

## Transient surface potential gradients as a driving force for the bulk conduction mechanism of iron oxide recrystallization

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Most environmentally and biologically relevant processes are controlled by the acidity of the surrounding environment. For instance, mineral transformation, biogeochemical reactions, remediation and sorption dynamics are profoundly affected by a charge developed at mineral surfaces, which in turns depends primarily on the environmental pH.

Here we report simulation results obtained by using our recently developed constant-pH molecular dynamics (cpHMD) scheme, which we used to sample the time-dependent protonation imbalance between dominant crystal faces of two iron oxide minerals: goethite and hematite. Our cpHMD implementation employs a discrete protonation sampling with the advantage of replica-exchange in an explicit solvent model [1] and employing an accelerated sampling of protonation-space by a simulated-annealing algorithm [2].

In particular, we show that electrostatic potential gradients spontaneously arise between intersecting low-index crystal faces and across explicitly treated oxide nanoparticles. Our studies indicate that in some cases this fluctuating potential bias is large enough to sustain either a through-bulk or subsurface conduction of electrons provided that the electron-hopping rate is more frequent than the repolarization of exposed surfaces. Our results provide atomistic proof of spontaneous electrostatic gradients that couple nanoparticle morphology to charge flow, gradients that can couple bulk oxide conduction and its surface reactivity, as postulated previously by Yanina and Rosso [3]. The findings are also directly relevant to observed iron isotope exchange and inferred recrystallization of goethite nano- and microrods in contact with Fe(II) solution [4].

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