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Facet-Selective Adsorption of Fe(II) on Hematite Visualized by Nanoscale Secondary Ion Mass Spectrometry

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Environmental Significance

The interaction of Fe(II) with hematite (Fe(III)₂O₃) particles and exposed facets imparts powerful catalytic reduction capacities, with broad environmental implications from contaminant remediation to the biogeochemical cycling of metals. This study explicitly illustrates site- and facet-selective adsorption of Fe(II) onto multifaceted hematite particles, enabled through utilizing isotopic tracers and nanoscale secondary ion mass spectrometry (NanoSIMS). NanoSIMS images reveal strongly preferred Fe(II) adsorption on basal (001) surfaces relative to edge facets (e.g., (012). These findings shed new light on the substantial anisotropy in interfacial reactivity of iron oxide crystallites. Additionally, the developed approach enables visualization and simultaneous characterization of the reactivity across various facets intact on single crystallites, and can be applied to better understand reaction-selective catalysis on (engineered) multifaceted particles.

Facet-Selective Adsorption of Fe(II) on Hematite Visualized by Nanoscale Secondary Ion Mass Spectrometry

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Abstract

Facet-specific reactivity of metal oxide particles is a well-known but at times difficult to probe phenomenon. Furthermore, in semiconductor metal oxides where crystal facets enclosing particles are electrically connected, separating them to enable detailed characterization defeats the purpose; the study of intact individual crystallites is necessary. Here we develop a masssensitive imaging approach to do so, and demonstrate its potential by unveiling the preferential binding of Fe(II) to various surfaces of the Fe(III) oxide hematite. Using isotopic tracers to follow iron provenance, ⁵⁶Fe-hematite microplatelets with various enclosing facets are reacted with aqueous ⁵⁷Fe(II) at circumneutral pH. The resulting distribution of ⁵⁷Fe across the hematite surfaces is directly visualized and quantified using nanoscale secondary ion mass spectrometry (NanoSIMS). The results unambiguously show Fe(II) sorption is highly selective for the basal (001) surface, while edge surfaces such as (012) and (110) are enriched to a lesser extent (up to 10× lower). Crystal intergrowth defects exposing poorly-ordered, nanoscale surface structures show the least enrichment. These results resolving Fe(II)-Fe(III) reaction fronts across multifacetted crystals provide a clear correlation between uptake and particle surface structure. The illustrated approach to understanding facet-specific ion uptake is also likely generalizable to other interfacial processes such as electron transfer and heterogeneous catalysis, across a broad range of particle and thin-film based systems.

1. Introduction

It is well established that the chemical and catalytic activity of crystalline materials can strongly depend on the types and proportions of their exposed facets. This is especially true when the crystal structure is anisotropic, such that the enclosing facets of individual particles will intrinsically expose two or more distinct sets of surface atomic structures. For example, among common binary metal oxides used or being developed as catalysts, reactivity differences for processes such as metal ion adsorption can more than double depending on the distinct terminations present.¹⁻⁴ Because of close ties between surface atomic structure and interfacial reactivity, synthesis of particles with a well-defined set of facets has been a growing frontier, aiding in the development of advanced materials with tailored catalytic functionality.⁵⁻¹⁰

The Fe(III)-oxide hematite (α -Fe₂O₃) is one such material for which morphology effects on reactivity have been demonstrated and are increasingly being exploited to optimize performance. This environmentally benign and versatile semiconductor has a range of important applications, such as in light-induced water splitting/photocatalysis,¹¹⁻¹⁶ energy storage,^{17, 18} and in contaminant remediation.^{1, 2, 19} Common particle shapes include platy, rhombohedral, and rounded, often based upon (001), (012), (110), and (104) facets.²⁰ Its hexagonal crystal structure imparts anisotropy in the types and distributions of amphoteric sites from one facet to the next, which collectively define the pH-dependent interfacial charge density per particle.²¹⁻²³ Particle morphology can thus strongly influence the reactivity of hematite/solution interfaces for any process that depends on interfacial electrostatics, such as ion sorption,^{2, 24-31} particle aggregation,³²⁻³⁴ and interfacial electron transfer.¹⁹ Likewise, for nanocrystalline hematite photoelectrodes, morphology optimization strategies include taking advantage of higher charge

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carrier mobility directions in the bulk crystal structure^{35, 36} to increase the efficiency of interfacial charge separation.^{9, 37, 38}

However, conventional studies that seek to unravel morphology-dependent reactivity highlight present-day gaps in experimental approaches that can do so. Current approaches are typically focused on either morphology-controlled nanoparticulate powders, which examine average ensemble behavior,^{1,2} or isolated facets of single crystals, which examine one surface independent of the others.^{4, 21, 39-42} Neither approach is ideal, particularly in cases where crystal facets on individual particles are mutually interactive and interdependent. For example, for semiconductors such as iron oxides, the electrostatic properties at particle surfaces have been shown to be a collective phenomenon, given a specific set of surfaces that enclose individual particles, an effect that is likely even more prevalent in particles at the nanoscale.^{43, 44} For example, macroscopic basal (001) and edge facets on hematite crystals in Fe(II) and oxalic acid solutions were shown to react differently simply on the basis of whether they were electrically connected or not.^{41, 45} While connected, facet-specific surface potential differences enabled conduction currents that enabled growth of (001) facets by oxidative adsorption of Fe(II) and dissolution of edge facets by Fe(II) release. It was furthermore shown that the direction of these inter-facet currents are pH dependent due to the different charging behaviors of (001) versus edge facets. On nanoparticles, such interactions remain difficult to unravel in experiments that probe only the average behavior of powders.

Likewise, measurements focused on isolated surfaces miss the collective behavior arising from interaction with other enclosing facets. Synchrotron X-ray reflectivity and scattering^{4, 39, 40} and atom probe tomography studies⁴⁶ on hematite (001) are all consistent with the notion that

Fe(II) undergoes oxidative adsorption leading to growth of this face. However, on isolated edge facets such as (012), Fe(II) appears to adsorb to and initiate reconstruction as well.^{4, 39, 40} Thus, while such studies provide valuable information on the structure and reactivity of individual facets, the prospect of those assumptions changing on intact particles is real and devoid of a straightforward means to predicting outcomes. Developing the ability to trace the interaction of reactants with various facets on individual crystallites simultaneously is, therefore, crucial for real progress in unraveling morphology dependent behavior.

Here, we lay out a new strategy that enables us to explicitly examine this collective behavior on individual hematite particles for the first time. We focus on mapping adsorbed Fe(II) distributions across single euhedral microparticles that expose a range of well-defined facets such as (001), (012), and (110). To do so, we combined stable isotopic labelling strategies with the power of nanoscale secondary ion mass spectrometry (NanoSIMS), enabling visualization of the selectivity of aqueous ⁵⁷Fe(II) adsorption onto ⁵⁶Fe-dominant platelets synthesized using iron isotopes at their natural abundance (NA) level. To be consistent with prior powder studies on this system, pH 7.5 was used,^{29, 47} which is also close to the point of zero electrostatic potential for most low-index hematite facets.²³ The latter indicates that the facet selectivity of Fe(II) being explored is primarily based on strength of interaction with specific surface structure (i.e., inner-sphere complexation), as opposed to non-specific electrostatic attraction (i.e., outer-sphere).

The observed spatial distribution of ⁵⁷Fe/⁵⁶Fe clearly reveals a prevailing affinity of Fe(II) for the (001) facet relative to edge facets at the selected experimental conditions, and complex interactions with a variety of possible microscale defects. Because all sites are intrinsically connected and exposed to identical conditions, the findings establish the real affinity of Fe(II) for

various facets on hematite particles, and likely that on nanoparticle powders and polycrystalline thin films. The experimental approach is likely generalizable to other metal oxide/adsorbate systems where facet and site-selectivity of interaction is an important consideration.

2. Methods

2.1 Batch experiments

The reader is referred to Taylor, *et al.* ^[46] for a detailed description of the materials and reaction conditions. In brief, micrometer-sized hematite platelets were synthesized according to Sapieszko and Matijevic ^[48], where a solution of 0.4M ferric nitrate, 0.2 M triethanolamine, 1.0 M sodium acetate, and 1.2 M sodium acetate was hydrothermally aged and agitated at 250°C for 2.5 hours. The specific surface area of the particles was measured to be $0.2 \text{ m}^2 \text{ g}^{-1}$ using the Brunauer-Emmett-Teller method with N₂ adsorption and a degas temperature of 100°C.

The hematite particles (200 g L⁻¹) were reacted at room temperature for 24 hours in a pH 7.5 solution (25 mM KBr, 25 mM 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) buffer) bearing 2 mM ⁵⁷Fe(II). Control samples were reacted in buffer solution without addition of ⁵⁷Fe(II) under the same conditions.⁴⁶ These sample types are referred to as reacted and unreacted hematite, respectively. All experiments were conducted in an anoxic glovebox (N₂/H₂ atmosphere) and all solutions were mixed using anoxic, degassed water. The water was prepared by boiling ultrapure Milli-Q water in Pyrex Corning glass bottles on a hot plate for ~30 minutes under vacuum, and then sparging it with purified N₂ in the glovebox.

Following reaction the supernatant was removed via centrifugation and analyzed with the ferrozine method (using a wavelength of 562 nm on a UV-vis spectrophotometer) to determine

the amount of Fe(II) remaining in solution, $[Fe(II)_{aq,24h}]$. Weakly bound Fe(II) on the hematite was removed by rinsing the particles with water and exposing them to 0.4 M HCl for 10 minutes; this was also measured, $[Fe(II)_{extr,24h}]$. This allowed us to feature more specifically the strongly interacting Fe(II) fraction, such as that attributable to the process of oxidative adsorption consistent with surface recrystallization. The amount of sorbed Fe $[Fe(II)_{sorbed, 24h}]$ across the entire powder was determined (Equation 1):

$$[Fe(II)_{sorb, 24h}] = [Fe(II)_{aq, 0h}] - [Fe(II)_{aq, 24h}] - [Fe(II)_{extr, 24h}]$$
(1)

Following the acid extraction step, the particles were rinsed two more times with the anoxic Milli-Q water. The unreacted and reacted particles were dispersed onto high purity vitreous carbon planchets (Ted Pella Inc.) using water and dried. From this point anoxia was no longer necessary to maintain. A scanning electron microscope (SEM; Thermo Fisher Scientific Helios Nanolab 600i) was used to identify particles from the unreacted and reacted samples and their respective regions of interest (ROI).

2.2 NanoSIMS Analysis

Isotopic image analyses were performed on select particles to determine the nature of the sorbed Fe with respect to crystallographic termination using a Cameca NanoSIMS 50L. Two types of analyses were performed – surface imaging and image analyses interleaved between aggressive sputtering cycles. For imaging alone, a 16 keV, ~4pA O⁻ primary ion beam with a diameter of approximately 200 μ m was employed. The two-dimensional image dimensions were set to encompass entire particles and were typically 30 × 30 μ m at 256 × 256 pixels, and 50 frames were typically collected. The entrance slit, aperture slit, and exit slits were set to 20 μ m, 350 μ m, and 100 μ m respectively. A centered energy window was used with an apparent energy

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width of 35 eV (10%). NMR regulation was employed in all analyses. The secondary Fe⁺ ions were accelerated to 8 keV and ⁵⁴Fe⁺, ⁵⁶Fe⁺, and ⁵⁷Fe⁺ were detected simultaneously using three electron multiplier detectors. ⁵²Cr⁺ was also monitored in a few cases where it was shown to be negligible and thus ⁵⁴Cr corrections on the ⁵⁴Fe signal were not employed. Major isobaric interferences on ⁵⁴Fe⁺ and ⁵⁶Fe⁺ (i.e., Al₂⁺ for ⁵⁴Fe⁺, CaO⁺ and Si₂⁺ for ⁵⁶Fe) were negligible for this system. Particular emphasis was paid to resolve ⁵⁷Fe⁺ from ⁵⁶Fe¹H⁺ and the 57 mass peak was checked frequently for drift and re-centered onto the ⁵⁷Fe signal as needed. These measurements map the Fe isotopic distributions at the near surface environment and do not reach the bulk, as NA isotopic values were not reached for the reacted particles (i.e., the ⁵⁷Fe/⁵⁶Fe ratios gradually decrease over time, and remain an order of magnitude above NA values).

An interleaved image-sputtering collection technique was applied to several particles to better observe the isotopic evolution from the enriched-surfaces into the bulk. Fe isotope images were interleaved with sputter cycles. Image cycles were acquired with similar conditions as described above, except that a dwell time of 13,500 μ s pixel⁻¹ was applied and followed by a 40 μ m × 40 μ m sputter cycle with a 500 pA beam. This cycle was repeated 5-6 more times to reach NA values. Measurements were conducted on an unreacted particle after every 3-4 reacted particles to ensure the ⁵⁷Fe/⁵⁶Fe ratios were consistent with NA values and that the instrument remained well calibrated.

Fe isotopic image processing was performed using the OpenMIMS plugin for ImageJ.⁴⁹ Images were pixel by pixel dead time–corrected and aligned using the Stack Editing tools in OpenMIMS.⁵⁰ The particles were analyzed in terms of ROIs (e.g., (001) vs (012)) in an Excel spreadsheet. ⁵⁷Fe within each of the ROIs was determined relative to ⁵⁶Fe in each ROI, as

⁵⁷Fe/⁵⁶Fe ratios. Hue-saturation-intensity (HSI) maps of ⁵⁷Fe/⁵⁶Fe were used to visualize the extent of ⁵⁷Fe-enrichment across the different ROI of a single particle. A median filter with a five-pixel radius was applied to the HSI images to reduce noise. While this makes the image data easier to interpret, it also causes minor artefacts due to spatial dilution of signals. Nevertheless, ROI isotopic data derived from ROI are not subject to these artefacts.

For the Fe isotopic measurements, the unreacted hematite particles were used as a standard to calibrate the instrument to NA Fe isotopic ratios. Instrumental mass fractionation corrections were implemented using the unreacted hematite particles as an external standard, accounting for any artificial changes in isotopic ratios produced during the measurement. The propagated uncertainty (σ) was also calculated to account for variability due to counting statistics for an individual ROI as well as the mass bias correction factor. Deviations of the ⁵⁷Fe/⁵⁶Fe isotopic ratios from NA were also considered. That is, variations in isotopic ratios can potentially result from relative differences in ROI heights and orientations, for instance, which impacts sputtered yields, secondary ion counts, and secondary ion energies.⁵¹ Previous studies using SIMS have shown that there is a potential instrumental bias affecting high precision δ^{18} O measurements for magnetite⁵² and δ^{56} Fe measurements for hematite⁵³ due to crystal orientation effects. The calculations and analyses performed on the standard unreacted particles are described in the *Electronic Supplementary Information (ESI)*.

In brief, the ⁵⁷Fe/⁵⁶Fe ratios across ROI at various orientations and heights for the standard unreacted particles were found to be within uncertainty of NA (0.023); e.g., the average ⁵⁷Fe/⁵⁶Fe for both the basal and edge surfaces was 0.024 ± 0.01 (considering 2σ , 95% confidence interval). Furthermore, as will be shown shortly, the isotopic contrast for the ⁵⁷Fe-reacted

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particles is significant and outside the uncertainty produced from these effects. Thus the ⁵⁷Fe/⁵⁶Fe ratios are reliable for observing the relative isotopic enrichment between the different ROI on the reacted particles. ⁵⁴Fe/⁵⁶Fe ratios were monitored as an additional check on data quality and were in all cases within uncertainty of NA ratios. The reader is referred to the *ESI* for additional detailed information about these analyses.

2.3 TEM characterization

The crystallographic structure of the hematite particles and its facets was characterized using transmission electron microscopy (TEM). A cross-section of an unreacted particle was prepared for TEM using conventional focused-ion beam (FIB) lift-out techniques with the dual-beam SEM.⁵⁴ In brief, electron-beam induced deposition of a Pt-capping layer on a rectangular section of the particle surface (i.e., $\sim 2 \ \mu m$ wide $\times \sim 20 \ \mu m$ long) was first done to protect the specimen from damage and Ga contamination during ion milling. This was followed by protective Pt- and C-capping layers via ion-beam induced deposition. A lamellar section ($\sim 1 \ \mu m$ long $\times \sim 20 \ \mu m$ long $\times \sim 2 \ \mu m$ depth) was extracted by perpendicularly milling on both sides of the coated region with the ion beam (Ga⁺ ion, 30 kV). The section was lifted-out with the Omniprobe micromanipulator and Pt-welded onto the post sidewall of a four-finger Cu FIB lift-out TEM grid (TedPella). The section was thinned down to <100 nm thickness for high-resolution TEM imaging.

TEM characterization of the specimen was performed with JEOL JEM-ARM200F operated at 200 kV. The microscope incorporates CEOS GmbH double-hexapole aberration corrector for the probe-forming lens, which allows imaging with ~0.8 nm resolution in scanning TEM (STEM) mode. The presented images were acquired in STEM mode using a High Angle

Annular Dark Field (HAADF) detector with a beam convergence of 27.5 mrad and a collection angle of 68-280 mrad. All images were acquired with Gatan's Digital Micrograph software package.⁵⁵

3. Results and Discussion

3.1 Hematite particle morphology and microtopography

Synthesis of euhedral hematite microplatelets enabled exploration of Fe(II) sorption on four different ROI: the three major low-index facets (001), (012), and (110), as well as defectrich vicinal surfaces resulting from grain intergrowths (**Figure 1a**). The platelets express dominant (001) basal facets bound primarily by (012) edge facets. The basal surface displayed characteristic microtopography including growth features defined by concentric step bunches centered on spiral dislocations, and/or composite spirals concentrated in platelet interiors. These step bunches separate relatively large atomically flat terraces that span several hundred nanometers.⁵⁶⁻⁵⁸ Expression of (110) edge terminations were observed as a minor facet; e.g., out of a random sampling of 50 particles, (110) surfaces were displayed on <10%.

Crystal twinning could also be readily observed in many of the larger particles (often > $15 \ \mu$ m). Defect-rich regions resulting from grain intergrowths that appear related to twinning were common.^{59, 60} In some cases intergrown platelets remained intact, revealing the high incident angle of intersection yielding stellate clusters. In other samples intergrown crystals had detached, leaving negative crystal pits referred to here as simply 'growth pits.' In the latter cases it could be seen that growth of the principal 'host' platelet was considerably impeded by the

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intergrown grain(s); the walls of these growth pits consist of the terminated edges of basal step bunches.

In general, the facet-specific reactivity within different ROI is expected to be controlled by the surface atomic structure. That the atomic structures of (001), (012), and (110) facets should be different is readily apparent through illustration of their nominal topologies from bulk terminations (Figure 1b). It is conventionally considered that a higher density of undercoordinated atoms leads to a higher surface energy and higher reactivity.⁶¹ Under this premise, the predicted trend from simplistic bulk termination models is: (110) > (012) >> (001).¹² However, because terminations in realistic systems are responsive to the chemical environment at the interface, at times even exhibiting multiple co-existing atomic configurations for a given facet, their structures are often quite different than simple bulk terminations.^{14, 62} Many studies have been devoted to probing the actual reconstructed and relaxed atomic structure of these hematite facets in situ.^{4, 21, 22, 62-64} But for the purpose of the present study, which requires no presumptions about such structural details under our selected experimental conditions, because their bulk truncations are clearly different it is safe to assume that their respective atomic structures are also different. Hence, the four ROI chosen, which are clearly distinguishable using SEM, likely capture a broad range of atomic surface structure possibilities for hematite particles.



Figure 1: (a) SEM image highlighting general particle morphology and ROI as well as grain intergrowths. (b) Approximate surface termination models for the different facets based on X-ray reflectivity measurements by Catalano, et al. ^[4], *visualized using Vesta v.3.3.2 software.* ⁶⁵ Small, blue atoms are iron and large, red atoms are oxygen. Dashed black line through (001) indicates one potential termination through an iron layer.

3.2 Facet-selective Fe(II) adsorption

The hematite particles were reacted at pH 7.5 for 24 hours in the absence and presence of 2 mM 57 Fe(II) under anoxic conditions (referred to as the unreacted and reacted samples, respectively). For the reacted samples, UV-vis measurements of the aqueous solution after reaction indicated an average sorbed Fe concentration of ~1 µmol g⁻¹, corresponding to an approximate surface coverage of ~1 – 2 monolayers. Recent prior APT analyses specifically on the basal surface indicated an average of 3 – 4 Fe atoms nm⁻².⁴⁶ The unreacted and reacted

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particles were dispersed onto high purity vitreous carbon planchets. Individual crystallites and their respective ROI were identified with SEM, and then analyzed with NanoSIMS.

NanoSIMS imaging of the ⁵⁷Fe/⁵⁶Fe ratio across the reacted and unreacted hematite particles clearly revealed significant heterogeneity in Fe(II) adsorption onto specific facets and site types (**Figure 2**). Unreacted particles, synthesized from NA-iron isotopes and exposed only to control solutions devoid of ⁵⁷Fe(II), show only a homogeneous distribution of their intrinsic minor ⁵⁷Fe content relative to dominant ⁵⁶Fe at any location on particle surfaces (**Figure 2a**). This manifested as a NanoSIMS map of effectively zero contrast. ⁵⁷Fe/⁵⁶Fe ratios for the different ROI of the unreacted particles were measured to be within [0.014, 0.038] (considering 2σ , 95% confidence interval; see *SI*), which are within range of NA (i.e., 0.023). Additional technical value stemming from these maps include the indication that the prospect of geometrical interferences leading to location-specific artificial signal were insignificant, and that such image data could be used to calibrate the ⁵⁷Fe/⁵⁶Fe signal intensity to its expected value at NA (see *ESI*).





Figure 2: Corresponding SEM and ${}^{57}Fe/{}^{56}Fe$ maps from NanoSIMS on (a) unreacted and (b) reacted particles. NA refers to the ${}^{57}Fe/{}^{56}Fe$ ratio at natural abundance (i.e., 0.023). (c) Trends in Fe(II) sorption with respect to ROI from imaging measurements. The ${}^{57}Fe/{}^{56}Fe$ ratios for each ROI of the particles are plotted. The gray vertical bars represent the uncertainty within 2σ (95% confidence interval) across the unreacted and reacted particles.

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In striking contrast, NanoSIMS maps collected in identical fashion on the particles reacted in aqueous ⁵⁷Fe(II) clearly showed that Fe(II) adsorption to hematite was strongly location-specific (**Figure 2b**). On all three major exposed facets, the measured ⁵⁷Fe/⁵⁶Fe ratios were generally an order of magnitude higher than NA (**Figure 2c**), thus indicating that net adsorption of Fe(II) occurred on all exposed low-index surfaces under our experimental conditions. However, regions where Fe(II) selectively adsorbed were strongly enriched in ⁵⁷Fe. The largest ⁵⁷Fe/⁵⁶Fe values were routinely observed on the basal (001) facets, which were consistently higher than those observed for the (110) and (012) edge facets. For instance, for the particles shown in **Figure 2b**, the maximum ⁵⁷Fe/⁵⁶Fe measured for (001) was 0.26±0.01 (2 σ) compared to 0.15±0.01 and 0.19±0.01 for (110) and (012) facets, respectively.

⁵⁷Fe/⁵⁶Fe imaging measurements were collected over seven different particles, and in all cases the same facet-dependent trend of preferred enrichment on (001) was found. The extent of ⁵⁷Fe-enrichment for each ROI were shown to vary slightly from particle to particle. For instance, ⁵⁷Fe/⁵⁶Fe measured for (001) surfaces across the seven crystallites fell within the range of [0.10, 0.32] (considering 2σ , **Figure 2c**). While this variation is within the measurement uncertainty, it is also possible that some arises from inherent reactivity differences between particles, such as variability in the ratio of edge to basal surface area (e.g., surface area of (012) relative to (001)). Nonetheless, basal surfaces were consistently more ⁵⁷Fe-enriched than (012) and (110) edge surfaces. Thus, a strong preferential facet selectivity for Fe(II) adsorption clearly emerged in the order (001) >> (012) ≈ (110).

The preference for Fe(II) adsorption to the (001) facet relative to edge surfaces is in conceptual agreement with prior studies on isolated single crystal surfaces. But because the

current data encompass whole particle behavior we now have a basis for calibrating and unifying those results. For example, at similar experimental conditions (i.e., 7.2 μ mol Fe m⁻² sorbed on (001) at pH 7) X-ray reflectivity measurements of Fe(II) sorbed on separated (001), (012), and (110) facets of large single crystals indicated that the (001) facet undergoes the most structural change upon reaction, nominally due to oxidative adsorption of the Fe(II) that nucleates hematite growth islands on (001).⁴ This result was confirmed by APT at a similar pH, where sorbed Fe at the (001) surface was consistent with island-like deposition.⁴⁶ X-ray reflectivity further suggested that the interfacial roughness and/or termination of the (012) and (110) facets changed after reaction with Fe(II), but in a manner distinct from that on (001); i.e., structural changes were speculated to occur via layer-by-layer growth or dissolution.⁴ Similarly, using crystal truncation rod X-ray scattering to characterize hematite reacted with Fe(II)_{aq} at pH 5, only one adsorbed Fe layer was found on the (012) surface whereas multiple adsorbed layers were observed on the (001) surface (i.e., two adsorbed Fe layers on the hydroxylated Fe-termination and one on the O-layer termination).^{39, 40} Most of these prior studies, however, were not able to conclusively differentiate iron addition from iron subtraction due to the methodological ambiguities of locating the original surfaces.

3.3 Inhibited Fe(II) adsorption at growth pit defects

In addition to observing the preferential adsorption of Fe(II) onto particular facets, locations where Fe(II) adsorption was not favored were also found. Our NanoSIMS data indicate the least amount of ⁵⁷Fe-enrichment in the locations of growth pits – here the associated ⁵⁷Fe/⁵⁶Fe ratios were typically within the same order of magnitude as NA values, indicating at

best only minor adsorption (**Figure 2b, c**). This weak interaction is somewhat surprising given that according to SEM images the surfaces in pit bottoms appear co-planar with the strongly interacting (001) facet (**Figure 3a**). However, the low depth resolution of SEM does not allow for a definitive conclusion in that regard, nor does it allow detection of more detailed microtopographic differences that likely exist between the (001) facets and pit bottom surfaces. In addition, NanoSIMS data also indicated weak adsorption to growth pit sidewalls. TEM and STEM characterization of these locations suggests that this behavior is related to the relatively low Fe(II) affinity of (012) and (110) edge facets, because the sidewalls appear micro-faceted with these same edge facets, as well as higher-index edge facets like (014) (**Figure 3b, c**).



Figure 3: (a) Growth pits observable by SEM. The area in the black box was imaged with TEM (b), where the micro-facetted character of the growth pit sidewalls can clearly be observed in cross-section, along $(100)_{hematite}$. The atomic structure for the steps in the block box was resolved with STEM (c). This section of the sidewall is comprised of (012) and (014) micro-facets; lattice planes are notated in the figure for clarity. The structural complexity within a single step, including twinning, is also highlighted.

The apparent lack of affinity for aqueous Fe at these locations is generally consistent with their history as sites where growth was inhibited during the initial synthesis, due to the presence of intersecting crystallites. The atomic-scale properties of the grain-boundary surfaces that define these growth pit features are unknown and potentially complex. For instance, these regions may be replete with dislocations due to stress accumulation along the grain boundaries between imperfectly aligned intersecting crystallites during growth. At fine length scales beyond SEM resolution these grain boundaries may be vicinal or high-index surfaces that do not present high affinity binding sites for Fe(II), although the data do not allow conclusiveness in this regard. Further exploration of these features at high resolution would be a challenge but of interest for deeper insight into fine-scale surface properties that influence Fe sorption and growth.

These observations contrast with some generally accepted notions regarding reactivity at structural defects sites. Defects are often assumed to be sites of higher interfacial reactivity and, in systems closely related to the present one, important sites for Fe(II) adsorption and electron transfer.^{44, 66} For instance, recent studies utilizing isotopic tracer techniques and atom probe tomography suggested preferential Fe(II) adsorption and atom exchange on goethite particles (α -FeOOH) within nanoscale pores and/or grain boundaries.⁶⁷ The opposite generally appears to be true for the present hematite system. It is thus noteworthy that such reactivity may be sensitive to the specific structural details of the defects present (e.g., vacancies vs. grain boundaries vs. twin boundaries, etc.), conceptually consistent with the overarching observation that the reactivity is likewise sensitive to the structural details of different exposed facets.

3.4 Temporal distribution of adsorbed Fe(II)

To gain insight into the relative depth of the ⁵⁷Fe enrichment on the various facets, we performed image-sputter measurements to map the isotopic distribution from the outermost surface to deeper within the near-surface across the different ROI. During this mode of analysis, sequential NanoSIMS images are interleaved with sputtering rasters under more aggressive ion beam conditions. Because the depth sensitivity is material specific and the structure of the adsorbed Fe layer, which is only a few monolayers thick according to combined UV-vis and APT measurements,⁴⁶ may differ significantly from hematite, the actual depth scale during profiling is not easily calibrated or predicted. As described in the imaging-only measurements above, the isotopic images obtained were used to map and quantify of ⁵⁷Fe/⁵⁶Fe across the different ROI of crystallites.

Image-sputter measurements on a crystallite formed from intergrown particles (**Figure 4a**) illustrate the ⁵⁷Fe enrichment observed with depth. Prior to sputtering, ⁵⁷Fe/⁵⁶Fe ratios across the different ROI are within the range of that observed for the imaging measurements discussed above (**Figure 4b, c**). Again, the (001) surface is the most enriched in ⁵⁷Fe relative to the edges and the defective growth pits are the least enriched. Interestingly, ⁵⁷Fe-enrichment on the basal surface is non-uniform as the ⁵⁷Fe/⁵⁶Fe maps shows slight variations in ⁵⁷Fe-enrichment between three main regions on the basal surface; the ⁵⁷Fe/⁵⁶Fe ratios across these three regions are 0.32±0.08, 0.25±0.06, and 0.21±0.05. While within uncertainty, the variation appears to depend on location. These distinct sub-regions are separated by growth pit defects arising from intergrown particles, suggesting affinity differences of basal surfaces related to location with respect to intergrown particles.

After the first sputter cycle, the ratios decrease by less than an order of magnitude for all ROI. The ratios for more highly enriched ROI (e.g. the (001) facets) are still slightly above NA, thus indicating that a considerable amount of ⁵⁷Fe at the surface has been removed by sputtering but that the depth of the original surface has not been reached. After three sputter cycles the ratios for all the ROI are within uncertainty of NA levels, consistent with intersecting the relict hematite surface. The rapid recovery of NA ⁵⁷Fe/⁵⁶Fe ratios with depth in general suggests that ⁵⁷Fe was most likely deposited upon the hematite surface rather than buried within it, such as by redox-catalyzed recrystallization. Recrystallization would likely have a larger isotopic contrast at depth rather than at the uppermost surface plane.^{46, 67}



Figure 4: (a) SEM characterization of a crystallite formed by intergrown particles. Black dashed lines separate the three regions correlating to intergrown particles. The area within the black box is further magnified in the right image, highlighting microstructural growth pits correlating to intergrown particles. (b) Corresponding sequential image-sputter data highlighting the depth distribution of ⁵⁷Fe from the outermost surface to deeper within the near-surface. Image numbers indicate the ratios measured following sputter cycles; e.g., image 0 is the first image taken before sputtering, image 1 is taken after the first sputter cycle, and so on. Note the ⁵⁷Fe/⁵⁶Fe color scale changes from image 0 vs. images 1 - 3 in panel b. (c) Quantification of ⁵⁷Fe/⁵⁶Fe concentrations progressing from the outermost surface into the bulk. ⁵⁷Fe/⁵⁶Fe ratios for each individual ROI are measured and

plotted; e.g., for the basal surface of the crystallite, the three regions with varying enrichment are plotted as separate (001) profiles. 2σ is plotted for select ROI.

3.5 Basis for facet-selectivity of Fe(II) adsorption

The facet-selectivity for Fe(II) sorption onto hematite was explicitly visualized for the first time. The findings clearly point to strong preferential adsorption of Fe(II) on the (001) facet and weaker adsorption to edge (012) and (110) facets, simultaneously, on individual hematite crystallites at circumneutral pH. They also reveal little to no adsorption at locations defined by detached intersecting crystallites, likely of unique atomic-scale structure and possibly defectrich. A key aspect of the findings is that facets were analyzed on intact particles, on an equal analytical footing, such that true adsorption behavior for whole particles is revealed, leaving no doubt that the (001) surface has the highest relative affinity for Fe(II).

While these results are consistent with previous studies,^{4, 39, 40} the explanation for this facet selectivity at the atomic scale remains somewhat in debate. For example, bond valence calculations and surface complexation modelling on idealized structure models of hematite surface terminations generally infer a higher binding affinity at surfaces bearing the highest density of under-coordinated surface ligands,⁶¹ leading to the expectation that edge facets such as (012) should outcompete (001). This was reinforced by molecular dynamics simulations that suggest weak outer-sphere binding of Fe(II) to one idealized (001) termination.⁶⁸ However, the differences between such models and real terminations in equilibrium with aqueous solution are substantial. This includes the prospect of mixed terminations on the (001) facet in water that present singly-coordinated hydroxyl groups on the (001) surface co-existing with doubly-coordinated functional groups,^{62, 69, 70} as well as the prospect of non-stoichiometric terminations

of (012).^{21, 40, 63, 64} Furthermore, the measured pH-dependence of the electrostatic potentials for individual facets suggests that edge facets such as (012) should indeed electrostatically outcompete (001) for Fe(II) at low pH.^{23, 41, 71} At the circumneutral pH of the present study, preferential binding to (001) likely reflects formation of an inner-sphere surface complex attaining a stable low energy structure, which was shown to be possible for our conditions by second harmonic generation spectroscopy.⁴² Further work is needed to understand the structure of these terminations in more realistic detail, so that sorption complexes of Fe(II) can be better predicted.

Further along these lines, it is noteworthy that the assumptions in many previous studies that reference or rely upon concepts such as 'monolayer coverage' of adsorbed ions may be highly inaccurate. In the context of the present study, the interaction between Fe(II) and Fe(III)- (oxyhydr)oxides often has been investigated using particulate powders^{1, 2, 42, 47, 72} or isolated single crystal surfaces in which the information is averaged over macroscopic length scales. ^{4, 21, 39-42} In such cases, because ion adsorption is typically assumed to occur as uniform mono- or multilayers, the true linkage between sorption capacity and surface coverage remains tenuous. The present study clearly demonstrates that ion sorption on single crystallites is heterogeneous in a manner that strongly depends on local atomic structure of specific facets, as well as the complex structure of defects. Furthermore, the reactivity from particle to particle may collectively span a wide distribution due to their inherent structural differences (e.g., proportions of exposed basal vs. edge surfaces, polycrystallinty, type and density of defects, etc.).

The isotopic labelling and NanoSIMS approach developed here can be applied to further probe morphology- and facet-dependent reactions as a function of different crystallographic

structures and/or experimental conditions (e.g., pH). For instance, for future work, it is of interest to systematically probe the interaction of Fe(II) with batches of synthesized, monodisperse hematite particles tailored with decreasing fractions of (001) relative to (012) (i.e., progressing from platelet to pseudo-cubic morphologies),^{19, 73, 74} effectively creating particles with a set range of reactivities.⁷ Trends for the different morphologies can then be determined using the isotopic imaging measurements. In turn, this knowledge can be used to develop new adsorption isotherm models that account for the distribution of a given set of facets of specific reactivity, enabling more accurate representation of the ensemble behavior for anisotropic materials. We note, given that the current spatial resolution of NanoSIMS is approximately 250 – 300 nm (with the system configuration used in this study), the approach ultimately finds its limits with smaller particles or particles and thin films with complex morphology- and facet-dependent studies on micrometersized particles^{48, 75, 76} could be investigated, comparing and extrapolating the results down-scale to understand facet-specific reactions on nanoparticles.

At these experimental conditions, because of the similarity of points-of-zero-potential²³ electrostatically driven currents linking the chemical transformations of one surface to another⁴¹ is not expected, nor was it observed. However, this tendency is expected to increase at either lower or higher pH,²³ as well as in the presence of potential-determining ions that can selectively bind to particular facets, such as oxalate.^{41, 77} In future work, our experimental approach can be adapted to such systems to improve understanding of interlinked surface reactivity. For example, redox-based growth and dissolution fronts will need to be concurrently identified using a combination of isotopic mapping and topographic measurements capable of monitoring surface

transformation relative to a fiducial marker of the original surface position. Identification of dissolution fronts cannot be inferred based only on the lack of ⁵⁷Fe-enrichment, but requires monitoring changes in the particle morphology and topography (e.g., etch pits) simultaneously.

4. Conclusions

By using isotopic labelling and mass-sensitive mapping techniques the facet-selective adsorption of Fe(II) across intact hematite surfaces at circumneutral pH was clearly resolved. Visualization and quantification of the ⁵⁷Fe distributions demonstrates that Fe(II) preferentially binds to the basal surfaces more readily than edge surfaces when electrostatic surface potential gradients are minimal. Additionally grain-intergrowth defects exposing unique micro-facets generally exhibit the least enrichment. The findings clearly demonstrate that the interfacial reactivity of individual iron oxide crystallites can be substantially anisotropic.

This approach using isotopic labelling and NanoSIMS enables further exploration into facet-selective reactions for anisotropic materials. The findings also have important general implications for advancing a means to probe and understand a wider variety of heterogeneous chemical processes for metal oxides, including crystal growth and metal uptake. For example, the macroscopic uptake of heavy toxic metal ions on different surfaces of a single crystallite³ could, in principle, easily be spatially resolved with NanoSIMS. Ideally the chemistry of the system of interest should be free of material-specific overlapping mass signal interferences, which to some extent can be circumvented through stable isotopic manipulation, as was done in the present case. Success could help substantiate spectroscopic observations and enable a more thorough understanding of how metal oxides influence, for example, contaminant transport in

 soils and sediments. The ability to resolve facet-specific reaction mechanisms would also aid in developing more effective adsorbents and catalysts, and/or to enable more insightful tailoring of particle or grain shape.^{2, 12}

Supplementary Information

Electronic Supplementary Information is available as a separate file.

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Toc Entry



Novel isotopic labelling and imaging techniques are used to directly observe the autocalatytic reaction and facet-selective adsorption of Fe(II) onto individual hematite (Fe₂O₃) crystallites.