

## Assessing iron oxide reduction using mediated electrochemical analysis

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The reduction of iron (oxyhydr-)oxides (hereafter Fe oxides) to ferrous iron plays a key role in many important biogeochemical electron transfer processes and in pollutant redox transformations. To date, most studies relied on using bulk chemical reductants or dissimilatory metal-reducing bacteria to investigate Fe oxide reduction. However, since these approaches offer only poor control on the thermodynamics of Fe oxide reduction, linking Fe oxide structure to reactivity has been challenging.

In this contribution, we demonstrate the applicability of mediated electrochemical reduction (MER) — a technique that employs dissolved electron transfer mediators to facilitate redox equilibration during electrochemical measurements — to directly quantify the reduction rates and extents of suspended Fe oxide particles under well-defined thermodynamic conditions set by solution pH (varied between pH 5 and 8 at constant applied reduction potential of  $E_h = -0.35\text{V}$ ), applied  $E_h$  (varied between  $-0.53$  and  $-0.17\text{V}$ , at pH 7) and the activity of dissolved ferrous iron.

MER of 6-line ferrihydrite was fast and complete at all studied pH and  $E_h$ , consistent with the highly exergonic reaction conditions in all systems. Conversely, MER of goethite and hematite showed decreasing rates and extents of reduction with increasing pH and increasing  $E_h$ , consistent with a decreasing thermodynamic driving force for reduction. A thermodynamic control of goethite and hematite MER was substantiated by good agreement in the decreases of their surface-area normalised reduction rates with increasing reduction free energies to less negative values. The results from the analyses of Fe oxides highlight the capabilities of MER to link rates and extents of Fe oxide reduction to reduction thermodynamics and, thus, to Fe oxide structure.

In an outlook, we will show that MER can also be used to characterise changes in the rates and extents of Fe oxides in dynamic systems: the pH-dependent conversion of 6-line ferrihydrite to goethite and magnetite in the presence of ferrous iron can be directly monitored using MER, which shows decreasing rates and extents of oxide reduction with increasing extent of mineral transformation.