

## Overview of the role of surface defects on goethite's biogeochemistry

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Iron (Fe) oxides participate in a variety of environmental processes, influencing the cycling of C, N, S, the speciation and mobility of contaminants and ultimately the respiration of microbes. Significant advances have been made in understanding the redox reactions between soil and groundwater. These redox reactions, especially the Fe(II)-Fe(III) oxide electron transfer, ultimately demonstrate that the oxidation of an Fe(II) that sorbs onto the mineral leads to the formation of a new layer similar to the original mineral. Despite substantial experimental evidence of Fe(II)-Fe(III) oxide electron transfer, computational chemistry calculations suggested that oxidation of sorbed Fe(II) by goethite is kinetically inhibited, unless surface defects are present. Here we explored the connections between surface defects and Fe redox chemistry and provided an overview of our findings. Specifically, we investigated how surface defects influence: (i) Fe(II)-Fe(III) electron transfer, (ii) the continuity of Fe(II)-Fe(III) electron transfer and (iii) microbial Fe(III) reduction. By using a hydrothermal treatment to remove defects and a suite of experiments with Fe isotopes we were able to demonstrate that surface defects play a commanding role in Fe(II)-goethite redox interaction, as predicted by computational chemistry. We also demonstrated that reaction with Fe(II) inhibits further electron transfer between Fe(II) and goethite. Importantly, however, transient geochemical fluctuations may restore Fe(II)-goethite electron transfer. Finally, by using isotope-labelled microbial respiration experiments, we were able to demonstrate that minerals with defects are a preferential electron acceptor for microbial respiration in the presence of an extracellular electron shuttle. Ultimately, the investigation on the effects of defects on the redox reactions involving iron minerals provided new insights into the mechanism allowing us to make better predictions of their behavior. In the environment, iron minerals likely contain defects, suggesting that crystalline phases such as goethite may be both more reactive and important bioavailable sources of Fe(III) than currently considered.