

Interaction of cytochromes with oxide surfaces: Adsorption-induced conformation change?

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The interaction of redox metalloproteins such as cytochromes with oxides is relevant to certain biosensors, to sensitized photovoltaics, the use of cytochromes as environmental redox catalysts, and the respiration of certain bacteria. Here, we use mitochondrial cytochrome c (Mcc) as a model because it is well studied (with a wealth of comparative background information) and is known to adopt conformational states with redox properties similar to the native states of key bacterial cytochromes. A key question is that of adsorption-induced conformation change, because such change can alter the redox potentials of the cytochrome and thereby induce electron transfer.

The pH- and ionic strength-dependence of Mcc sorption on hematite is consistent with mainly electrostatic interaction. A narrow peak in adsorption occurs between pH 8.5 and pH 10, which are the point of zero charge of hematite and the isoelectric point of Mcc respectively. Adsorption is enhanced on the low pH side of this peak in the presence of aqueous phosphate. Sorption declines with ionic strength. However, adsorption is non-zero over a broader pH range, which suggests that other interactions play a role as well.

Contact-mode versus AC-mode AFM imaging shows that Mcc is loosely bound to the hematite surface, and electrochemical STM of Mcc on graphite reveals a possible electrochemical resonance peak along step edges (but not from terraces) that is consistent with native Mcc. Direct electrochemistry of Mcc on hematite and SnO₂ electrodes is consistent with native-state protein, but XANES/EXAFS data suggest the adsorbed protein is significantly different from the native state and similar to states induced by denaturants. Possibly the oxide surface becomes “coated” with denatured protein that then insulates it from direct interaction with further protein.

Sorption of proteins and other organic molecules can be studied using optical second harmonic generation (SHG), which will be demonstrated and discussed here. In summary, our results suggest that there are some subtle structural rearrangements that occur upon Mcc adsorption to oxide surfaces, and these can have a direct effect upon the electron transfer properties of Mcc.

Surface reactivity, bacteria, and metal isotope fractionation

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The use of isotopes to investigate mechanisms of mineral reaction, well established for the light isotopes, has only recently been attempted with transition metal isotopes. Isotopic fractionation during mineral-water reaction could elucidate complex mineral reactions under abiotic and biotic conditions. For example, during adsorption of Fe(II) onto goethite under anaerobic and abiotic conditions, isotopic fractionation occurs such that sorbed Fe becomes isotopically heavy. The addition of a siderophore affects the fractionation, perhaps suggesting that the siderophore effectively blocks the complexation of ⁵⁶Fe(II) with surface sites on goethite. *In vitro* reduction experiments show that the membrane fraction of an iron-reducing bacterium could also have a similar effect as the siderophore, perhaps indicating complexation reactions between Fe(II) and membrane fractions. However, isotopic mass balance suggests that sorption of Fe(II) at the surface is accompanied by increasing incorporation of structural Fe within the goethite. We are investigating how the time-dependent incorporation of Fe at the mineral surface affects metal isotope fractionation in order to clarify the processes of aging of goethite in aqueous solutions with and without the presence of dissimilatory iron-reducing bacteria. Such isotopic investigations provide a new probe to elucidate mineral-water-bacteria reactions.