# Theoretical Evaluation of Electron Transfer Kinetics at Fe(III)-Oxide Surfaces with Implications for Microbial Respiration

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The respiration of dissimilatory Fe(III)-reducing bacteria involves a poorly understood heterogeneous electron transfer (ET) step to terminal acceptor sites at Fe(III)-oxide surfaces. Recent discussion centers around the relative efficacy of Fe(III) reduction by ET from outer membrane cytochromes versus exogenous electron shuttle species. Because the kinetics of elementary ET reactions at surfaces are difficult to access experimentally, theoretical treatments could be of great utility for developing a mechanistic understanding of macroscopically observable kinetics.

For the purposes of building atomistic kinetic models to evaluate hypothetical ET reactions at various Fe(III)-oxide surfaces, we utilize a combination of Marcus theory and ab initio calculations. This approach has allowed us to compute the physical quantities controlling rates of ET involving surface and near-surface Fe(III) sites at hematite (001) and (012), and magnetite (100) and (111) surfaces. Marcus principles relate the activation free energy ($\Delta G^*$) to the driving force ($\Delta G^o$) and the energy to reorganize bonds in the inner spheres of the reactants ($\lambda_{is}$) and the surrounding dielectric media in the outer sphere of the encounter complex ($\lambda_{os}$). Using known possibilities for the surface structures and including sorbed water species, we utilize a molecular orbital cluster-based strategy to calculate the $\lambda_{is}$ explicitly for all Fe(III) site possibilities at the density functional level of theory. The cluster calculations also provide estimates of the relative redox potentials for each site leading to estimates of $\Delta G^o$. $\lambda_{os}$ is calculated using Marcus continuum equations.

We have applied these methods to estimate rates of heterogeneous ET reactions from anthraquinone 2,6 disulfonate (AQDS), a model electron shuttle compound, and from model outer membrane cytochromes (OmcA) to acceptor sites on the different of Fe(III)-oxide surfaces. Primary factors which differentiate the ET rate are the reorganization energy terms and the density of Fe(III) sites in the near-surface region. For the different possible sites at the various surfaces, $\lambda_{is}$ may be generally ranked according to $Fe_{surface} > Fe_{bulk}$ because of increased degrees of freedom at the surface to accommodate conformational changes in Fe-O bonding through the $Fe^{2+/3+}$ transformation. The ET distance is a primary factor in differentiating the ET rate between AQDS to surface sites from OmcA to surface sites. The model results are in qualitative agreement with recent experimental observations of bacterial growth on these surfaces being used as the sole electron acceptor.

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# Geochronology of the Peloritani Mountains (Sicily): Hercynian, pre-Hercynian, but not Alpine

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The Peloritani Mountains are a fragment of the Hercynian belt whose metamorphic units show different metamorphic paths. The Ar-Ar, U-Pb stepwise leaching and Rb-Sr data reported here demonstrate that the medium-high grade units (Aspromonte and Mela Units) also differ in their geochronological evolution.

The main thrusting of the Aspromonte Unit over the lower grade units (Mandanici Unit) took place at 301±2 Ma. Brittle Tertiary reactivation of Hercynian thrust planes did not produce any rejuvenation of white micas.

The Aspromonte Unit is geochronologically heterogeneous. Proterozoic ages are preserved both in amphibole relics and in titanite from the Cumia sub-unit; Devonian amphibole and apatite ages are found in the Saponara sub-unit; Carboniferous amphiboles occur in other sub-units; no Tertiary amphiboles were formed. We propose to consider the chronologically heterogeneous sub-units as accreted pre-Hercynian terranes (microplates) amalgamated late during the Hercynian orogeny.

The Mela Unit amphiboles are Carboniferous, younger than those of the Aspromonte Unit, in parallel with the different P-T path which is characterized by pervasive retrogression of peak assemblages.

Micas in both units give scattered Mesozoic Ar-Ar and Rb-Sr ages, with evidence for heterochemical mica generations. We interpret them as a result of widespread hydrothermal circulation event(s).

Tertiary metamorphic minerals are generally absent, with the exception of a small area near Messina where biotite and muscovite underwent a complex recrystallization history in the interval 48-61 Ma.