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Interaction of redox metalloproteins with hematite surfaces

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Proteins that catalyze electron transfer between organisms and ferric mineral surfaces can in some cases be thought of as nanomachines. For example, adsorption-induced unfolding of a cytochrome on a gold electrode results in a shift in the reduction potential of the cytochrome by nearly 400 mV to the negative, to a point coincident with the base of the hematite conduction band. Thus, unfolding of reduced cytochrome c on a hematite electrode would tend to promote electron transfer to the hematite conduction band. In another example, redox-induced movement of iron sulfur proteins (ferredoxins) may point toward an extension-retraction mechanism for interaction with a mineral surface in concert with cytochromes. One study shows that an iron-sulfur protein is part of the DIRB iron reduction process and is associated with the outer membrane. Ferredoxins have been shown to catalyze electron transfer between an oxide surface and cytochrome P450. Such processes may be important in understanding the biochemical pathways utilized by dissimilatory iron reducing bacteria (DIRB) in Fe(III) reduction.

In these examples, ferredoxin and c-type cytochrome act as conformationally "triggered" nanomachines in which mechanical changes in the folding or orientation of the molecules is key to their reactivity. It has been suggested that these proteins could be utilized, separately from the organisms that synthesize them, in environmental remediation strategies such as reductive dehalogenation. To realize this potential, however, much more must be learned about the protein-iron oxide interaction.

Here we take initial steps in the extension of such studies to interaction of c-type cytochrome and Fe-S protein with hematite electrode surfaces.

Adsorption of c-type cytochrome on hematite is quite strong, and more extensive at high pH than at low pH. AFM imaging of adsorbed cytochrome layers in aqueous phosphate solutions reveals layers of aggregated cytochromes that are relatively difficult to remove from the surface. We have also conducted cyclic voltammetry experiments using hematite electrodes in aqueous cytochrome and ferredoxin solutions. The reduction and oxidation peaks of the adsorbed proteins shifts with surface coverage, which is qualitatively consistent with the behavior of these proteins on metal electrodes and their apparently environment-dependent conformation changes.

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Packing schemes of cavities in selected clathrasils and zeolites and their analogues in crystal structures

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Sizes of cavities and their packing schemes in edingtonite, natrolite, paulingite, sodalite melanophlogite, dodecasil 3C and 1H were studied by means of least squares fitting of circumscribed spheres to them. Resulting packing of spheres of different diameters was analysed by the coordinates of their centers, volumes and sphericity and interpreted by comparing with analogues found among compound and alloy structures. The topology of the cavities are described qualitatively by 3D-imaging of the structures formed by the cavities.

Edingtonite and **natrolite** have very similar types of cavities but the packing schemes are different. Both are built from two types of cavities, tetragonal scalenohedra and cavity [8⁶]. The latter make two sets of intersecting channels delimited by 8-rings. The free diameter of these rings is 2.8 Å. The [8⁶] cavities have different shape and packing in the two structures.

Paulingite has a cubic arrangement of seven different types of cavities. The largest cavity, a great rhombicuboctahedron [4¹²6⁸8⁶] (df = 11.02 Å), in a body centered configuration, is interspaced by the other six types of cavities (df = 5.1 Å – 8.2 Å) arranged in a complex pattern. In this structure there are three non-intersecting channel systems, the two broadest are identical and one is different. Cavity arrangements mimick sodalite and modified perovskite structures.

Sodalite has only one type of cavity in the cubic structure, a truncated octahedron [4⁶6⁸] (df = 6.4 Å) arranged in a cubic closest packing or ABC stacked along [111]. The coordination of every such octahedral cavity is 8 + 4 cavities, resulting in rhombododecahedral coordination. This arrangement of cavities are analogous with the packing of atoms in α-Fe structure types.

Melanophlogite, dodecasil 3C and **1H** are all clathrasils and have isolated cavities. They all have the same type of cavity among others in their structure; pentagonal dodecahedra [5¹²]. The packing of cavities in melanophlogite is analogous to the packing in the structure of Cr₃Si, where the Cr atoms form icosahedra about the Si sites. Dodecasil 3C has a cubic arrangement of [5¹²] cavities and this can be described as stacking of kagomé nets. This type of packing is an analogue to the packing in the cubic Laves phase MgCu₂. Dodecasil 1H has an arrangement of [5¹²] cavities in an AA stacking of kagomé nets and is analogue to the atomic structure type CaZn₅.