments, lepidocrocite was dissolved at rates proportional to the surface concentration of BM, rather than to the total adsorbed concentration. Under UV-light (365 nm), BM was photolyzed at a higher rate than MM and OS. Although the comparison of measured spectra with calculated frequencies cannot exclude additional possible structures, the combined results allowed the assignment of three main structures with different reactivities consistent with experiments. The results illustrate the importance of the surface speciation of adsorbed ligands in dissolution and photochemical reactions.

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