

## **Proton-Promoted and Electron Transfer Dissolution of Nano-sized Hausmannite: Implications for Cr Cycling in Surficial Environments**

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Hausmannite, the fifth most common Mn oxide, is often found as small nanoparticle aggregates on the surface of stream sediments, making it critical to biogeochemical processes like heavy metal sorption and/or redox reactions, as well as microbial processes in surficial environments. Many of these, however, involve mineral dissolution through reduction of higher valence Mn (Mn(III)) to soluble Mn(II) in conjunction with oxidation of other redox-active heavy metals or organic compounds in the environment. Solution pH is also important in such environments to control not only the extent of hausmannite dissolution, but also the degree of hausmannite oxidation potential with heavy metals; yet these relations are not fully understood. Additionally, previous studies have only investigated hausmannite dissolution reactions using bulk materials, not nanoparticles, as would be found in natural environments.

In this study, we examine the rates of the proton promoted and electron transfer dissolution reactions of hausmannite both individually and in conjunction to identify any synergistic effects between the two pathways. Computer modelling and batch reaction experiments are conducted using chromium (Cr) as a redox-active constituent for the electron transfer reaction. Treatment variables include solution pH (3, 5, and 8) and initial Cr concentrations ( $1.67 \times 10^{-5}$ ,  $1.27 \times 10^{-4}$ , and  $1.27 \times 10^{-3}$  M). The results of batch reactions show that proton-promoted dissolution is dominant in pH 3, while Cr-induced dissolution in pH 8. Hausmannite dissolution rates at pH 5 indicate little synergism, as its rate is similar to the sum of the dissolution rate from both reactions. Thermodynamic models are run in the same conditions as batch experiments using HSC 5.1 for mineral and chemical species stability, and USGS PHREEQC 3.4 for equilibrium concentration. These results are then compared to the batch reaction results. Thus, the present study highlights the important role of hausmannite in Cr oxidation state and thus, toxicity in surficial environments. This also addresses the complexity of dissolution reactions at the nano-scale, and discrepancies between modeling and batch experiments for predictions concerning Cr behavior in nature.