

# Probing Interfacial Molybdate– Ferrihydrite Reactions Using Reactive Molecular Dynamics and Synchrotron X-Ray Spectroscopy

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Molybdenum occupies the active sites in metalloenzymes that support diverse metabolic processes in plants, animals, and microbes. Cellular uptake of bioavailable molybdate ( $\text{MoO}_4^{2-}$ ) enables biosynthesis of these metalloenzymes, which support global biogeochemical cycles that have shaped the biological and environmental co-evolution of Earth. Interfacial reactions with metal (oxyhydr)oxides often control molybdate mobility and bioavailability in soils, sediments, and water, yet our current understanding of these metal-mineral interactions remains incomplete [1]. Although surface complexation modelling and synchrotron X-ray spectroscopy have improved understanding of these interactions, these equilibrium approaches offer limited insight into complex reaction pathways [2].

Reactive Molecular Dynamics (MD) can simulate kinetic effects, surface dynamics, ion-ion interactions, and competitive adsorption using fundamental atomic properties derived from quantum mechanics. Our research explores interfacial molybdate-ferrihydrite interactions using coupled reactive force field (ReaxFF) simulations and synchrotron X-ray spectroscopy. Unlike classical MD, ReaxFF uses interatomic potentials to simulate bond formation and bond breaking through time. ReaxFF simulations can offer insight into reaction pathways that may involve protonation/deprotonation, hydration/dehydration, polymerization, and crystallization.

We developed ReaxFF simulations to examine interfacial reactions between aqueous molybdate and ferrihydrite. These simulations used aqueous  $\text{Na}_2\text{MoO}_4$  concentrations ranging from 0.025 to 0.2 M. The simulations are pre-equilibrated using harmonic restraints, followed by reactive equilibration and production. The resulting trajectories provide information on concentration-dependent electron density profiles, radial distribution functions, and diffusion coefficient profiles. Umbrella sampling is used to study the free energy profile of the adsorption.

Although classical MD and equilibrium models often treat both surfaces and molecules as rigid bodies, our preliminary simulations show that ferrihydrite undergoes restructuring in response to atom exchange. These dynamics modulate solute diffusivity at the mineral-water interface, and influence molybdate adsorption mechanisms on ferrihydrite. Ongoing efforts will incorporate synchrotron X-ray spectroscopy methods to substantiate ReaxFF simulation results. Overall, this research

aims to improve understanding of atomic-scale reaction dynamics that regulate Mo mobility and bioavailability globally.

[1] Zhang et. al. (2022), *Journal of Hazardous Materials*, 431, 128564.

[2] Satpathy et. al. (2021) *Environmental Science & Technology*, 55(13), 9352-9361.