

Strain Evolution Imaging during Hydrogen Reduction of Magnetite: Supporting Information

Ruiyang Duan¹, David Yang², Yue Dong³, Jialun Liu¹, Sooyeon Hwang⁴, Kim Kisslinger⁴, Jiangtao Zhao⁵, Steven Leake⁵, Marie-Ingrid Richard^{5,6}, and *Ian K. Robinson^{1,2}

1. London Centre for Nanotechnology, University College, London WC1E 6BT, UK

2. Condensed Matter Physics and Materials Science, Brookhaven National Laboratory, Upton NY 11973, USA

3. Department of Physics, University of Oxford, OX1 3PU, UK

4. Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton NY 11973, USA

5. European Synchrotron Radiation Facility, 71 Avenue des Martyrs, 38000 Grenoble, France

6. Universite Grenoble Alpes, CEA Grenoble, IRIG, MEM, NRX, 17 rue des Martyrs, 38000 Grenoble, France

Supplementary I. Amplitude range for crystalline volume

The amplitude was normalized to $0 \leq A \leq 1$. We inspected scan 153 in ParaView, corresponding to the start of the final H₂ reduction step at 475C. Most signal below $A = 0.2$ lay outside the main crystal boundary and filled the reconstruction box as diffuse background. The $0.2 < A < 0.4$ interval follows the crystal exterior. The $0.4 < A < 1.0$ interval covers the compact interior. We take $A = 0.2$ as the boundary of the BCDI-visible crystalline volume. The threshold $A = 0.4$ separates the higher-amplitude interior.

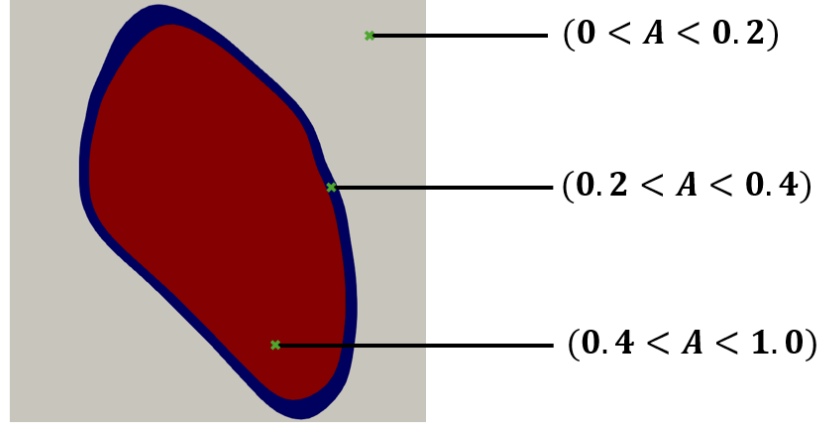


Figure S1. Representative spatial distribution of the operational amplitude ranges. Cross-sectional cut through the reconstruction of scan 153 in ParaView. Amplitude in $0 < A < 0.2$ is mostly outside the crystal. The $0.2 < A < 0.4$ interval lies around the exterior. The $0.4 < A < 1.0$ interval is the compact interior. The same separation was checked in other reconstructions.

Supplementary II. Real-space resolution estimated from the local amplitude-edge response

We estimated real-space resolution from the amplitude edge at the crystal-background boundary. The $A = 0.2$ isosurface gave the approximate crystal extent. For each direction, the opposite boundary regions were treated as a pair. A 15×15 voxel grid covered the central 65% of each face. Sampling lines ran from 160 nm outside the crystal to 220 nm inside. Each line crossed one boundary and did not reach the opposite surface.

We smoothed $A(s)$ with a Gaussian kernel of $\sigma = 8$ nm and calculated dA/ds . Near the expected boundary, the strongest positive derivative peak was fitted over an 80 nm window to a Gaussian plus constant:

$$\frac{dA}{ds} = B \exp \left[-\frac{(s - s_0)^2}{2\sigma_{\text{edge}}^2} \right] + c,$$

In this fit, s_0 is the edge position. σ_{edge} is the local edge width. The full width at half maximum is

$$\text{FWHM} = 2\sqrt{2 \ln 2} \sigma_{\text{edge}}.$$

We rejected profiles with too little outside-to-inside contrast or an unsuitable baseline. Fits were also rejected when the derivative peak was misplaced or the width was unstable. Any fit with $R^2 < 0.35$ was removed. We then applied a median-absolute-deviation filter within each boundary. A boundary region required at least eight

accepted profiles. For each direction, one of the two opposing regions was retained. The score favored a smaller median σ_{edge} , a smaller interquartile range, and more accepted profiles. The directional edge width was the median σ_{edge} for the selected region. For stable reconstructions through scan 153, it was approximately 40–45 nm along (x) and (y), and approximately 30 nm along (z). Later reconstructions had more irregular boundaries, so their fitted widths were not used to infer changes in spatial resolution.

Figure S2 shows one selected face from scan 153. The example profile has $\sigma_{\text{edge}} = 34.8$ nm (FWHM 81.9 nm). Across 68 accepted profiles, the median is 34.5 nm. The interquartile range is 13.4 nm.

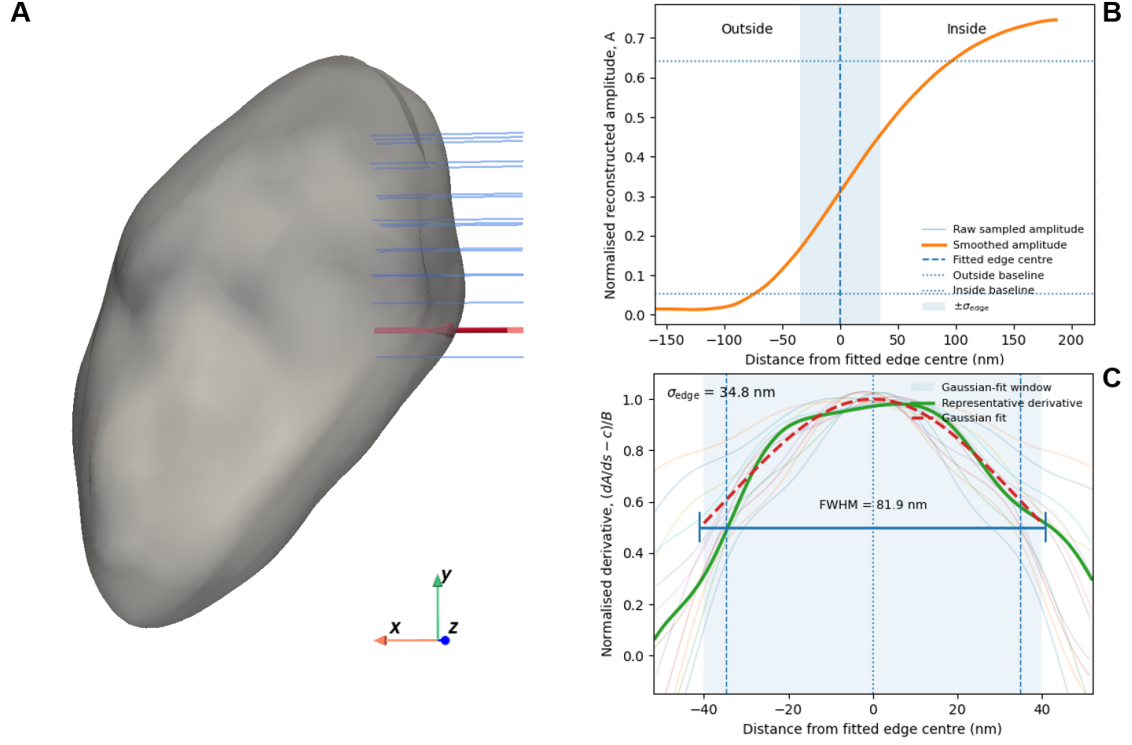


Figure S2. (A) $A = 0.2$ amplitude isosurface of scan 153 showing representative sampling lines across the selected face. Each line extends from outside to inside the reconstructed crystal and crosses only one crystal boundary. Blue lines show a subset of the accepted profiles, while the red line is the representative profile displayed in panels B and C. (B) Complete outside-to-inside normalized-amplitude profile along the representative sampling line. The raw and Gaussian-smoothed amplitude profiles are shown together. The dashed vertical line is the fitted edge center, the dotted horizontal lines are the outside and inside amplitude baselines, and the shaded region is $\pm\sigma_{\text{edge}}$. (C) Spatial derivatives of representative accepted amplitude profiles after alignment to their fitted edge centers. The green curve is the derivative of the representative profile, and the red dashed curve is the corresponding Gaussian fit. The shaded region is the 80 nm fitting window. The fitted Gaussian standard deviation is $\sigma_{\text{edge}} = 34.8$ nm, corresponding to an FWHM of 81.9 nm. Across the selected face, the median σ_{edge} is 34.5 nm, with an interquartile range of 13.4 nm from 68 accepted profiles.

Supplementary III. Evolution of the Bragg-peak intensity

Two methods were used to estimate the total peak intensity. Each rocking scan gave an integrated Bragg intensity and a peak-frame maximum. The first is the signal summed over the selected Bragg-peak region throughout the rocking curve. The second is obtained from a single diffraction frame. Each trace was divided by its own maximum for normalization.

Both traces rise during the early scans and decrease later. Small fluctuations remain during the later H₂ exposure. Other fluctuations may arise from changes in the beam or sample alignment.

The final scans have the lowest intensities. Their interpretation is therefore limited, and they are not detailed in the main text. During this H₂ exposure at 475 °C, the diffraction intensity and reconstructed volume both decrease overall, with unmatched fluctuations.

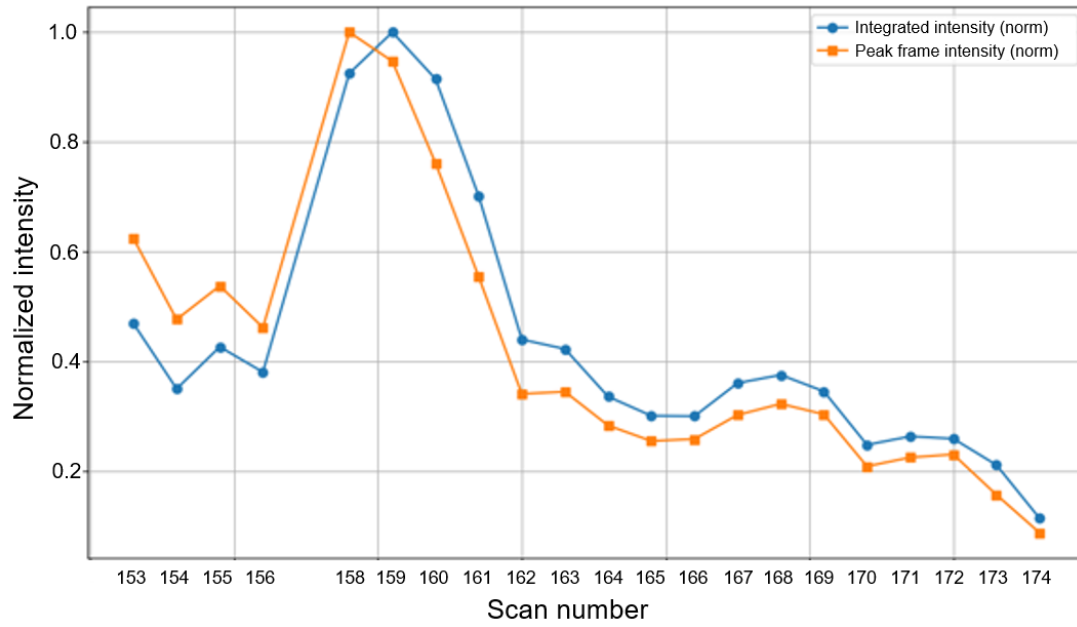


Figure S3. Evolution of the Bragg-peak intensity during the 475 °C H₂ exposure series. The two curves are the integrated intensity and the largest single-frame intensity. Each is divided by its own maximum. Both rise early in the H₂ exposure and fall later; the final scans are lowest.

Supplementary IV. Lattice-parameter evolution during the in situ sequence

For each scan, the PyNX reconstruction provided a three-dimensional lattice-parameter field. We averaged this field over the voxels within threshold $A \geq 0.20$ to obtain a mean lattice parameter for that scan. Okudera et al. [1] report the non-linear temperature dependence of the magnetite lattice parameter as

$$a_{\text{Oku}}(T) = 0.83856 - 2.0 \times 10^{-7}T + 1.03 \times 10^{-8}T^2 \text{ nm},$$

with T in K. Figure S4 plots this published relation directly over the reconstructed values. The

measured averages remain close to the reference, although the separation increases at higher temperature. For $A \geq 0.20$, the average is about 8.399 Å at 75 °C and 8.452 Å at 475 °C. the difference can be Our measurements and the reference used different atmospheres, also Magnetite thermal expansion depends on atmosphere [2].

We also see small, but clear changes within each isothermal region. Especially during the last three temperatures the lattice is seen to contract slightly during the H₂ exposure. This contraction may contribute to the negative shift of the total-strain distributions reported in the main text. Under H₂, a small decrease begins at 375 °C. At 475 °C, the $A \geq 0.20$ mean is about 8.4519 Å near the start of H₂ exposure. It is 8.4503 Å around scan 163 and about 8.4517 Å in later scans. This return occurs during scans 162–164, where the volume–strain transition lies.

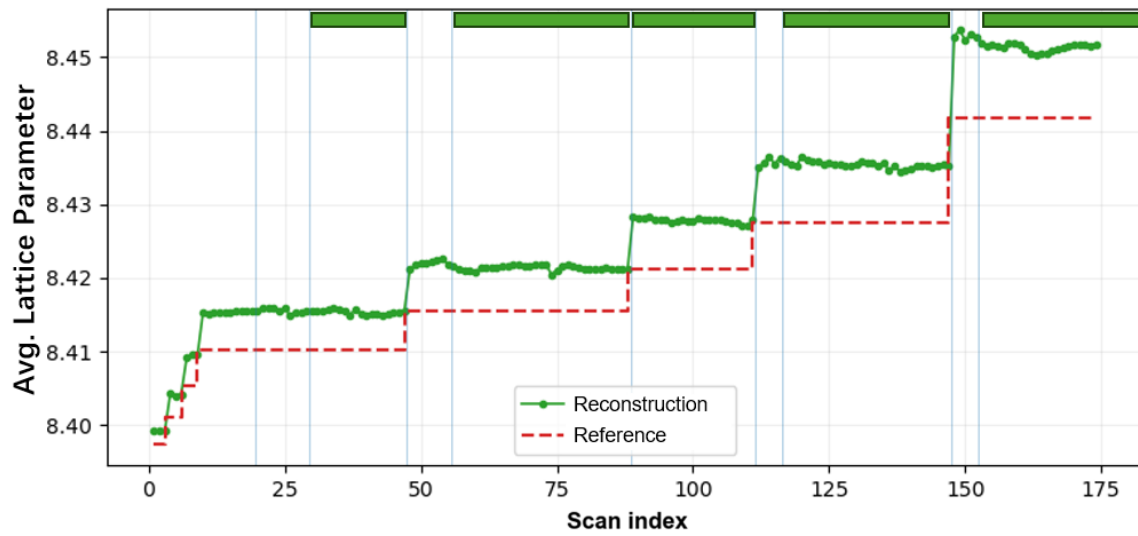


Figure S4. Mean lattice parameter during the in situ sequence. The green line is the reconstructed lattice parameter. The red dashed line is the Okudera et al. reference [1]. Green bars are H₂ periods. Blue vertical lines separate measurement groups.

Supplementary V. Coordinate convention and crystallographic orientation, compared with SEM

Figure S5 places the SEM images beside matched views of the scan 30 reconstruction where the effects of annealing are complete. The main facets and crystal outline reproduce extremely well. We assigned the crystallographic directions in Fig. S5A from the morphology of the (111)-oriented parent crystal used during the FIB milling. In the side view, [111] is 35.3° from [110]. The other directions lie within the (111) surface as drawn in the top view. The same facets are recognized in the BCDI reconstruction and define the orientation in Fig. S5B.

The xyz axes, also used in the figures of the main paper, are the laboratory coordinates defined in the PyNX software. The +x axis points along the incident beam direction; the +y axis is vertical and the z-axis is mutually perpendicular. In the top-down view, y lies close to the [111] surface normal, while the x-z directions are rotated about about 15° representing the angle at which the sample happened to be mounted on the diffractometer.

The tilted views of the reconstruction are shown with the same tilt angles used in the SEM. The x and z axes

are therefore not exact crystallographic directions.

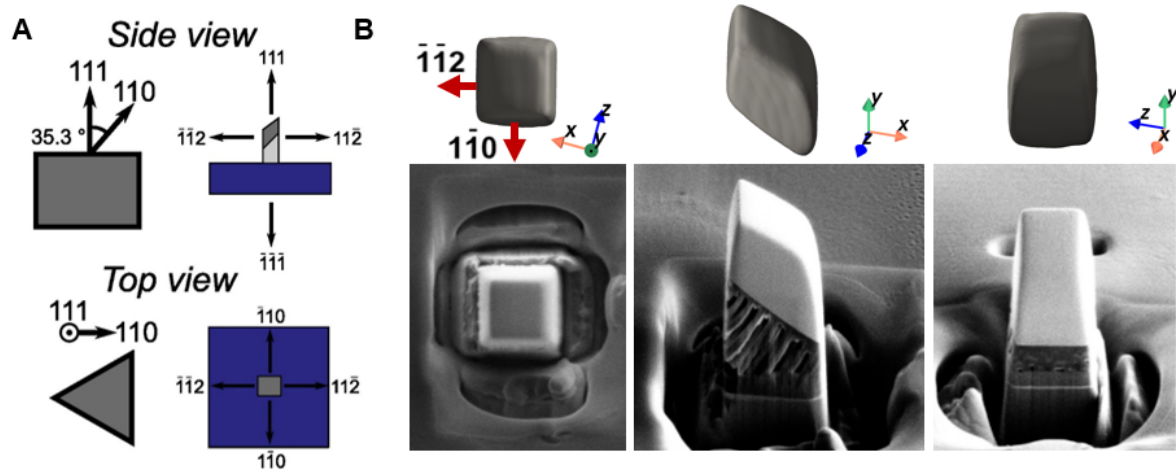


Figure S5. (A) Crystallographic directions assigned to the FIB-cut crystal facets during the sample preparation, based on the parent crystal morphology. (B) BCDI reconstructions and SEM images with matched orientations and scale. The orange-green-blue arrows show the reconstruction “laboratory” coordinates used in the PyNX software.

Supplementary VI. Post-experiment EDX analysis

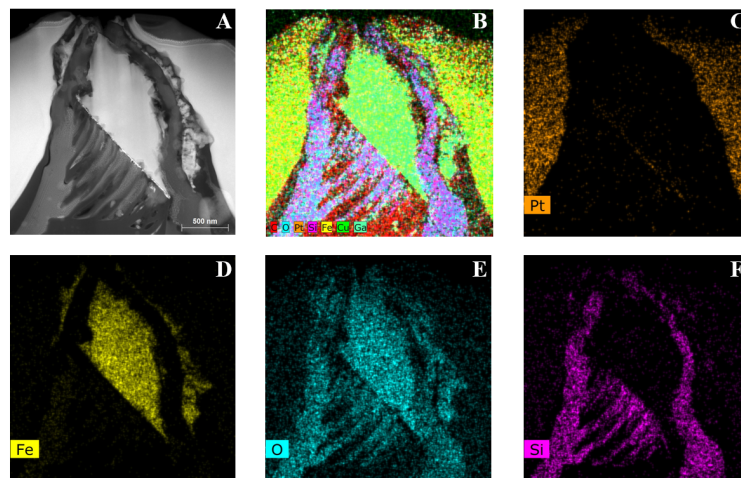


Figure S6: Cross-sectional high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and corresponding Energy-dispersive X-ray spectroscopy (EDX) elemental maps of the sample after hydrogen reduction. (A) HAADF image. (B) Composite EDX map. (C–F) Pt, Fe, O, and Si maps. The lamella is viewed from the side with the (111) facet upward. Scale bar = 500 nm.

After the experiment, we cut a TEM foil from the magnetite crystal, following its exposure to both X-rays and H_2 and subsequent transfers in air, using an FEI Helios G5 UX DualBeam FIB and EasyLift Nanomanipulator. The sample was first covered by 2 μm of Pt and then 500 nm of carbon, to form a wall around the magnetite crystal. We extracted the lamella at 30 kV and 2.6 nA. Final polishing at 16 kV and 63 pA gave a thickness of 100 nm.

We collected the post-reduction EDX maps on an FEI Talos F200X analytical scanning/transmission electron

microscope at 200 kV. HAADF-STEM images came from the same instrument. A Super-X detector was used for STEM-EDS.

In Fig. S6A, the central region is about 830 nm wide, slightly smaller than the crystal in the pre-experiment SEM. Around it is a roughly 200 nm thick region with strong Si signal. Figure S6B combines the EDX maps of Pt, Fe, O and Si in figures S6C to S6F.

Pt is seen to follow the outside of the structure in Fig. S6C. This is the support deposited during preparation, with the crystal surrounded by it.

The Fe map in Fig. S6D has a compact center, again slightly smaller than the crystal in the pre-experiment SEM. Fe also occurs in the rough outer regions seen after the experiment. Across both regions, the Fe signal extends about 1260 nm. This is wider than the original crystal, and the outer morphology cannot be assigned directly to its initial shape.

In Fig. S6E, oxygen extends beyond the Fe-rich center and into the gap toward the outer Fe-containing region. The outer oxygen signal is weaker. Several weeks passed before this measurement, and exposure to air may have changed the oxygen distribution. Oxygen and Fe still overlap after reduction.

The gap between the Fe-rich center and the outer Fe-containing material is rich in Si (Fig. S6F), with weaker oxygen in the same region. The Si signal continues toward the Pt support. We do not assign it to the magnetite crystal; it probably comes from the substrate or mounting material and may include silicon oxide.

These are post-mortem maps, so there is no direct elemental comparison with the initial state. EDX also cannot identify the chemical phase of the iron-oxide, which remains unknown. Fe is concentrated at the center and also occurs in the outer morphology.

Supplementary VII. EELS Analysis:

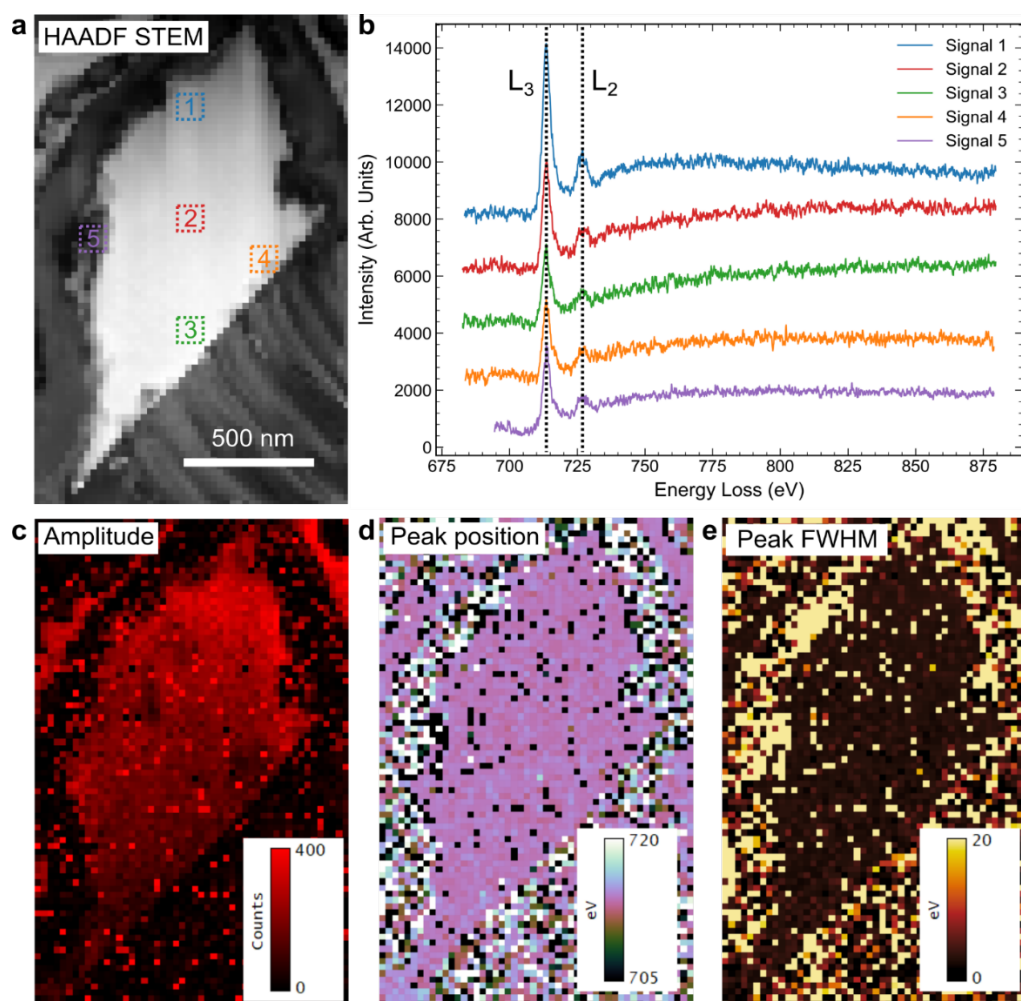


Figure S7: Postmortem EELS characterization. (a) HAADF-STEM image of the FIB-manufactured magnetite sample. Five regions of interest, labelled 1-5, are marked, corresponding to the average background-subtracted Fe $L_{2,3}$ energy loss spectra in (b), with the $L_{2,3}$ edges marked by the dashed lines. The Fe L_3 spectra were fitted using nonlinear least square fitting (NLLS) with a Gaussian function and the optimized amplitude (c), peak position (d), and full width at half maximum (e) are shown. The scale bar in (a) also applies to (c)-(e).

Electron energy-loss spectroscopy (EELS) and HAADF-STEM were performed on a FEI Talos F200X analytical scanning/transmission electron microscope with a Gatan Enfium spectrometer, which offers dual-EELS capability (Figure S7(a)). An acceleration voltage of 200 kV, beam convergence of 10.5 mrad and collection of 8.1 mrad were used. All acquired spectra in the spectrum-image were aligned by the position of the zero-loss peak. Figure S7(b) shows the EELS spectra at various regions of interest in the TEM sample. A power law was used to fit and subtract the background from the spectra, and the Fe $L_{2,3}$ edges were fitted using NLLS with a Gaussian profile, with the fitted amplitude, peak position, and FWHM shown in Figure S7(c-e). Figure S7(d) indicates that there is no shift in the fitted Fe L_3 edge, indicating there is no observed spatial variation of oxidation state of the sample.

Supplementary VIII. Inward-depth amplitude profiles and characteristic depth

This section defines the characteristic depth used in Figure 5 of the main paper and the scan-specific threshold used to divide the images into high- and low-amplitude layers. Within the $A \geq 0.2$ mask, we calculated Euclidean distance s from each voxel to the nearest surface, using the reconstruction voxel dimensions. The distance is small at the $A = 0.2$ boundary and increases inward. For each reconstruction, we divided it by the maximum distance inward, measured to the center of the sample,

$$d = \frac{s}{s_{\max}},$$

At $d = 0$, the voxel is on the crystal boundary. At $d = 1$, it is at the deepest point in the $A \geq 0.2$ region. This assigns one scalar value to each voxel. We grouped the voxels into 45 equal intervals of depth and averaged $A(d)$ in each interval. Bins with fewer than 80 voxels were left out.

The resulting depth profiles were fitted using a stretched-exponential recovery function,

$$A(d) = 0.2 + \Delta A \left[1 - \exp \left(- \left(\frac{d}{\tau} \right)^\beta \right) \right],$$

The boundary amplitude was fixed at 0.2. The fitted rise toward the interior is ΔA . We fixed β at 1.5. The fit parameter τ is the characteristic inward distance. Fits used only $0 \leq d \leq 0.88$ because the deepest bins contain few voxels.

For τ , take $d = \tau$,

$$\left(\frac{d}{\tau} \right)^\beta = 1,$$

which gives

$$A(\tau) = 0.2 + \Delta A(1 - e^{-1}) \approx 0.2 + 0.632 \Delta A.$$

At τ , the fitted amplitude has completed 63.2% of its rise from the $A = 0.2$ boundary to the fitted interior value,

$$A_c = 0.2 + \Delta A.$$

The normalization of d is separate for each reconstruction. τ is dimensionless and is a fraction of the maximum crystal depth. The physical depth is

$$\tau_{\text{abs}} = \tau s_{\max}.$$

We also calculated the amplitude at this depth,

$$A_\tau = A(\tau) = 0.2 + \Delta A(1 - e^{-1}),$$

and used it as a scan-specific threshold. The lower-amplitude exterior was $0.2 \leq A < A_\tau$. The higher-amplitude interior was $A \geq A_\tau$.

Supplementary IX. Decomposition of the total strain field

For each scan, we separated the total strain along the measured scattering direction into a local field and one homogeneous value,

$$\varepsilon_{\text{total}}(r) = \varepsilon_{\text{het}}(r) + \varepsilon_{\text{hom}}.$$

ε_{het} is the local variation within the reconstructed crystal. ε_{hom} is the uniform lattice-spacing offset relative to scan 153.

Histograms for $A \geq 0.2$ in scans 153–163 are in Fig. S8A. Scans 164–174 are in Fig. S8B. Bin width $\times$ density sums to 1. Peak height is not separately set to 1. Once the homogeneous term is removed, the centers stay near zero. Before scan 164, most curves are narrower and higher. From scan 164 they are broader and lower. Their asymmetry changes, but the center does not remain displaced.

The homogeneous strain is referenced to scan 153 and is mostly negative (Fig. S8C). Negative values mean smaller average lattice spacing along the measured scattering direction. Scans 157–160 contain several excursions. A separate positive step lies between scans 167 and 168. Their origin is unclear. Neither occurs at the volume–strain transition around scans 163–164, so they may contribute little to that transition.

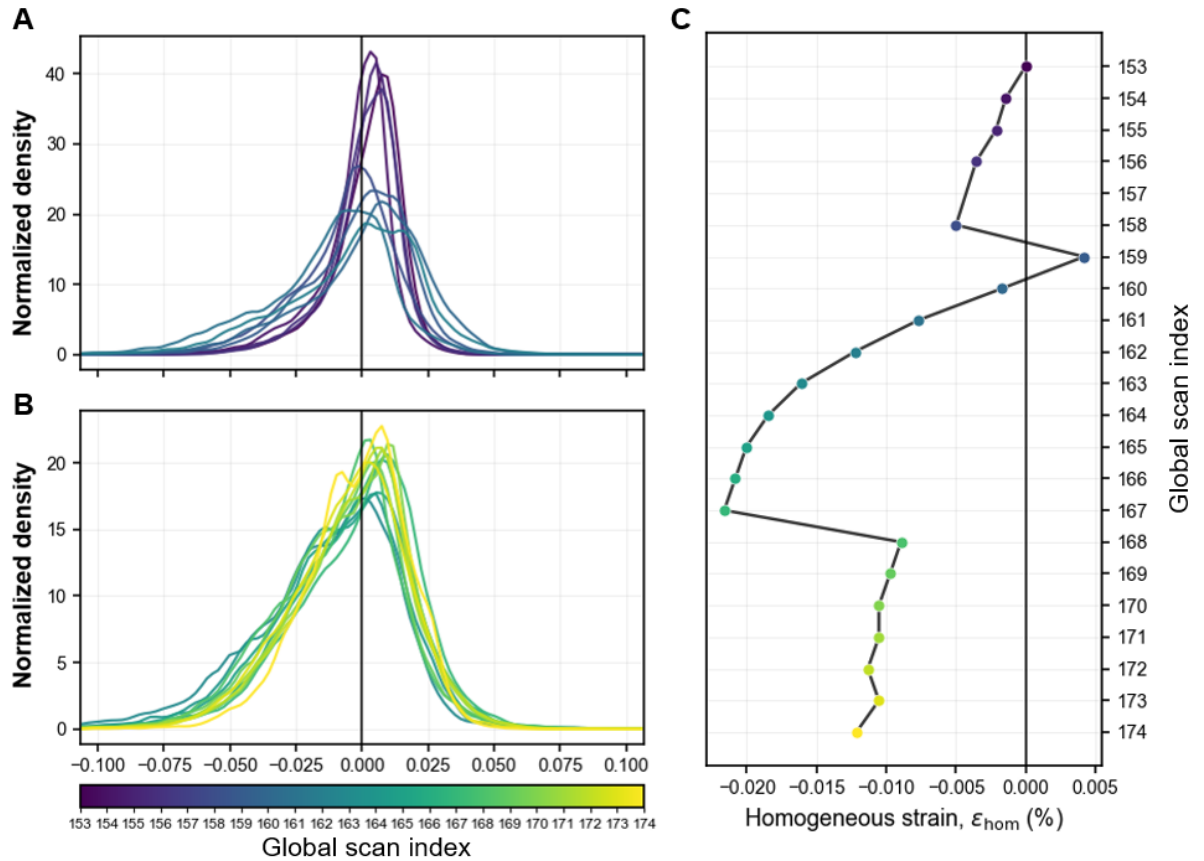


Figure S8. Decomposition of the total strain into heterogeneous and homogeneous components during the 475 °C H₂ exposure series. (A, B) Probability density of ε_{het} for voxels inside $A \geq 0.2$. Panel A covers scans 153–163 and panel B covers 164–174. Each curve has unit area. Color gives the global scan index. The black vertical line is zero. (C) ε_{hom} relative to scan 153. Negative values are contraction of the average lattice spacing along the measured scattering direction. Successive points are joined as a guide; the black vertical line is zero.

- (1) Okudera, H.; Kihara, K.; Matsumoto, T. Temperature Dependence of Structure Parameters in Natural Magnetite: Single Crystal X-Ray Studies from 126 to 773 K. *Acta Crystallogr. B* **1996**, *52* (3), 450–457.
<https://doi.org/10.1107/S0108768196000845>
- (2) Levy, D.; Artioli, G.; Dapiaggi, M. The Effect of Oxidation and Reduction on Thermal Expansion of Magnetite from 298 to 1173K at Different Vacuum Conditions. *J. Solid State Chem.* **2004**, *177* (4–5), 1713–1716.
<https://doi.org/10.1016/j.jssc.2003.12.032>