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

KENICHI SHIMIZU1*, ANDREY SHUCHKAREV1, ANDRZEJ LASIA2, JOSEPHINA NYSTRÖM2, PAUL GELADI3, BRITTA LINDBOM-SETHSON1, JEAN-FRANÇOIS BOILY1

1Department of Chemistry, Umeå University, Sweden, kenichi.shimizu@chem.umu.se (*presenting author)
2Department of Chemistry, University of Sherbrooke, Canada
3Unit of Biomass Technology and Chemistry, Swedish University of Agricultural Sciences, Sweden

Hematite (α-Fe₂O₃) 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⁺, Li⁺, Cs⁺, NH₄⁺, F⁻) and divalent ions (Ca²⁺, Mg²⁺, Sr²⁺, Ba²⁺). Ammonium ion sorption occurs through surface-bound NH₃ species (e.g. =Fe-OH–NH₃) shifting the protonation constant of the cation from pKₐ = 9.3 in bulk solution to pKₐ = 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 NH₄Cl 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.

The Structure and reactivity of iron-organic matter coprecipitates

MASAYUKI SHIMIZU1*, MARTIN OBST2, ANDREAS KAPPLER3, THOMAS BORCH1,4

1Department of Soil and Crop Sciences Colorado State University, Fort Collins, U.S., masayuki.shimizu@colostate.edu (*presenting author)
2Center for Applied Geosience Eberhard Karls University Tübingen, Tübingen, Germany, martin.obst@uni-tuebingen.de
3Center for Applied Geosience Eberhard Karls University Tübingen, Tübingen, Germany, andreas.kappler@uni-tuebingen.de
4Department of Chemistry Colorado State University, Fort Collins, U.S., thomas.borch@colostate.edu

Introduction

Iron (Fe) (oxy)hydrates 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 in both structural 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 compositional variation, such as that of 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. Electrokinetic 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 particles 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 bound forms within specific Fe and C surface functional groups. The STXM analysis indicated that Fe and C were 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 characterisation. Our results indicate that both the ferrihydrite morphology and reactivity is strongly influenced when coprecipitated with soil organic matter.