Electrolyte Ion Adsorption at the Hematite/Water Interface: Cryogenic X-ray Photoelectron and Electrochemical Impedance Spectroscopic Studies

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Hematite (α-Fe_2O_3) is a commonly occurring mineral in natural environments and its (electro)chemical attributes are of great importance to various geochemical and technological settings. A fundamental understanding of reactions taking place on hematite surfaces is particularly important in this regard. In this study, electrolyte ion adsorption and electrostatic potential development across the hematite/water interface are respectively probed by cryogenic X-ray photoelectron spectroscopy (XPS) and by electrochemical impedance spectroscopy (EIS).

Cryogenic XPS measurements are carried out on colloidal hematite particle surfaces equilibrated in 50 mM aqueous solutions of monovalent ions (Na^+, K^+, Rb^+, Cs^+, NH_4^+, F^-, Cl^-, Br^-, I^-) at pH 2-11. Results consistently reveal coexisting cations and anions both below and above the point of zero charge of hematite. Inverse correlation between pH dependent surface loadings and hydrous ionic radii is observed in both alkali metal ($Na^+ > K^+ > Rb^+ \approx Cs^+$) and halide ($F^- > Cl^- \approx I^- > Br^-$) ions. Ammonium ion sorption occurs through surface-bound NH_3 species (*e.g.* $\equiv$Fe-OH$\cdots$$NH_3$) shifting the protonation constant of the cation from pK = 9.3 in bulk solution to pK = 8.4 at the interface.

Hematite single crystal electrodes with various crystallographic orientations are used to obtain the pH dependence of electric surface potentials in NaCl and NH_4Cl solutions. Three distinct interfacial processes, space charging, electrical double layer, and adsorption of proton and/or electrolyte ions, are extracted by fitting experimental impedance data using an equivalent circuit model (Fig. 1). Double layer capacitance values vary with pH and exhibit a minimum at pH around 8.7, close to the point of zero charge of this mineral. This capacitance-pH behavior closely resembles that of the interfacial concentrations of electrolyte ions on colloidal hematite particles obtained by XPS. Our results reveal systematic effects of pH and electrolyte ion identity on the intrinsic activity of hematite surfaces.

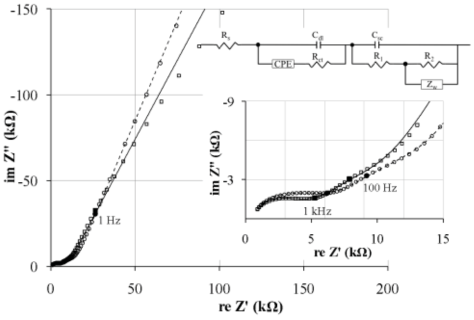

Fig. 1 *Complex plane plots of hematite in 0.1 M NaCl (pH 3.8, ○) and NH_4Cl (pH 3.5, □), including an equivalent circuit model.*

The Structure and reactivity of iron-organic matter coprecipitates

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Introduction

Iron (Fe) (oxy)(hydr)oxides can have large specific surface areas and reactive functional groups, which make them important sorbents for soil nutrients, contaminants, and organic matter (OM). Thus, Fe oxides play a critical role in stabilizing soil organic matter. In the natural environment, pure Fe oxides, such as ferrihydrite, are rarely formed. For instance, OM can be incorporated in the ferrihydrite structure via coprecipitation, likely resulting inboth structual and reactivity changes. Despite the high natural abundance of Fe-OM coprecipitates, only few studies have attempted to determine their reactivity and characterize their chemical and physical properties. In this study, we synthesized Fe-OM coprecipitate with various methods, such as hydrolysis vs. oxidation and with different composition of OM, such as humic acid or fulvic acid. We then characterized the morphology, structure, and reactivity of these coprecipitates to gain new insight into how OM controls the biogeochemical cycling of Fe oxides.

Results and Conclusion

X-ray diffractometry (XRD) analysis indicated that coprecipitated OM did not change the crystal structure of 2-line ferrihydrite. Electrophoretic mobility (EM) analysis was conducted to study the impact of coprecipitated OM on the zeta potential of suspended Fe oxide particles between pH 5 and 9. The EM measurements clearly showed that the addition of OM resulted in more negatively charged partiles of coprecipitates compared to ferrihydrite. Particles with higher C/Fe ratios were more negatively charged than particles with lower C/Fe ratios. Scanning transmission X-ray microscopy (STXM) was used to obtain both two and three dimensional chemical maps of the Fe-OM coprecipitates as well as information about the most likely bounds formed between specific C and Fe surface functional groups. The STXM analysis indicated that Fe and C are evenly distributed within particles and that carboxylic-C may play an important role in complexation with Fe oxides. Complementary techniques, such as X-ray absorption spectroscopy, Mössbauer spectroscopy, TEM, SEM, specific surface area analysis were also conducted for the additional characterization. Our results indicate that both the ferrihydrite morphology and reactivity is strongly influenced when coprecipitated with soil organic matter.