Dose Rate Dependent Cation and Anion Radiation Enhanced Diffusion in Hematite

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Supplemental Information

1. Further Sample Details and Irradiation Conditions
This section provides details on the sample stacks grown by MBE (Figure S1 and S2), irradiation setup and stage temperature (Figures S3 and S4), dose calculation by Stopping Range of Ions in Matter (SRIM) (Figure S5) and tabulated final irradiation values (Table S1).

Figure S 1: Schematic illustration of the multilayer film stack designs for (a) irradiated and (b) thermally annealed films used in the current study. Isotopic species are noted as either natural abundance (NA) or enriched in the indicated isotope.

Figure S 2: Additional STEM BF imaging of as-grown MBE film. Black arrows denote vertical growth dislocations. No dislocation loops or voids are present in the Fe$_2$O$_3$ or Cr$_2$O$_3$ films.
Figure S 3: Optical photographs of the ~5x5 mm$^2$ chips irradiated in this study. Chips irradiated at mid and low dose rates (2.3×10$^4$ and 2.3×10$^5$ dpa/s, respectively) were partially shielded with foil during irradiation. Silver paste was used to hold samples to stage.

Figure S 4: Thermocouple-measured sample temperature cooling profile after irradiation at 500 °C.
Figure S5: SRIM profiles of (A) sample dose (solid line, left axis) and Ar implantation (dashed line, right axis) as a function of sample depth based on the stack geometry shown in Fig. S1 and (B) the corresponding dose rate dependencies as a function of depth.
Table S 1: Sample irradiation parameters from this study (high, mid, and low dose rates) and from prior work using proton irradiation – ref. 2

<table>
<thead>
<tr>
<th>Name</th>
<th>Temperature (°C)</th>
<th>Irradiation Time (s)</th>
<th>Dose (dpa)</th>
<th>Ion Fluence (ions/cm²)</th>
<th>Dose rate (dpa/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High dose rate</td>
<td>500</td>
<td>254</td>
<td>0.6</td>
<td>1.15E15</td>
<td>2.5E-3</td>
</tr>
<tr>
<td>Mid dose rate</td>
<td>300</td>
<td>2,729</td>
<td>0.6</td>
<td>2.3E-4</td>
<td>2.3E-4</td>
</tr>
<tr>
<td>Low dose rate</td>
<td>500</td>
<td>23,580</td>
<td>0.6</td>
<td>1.15E15</td>
<td>2.6E-5</td>
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<tr>
<td>Proton irradiation</td>
<td>450</td>
<td>86,400</td>
<td>0.1</td>
<td>4.65E18</td>
<td>1E-6</td>
</tr>
</tbody>
</table>

2. Supplemental APT and TEM Data

Included here are additional details and experimental results from both the APT and TEM characterization. These details are split into three sub-sections. The first is on the quantification of isotopic enrichment by APT (Figures S6-S8), the second into APT reconstruction methods (Figures S9 – S11), and finally into identification of the Fe₃O₄ phase after irradiation (Figures S12-S14).

2.1. Quantification of Isotopic Enrichment

The mass spectra for the specimens consists primarily of the ions Fe, Cr, CrO, FeO, and O (Figure S6). When evaluating the isotopic enrichment of the oxygen species, the O¹⁺ peaks at 16 and 18 Da are used (Figure S7a). For the iron isotopic enrichment the Fe²⁺ peaks at 28 and 28.5 Da are used (Figures S7b). These isotope-specific O¹⁺ and Fe²⁺ peaks are used to calculate the fraction of ¹⁸O and ⁵⁷Fe as:

\[ f_{18O} = \frac{N_{18O}}{N_{18O} + N_{16O}} \]  \hspace{1cm} (1)

and

\[ f_{57Fe} = \frac{N_{57Fe}}{N_{57Fe} + N_{56Fe}} \]  \hspace{1cm} (2)

Here \( N_{18O} \) and \( N_{16O} \) represent the counts of the 16 Da and 18 Da O¹⁺ peaks while \( N_{57Fe} \) and \( N_{56Fe} \) represent the 28 and 28.5 Da Fe²⁺ peaks, respectively. Fractional ¹⁸O and ⁵⁷Fe profiles for two as-grown specimens are included in Figure S8. Uncertainty in the \( f_{18O} \) and \( f_{57Fe} \) profiles can be estimated by standard counting error (\( \sigma \)) as:
\[
\sigma_{18O} = \sqrt{\frac{f_{18O} \times (1 - f_{18O})}{N_{16O} + N_{18O}}}
\]

\[
\sigma_{57Fe} = \sqrt{\frac{f_{57Fe} \times (1 - f_{57Fe})}{N_{57Fe} + N_{56Fe}}}
\]

Although these uncertainties are locally dependent on the number of counts in each datapoint, typical uncertainties are ~0.02 in the profiles provided here and never exceed 0.05 in the presented data.

Figure 5 6: Representative APT mass spectrum, taken from an as-grown film stack with most major peaks labeled.
2.2. Scaling of APT reconstructions and effect of assumed resolution limits

The bilayer spacings of Fe$_2$O$_3$ and Fe$_3$O$_4$ (2.3 Å and 4.8 Å – Figure S9) are used to scale the APT reconstructions accurately based on the observable spatial distribution map (SDM) (Figure S10). Combining these interplanar spacings with our previously discussed isotopic fraction uncertainty ($\sigma<0.05$), we can visualize how an idealized APT measurement of different characteristic diffusion distances and corresponding diffusion profiles appear. This is presented in Figure S11, where each profile represents the error function solution to Fick’s 2nd law using $D$ and $t$ values to reproduce characteristic diffusion distances ($l = \sqrt{4Dt}$) from 0.3 nm to 1 nm. From these plots, it is clear that $l = 0.5$ nm is readily observable, and 0.3 nm is likely near the resolution limits of the technique. This relationship between $D$, $t$, and assumed resolution limits are visualized in Fig. S11 for a few assumed resolution limits, defining zones where APT can be expected to resolve diffusion or any diffusion may be undetected. In general, we view that $l = 0.5$ nm is a reasonably conservative estimate of our detection...
limits, and more rigorous statistical analyses may extend this further. Our experimental measurements
are plotted against these curves, and the time scale has been extended out to waste form relevant
values (100 yrs or 3 × 10^9 sec). Even with APT's exceptional spatial resolution, the previously noted
Arrhenius extrapolation of O diffusion in Fe₂O₃ to 300C (~10^-45 m^2/s) is 14 orders of magnitude away
from the detection limit after 100 years of annealing. On the other hand, at times of 5 minutes the
minimum diffusivity resolvable is 2 × 10^-22 m²/s. It can therefore be challenging to balance the extremes
of experimental detectability, practical laboratory time scales, relevant diffusivity values, and even dose
rates and cumulative dose (i.e. 10⁻³ dpa/s in minutes vs 10⁻⁵ dpa/s in hours vs 10⁻¹³ dpa/s in hundreds of
yrs). However, it is also worth emphasizing that APT’s resolution and detection limits provide new
opportunities for nanoscale mass transport that were previously impossible by other techniques that
required micrometers of diffusion for reliable quantification.

![Figure S 9: Ball and stick models of (A) Fe₂O₃ and (B) Fe₃O₄ with the indicated [0001] / [111] bilayer spacing.](image)

Figure S 9: Ball and stick models of (A) Fe₂O₃ and (B) Fe₃O₄ with the indicated [0001] / [111] bilayer spacing.
Figure S 10: APT derived spatial distribution maps (SDMs) of interplanar spacing along the Z-axis used for scaling of the APT reconstruction in (a) Fe$_2$O$_3$ and (b) Fe$_3$O$_4$. The red dashed lines indicate the true O bilayer spacing expected in the data versus the experimentally measured SDM (black lines).

Figure S 11: Representative calculated diffusion curves for characteristic diffusion distances of 0.3 nm, 0.5 nm, and 1.0 nm. The curves are sampled at 0.2 nm spacings, as would be done in the APT measurement. Vertical and horizontal lines indicate 0.23 nm interplanar spacings of Fe$_2$O$_3$, and the f$_{18O} = 0.05$ uncertainty limit from counting statistics, respectively. These plots show that at the $l = 0.5$ nm resolution limit ($D_{mon}$) approximately ~5-7 APT data points are within counting error limits, or ~5 monolayers of interdiffusion.
Figure S 12: Resolution limit of the APT and isotopic tracer technique. Limits of 0.3 nm, 0.5 nm, and 1 nm are provided to give an idea of the range of D values based on more (1nm) or less (0.3 nm) conservative estimates of the resolution limit. Experimental D values are included for context.

2.3. Identification and impact of localized Fe$_2$O$_3$ reduction to Fe$_3$O$_4$

Regions of the Fe$_2$O$_3$ near the Cr$_2$O$_3$ interface reduced to Fe$_3$O$_4$ and this transformation was captured by TEM (Figure S13) and APT (Figures S14 and S15) in both low and high dose rate samples (500°C) but not in the mid dose rate sample (300°C). The depth of Fe$_3$O$_4$ reduction varied across the samples reaching at most (in the regions captured by TEM) 40 nm from the Cr$_2$O$_3$ interface. In regions where the Fe$_3$O$_4$ transformation reached the isotopic tracer layer, the $^{57}$Fe tracer rapidly diffused through the reduced volume, while the $^{18}$O did not (Figure S15). This phenomenon will be the subject of a future paper.
Figure S 13: Darkfield TEM image and corresponding diffraction pattern to visualize the extent of Fe$_3$O$_4$ formation in high dose rate sample. The observed Fe$_3$O$_4$ region is directly beneath the Cr$_2$O$_3$ film, extending at most (in this region) 40 nm into the Fe$_2$O$_3$ film.

Figure S 14: APT-measured mixed atomic and isotopic concentration profiles across a film stack in which the irradiated Fe$_2$O$_3$ has partially transformed to Fe$_3$O$_4$. While the $^{18}$O tracer remains relatively in-place, the $^{57}$Fe is seen to rapidly diffuse throughout the transformed Fe oxide.
Figure S 15: APT-measured $f_{^{18}O}$ and $f_{^{57}Fe}$ profiles of irradiated and as-grown samples. An APT specimen from the high dose rate irradiation exhibits partial $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$ transformation to the indicated positions (orange). When the transformation has not yet reached the tracer layer, the transformation seems to have no perceived effect on the tracers. Conversely, when the conversion reaches the tracer layer (as in a specimen from the low dose rate irradiation – blue), the $^{57}\text{Fe}$ cation distributes throughout the transformed region and $^{18}\text{O}$ does not.

3. References