

Resolving Atomic Transport Through Iron Oxide Under Irradiation Using Isotopic Tracers

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Structural materials in nuclear environments are exposed to complex and harsh conditions, including high temperatures, corrosive solutions, and irradiation. Material stability and likewise degradation are fundamentally controlled by atomic transport mechanisms. Here, we investigate the influence of radiation-induced, non-equilibrium point defect populations on mass transport within model oxide systems using isotopic tracers and atom probe tomography (APT).¹

An isotopically labelled hematite (α -Fe₂O₃) film was synthesized with ¹⁶O- and ¹⁸O-rich layers (>30nm and 10 nm, respectively) sequentially deposited via molecular beam epitaxy. A metallic Cr cap was also deposited to protect the underlying tracer layers during irradiation. One region of the film was proton irradiated to ~0.1 dpa at 450°C, and regions outside the beam spot provided a non-irradiated control of thermal annealing only. 3D APT was used to directly visualize the elemental and O-isotopic redistribution following both thermal and combined thermal and irradiation conditions. Complementary scanning transmission electron microscopy (STEM) was also employed to study the microstructural evolution.

Baseline characterization of the as-grown films shows the crystallinity and distinct O-isotopic stacking within hematite films (Figure 1A). After annealing and irradiation at 450°C (Figure 1B), structural changes are readily observed, where hematite (Fe₂O₃) has transformed to a magnetite (Fe₃O₄) phase and Cr cap has oxidized forming chromia (Cr₂O₃). These transformations are driven by the flux of O from hematite into the Cr metal. Within the hematite bulk, the 3D APT also reveals more subtle self-diffusion of ¹⁸O from the initial tracer layer from both thermal annealing and irradiation. Fitting the APT-measured ¹⁸O-concentration profiles using error function fits (Figure 2) enables quantification of diffusion coefficients, including slightly enhanced O mobility during irradiation than thermal annealing alone. Further improvements, particularly to prevent unwanted phase transformations and surface reactions, are being pursued to further improve our quantification of this apparent radiation enhanced O diffusion through hematite. Cation isotopic tracers (e.g. ⁵⁷Fe) are also being pursued to compare anion and cation mobility under irradiation through these model oxide systems.

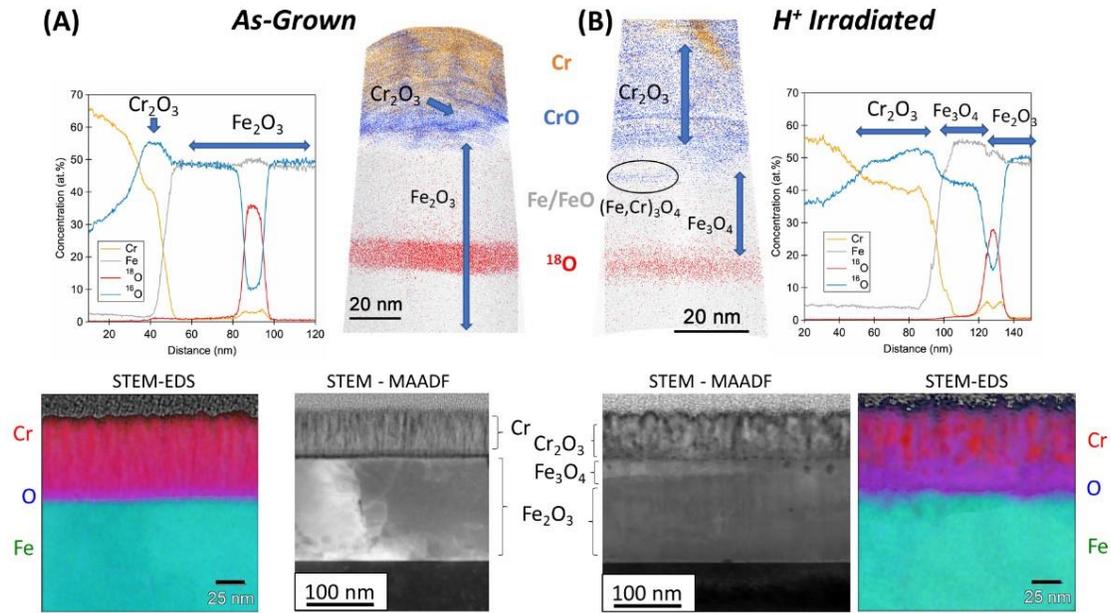


Figure 1. Microstructure and elemental distribution for (A) as-grown vs. (B) proton-irradiated hematite films, characterized by 3D APT (top) and STEM imaging (bottom). Approximately 20 nm of Fe₂O₃ adjacent to the Cr coating has converted to Fe₃O₄ as the Cr metal oxidized to Cr₂O₃.

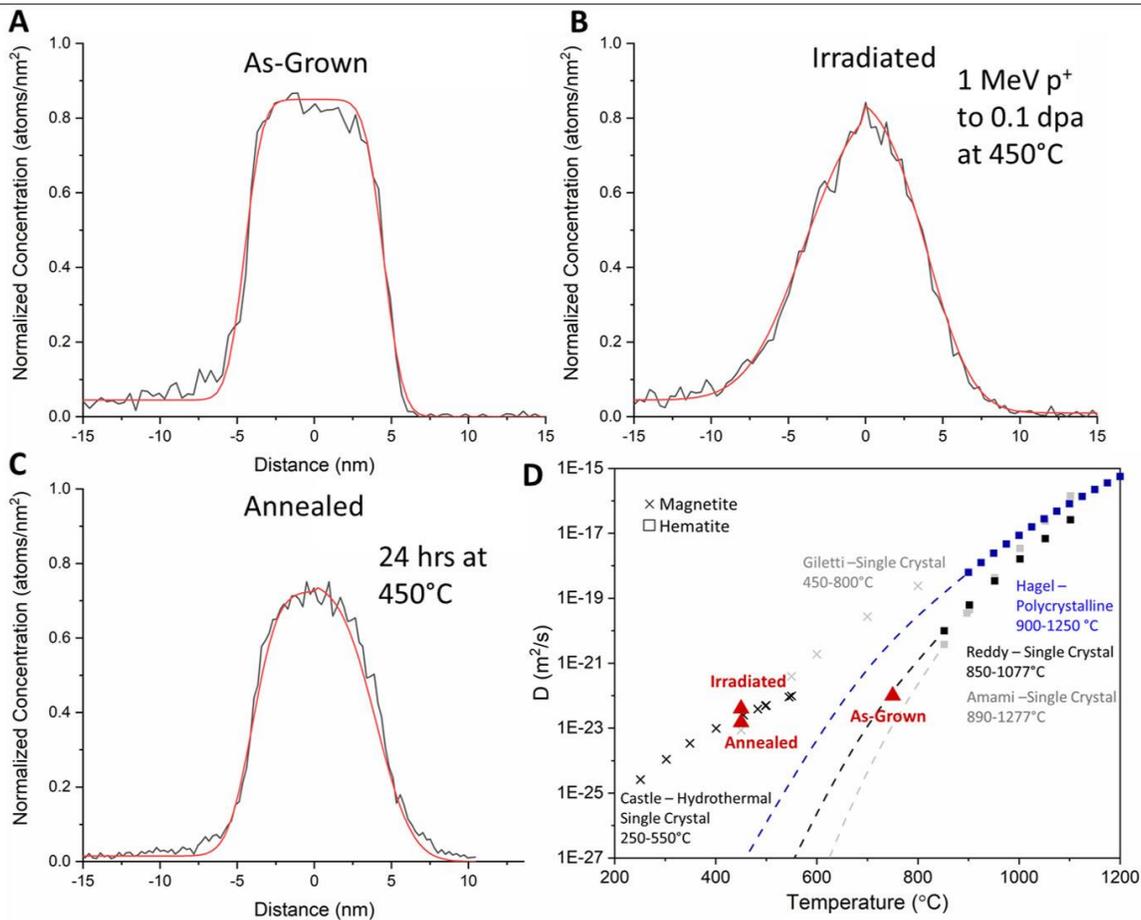


Figure 2. Diffusion coefficients extracted from ^{18}O concentration profiles in (A) as grown, (B) proton irradiated, and (C) annealed hematite compared to (D) literature results for hematite (square symbols) and magnetite (' \times ' symbols).

References

1. Taylor, S. D. *et al.* Resolving Iron(II) Sorption and Oxidative Growth on Hematite (001) Using Atom Probe Tomography. *J. Phys. Chem. C* **122**, 3903–3914 (2018).