

## Electrochemical characterisation of microbial Fe(III) reduction

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Extracellular electron transfer by Fe(III)-respiring bacteria is often accompanied by mineral dissolution, secondary (bio)mineralization and changes to Fe reactivity and bioavailability, and exerts significant controls on the availability and toxicity of contaminants and major and trace elements. As a consequence, there is a requirement to assess rates and extents of Fe(III) reduction in terms of thermodynamic parameters of key Fe-bearing minerals.

Here, we show that a new amperometric technique - mediated electrochemical reduction and oxidation (MER/MEO) - allows the direct and sensitive quantification of both Fe(III) and Fe(II), as well as the apparent standard reduction potential of the mineral-Fe system, without the sample preparation or acid digest steps required for conventional colourimetric assays. First, we demonstrate that this technique can be used to quantify the extracellular electron transfer to ferrihydrite by *Shewanella oneidensis*. In addition, MER analyses over a pH range of 5 to 7.25, complemented by TEM and XRD, reveals that the rates and extents of microbial reduction can be related to reaction free energy as the mineral-Fe(II) system evolves.

Second, amperometric analyses performed over a wide range of potentials ( $E_H$  -0.6 to +0.6V SHE) indicate that the type of interlayer cation (e.g. Na<sup>+</sup> vs. K<sup>+</sup>) alters the electron-accepting properties of an Fe-rich smectite, SWa-1. To address the impact of interlayer cations and altered interlayer accessibility for electron transfer on microbial reduction dynamics and redox driven structural transformations, we probe mineral redox properties and follow the chemical (e.g. dithionite) versus enzymatic reduction of Fe(III) in Na- and K-exchanged SWa-1 incubated with *S. oneidensis* and *Geobacter sulfurreducens*.

The proposed analyses pave the way toward a more comprehensive understanding of thermodynamic driving forces which define microbial Fe(III) reduction in poorly soluble Fe-bearing minerals and, in turn, reactivity towards contaminants and trace elements.