

Electron-transfer rates in magnetite surfaces: Implications for Uranium reduction

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The reductive adsorption of U^{6+} in solution by Fe^{2+} in magnetite (Fe_3O_4) retards radionuclide transport in some sub-surface environments, and helps minimize radionuclide release from waste-packaging materials surrounding spent nuclear fuel. Experimentally, magnetite reduces U^{6+} to U^{4+} , however reduction is not always complete, resulting in mixed-valent U on the magnetite surface [1, 2]. In order to explore whether heterogeneous electron transfer could be a rate-limiting step in this process, we combine quantum-mechanical methods with Marcus theory to calculate the energetics and rates of individual electron transfer events for near-surface iron-dimers (e.g., between Fe^{2+} and Fe^{3+} in magnetite), and for uranyl complexes bonded to iron-dimers in an inner-sphere fashion.

At room temperature, charge hopping occurs on the octahedral sub-lattice of magnetite, which is populated by equal numbers of Fe^{2+} and Fe^{3+} atoms. A localized-electron, computational approach is used to determine charge ordering in bulk magnetite and in hydrated and vacuum-terminated (001) slabs. Ferric-ferrous iron dimers are extracted from bulk, slab and surface environments surrounded by different Fe^{2+} and Fe^{3+} distributions in order to determine the effect of local charge ordering and coordination environment on rates of electron transfer. Rates calculated for bulk and near-surface environments span two orders of magnitude, while those calculated for the uppermost surfaces span six-orders of magnitude. The latter range is attributed to greater distortion of bond lengths in surface environments relative to the bulk, and the presence or absence of water. Such differences in electron-transfer rates may influence the kinetics of abiotic or microbially-mediated oxidation and reduction reactions at magnetite surfaces.

Finally, a cluster approach is used to evaluate the rate of electron transfer between U^{6+} and Fe^{2+} -dimers. *Ab initio* total energy calculations suggest that a change from a uranyl-like conformation to a more highly-coordinated structure may be necessary in order for the reduction reaction to proceed in an energetically favorable manner beyond U^{5+} to U^{4+} .

[1] Missana *et al.* (2003) *J. Colloid Interface Sci.* **261**, 154-160. [2] Scott *et al.* (2005) *GCA*, **69** (24) 5639-5646.

The effect of induced sediment-surface redox conditions on fluxes of organic carbon, phosphate, iron, and manganese over the sediment-water interface of coastal sediments

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The role of seasonal anoxia in coastal compound budgets and nutrient fluxes is unknown. Our objectives were to determine the effect of onset of anoxia and subsequent reoxygenation on sediment-to-water fluxes of DOM, PO_4^{3-} , Fe^{2+} , and Mn^{2+} . To date, no study has determined the effect of inducing anoxia and then restoring oxic conditions on fluxes of this suite of organic and inorganic compounds.

We carried out a laboratory incubation of surface sediment with five mesocosms during 35 days. The control treatment consisted of three mesocosms amended with O_2 . The oxygen-depleted treatment consisted of two mesocosms that developed anoxia by bacterial consumption of oxygen during OM degradation. The oxygen-depleted treatment was reoxygenated during the last seven days of the experiment.

Benthic fluxes of DOC, POC, PO_4^{3-} , and Fe^{2+} increased during anoxia in the oxygen-depleted treatments. The DOC and Fe^{2+} concentrations started increasing at onset of anoxia and increased concomitantly towards a maximum at day 12. The concomitant increases in Fe^{2+} and DOC concentrations may have indicated dissolution of $FeOOH$ and associated DOC. The concentration maxima in Fe^{2+} and DOC were followed by concentration decreases of both compounds, which could have been a result of coprecipitation of DOC with Fe-containing minerals. In contrast, the PO_4^{3-} concentration increase occurred several days after onset of anoxia. We suggest that the delayed PO_4^{3-} concentration increase was a result of formation of $Ca_{10}(PO_4CO_3)_6F_2$, carbonate fluoro apatite. Restoring oxic conditions resulted in a decrease in DOC, POC, and PO_4^{3-} concentrations.