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Supplementary Information for

Facet-selective adsorption of Fe(II) on hematite visualized by nanoscale secondary ion mass spectrometry

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NanoSIMS standards analysis

For the Fe isotopic measurements with nanoscale secondary ion mass spectrometry (NanoSIMS), the unreacted hematite particles were used as a standard to calibrate the instrument to natural abundance (NA) Fe isotopic ratios. As described in the main text, these hematite particles were reacted at similar conditions as the ^{57}Fe-reacted hematite particles, but without addition of the $^{57}Fe(II)_{aq}$, and thus possess a Fe isotopic composition at NA; i.e., they were reacted at room temperature for 24 hours in a pH 7.5 solution (25 mM KBr, 25 mM HEPES buffer). The $^{57}Fe/^{56}Fe$ ratio was utilized to probe enrichment of ^{57}Fe across particles and their respective regions of interest (ROI). In turn, the ratios for the unreacted particles were carefully analyzed to determine ratio variations across ROIs (described below). In general, analyses of the unreacted samples shows that the $^{57}Fe/^{56}Fe$ measurements are in agreement with NA values and also demonstrate that relative ^{57}Fe-enrichments between different ROI can be statistically differentiated in ^{57}Fe-reacted particles.

To account for any artificial changes in isotopic ratios produced during the measurement an instrumental mass fractionation correction factor (k) was determined (Equation S1):

$$k = \frac{(\frac{R}{R_{obs}} - 1)}{\Delta m} \quad \text{(S1)}$$

where R is the theoretical value of the isotope ratio of interest at NA, R_{obs} is the measured value, and Δm is the difference in mass between the two isotopes. The corrections were averaged across all regions (k_{avg}) and applied to obtain mass-bias corrected isotopic ratios (R_{cor}, Equation S2):

$$R_{cor} = R_{obs}(1 + k_{avg} \cdot \Delta m) \quad \text{(S2)}$$

As part of characterizing the unreacted samples as controls it was important to consider how the Fe isotopic ratios on the different surfaces and features of the unreacted particles could vary. That is, the magnitude of counts can vary between different ROI depending on the amount of exposed areas (e.g., the basal surface has a larger exposed area than the edges) and the crystal orientation (e.g., the basal surface will be oriented to the beam and detector differently than the edges). Additionally, the crystal orientation impacts the sputtered yield, secondary ion counts, and secondary ion energies.[1] Previous studies using SIMS have shown that there is a potential instrumental bias affecting high precision $\delta^{18}O$ measurements for magnetite[2] and $\delta^{56}Fe$ measurements for hematite[3] due to crystal orientation effects. It is important to analyze these effects to determine whether enrichment observed is dependent on the feature/orientation. However, these effects manifest themselves on the scale of a few per mil and are not expected to have a significant effect on our highly ^{57}Fe-enriched samples.

These effects were analyzed in terms of the $^{57}Fe/^{56}Fe$ ratios for the different ROI on the unreacted sample, where the ratio will be at NA (i.e., 0.023). Additionally, the uncertainty in $^{57}Fe/^{56}Fe$ for different ROI was calculated to determine the range in which the ratios could theoretically lie within. In particular, the propagated uncertainty (σ) was calculated to account for variability due to counting statistics for an individual ROI as well as the mass bias correction factor (Equation S3):

$$\sigma = \sqrt{(1 + k_{avg} \cdot \Delta m)^2 \cdot \sigma_{abs}^2 + (R_{obs} \cdot \Delta m)^2 \cdot \sigma k_{avg}^2} \qquad \text{(S3)}$$

where σk_{avg} is the standard deviation of the average of the mass bias correction factors from the individual ROI. σ_{abs} is the absolute uncertainty in $^{57}Fe/^{56}Fe$ based on counting statistics, and is calculated as (Equation S4):

$$\sigma_{abs} = R_{obs} \cdot \sqrt{\frac{1}{N_1} + \frac{1}{N_2}} \quad \text{(S4)}$$

where N_1 and N_2 are the counts for ^{57}Fe and ^{56}Fe, respectively for a given ROI. We plot error bars as 2σ to represent an approximate 95% confidence interval of a $^{57}Fe/^{56}Fe$ ratio for a given ROI.

For the unreacted particles, the $^{57}Fe/^{56}Fe$ isotopic ratios on the different surfaces and features of the unreacted particles at various orientations and heights relative to one another were within uncertainty of NA. For instance, if using 2σ to represent the range the ratios fall within, the average $^{57}Fe/^{56}Fe$ for both the basal and edge surfaces was 0.024±0.01. In general, significant differences in the ratios between the different ROI are not observed.

Additionally, particles with protruding growth twins were also utilized to further probe particle height and orientation effects on the Fe isotopic measurements (**Figure S 1**). That is, as shown in the scanning electron microscope (SEM) image of the unreacted sample in Figure 1 of the main text, growth twins can protrude from the basal surface of the parent particle, thereby providing surfaces at various orientations relative to the beam. The edges of the growth twins can be considered to be at a greater height and more normal to the beam relative to (012) surfaces on the flat-lying parent particle. $^{57}Fe/^{56}Fe$ measurements for (012) surfaces of protruding growth twins and the flat-lying parent particle were compared to observe whether significant variations in the ratio existed based on differences in the surface orientation. The average $^{57}Fe/^{56}Fe$ for the

(012) surfaces of the protruding growth twins and parent particles were within the ranges of 0.025±0.01 and 0.024±0.01, respectively. Thus, the uncertainty calculations indicate that particle height and orientation do not affect quantification of the Fe isotopic ratios for the purposes of this study, whereby isotopic contrast for the ^{57}Fe-reacted particles is significant (i.e., ^{57}Fe/^{56}Fe is an order of magnitude higher than NA) and outside the uncertainty produced from these effects. Thus, the ^{57}Fe/^{56}Fe ratios measured on the reacted particles are reliable for observing the relative isotopic enrichment between different ROI of the reacted particles.

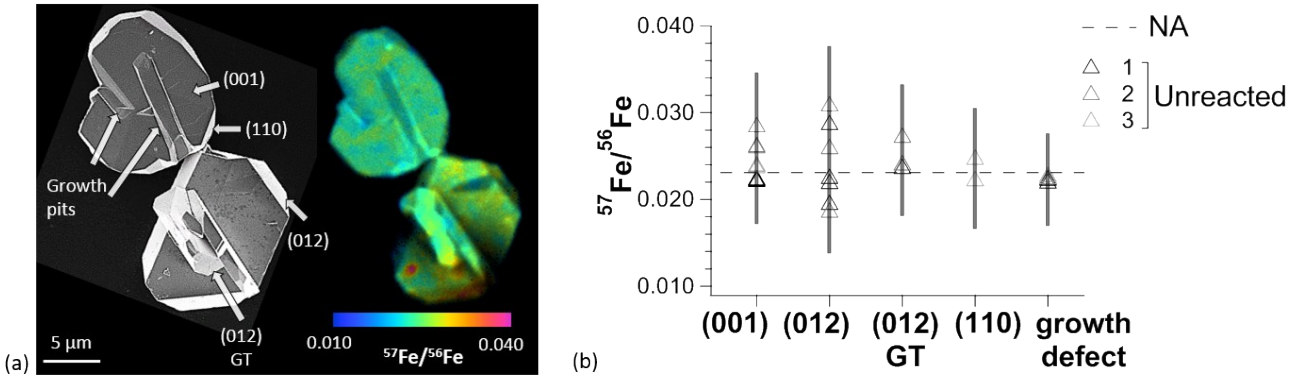

Figure S 1: (a) SEM image and corresponding ^{57}Fe/^{56}Fe map of an unreacted particle, highlighting flat vs. non-flat lying regions. (b) ^{57}Fe/^{56}Fe ratios for unreacted particles from imaging measurements, where error bars represent 2σ-95% confidence intervals. "(012) GT" refers to (012) surfaces of the protruding growth twins at different heights and orientations to the ion beam relative to the (012) surfaces of the flat-lying parent particle. The gray dashed line represents the theoretical ^{57}Fe/^{56}Fe value at NA (i.e. 0.023).

$^{54}Fe/^{56}Fe$ ratios for unreacted and reacted particles

As a secondary check the $^{54}Fe/^{56}Fe$ ratios were also computed for the unreacted and reacted particles (**Figure S 2**), similar to that done for the $^{57}Fe/^{56}Fe$ ratios. The ratios for the both unreacted and reacted particles are within range of that expected for NA values (i.e., 5.85 $^{54}Fe/91.75$ $^{56}Fe = 0.064$), as expected. This demonstrates that the Fe isotopic measurements were effectively calibrated during the NanoSIMS measurements.

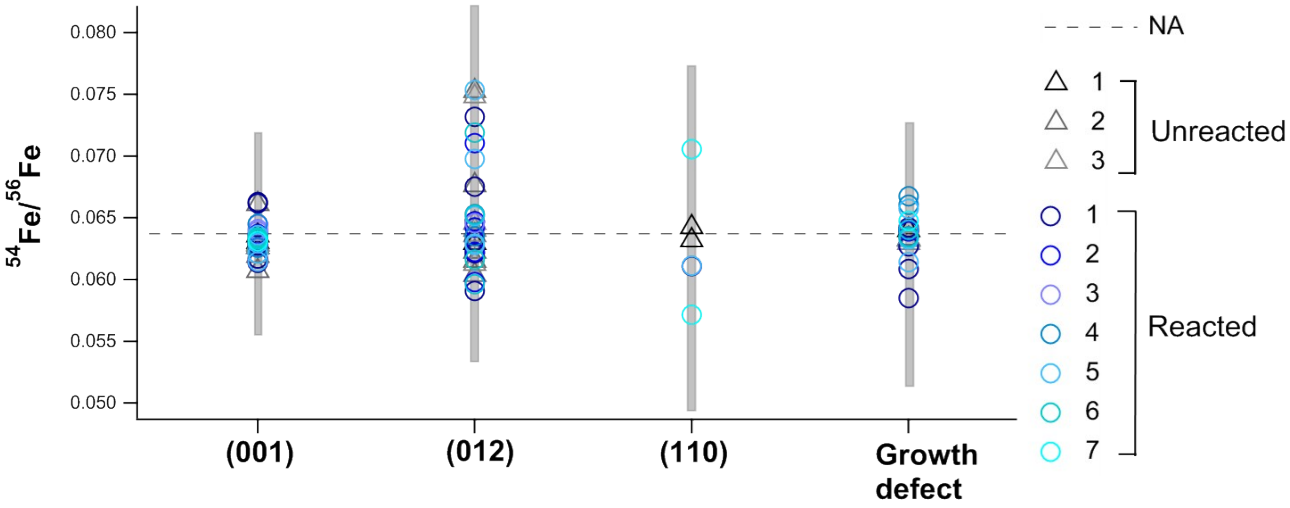

Figure S 2: $^{54}Fe/^{56}Fe$ ratios for the unreacted and reacted particles. 2σ (95% confidence intervals) across all the particles is plotted as gray vertical bars.

References

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