Chasing Atom Exchange Fronts During Fe(II)-Catalyzed Recrystallization of Hematite Using Isotopic Mapping Probes

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To obtain a detailed understanding of the mechanisms and atom exchange pathways involved in the Fe(II)-accelerated recrystallization of Fe(III) oxides, we employed isotopic mapping probes to explore Fe sorption and growth on hematite microparticles reacted with ^{57}Fe(II)$_{aq}$ as a tracer. Nanoscale secondary ion mass spectrometry (NanoSIMS) and atom probe tomography (APT) were used to obtain information on the depth and spatial distribution of growth and atom exchange fronts in individual crystallites. These powerful tools help establish the physical location(s) of growth and/or atom exchange fronts at the dynamic interface between aqueous ^{57}Fe(II) and Fe(III) (oxyhydr)oxides that can, in turn, be used to infer the recrystallization mechanisms. ^{57}Fe-enrichment at the hematite surfaces could be unambiguously resolved using both techniques, where in general results indicate apparent atom exchange front distributions are heterogeneous with respect to different crystallographic surface terminations and morphological features. NanoSIMS measurements of ^{57}Fe/^{56}Fe ratios across individual crystallites shows the basal surface (i.e. (001)) is up to 10×s more enriched relative to edge surfaces (e.g. {012}). Defects such as twin planes observed the least amount of enrichment, sometimes observing ^{57}Fe/^{56}Fe ratios at natural abundance. APT was used to spatially and temporally resolve ^{57}Fe-enriched regions on the basal surface at the sub-nanometer level. An average net adsorption of 3.2 – 4.3 ^{57}Fe atoms nm^{-2} was calculated. Furthermore, statistical analyses of the sorbed Fe distribution revealed heterogeneous atomic segregation and clustering, demonstrating that Fe sorption and growth on (001) occurs via nucleation of island-like features. These techniques provide an unprecedented means to explicitly characterize and visualize the distribution of sorbed Fe atoms on hematite surfaces, a scientific challenge that has persisted for nearly two decades. The collective findings shed new light on potential electron and atom exchange pathways between Fe(II)$_{aq}$ and dominant Fe(III) (oxyhydr)oxides minerals, with important and broad implications on our understanding biogeochemical cycling of elements in the environment.