

# Transverse Electron Exchange Pathways in Nontronite from First Principles

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Fe-bearing clay minerals are important redox-active components of the subsurface and engineered barriers. Their interfacial reactivity plays an essential role in environmental processes such as biogeochemical cycling of various elements and contaminants. A detailed mechanism of Fe(II) surface speciation and interfacial electron transfer (ET) to Fe(III) in the octahedral sheet is still under debate despite its well-established consequence as one of the most effective reductants in anoxic environments. Recent developments have shown that edge-bound Fe(II) adsorption complexes at different surface sites may coexist on different edge facets. It has also been shown that complexes at ferrinol FeO(H) edge sites are the most energetically favorable and ET at these sites is facile and coupled to proton exchange. However, ET from Fe(II) sorbed to the external basal surface to octahedral Fe(III) is predicted to be predominantly thermodynamically uphill. A major enduring uncertainty in experiments is the extent to which Fe(II) can displace interlayer cations through cation exchange and there become a more effective reductant for Fe(III) in the octahedral sheet. Herein, we apply density functional theory (DFT) calculations to provide atomistic insights into the valence-interchange ET energetics and kinetics between Fe(II) in the interlayer site and an Fe(III) in the octahedral sheet, which reveals a lower ET barrier due to desolvation of interlayer Fe(II).

