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Aspects of goethite surface microtopography, structure, chemistry, and reactivity

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ABSTRACT

Goethite (010), (110), and (111) growth faces and (010) cleavage surfaces of large, natural single crystals, as well as a high surface area synthetic sample were characterized using various surface sensitive microscopies and spectroscopies. Differential interference contrast and atomic force microscopy characterization of the natural single crystal faces showed microtopography indicative of growth, dissolution, and cleavage. Low energy electron diffraction patterns of the goethite (010) surface exhibit sharp, intense diffraction spots, indicating long-range order on this important surface. These patterns have two-dimensional point group symmetry 2*mm*, consistent with an undistorted surface structure and unit-cell parameters $a = 4.62 \pm 0.14$ Å and $c = 2.99 \pm 0.08$ Å. These parameters equal the equivalent bulk cell dimensions given the uncertainties. Ultra-high vacuum scanning tunneling microscopy was performed on (010) cleavage faces, although the tunneling properties of the surface were very heterogeneous. Atomic resolution was not obtained; however, microtopographic images are identical to those collected with AFM. XPS spectra from the (010) faces of two natural samples as well as the synthetic powder all have peak maxima for Fe ($2p_{3/2}$) at 711.5 ± 0.1 eV. The O(1s) line originating from the goethite can be fit with two peaks with a chemical shift of 1.3 eV. The peak at higher binding energy (531.3 eV ± 0.1 eV) represents the protonated oxygen in the structure, and the peak at lower binding energy (530.0 eV ± 0.1 eV) represents the proton-free oxygen in the structure. Ab initio and semi-empirical models of the (010) surface suggest that cleavage occurs through the hydroxide plane at 1/4 *b* in the structure. This is contrary to cleavage through the oxide plane at 1/2 *b*, which has been assumed in several previous studies.