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The surface structure of α-Fe_2O_3 (001) by scanning tunneling microscopy: Implications for interfacial electron transfer reactions

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ABSTRACT

STM images of hematite (α-Fe_2O_3) (001) surfaces taken under a wider variety of conditions than in previous studies are presented. The results strongly suggest that only Fe sites contribute to the tunneling current. Specifically, corrugated unit-cell structures expected of the Fe sublattice are observed under both occupied- and unoccupied-states imaging conditions. A pattern of apparent vacancies was observed under conditions previously attributed to oxygen states; this is most simply interpreted either as Fe vacancies, or Fe sites whose electronic structure has been altered by a (unknown) coordinating anion, but difficult to explain as the oxygen sublattice. For unoccupied states imaging, decreasing the tip-sample distance (increasing the tunneling current) results in an image change from only one site per unit cell to three sites per unit cell. This is also relatively easy to explain using the Fe sublattice, but difficult to explain using the oxygen sublattice. These results are modeled using resonant tunneling theory, which shows that changes in bias voltage, tunneling medium, and tip-sample distance can have the observed effects only if Fe atoms are being imaged. The results have implications for modeling electron transfer across mineral-water interfaces more generally because they provide a framework for understanding site-specific electron transfer kinetic parameters.