

Electrochemical STM of quinones at hematite (0001) surfaces: Adsorption of a biological electron "shuttle."

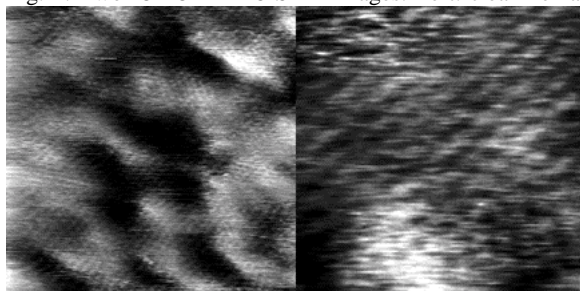
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Iron may be the second most common biological electron acceptor after oxygen¹. A variety of molecules with a quinone moiety are implicated in biological electron transport, including the reduction of Fe(III) by dissimilatory iron-reducing bacteria (DIRB) via electron shuttle compounds such as AQDS or humic substances. Our study was prompted by an interest in better understanding the mechanisms of electron transport from organisms to ferric mineral surfaces. As a first step, we have investigated the packing of hydroquinone molecules onto the hematite (0001) surface by electrochemical scanning tunneling microscopy (EC-STM).

We have imaged hematite (0001) surfaces in acidic aqueous solutions both in the absence and presence of varying amounts of hydroquinone. In the absence of hydroquinone a periodicity of ~0.5 nm is observed, characteristic of a clean hematite (0001) surface. In the presence of hydroquinone, a periodicity of $\sim 1.1 \pm 0.2$ nm is observed; this is similar to the periodicity observed for hydroquinone self-assembled monolayers on Pd (111)² and suggests that the quinone molecules may lie nearly flat on the hematite surface. Cyclic voltammetry studies also reveal current densities consistent with monolayer coverage. Following the structural suggestions of Soto et al.³ for hydroquinone on Pd(111), we speculate that the ring portion of the quinone coordinates surface Fe atoms in a η -6 configuration (on the hematite Fe-termination). This type of organometallic bonding is well known for other aqueous metal-ligand complexes. Some images show different quinone domains that may be related to the underlying Fe- and O-terminations of the hematite.

Fig. 1: Two 15x15 nm EC-STM images. Left: clean hematite



(Z scale 0.25 nm). Right: In the presence of a QH2 monolayer (Z scale 0.3 nm).

¹Lovley, D.R. (1991) *Microbio. Rev.* 55, 259-287.

²Kim, Y.-G., Soriaga, M.P. (2001) *J. Coll. Interf. Sci.* 236, 197-199.

³Soto, J.E., Kim, Y.-G., Soriaga, M.P. (1999) *Electrochem. Comm.* 1, 135-138.

Isotopic and elemental studies at a 50 nm scale with the NanoSIMS

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The NanoSIMS is a revolutionary new type of ion microprobe with a wide range of applications in areas like biology, material science and geochemistry. The first commercial NanoSIMS was installed in St. Louis in December 2000 and has since been used for a large number of microanalytical studies of extraterrestrial materials that would not have been possible with any other instrument. The most important features of the NanoSIMS are a primary beam diameter at the sample of less than 50 nm, a very high secondary ion transmission – even at high mass resolution – and the capability of measuring several secondary ion signals simultaneously.

One of the most fascinating aspects of the work with the NanoSIMS is that it can be used as a complement to the transmission electron microscope (TEM). Previous generations of ion microprobes could determine the isotopic compositions of micrometer-sized (and larger) sample components, but it was not possible to determine the mineralogical context of the observed features due to differences in size scales and sample mounting requirements. With the NanoSIMS it is not only possible to measure isotopes at a spatial resolution that comes close to that of the TEM, but it is possible to do so directly in TEM sections, without any modifications to the sample itself. A sample can first be characterized in the TEM and then be transferred to the NanoSIMS for raster imaging SIMS analysis. It is thus possible to directly correlate isotopic and mineralogical information of a sample and its sub-components on a scale of 50 nm. This combination of two powerful microanalytical techniques may become one of the strongest tools for the investigation of extraterrestrial materials.

References

See <http://presolar.wustl.edu/nanosims/> for more detailed information about the St. Louis NanoSIMS.