Direct electrochemistry of cytochrome c on oxide electrodes

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Redox metalloproteins involved in biochemical electron transfer can interact with mineral surfaces. Cytochromes, and in particular cytochrome c (mitochondrial), have been used in the construction of biosensors based on semiconducting iron oxide; photovoltaic devices have been built based on cytochrome c sensitized titanium oxide nanoparticles, and cytochromes have been used as environmental remediation catalysts for reductive dehalogenation of contaminants (e.g., TCE). It has been proposed that c-type cytochromes anchored to the outer membrane of dissimilatory iron-reducing bacteria effect electron transfer to solid ferric minerals. Electron transfer between an oxide and the cytochrome is important in all of these settings. A key properties of cytochromes is "redox-linked conformation change" in which conformational changes of the protein affect redox potentials. The interaction of cytochromes with surfaces can induce conformational changes that trigger electron transfer. Here, we use cytochrome c a model cytochrome in an investigation of the effects of conformation change on reduction potential in the presence of oxide surfaces.

In this presentation, direct electrochemistry of cytochrome c using iron oxide electrodes is demonstrated. The results are compared and contrasted to those for Indium-doped tin oxide electrodes, which have been used previously. Cyclic voltammetry shows that the reduction potential of cytochrome c on hematite electrdoes is similar to that of the native protein, suggesting that there is little or no denaturation of the protein at the electrode surface. This is in agreement with results for other hydrophilic electrodes, and in contrast with results for certain hydrophobic and metal electrodes. We therefore used tin oxide electrodes in subsequent studies of denaturation.

Following biochemical studies of guanidine-induced cytochrome c denaturation, we observed the direct electrochemistry of cytochrome c on tin oxide electrodes in the presence of varying concentrations of guanidine. The "native" reduction potential disappeared with increasing guanidine concentration, and two new reduction waves at more negative potential appeared (with higher current than the native reduction peak). These two peaks can be attributed to a "molten globule" intermediate unfolding state at intermdiate reduction potential, and to a fully unfolded state at the most reducing potentials.

Transformation of hematite into magnetite – How do bacteria contribute?

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Formation of secondary iron minerals frequently accompanies dissimilatory iron reduction. In particular, the formation of magnetite has received much attention as it affects the magnetic characteristics of the medium and because of the high capacity of biogenic magnetite to reduce environmental contaminants. However, the precise role of bacteria in magnetite formation during iron reduction is still enigmatic. The abiotic transformation of highly reactive iron oxyhydroxides, such as ferrihydrite and lepidocrocite, into magnetite under environmentally relevant conditions is well documented. For iron oxyhydroxides of low reactivity, such as goethite and hematite, no such transformation has so far been reported. In incubations with the bacteria *Shewanella putrefaciens* we observed the formation of magnetite as a product of bacterial reduction of nanoparticulate hematite. This model system thus appears to be a very suitable to unravel the role of bacteria in the formation of magnetite. We performed incubation experiments to constrain the optimal conditions for magnetite formation. Magnetite formation was enhanced by relatively high dissolved carbonate concentrations, while relatively low concentrations of phosphate or arsenate inhibited magnetite formation. Experiments were also run in which a fraction of the hematite suspension was separated from the rest of the suspension in a dialysis bag. Bacteria were present outside, but not inside the bag. Surprisingly, significant magnetite formation was observed inside the dialysis bag, but not outside the bag. These results suggest that transformation of hematite into magnetite is an abiotic process, with the role of bacteria restricted to the supplying of reduced iron. However, all attempts to induce magnetite formation from hematite in abiotic controls have not been successful so far. In the presentation, we will discuss possible mechanisms, which may explain how bacteria regulate the transformation of hematite to magnetite in the experimental systems. Furthermore, we will discuss the environmental significance of our observations.