

## **Capturing atom exchange fronts during Fe(II)-catalyzed recrystallization of Fe(III)-oxide minerals using isotopic mapping probes**

SANDRA D. TAYLOR\*, JIA LIU, XIN ZHANG, LIBOR KOVARIK, JOHN B. CLIFF, DANIEL E. PEREA, THAK SANG BYUN, DANIEL K. SCHREIBER, KEVIN M. ROSSO

Pacific Northwest National Laboratory, Richland, WA, USA

\*Corresponding author: sandra.taylor@pnnl.gov

The autocatalytic redox interaction between aqueous Fe(II) and Fe(III)-(oxyhydr)oxide minerals leads to rapid recrystallization marked, in principle, by an atom exchange (AE) front, according to bulk iron isotopic tracer studies. Here, we present recent developments using isotopic mapping probes that enable direct microscopic visualization and characterization of these AE fronts for the first time. Batch aqueous experiments were conducted to investigate Fe oxidative sorption and growth on hematite ( $\text{Fe}_2\text{O}_3$ ) microplatelets and goethite ( $\text{FeOOH}$ ) microrods reacted with  $^{57}\text{Fe}(\text{II})_{\text{aq}}$  as a tracer at circumneutral pH. Nanoscale secondary ion mass spectrometry (NanoSIMS) and atom probe tomography (APT) were then used to identify the spatial and temporal characteristics of iron AE fronts in individual crystallites. The collective findings clearly reveal that the interfacial redox reactivity depends on the specific crystallographic terminations and the presence of defects. For hematite,  $^{57}\text{Fe}$  distributions across single euhedral microplatelets suggest that Fe(II) strongly preferentially binds to (001) facets with up to  $10\times$  more  $^{57}\text{Fe}$ -enrichment than on edge surfaces such as (012). For goethite, APT shows the Fe(II)-catalyzed AE front was spatially correlated with defect content. High defect populations within the microrods, in the forms of nanovoids and intergranular boundaries, were observed using high resolution transmission electron microscopy. 3D APT reconstructions on cross-sections on prismatic surfaces revealed AE fronts with spatial characteristics consistent with these defect features. These powerful techniques and the knowledge gained are being applied to investigate recrystallization under corrosive, high temperature reaction conditions where AE is expected to be more complex and/or extreme. Ultimately, given very limited alternative analytical options, such studies are essential for gaining detailed insight into fundamental mechanisms controlling the redox recrystallization, trace element cycling, and even metallic alloy corrosion.