Goldschmidt 2026 Abstract
https://doi.org/10.46427/gold2026.37012

Quantifying Thermodynamic and Structural Controls on Manganese Oxide Reduction Kinetics

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Manganese (oxyhydr)oxides are abundant redox-active minerals that influence diverse biogeochemical processes, yet their redox reactivity remains difficult to predict because it varies with both mineral structure and manganese oxidation state. This uncertainty limits our ability to forecast Mn-mediated transformations that affect carbon and nutrient cycling, contaminant dynamics, and trace metal(loid) behavior across environmentally relevant redox gradients.

Here, we quantified the reduction kinetics of three geochemically relevant manganese oxides—birnessite, manganite, and hausmannite—using extracellular electron shuttles with different redox potentials to systematically modulate the thermodynamic driving force for electron transfer. For each individual oxide, reaction kinetics were well described by the Gibbs free energy of reaction. However, the Pourbaix free-energy difference provided a distinct advantage as a predictive metric because it captures variations in pH and without requiring detailed knowledge of specific reaction pathways. This makes the Pourbaix free-energy difference especially useful in natural and experimental systems where the exact redox reactions are not fully constrained. To further resolve kinetic controls, we developed a coupled kinetic-mass transport model. The model indicates that electron-transfer rate constants differ among Mn oxide phases, whereas mass-transfer coefficients are comparatively similar. These results suggest that phase-dependent reactivity is controlled primarily by intrinsic interfacial electron-transfer properties at low thermodynamic driving forces and by mass-transport at high thermodynamic driving forces. We then applied classical nucleation theory to contextualize these differences, showing that the interplay between surface and bulk energies governs the dissolution barrier and helps explain phase-specific kinetic behavior.

Together, our results demonstrate that manganese oxide reduction kinetics are jointly controlled by reaction thermodynamics and mineral phase properties. More broadly, this work provides a mechanistic and generalizable framework for predicting the reactivity of redox-active minerals across diverse environmental conditions, with implications for understanding and modeling biogeochemical processes and the environmental fate of trace metal(loid)s.