

Science Made Possible

Growing Hematite, Slowing Pollution

PNNL scientists and university partners join forces to provide a new research direction

Understanding subsurface processes like the uptake and release of technetium and other redox-active contaminants at the molecular-level will play a major role in the future of environmental cleanup and pollution prevention. To elucidate one of the influential reactions involved in these processes—electron and atom exchange between aqueous Fe(II) and structural Fe(III) in minerals—researchers from Pacific Northwest National Laboratory (PNNL), the University of Iowa, and Yale University collaborated to connect previous, separate studies on this topic. Using x-ray diffraction and scanning electron microscopy tools at the Department of Energy's EMSL to make the connection, the team designed a set of experiments that used novel measurement approaches in one of the previous studies to characterize reaction products grown under the conditions of the other study.

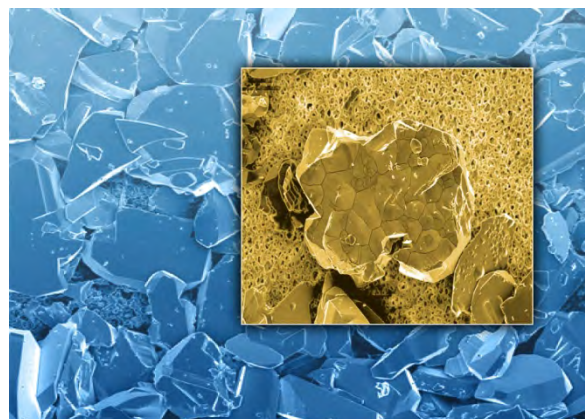
Prior to this work, separate studies by Larese-Casanova (from Yale) and Scherer (from Iowa) and Rosso and Yanina (from PNNL) had come to a similar conclusion: that Fe(II) interaction with hematite causes hematite deposition by $\text{Fe(II)}_{\text{ads}} \rightarrow \text{Fe(III)}_{\text{oxide}}$ interfacial electron transfer into the solid. However, differences in the experimental conditions and materials made it unclear whether the separate observations were both enabled by a bulk charge transport mechanism shuttling electrons from points of iron deposition to points of iron release. Using isotopically distinct pools of labeled Fe(II) and Fe(III) in hematite, the team was able to show using Mössbauer spectroscopy that Fe(II)-catalyzed hematite growth indeed involves electron and atom exchange facilitated by bulk charge transport, and concluded that this process is operative over a wide range of environmental conditions. The work helps build an improved conceptual model of iron oxides and oxyhydroxides in contact with aqueous Fe(II), with implications for coupled uptake and release of contaminants that interact with these common subsurface components.

Scientific impact: This work exemplifies a key collaboration within the research community that accelerates research in a promising direction, as well as addressing the EMSL science theme of geochemistry/biogeochemistry and subsurface science. Unraveling molecular-level phenomena like iron electron and atom exchange is a top research priority because of potential impact on DOE's environment-related missions.

Societal impact: Electron transfer among different chemical states and phases of iron has an impact on the makeup and movement of environmental pollutants such as byproducts of nuclear energy production. Converting pollutants into less dangerous forms and reducing their mobility underground protects ecosystems and humans from harmful contact.

Reference: Rosso KM, S Yanina, CA Gorski, P Larese-Casanova, and M Scherer. 2010. "Connecting Observations of Hematite ($\alpha\text{-Fe}_2\text{O}_3$) Growth Catalyzed by Fe(II)." *Environmental Science & Technology* 44(1):61-67. doi: 10.1021/es901882a

Acknowledgment: This work was funded by DOE's Office of Basic Energy Sciences, Geosciences Program, and a Nanoscale Interdisciplinary Research Team (NIRT) grant from National Science Foundation NIRT.



Making a Deposit: Scanning electron micrographs of synthetic tabular hematite powder shown before (blue) and after (gold) a 24-hour reaction in 1 mM FeCl_2 + 10 mM oxalic acid at pH 2.10, temperature 348 K. The deposition of pyramidal hematite island overgrowths is seen after the reaction.