

Large-scale simulation of molecular structure and electron transfer in microbial cytochromes

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This research seeks to understand rates and molecular mechanisms used by microbial multiheme c-type cytochromes (c-Cyts) for mediating extracellular Fe valence transformation, an important biogeochemical process affecting the availability and supply of reactive Fe (II) in subsurface environments. The structure of MtrF, an outer-membrane decaheme c-type cytochrome from an iron-reducing bacterium, has been determined by synchrotron diffraction measurements. Results show that the ten hemes of MtrF are organized into a unique 'wire cross', in which a staggered 65 Å octa-heme chain transects the length of the protein and is crossed at the middle by a 45 Å tetra-heme chain. Each heme is within 7 Å of its nearest neighbors, in principle permitting rapid interheme electron transfer.

Large-scale molecular dynamics simulations are being carried out to understand the free energy landscape for electron hopping along various trajectories of the wire cross. Using the technique of thermodynamic integration, relative redox potentials of all possible intraprotein electron transfer steps have been computed, which shows that upon possible electron entry into heme 5, only a 0.84 kcal/mol (1.4 kT) activation free energy barrier for electron transfer to heme 4 opposes otherwise net thermodynamically downhill heme-to-heme conductance to hemes 2, 7, and 10 at the protein-environment interface. It is therefore proposed that heme 5 is the input site of electrons from partner proteins MtrDE up the electron transport chain, and that MtrF transfers electrons down the chain directly to Fe (III)-oxides via highly solvent-exposed heme 10. The combined experimental and computational simulation activity is collectively providing a comprehensive understanding of bacterial outer-membrane c-Cyt functioning at the level of individual heme redox potentials, heme-to-heme electron transfer rates across the protein, and insights into dynamical effects of protein fluctuation and solvent reorganization on overall electron transfer conductance.

Reactive Fe(II) and electron exchange dynamics in iron oxides

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Ferrous-ferric electron exchange is central to the biogeochemical cycle of iron and determines iron forms and availability in the subsurface. For most environmentally relevant conditions this exchange involves interaction between soluble ferrous iron and solid-phase iron oxides and oxyhydroxides, with complex involvement of solid-state charge migration. Examples include Fe (II)-catalyzed transformation of Fe (III)-oxides and oxyhydroxides, and spinel ferrite nanoparticles acting as a mineralogic source and sink for reactive Fe (II) due to their topotactic solid-solution property and stable multi-valent nature. This presentation focuses on the interdependence of Fe (II) fluxes at these mineral-water interfaces with structural and electronic properties of mineralogic iron oxide forms. Using combined experiment and computational molecular simulation, we examine the underlying mechanisms of observed complete iron atom exchange without change in mineralogy, crystallinity, crystal size or shape between an aqueous Fe (II) pool and well-defined goethite (FeOOH) crystallites, the accessibility of solid-state Fe (II) in titanomagnetite (Fe_{3-x}Ti_xO₄) nanoparticles in which the structural Fe (II)/Fe (III) ratio is intentionally tuned by the Ti (IV) content, and the highly time-resolved dynamics and fate of Fe (II) electrons photoinjected into maghemite (Fe_{8/5}O₄) nanoparticles. Aspects covered will include thermodynamic energy requirements for bulk crystal conduction and possible free energy sources sustaining bulk currents, ferrous iron adsorption energies at iron oxide surfaces and the kinetics of interfacial electron exchange, the structural dependence of ferrous-ferric electron exchange in the solid, and internal charge compensation mechanisms. These lines of research are collectively converging on a picture of rapid electron exchange dynamics between aqueous ferrous iron and iron oxides, with broad-reaching implications for the biogeochemistry iron in the subsurface.