

Understanding electron transfer at Fe-bearing mineral surfaces to optimize contaminant remediation

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In order to use natural or engineered materials for contaminant sequestration, it is necessary to fully characterize the material in terms of its structure and reactivity. Even within a nanoparticle, elemental distribution can vary from the interior to the surface, thus surface sensitive techniques must be employed to probe mechanisms of interaction between the mineral phase and chemical/biological components present in the subsurface environment.

Here, we present the use of model materials, as well as field samples, in combination with high-resolution spectroscopic and microscopic capabilities, to interrogate interfacial reactivity of Fe-bearing minerals with redox-active contaminants and electron-transfer proteins. A novel and well-characterized set of Fe_{3-x}Ti_xO₄ titanomagnetite nanoparticles was selected as the model mineral system. Replacement of Fe(III) by Ti(IV) in the lattice yield a naturally "tunable" solid-state Fe(II)/Fe(III) ratio, which in principle controls the thermodynamic reduction potential of the mineral phase. Also, the high specific surface area of the nanoparticles greatly improves experimental sensitivity to contaminant/protein interaction and accompanying changes to the solid surface. Nanoparticle properties such as size, morphology, crystallinity, element and valence distribution are characterized by STEM-EELS and micro-XRD. X-ray magnetic circular dichroism (XMCD) is used to distinguish between Fe oxidation states and crystallographic sites at the reactive surface with a probing depth of ~4.5 nm (~5 unit cells).

The mechanism and rate of heterogeneous electron transfer from Fe_{3-x}Ti_xO₄ nanoparticles, microparticles, and natural materials, isolated from Hanford nuclear reservation sediments, to Tc(VII) is investigated. Electron transfer at microbe-nanomaterial interfaces is characterized by examining the oxidation of Fe_{3-x}Ti_xO₄ nanoparticles by the bacterial electron transfer enzyme MtoA, a decaheme *c*-type cytochrome.

Cr isotope fractionation in reducing continental margin sediments

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Sedimentary records of redox sensitive metals are commonly used to assess the availability of dissolved oxygen in seawater. However the interpretation of such records is complicated by the fact that metal concentrations can also be influenced by factors such as the detrital flux and primary productivity. Redox sensitive isotopic variations may therefore provide a more robust means of assessing seawater oxygenation. The chromium (Cr) isotope system has considerable promise in this regard as the reduction of soluble Cr(VI) to insoluble Cr(III) has been shown to be associated with reversible isotopic fractionation [1]. Determining when and how Cr isotopes are fractionated in marine sediments will improve our understanding of the mechanisms that control Cr removal from seawater, and will provide a framework for interpreting redox-related variations in the δ⁵³Cr composition of seawater [2].

In order to evaluate the sensitivity of the Cr isotope system to variations in sedimentary conditions we present δ⁵³Cr data from continental margin sediments deposited under a range of redox settings. Oxic samples come from MANOP site H in the eastern Pacific Ocean, where a down core profile is used to assess the behaviour of δ⁵³Cr through the Mn reduction zone. Suboxic samples are analysed from sites along the Californian margin, while anoxic samples come from surface sediments deposited off the coast of Mexico. Previous characterisation of sediment properties at these localities enables variations in δ⁵³Cr to be compared to the behaviour of other redox sensitive metals such as molybdenum (Mo) and uranium (U) [e.g. 3, 4], and helps validate the utility of the Cr isotope system as a tracer of dissolved oxygen in seawater.

[1] Ellis *et al* (2002), *Science* **295**, 2060-2062. [2] Frei *et al* (2009), *Nature* **461**, 250-253. [3] Poulson-Brucker *et al* (2009), *G-Cubed* 10(6), Q06010. [4] McManus *et al* (2006), *GCA* **70**, 4643-4662.