

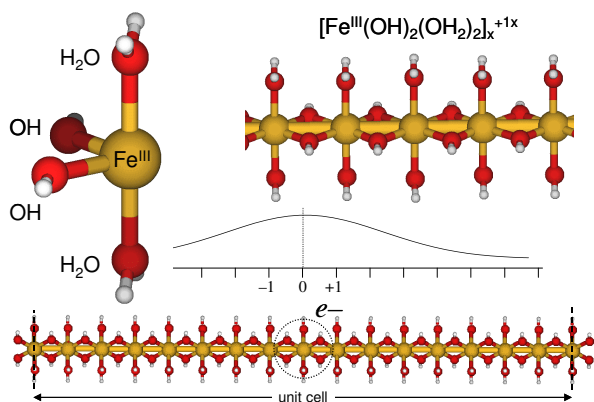
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Electron transfer in iron oxides: Theoretical assessment of electron hopping rates

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Rates of Fe(II/III) electron transfer (ET) reactions have an important impact in a wide range of abiotic and biotic geochemical processes, yet remain poorly understood partly because ET barriers are highly dependent on the local structural setting. Here we introduce a versatile atomistic kinetic model for Fe(II/III) reactions based on a combination of Marcus ET theory and quantum mechanical calculations. We illustrate the model for the transport of conduction electrons through the hematite lattice and also for the trioctahedral Fe sheet in annite. Electron hopping from one metal site to another across shared octahedral edges is modeled as a valence alternation of Fe cations, consistent with the small polaron model. Localization of a conduction electron at an Fe lattice site is accompanied by calculated Fe-O bond length increases that gives rise to a large internal component of the reorganization energy. For ET in hematite parallel to the basal plane, the electronic coupling matrix element is computed to be 0.20 eV, which leads to characteristic ET times of 10^{-12} sec [1]. In contrast, the coupling is small in annite, leading to characteristic ET times that are six orders of magnitude slower [2]. In annite, M1 Fe sites are predicted to be efficient electron traps and charge transport should occur by nearest-neighbor electron hops along the M2 Fe sublattice. Calculated electron mobilities agree well with experimental estimates. The effects of compositional defects on the ET rates can be significant and will be discussed.



References

- [1] Rosso K.M., Smith D.M.A., and Dupuis M. (2003) *JCP* **118**, 6455-6465.
[2] Rosso K.M. and Ilton E.S. (2003) *JCP* **119**, 9207-9218.

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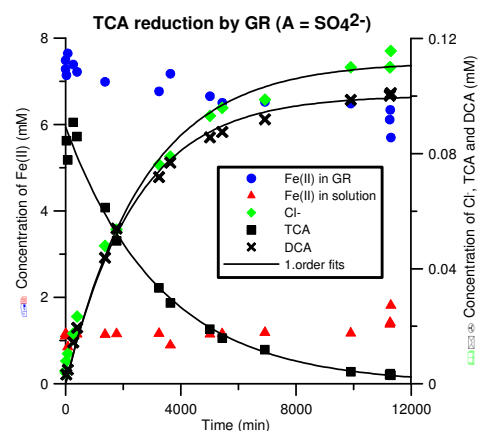
Reductive dechlorination of trichloroacetic acid by green rusts

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Trichloroacetic acid (TCA) is a widely distributed phytotoxic substance produced both by natural and industrial processes. In soils TCA may be reductively degraded to less chlorinated products, e.g. dichloroacetic acid (DCA). Previous studies have shown that layered mixed-valence iron hydroxides (green rusts, GR; $\text{Fe}^{\text{II}}_4\text{Fe}^{\text{III}}_2(\text{OH})_{12}\text{A} \cdot x\text{H}_2\text{O}$, $\text{A} = \{\text{SO}_4^{2-}; \text{CO}_3^{2-}\}$) which may be present in anoxic soils, can dehalogenate tetrachloromethane [1]. In this study we found that GRs (pH ~ 8) can reduce TCA to dichloroacetate (DCA) with the concurrent oxidation of GR to spinel-type iron oxides (see figure). Further reduction of DCA was found insignificant. The reaction follows 1.order kinetics with respect to TCA:

$$r = k_{\text{obs}} \cdot [\text{TCA}]$$

At initial concentrations of Fe(II) in GR of 5 - 10 mM, the surface-area normalized k_{obs} values for the GRs with CO_3^{2-} and SO_4^{2-} as the interlayer anions were $3.1 \cdot 10^{-5} \pm 3.1 \cdot 10^{-5} \text{ min}^{-1} \text{ m}^2 \text{ L}$ and $7.8 \cdot 10^{-6} \pm 1.79 \cdot 10^{-6} \text{ min}^{-1} \text{ m}^2 \text{ L}$, respectively. The rate constants are of similar size as the rate constants found for nitrate reduction by GRs [2] and demonstrates that Fe(II) in solid phases needs to be considered with respect to the geochemical balances of TCA.



References

- [1] Erbs, M., Olsen, C.E. and Hansen, H.C.B. (1999) *ES&T* **33**, 307-311.
[2] Hansen, H.C.B. et al. (1996) *ES&T* **30**, 2053-2056.