

Supporting Information for

“Iron Dissolution from Goethite (α -FeOOH) Surfaces in Water by *Ab Initio* Enhanced Free Energy Simulations”

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Ab initio molecular dynamics (AIMD) based simulations were performed to model dissolution of Fe from the (021) and (110) goethite surfaces. We investigated Fe dissolution from the two symmetrically inequivalent Fe sites of the (021) facet and from the three topmost Fe sites of the (110) facet (Figure 1) into aqueous solution considering three dissolution scenarios for each Fe species – nonreductive (as Fe^{3+}), nonreductive proton-assisted, and reductive (as Fe^{2+}) mechanisms. For each case AIMD based metadynamics simulations were employed to explore dissolution free energy landscapes and identify possible reaction mechanisms. Then, the Blue Moon ensemble simulations were carried out to accurately determine activation free energy barriers of iron dissolution. In total, about 800 ps AIMD trajectories were analyzed.

Below we provide computational details on the metadynamics and thermodynamic integration simulations including free energy profiles and gradients for the reaction steps of iron dissolution from both (021) and (110) goethite surfaces (see simulation cells in Fig. S1). Van der Waals corrections, statistical error and the Pauling electrostatic bond strength analyses are also described.

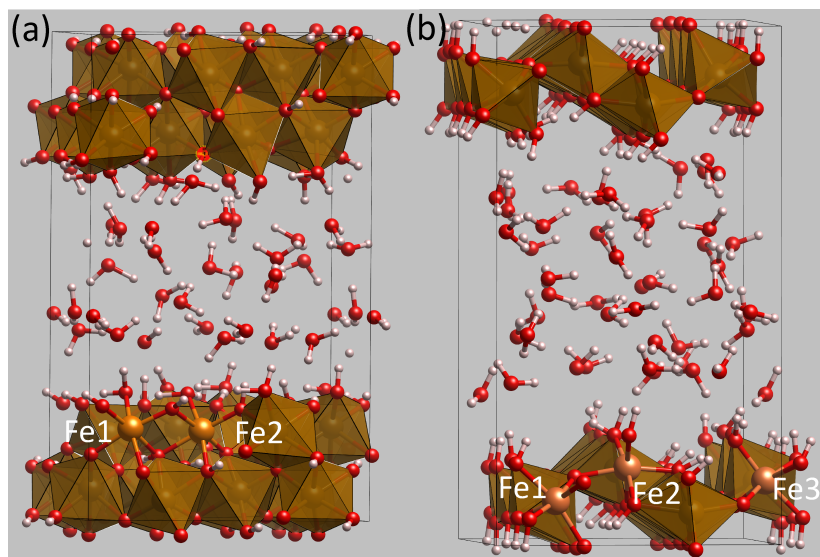


Fig. S1. Side view of the supercell models for the (021) (a) and (110) (b) goethite hydroxylated surfaces. Symmetrically inequivalent topmost Fe atoms investigated for dissolution are denoted.

Thermodynamic Integration - (021) Surface

We start by considering Fe^{3+} dissolution from the Fe2 surface site (see Fig. S1). We note that the results for the Fe2 and Fe1 sites turned out to be qualitatively similar with minor differences as alluded to below. The results of the metadynamics simulations for the dissolution trajectory of Fe from the (021) goethite surface are shown in Fig. S2. As it is seen from Fig. 1, iron at the Fe2 site is coordinated by six oxygen atoms – 2 two-fold coordinated O atoms, 1 three-fold coordinated OH, 2 two-fold coordinated OH and 1 weakly bound H_2O molecule.

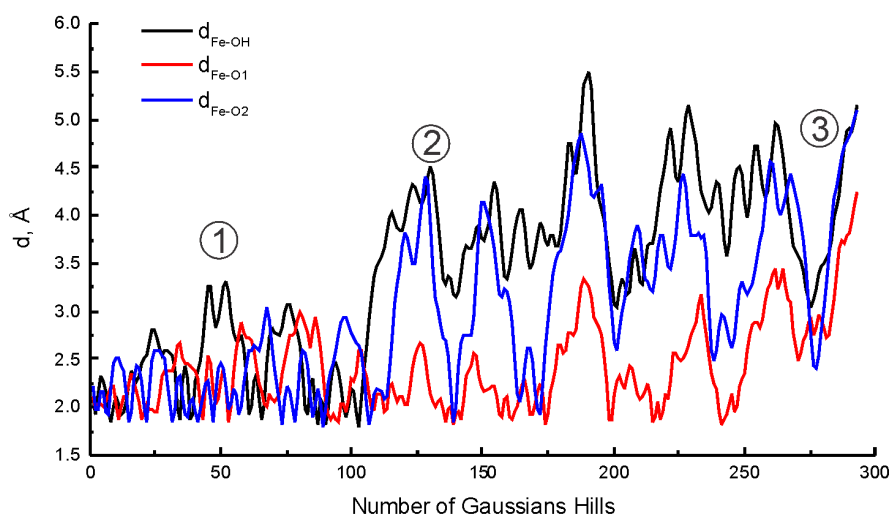


Fig. S2. Evolution of the collective variables (the bond distances between the dissolving Fe and structural O species) as a function of the number of Gaussians from metadynamics simulations of Fe^{3+} dissolution from the (021) surface.

According to our metadynamics simulations, Fe^{3+} dissolution proceeds through a number of intermediate metastable configurations shown in Fig. 2 for the Fe^{3+} case. As can be seen from Fig. S2, breaking of the first Fe-O bond does not result in a metastable intermediate state. However, if both Fe-O and Fe-OH bonds are simultaneously broken (region 2 in Fig. S2), the dissolving Fe ion becomes available for the attack by an H_2O molecule from solution. This H_2O rapidly dissociates to yield OH attached to Fe^{3+} that stabilizes this intermediate configuration (state *b*, Fig. 2). Additionally, dissolving Fe^{3+} forms one more bond with the neighboring structural OH, whereas in the case of Fe^{2+} dissolution this bond is only formed during the next step due to the lower oxidation state of Fe.

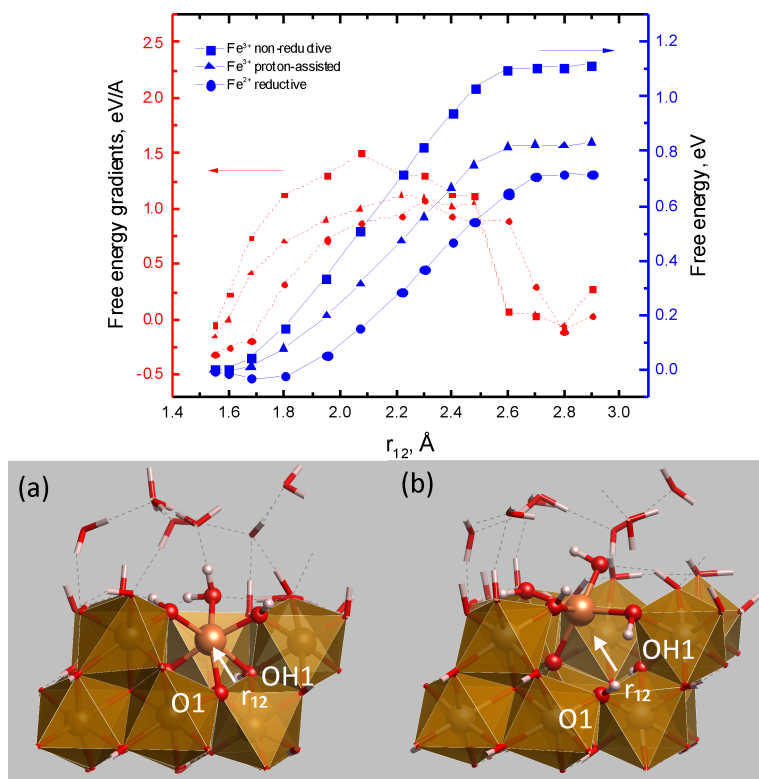


Fig. S3. Free energy gradients (left-hand scale) and integrated free energy (right-hand scale) vs. reaction coordinate r_{12} (the distance between Fe2 and the center of the bond between O1 and oxygen atom from OH1) for the transition between *a* and *b* states of dissolution from the (021) surface.

To estimate the activation barriers of simultaneous breaking of the two Fe-O1 and Fe-OH1 bonds we applied the Blue Moon ensemble simulations [1] and chose the

distance between the Fe atom and the center of the bond between O1 and oxygen atom from OH1 as a collective variable (Fig. S3). The forces and free energies for this dissolution step are presented in Fig. S3. When r_{12} reaches ~ 2.4 - 2.5 Å and both Fe-O1 and Fe-OH1 bonds are almost broken, we observe that the dissolving Fe atom becomes active for water attack followed by dissociation of water. From electrostatic point of view, after breaking the bonds with 3-fold coordinated O1 and 3-fold coordinated OH1 the sum of the electrostatic bond strengths to Fe2 decreases by 1 e. To preserve local electroneutrality, the H₂O molecule bound to the dissolving Fe³⁺ ion becomes deprotonated (1 e) leading to a new OH group and concurrently dissolving Fe forms a weak bond with the nearest surface OH group (1/2 e). After that the forces sharply drop down and become negative indicating the formation of a new intermediate state. As it will be shown later this step is rate limiting with the highest activation barrier of 1.12 eV. The reductive mechanism of Fe²⁺ dissolution is qualitatively very similar, but leads to a much smaller barrier of 0.72 eV.

We next investigated how protonation may promote Fe dissolution. In the proton-assisted dissolution mechanism we assume that the breaking bond may be protonated from acidic solution. It is worth noting that we also observed spontaneous protonation of under-coordinated O1 from a neighboring OH after the Fe-O1 bond is broken, which is due to internal proton migration. Expectedly, our results revealed that breaking of the Fe-OH bond occurs easier than Fe-O. It is natural to suggest that protonation of O weakens the bond with Fe. Fig. S3 demonstrates that when the distance r_{12} has increased up to 2.2 Å, the influence of external protonation vanishes due to spontaneous internal protonation. The effect of protonation from acidic environment decreases this barrier down to 0.84 eV.

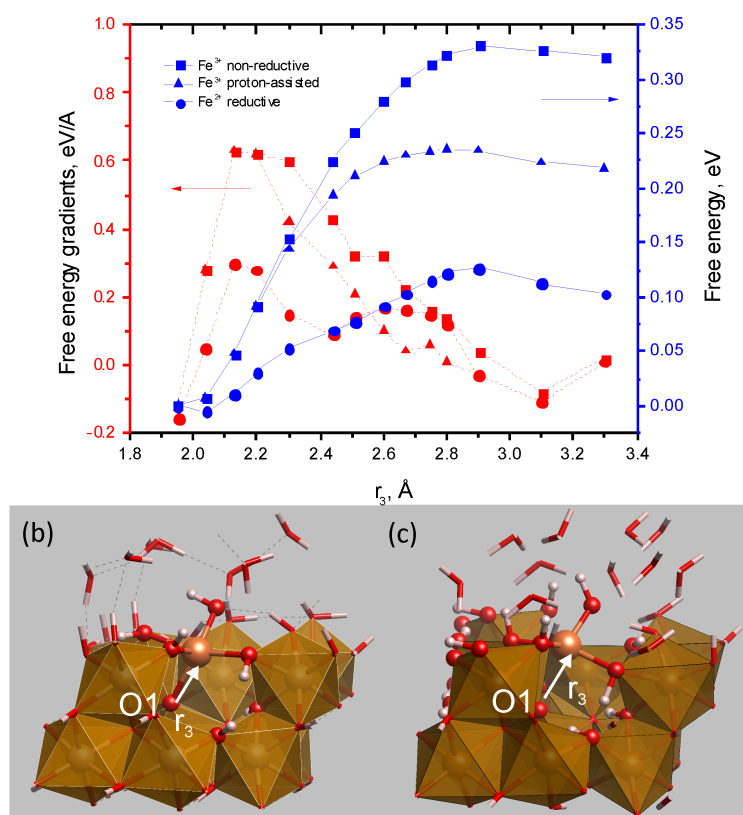


Fig. S4. Free energy gradients and (left-hand scale) and free energy (right-hand scale) vs. reaction coordinate r_3 (the distance between Fe2 atom and O2) for the transition between *b* and *c* states of dissolution from the (021) surface.

After that the system overcomes a barrier of 0.33 eV, which involves breaking of the Fe-O2 bond (r_3 reaction coordinate). By breaking this bond with 2-fold coordinated O ($-2/3$ e), the system recovers the local charge balance and the sum of the electrostatic bond strengths becomes equal to the charge on Fe^{3+} . The protonation of the O atom was found to be energetically unfavorable initially, while for $r_3 > 2.2$ Å a protonation becomes energetically favorable leading to a decreased barrier of 0.24 eV. In the case of reductive dissolution of Fe^{2+} , the barrier is only 0.12 eV, and the dissolving Fe ion is now coordinated by the 4 OH groups. The corresponding forces and energies for this case are presented in Fig. S4.

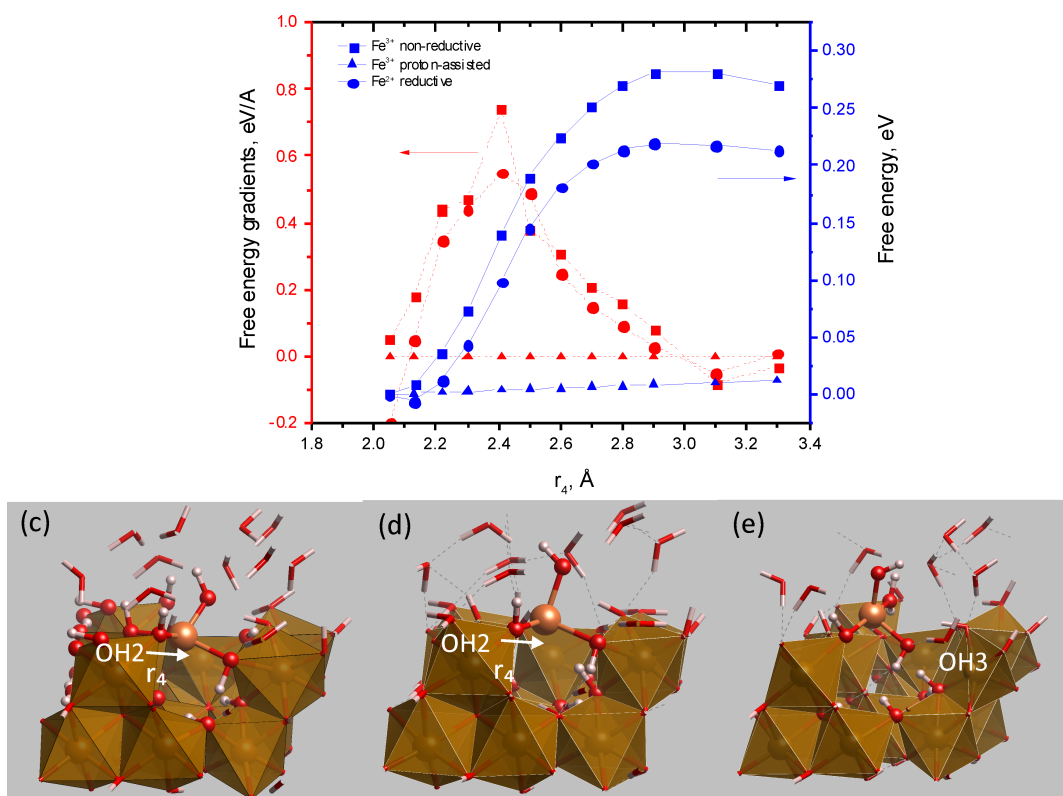


Fig. S5. Free energy gradients and (left-hand scale) and integrated free energy (right-hand scale) vs reaction coordinate r_4 (distance between Fe2 atom and OH2) for the transition between c and e states of dissolution from the (021) surface.

Next, we simulated the bond breaking between the dissolving Fe^{3+} ions and structural OH2 group (r_4 reaction coordinate, Fig. S5). Along the dissolution pathway one structural OH3 group bound to the outgoing Fe^{3+} ion detaches from a structural Fe^{3+} and leaves the surface together with the dissolving ion (Fig. S5). Concurrently, the H_2O molecule bound to the dissolving ion gets deprotonated. The mechanism described above can be analyzed using the Pauling's principle of electroneutrality: the bond breaking with 2-fold coordinated OH2 group ($-1/2$ e) is compensated by the formation of a stronger bond with 1-fold coordinated OH3 ($1/2$ e) and water dissociation ($1/2$ e). The protonation of Fe-OH2 was observed to be energetically favorable from the very beginning of the reaction, and the Fe-OH2 bond breaks immediately at low pH. In the case of reductive dissolution Fe^{2+} bonds are saturated and after water dissociation the bond with OH3 group breaks spontaneously, finally leading to $\text{Fe}(\text{OH})_2$ species bound to a structural hydroxyl.

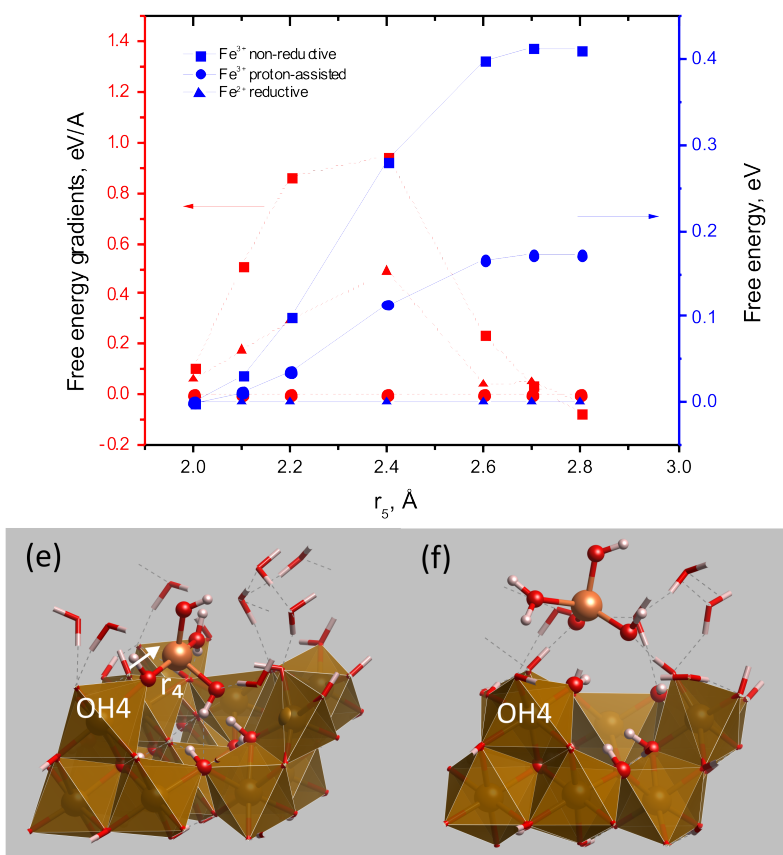


Fig S6. Free energy gradients and (left-hand scale) and integrated free energy (right-hand scale) vs reaction coordinate r_5 (distance between Fe2 atom and OH4) for the transition between *e* and *f* states of dissolution from the (021) surface.

The last dissolution step includes breaking of the Fe-OH4 bond and release of $\text{Fe}(\text{OH})_3/\text{Fe}(\text{OH})_2$ into water solution (Fig. S6). After the last Fe-OH bond breaking (-1/2 e) and formation of the $\text{Fe}^{3+}(\text{OH})_3/\text{Fe}^{2+}(\text{OH})_2$ complex the local charge balance recovers. Our AIMD simulations with the H_3O^+ ions embedded in aqueous solution in the vicinity of the Fe-OH4 bond showed spontaneous protonation of OH followed by Fe detachment from the surface. The complete free-energy profiles between these intermediate steps are shown in Fig 2b.

The second inequivalent dissolution site on the (021) surface is Fe1. The first coordination sphere of the Fe1 ion includes one 2-fold coordinated O, two 3-fold coordinated OH, two 2-fold coordinated OH and one single coordinated OH. According to the qualitative electrostatic bond strength analysis, the surrounding of the Fe1 site is more electronegative than Fe2. Consequently, the Fe1 ion is characterized by a smaller dissolution barrier. The total dissolution barrier decreases down to 1.81 eV as compared

to the Fe2 case (1.89 eV) which is mainly attributed to the first dissolution step. Subsequent dissolution steps for both Fe1 and Fe2 are found to be similar with negligible difference in activation barrier.

Thermodynamics integration – (110) surface

Below we briefly discuss Fe dissolution from various sites (see Fig. S1) on the (110) goethite surface.

Fe3 site

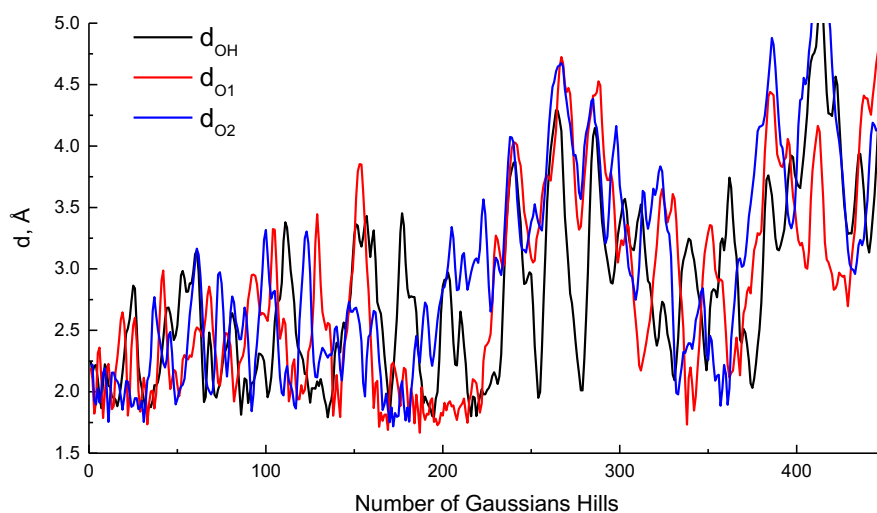


Fig. S7. Evolution of the collective variables (the bond distances between the dissolving Fe and structural O species) as a function of the number of Gaussians from metadynamics simulations of Fe^{3+} dissolution from the Fe3 site on the (110) surface.

From Fig. S8 it is seen that iron at the Fe3 site on the (110) surface is coordinated by six oxygen atoms: two 3-fold coordinated O atoms, three 3-fold coordinated OH, and a singly-bound OH. According to our metadynamics simulations (Fig. S7), Fe^{3+} dissolution proceeds through a number of intermediate metastable configurations that are depicted in Fig. S8. Similarly to Fe dissolution from the Fe2 site on (021) described above, breaking of the first Fe-O/Fe-OH bonds does not result in a metastable intermediate state. However, if both Fe-O and Fe-OH bonds are simultaneously broken, the dissolving Fe species becomes available for the nucleophilic attack by a neighboring H_2O molecule.

Upon breaking these two bonds, the dissolving Fe^{3+} ion forms a new bond with the nearest surface OH group (see Figure S8, state *b*). At the same time, the structural O atom left behind becomes protonated by a structural proton from the nearby OH group that facilitates the bond-breaking event. Then, the third Fe-O bond breaks leading to the intermediate state *c*. The next two states (*d* and *e*) involve breaking of two Fe-OH bonds

that takes place almost simultaneously with a very small activation barrier. First, the bond between the dissolving Fe^{3+} and structural OH is broken (state d), then another structural OH bound to the outgoing Fe^{3+} ion detaches from a structural Fe^{3+} (state e) and leaves the surface together with the dissolving Fe^{3+} ion. Concurrently, an H_2O molecule from solution binds to the dissolving Fe^{3+} ion and subsequently becomes deprotonated resulting in one more OH group. During the next step (from state e to f) the remaining bond between the dissolving Fe^{3+} and structural OH is being broken.

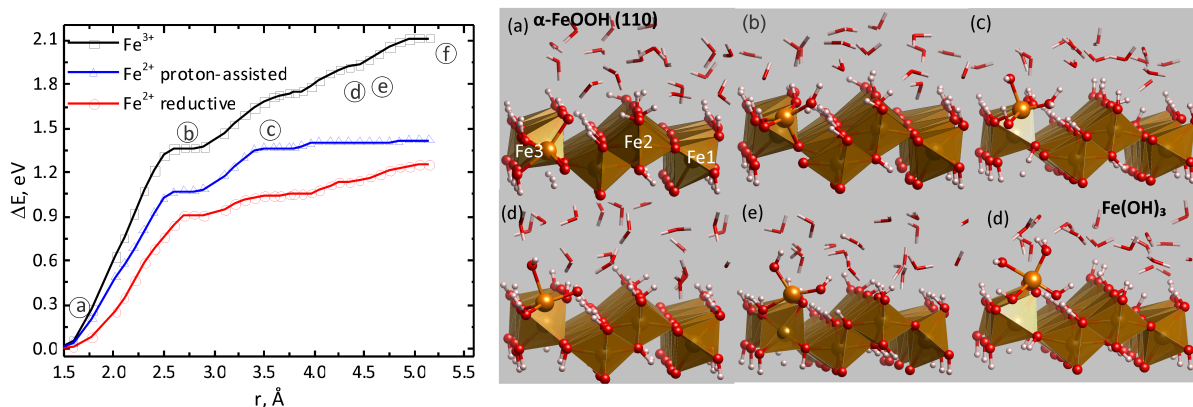


Fig. S8. Free energy profiles of iron dissolution from the Fe3 site of the (110) surface for the reductive (as Fe^{2+}) and nonreductive (as Fe^{3+} at neutral and acidic pH) mechanisms. (a)-(f) correspond to the initial, final and intermediate metastable structures along the dissolution pathway shown on the right for the Fe^{3+} case.

In the case of reductive dissolution, we observe a similar sequence of the bond-breaking events, while the activation barriers are considerably lower (by 0.85 eV) due to disruption of the Fe-O bonds. Proton-assisted mechanism also leads to a considerable reduction of the dissolution barrier by as much as 0.75 eV, mainly due to spontaneous breaking of the Fe-OH bonds exposed to solution.

Fe2 site

As can be seen from Fig S1, Fe at the Fe2 site on the (110) surface is coordinated by six oxygen atoms - one 3-fold coordinated O atoms, three 3-fold coordinated OH, and two 2-fold coordinated bridging OH.

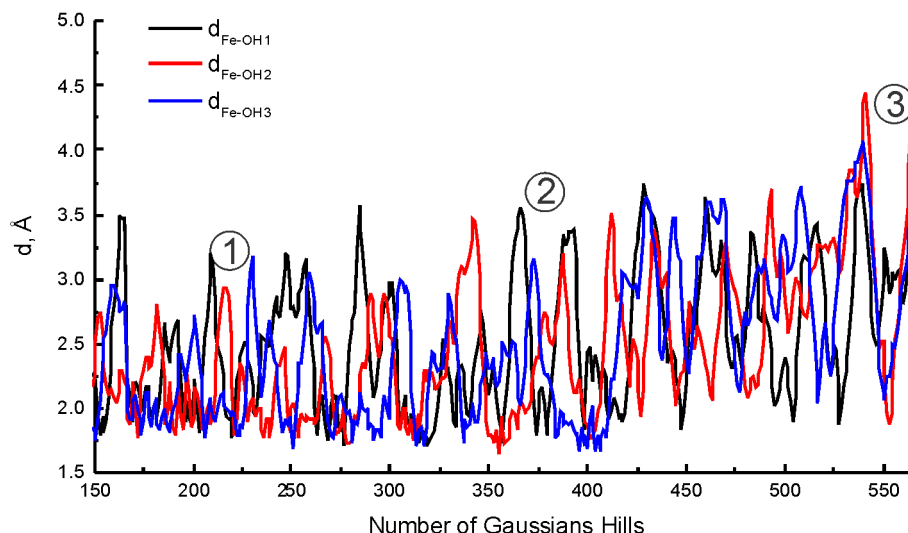


Fig. S9. Evolution of the collective variables (the bond distances between the dissolving Fe and structural O species) as a function of the number of Gaussians from metadynamics simulations of Fe^{3+} dissolution from the Fe2 site on the (110) surface.

In contrast to the previous cases metadynamics calculations for Fe dissolution from the Fe2 site of the (110) surface reveal (Fig. S9) that only simultaneous breaking of three Fe-OH bonds (Fig. S9, region 3) with bottom oxygen atoms leads to the stable intermediate state, as shown in Fig. S10b. At the end of this bond-breaking event (state *b*), the dissolving Fe^{3+} ion catches H_2O , which immediately dissociates to yield OH. Then, dissolution is followed by the Fe-O bond breaking (Fig. S10, transition *b* $\rightarrow$ *c*), which leads to the intermediate state *c*. In this case the bond-breaking event is not followed by internal protonation of the corresponding oxygen atom. Therefore, this step gives a considerable contribution to the activation barrier. Subsequently, the third Fe-OH bond breaks leading to the intermediate state *d*. At the end of this step the H_2O molecule from solution attacks the dissolving Fe^{3+} ion and becomes deprotonated resulting in one more OH group. During the next step (Fig. S10 transition *d* $\rightarrow$ *e*) the remaining bond between the dissolving Fe^{3+} and structural OH is being broken.

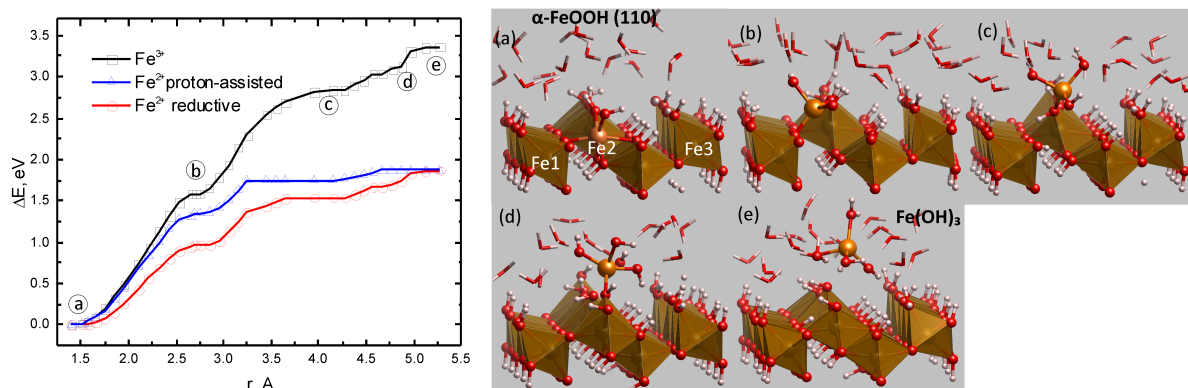


Fig. S10. Free energy profiles of iron dissolution from the Fe2 site of the (110) surface for the reductive (as Fe^{2+}) and nonreductive mechanisms. (a)-(e) correspond to the initial, final and intermediate metastable structures along the dissolution pathway shown on the right for the Fe^{3+} case.

In the case of reductive Fe dissolution, the activation barriers are determined to be considerably lower (by ~ 1.45 eV) due to destabilization of the Fe-O bonds. Sequential protonation of breaking bonds lower the total activation barrier by ~ 1.47 eV. For the proton-assisted mechanism we considered different scenarios that includes the protonation of top doubly-coordinated bridging OH groups. Our calculations showed that the bridging OH groups could only be protonated at very low pH, while under neutral conditions these groups can be considered as nonreactive. Specifically, after protonation of OH the newly formed H_2O molecules are stable during 1-2 ps, however, the proton eventually leaves the surface.

Fe1 site

Fe ion at the Fe1 site of the (110) surface is coordinated by six oxygen atoms - three 3-fold coordinated O atoms and three 3-fold coordinated OH groups (Fig. S1).

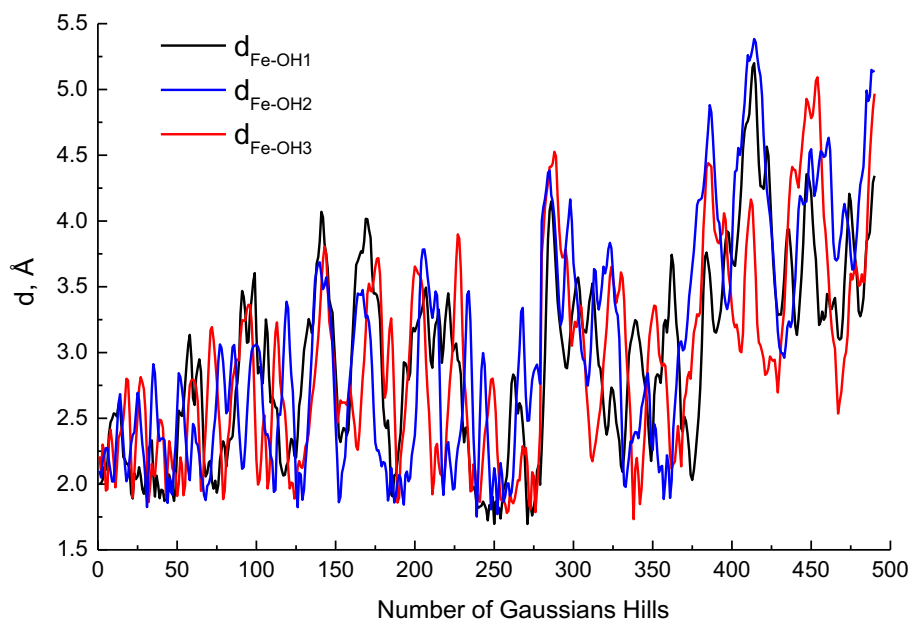


Fig. S11. Evolution of the collective variables (the bond distances between dissolving Fe and structural O species) as a function of the number of Gaussians from metadynamics simulations of Fe^{3+} dissolution from the Fe1 site on (110) surface.

According to metadynamics simulations (Fig. S11), the first metastable state for the dissolution of Fe1 ion from the (110) facet is observed after almost simultaneous breaking of three bottom Fe-O/OH bonds. Similar to all previous cases, stabilization of this intermediate state occurs upon nucleophilic water attack (Fig. S12, transition $a \rightarrow b$).

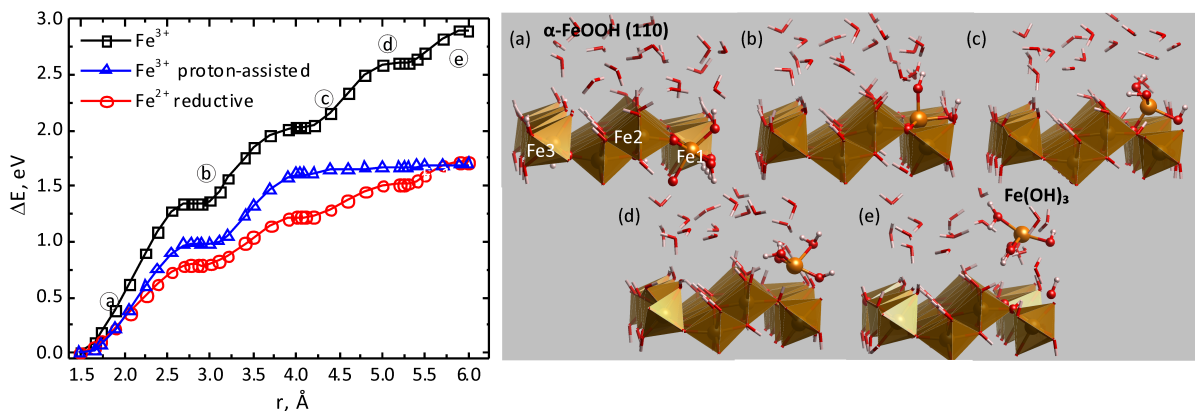


Fig. S12. Free energy profiles of Fe dissolution from the Fe1 site of the (110) surface for the reductive (as Fe^{2+}) and nonreductive (as Fe^{3+} at neutral and acidic pH) mechanisms. (a)-(d) correspond to the initial, final and intermediate metastable structures along the dissolution pathway shown on the right for the Fe^{3+} case.

Then, dissolution proceeds via Fe-O bond breaking step (Fig. S12, transition $b \rightarrow c$), leading to the intermediate state c . At the end of this bond-breaking event (Fig. S12, state c), Fe^{3+} catches H_2O which then dissociates to form an OH group. In this case the bond-breaking event is not followed by internal protonation of a surface oxygen atom, thus resulting in the relatively high activation barrier. Subsequently, the fifth Fe-O bond breaks leading to the intermediate state d . During the next step (Fig. S12 transition $d \rightarrow e$) the remaining bond between the dissolving Fe^{3+} and structural OH is being broken.

In the case of reductive dissolution, we observe a similar sequence of the bond-breaking events, while the activation barriers are considerably lower (by 1.2 eV) due to disruption of the Fe-O bonds. Proton-assisted mechanism also leads to a considerable reduction of the dissolution barrier by as much as 1.2 eV, mainly due to spontaneous breaking of external Fe-OH bonds.

Error estimation

The standard uncertainty in computing the free-energy gradients was estimated using the block average method [2]. As it was stated above, in our calculation we use 2 ps trajectories to collect free energy gradient and calculate the average. To estimate the error we considered a longer trajectory of 10 ps and accumulated 5 blocks of 2 ps each. Then, we calculated the standard deviation for the energy gradient after which the linear error propagation theory was used to calculate the uncertainty for activation energy barriers as shown in Fig. S13. Thus, the activation energy for the first step of Fe2 dissolution through the non-reductive mechanism is 1.11 ± 0.06 eV, which corresponds to the error of ~5%. Since the total dissolution barrier is about twice larger than the first dissolution step, the error is cumulative, but the gradients are decreasing, we can estimate that the overall error for the total activation barrier should be less than 10%.

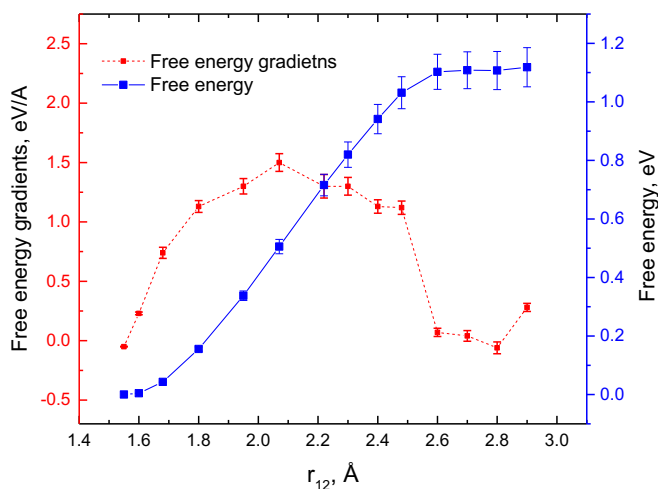


Fig. S13. Free energy gradients and (left-hand scale) and integrated free energy (right-hand scale) and corresponding uncertainties vs reaction coordinate r_{12} (distance between Fe atom and the center of bond between the atom O1 and atom oxygen atom from OH1) for the system evaluation between (a) and (b) states.

Van der Waals corrections

Although van der Waals (vdW) corrections may play an important role in description of water/solid interfacial processes [3-4], the choice of the functional was also found to be crucial for accurate estimation of interaction energies and bond distances. We found that the use of the PBE functional with D3 correction does not significantly affect our results on Fe dissolution. This agrees well with some previous first-principles studies of structural properties of liquid water [5] and water/solid interfaces [6]. Specifically, the average Fe-O distances (Fig. S14) and dissolution barriers (Fig. S15) are only weakly sensitive to Grimme's correction within the considered level of accuracy/theory. A more systematic study is needed to reveal the role of vdW corrections on interfacial properties of α -FeOOH considering different functionals (optPBE, revPBE, optB88) and levels of theory (D2, Tkatchenko-Scheffler, dDsC).

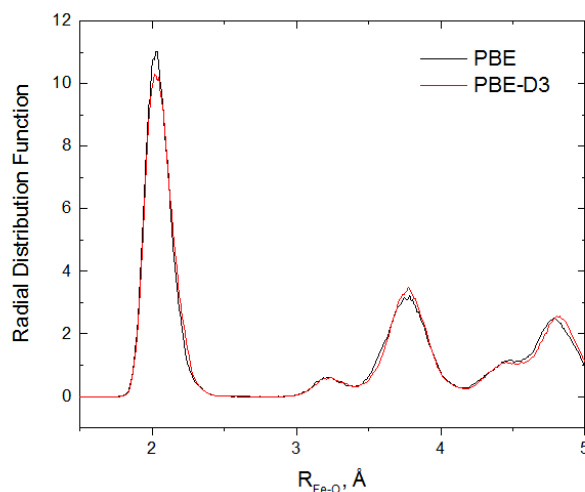


Fig. S14. Radial distribution function for the Fe-O bond between all Fe and O atoms in the system for the (021) surface.

To further demonstrate that our choice of computational scheme does not change the barrier heights significantly, we have performed additional Blue Moon simulations of breaking the first Fe-O bond for Fe^{2+} and Fe^{3+} dissolution from the Fe2 site at the (021) surface using PBE-D3. It is seen from Fig. S15 that the change of the dissolution barrier between simulations without vdW and 2 a.u. H mass (filled symbols) and with vdW and 3 a.u. H mass (open symbols) is very small being well within the estimated uncertainty of our simulations. Moreover, this change is systematic revealing that the difference between dissolution barriers for Fe^{2+} and Fe^{3+} stays the same.

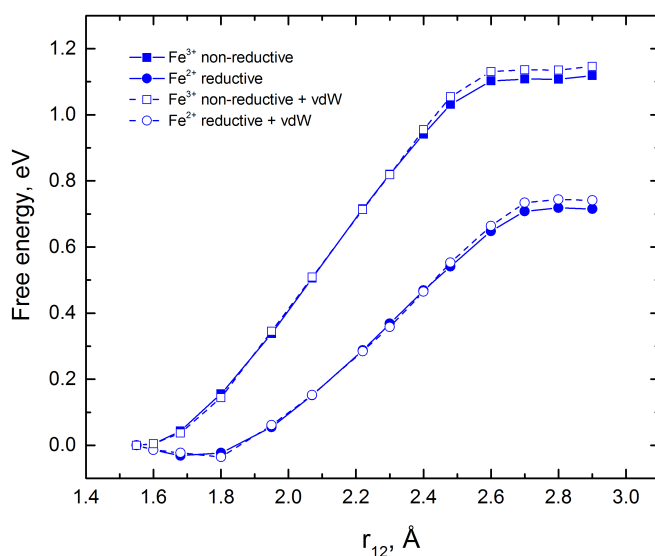


Fig. S15. Free energy profile of breaking the first Fe-O bond for Fe dissolution for the Fe2 site at the (021) surface.

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