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Size-dependent reactivity of Fe(III) (oxyhydr)oxides towards microbial and electrochemical reduction

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Fe(III) (oxyhydr)oxide minerals (hereafter referred to as iron oxides) such as goethite (α-FeOOH) and hematite (α-Fe_2O_3) are ubiquitous in nature and influence the (bio)availability of trace elements and the fate of contaminants via redox reactions. Depending on environmental conditions during formation, iron oxide particle size varies from nano- to micrometers. Beyond changes in specific surface area, the size-dependent behavior of these minerals is often non-linear and strongly affected by molecular-level interactions. Therefore, it is difficult to predict the properties of nanoscale iron oxides based on comparison with corresponding bulk minerals. Here, we study the size-dependent reactivity of iron oxides towards microbial and electrochemical reduction. In this work, we synthesized goethite and hematite with a broad range of sizes (20-1000 nm for goethite and 5-400 nm for hematite) and characterized them with XRD, Mössbauer spectroscopy, electron microscopy and BET surface area analysis. We conducted microbial reduction experiments using the Fe(III)-reducing microorganism *Shewanella oneidensis MR-1* (pH 7), and mediated electrochemical reduction experiments (pH 7, -0.49 V vs. SHE) to determine how the size influences the rates and extent of Fe(III) reduction and to compare the heterogeneity in reactivity towards biotic and abiotic reduction. Our results suggest that available surface area is the dominant factor controlling the electrochemical reduction of iron oxides. However, in microbial reduction, factors such as particle aggregation and electron transfer pathways between microbes and minerals also play a role on the process. For example, nanoscale goethite (20 nm diameter) was microbially reduced faster than 60 nm-sized goethite particles, even after accounting for surface area. In addition, iron oxides coexist in different sizes and mineral phases in nature. Hence, we used ^{56}Fe isotope-labeled particles to investigate whether there is a difference in reduction rate and extent when different-sized iron oxides are present together. Specifically, we performed microbial/electrochemical reduction experiments with a mix of different-sized goethite hematite. Our project will help elucidate the relationship between surface area and reduction kinetics at the nanoscale and understand differences in reducibility of iron oxides between single mineral systems and coexisting mineral systems that are more environmentally relevant.