Supplementary Information for

Ab Initio Thermodynamics Reveals the Nanocomposite Structure of Ferrihydrite

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Details of surface enthalpies calculated with Metadise:

| Surface direction | Goethite  | Hematite  | Lepidocrocite | Orthorhombic phase | Michel Model | Manceau Model |
|-------------------|-----------|-----------|---------------|--------------------|--------------|---------------|
|                   | $\Delta H_{surf}^p$ (J/m$^2$) | $\Delta H_{surf}^h$ (J/m$^2$) | $\Delta H_{surf}^p$ (J/m$^2$) | $\Delta H_{surf}^h$ (J/m$^2$) | $\Delta H_{surf}^p$ (J/m$^2$) | $\Delta H_{surf}^h$ (J/m$^2$) |
| [001]             | 1.68      | 0.64      | 1.78          | 1.21               | 0.93         | 0.69          | dipole        | -               | 1.70           | 0.71           |
| [100]             | 1.48      | 0.78      | 1.99          | 1.01               | 1.46         | 0.80          | 1.81          | 0.64            | 1.42           | 0.56           | 1.12           | 0.60           |
| [010]             | 0.68      | 1.01      | 1.99          | 1.01               | 0.25         | 0.25          | 1.86          | 0.58            | 1.80           | 0.54           | 0.58           | 1.16           |
| [011]             | 1.86      | 0.64      | 2.41          | 0.83               | 0.81         | 0.60          | dipole        | -               | dipole         | -              | 1.39           | 0.74           |
| [110]             | 1.18      | 0.50      | 2.03          | 0.81               | 1.49         | 0.84          | 1.40          | 0.59            | 1.73           | 0.81           | 0.96           | 0.72           |
| [101]             | 1.32      | 0.84      | 2.34          | 0.67               | 1.68         | 0.72          | dipole        | -               | dipole         | -              | 1.64           | 0.44           |
| [111]             | 1.33      | 0.61      | 2.41          | 0.84               | 1.66         | 0.73          | dipole        | -               | dipole         | -              | 1.38           | 0.75           |
| [021]             | 1.22      | 0.58      |               |                    |              |               |               |                 |           |                 | 1.13           | 0.59           |
| [012]             |           |           | 2.36          | 0.97               |              |               |               |                 |           |                 |               |               |
| [102]             |           |           | 1.88          | 0.97               |              |               |               |                 |           |                 |               |               |

**Table S1**: Calculated surface enthalpies of cleaved ($\Delta H_{surf}^p$) and hydroxylated ($\Delta H_{surf}^h$) surfaces for goethite, hematite, lepidocrocite, the orthorhombic phase, and the two ferrihydrite models.
- **Surface entropy and temperature-dependent surface energy:**

| Mineral phases | $\rho_{H_2O}$ (μmol/m$^2$) | $S_{H_2O}^{Chem}$ (J.mol$^{-1}$.K$^{-1}$) | $S_{H_2O}^{Phys}$ (J.m$^{-2}$.K$^{-1}$) |
|---------------|-----------------|-----------------|-----------------|
| Hematite ($\alpha$-Fe$_2$O$_3$) | 13.20 | -17.10 | -5×10$^{-5}$ |
| Manceau Model (FeOOH) | 10.58 | -17.10 | -5×10$^{-5}$ |
| Michel Model (Fe$_5$O$_8$H) | 12.10 | -17.10 | -5×10$^{-5}$ |
| Goethite ($\alpha$-FeOOH) | 11.02 | -17.10 | -5×10$^{-5}$ |
| Lepidocrocite ($\gamma$-FeOOH) | 10.26 | -17.10 | -5×10$^{-5}$ |
| Orthorhombic (Fe$_5$O$_8$H) | 12.47 | -17.10 | -5×10$^{-5}$ |

**Table S2:** Details of the surface entropy for each mineral phase investigated. $\rho_{H_2O}$, $S_{H_2O}^{Chem}$, and $S_{H_2O}^{Phys}$ are respectively the density of water, the entropy of chemisorbed and physisorbed water. While $\rho_{H_2O}$ has been calculated in this work, the values for $S_{H_2O}^{Chem}$ and $S_{H_2O}^{Phys}$ were obtained from the work of Hiemstra.$^1$

For each mineral phase, the temperature-dependence of the surface energy has been calculated using the following generic equation:

$$\gamma(T) = \Delta H_{surf}^{h} - T(\rho_{H_2O} \times S_{H_2O}^{Chem} + S_{H_2O}^{Phys})$$

**Table S3** summarizes the values of $\gamma(T)$ for the mineral phases considered.

| Mineral phases | Temperature (K) |
|----------------|-----------------|
|                | 0   | 100 | 200 | 298.15 | 300 | 400 | 500 | 600 | 700 | 800 | 900 | 1000 |
| Hematite       | 0.750 | 0.778 | 0.805 | 0.832 | 0.833 | 0.860 | 0.888 | 0.915 | 0.943 | 0.971 | 0.998 | 1.026 |
| Manceau Model$^a$ | 0.400 | 0.423 | 0.446 | 0.469 | 0.469 | 0.492 | 0.515 | 0.539 | 0.562 | 0.585 | 0.608 | 0.631 |
| Manceau Model$^b$ | 0.100 | 0.123 | 0.146 | 0.169 | 0.169 | 0.192 | 0.215 | 0.239 | 0.262 | 0.285 | 0.308 | 0.331 |
| Michel Model$^a$ | 0.400 | 0.426 | 0.451 | 0.477 | 0.477 | 0.503 | 0.528 | 0.554 | 0.580 | 0.606 | 0.631 | 0.657 |
| Michel Model$^b$ | 0.100 | 0.126 | 0.151 | 0.177 | 0.177 | 0.203 | 0.228 | 0.254 | 0.280 | 0.306 | 0.331 | 0.357 |
| Goethite       | 0.550 | 0.574 | 0.598 | 0.621 | 0.622 | 0.645 | 0.669 | 0.693 | 0.717 | 0.741 | 0.765 | 0.788 |
| Lepidocrocite  | 0.440 | 0.463 | 0.485 | 0.507 | 0.508 | 0.530 | 0.553 | 0.575 | 0.598 | 0.620 | 0.643 | 0.665 |
| Orthorhombic   | 0.590 | 0.616 | 0.643 | 0.668 | 0.669 | 0.695 | 0.722 | 0.748 | 0.774 | 0.801 | 0.827 | 0.853 |

**Table S3:** Calculated values of $\gamma(T)$ in J/m$^2$ at different temperatures.

$^a$ used $\Delta H_{surf}^{h} = 0.40$ J/m$^2$.

$^b$ used $\Delta H_{surf}^{h} = 0.10$ J/m$^2$. 
Effect of different (T,pH₂O) conditions on relative phase stability:

Figure S1: Particle-size dependency of the relative phase stability of the Manceau and Michel ferrihydrite models as well as for goethite, lepidocrocite, hematite and the orthorhombic phase for pH₂O=32 mbar and pH₂O=1 bar, and (a,d) T=100 K, (b,e) T=298.15 K, and (c,f) T=500 K. For the two ferrihydrite models, the curves with open squares were obtained using ΔH_{surf}^{h}=0.10 J/m², while the curves with open circles used ΔH_{surf}^{h}=0.40 J/m². Square filled curves used ΔH_{surf}^{h} calculated for hydroxylated periodic surface crystals. The red hatched area represents the size-range of particles for which the two ferrihydrite models can potentially coexist.
• AIT calculated Gibbs free energy and equilibrium reactions:

| Mineral phase       | $\Delta G_{\text{Calc.}}$ (kJ/mol) | $\Delta G_{\text{Expt.}}$ (kJ/mol) | Equilibrium reactions                                           | Log($K_{s0}^{\text{Calc.}}$) | Log($K_{s0}^{\text{Expt.}}$) |
|---------------------|------------------------------------|------------------------------------|----------------------------------------------------------------|-----------------------------|-----------------------------|
| Hematite            | -747.375                           | -744.400                           | $\text{Fe}_2\text{O}_3 + 6\text{H}^+ \leftrightarrow 2\text{Fe}^{3+} + 3\text{H}_2\text{O}$ | -3.627                      | -2.101                      |
| Michel model        | -1958.630                          | n/a                                | $\text{Fe}_5\text{O}_8\text{H} + 15\text{H}^+ \leftrightarrow 5\text{Fe}^{3+} + 8\text{H}_2\text{O}$ | -4.257                      | n/a                         |
| Manceau model       | -486.942                           | n/a                                | $\text{FeOOH} + 3\text{H}^+ \leftrightarrow \text{Fe}^{3+} + 2\text{H}_2\text{O}$ | -1.049                      | n/a                         |
| Goethite            | -490.372                           | -490.600                           | $\text{FeOOH} + 3\text{H}^+ \leftrightarrow \text{Fe}^{3+} + 2\text{H}_2\text{O}$ | -1.650                      | -1.020                      |
| Lepidocrocite       | -479.810                           | -482.700                           | $\text{FeOOH} + 3\text{H}^+ \leftrightarrow \text{Fe}^{3+} + 2\text{H}_2\text{O}$ | -0.202                      | 0.365                       |
| Orthorhombic        | -1944.192                          | n/a                                | $\text{Fe}_5\text{O}_8\text{H} + 15\text{H}^+ \leftrightarrow 5\text{Fe}^{3+} + 8\text{H}_2\text{O}$ | -1.725                      | n/a                         |
| $\text{H}_2\text{O}$ | -235.232                           | -237.141                           |                                                                  |                             |                             |
| $\text{Fe}^{3+}$    | n/a                                | -10.500                            |                                                                  |                             |                             |

Table S4: Comparison of AIT calculated and experimental Gibbs free energies and solubilities for virtual bulk lattices of the various mineral phases considered at $T=298.15$ K and $p\text{H}_2\text{O}=32$ mbar.

• Equilibrium solubility and hydrolysis reactions:

Based on the equilibrium reactions shown in Table S4, the equilibrium solubility of [Fe(III)] for each mineral phase has been calculated by following the methodology given in Ref[4,5] by:

$$K_{\text{Fe}_2\text{O}_3} = \frac{a_{\text{Fe}}^2 a_{\text{H}_2\text{O}}^3}{a_{\text{H}}^6}$$

$$K_{\text{Fe}_5\text{O}_8\text{H}} = \frac{a_{\text{Fe}}^5 a_{\text{H}_2\text{O}}^8}{a_{\text{H}}^{15}}$$

$$K_{\text{FeOOH}} = \frac{a_{\text{Fe}} a_{\text{H}_2\text{O}}^2}{a_{\text{H}}^3}$$

Where $a_i$ is the activity of the species $i$ and is defined by the product between the activity coefficient ($\gamma_i$) and the concentration of the species $i$ such that $a_i = \gamma_i \times [i]$. Considering pure water as the medium for the chemical reactions, we used the Davies formula to calculate the activity coefficients of the charged species involved in the chemical reactions, as well as the activity of water. The use of the Davies formula is justified for solutions with ionic strength lower than 0.3 mol/kg.

$$\gamma = 10^{-a z_i^2 \left(\frac{i}{2} \frac{I}{17} - 0.3 I\right)}$$

where $a$ is the Debye-Hückel parameter having the value of 0.50948, $z_i$ is the charge of the species, and $I$ (in mol/kg) is the ionic strength of the solution. The water activity has been determined by the following equation:
\[
(H_2O) = \frac{[H_2O]}{[H_2O] + \sum_{[\text{solute}]},}
\]

where \([H_2O]=55.5099 \text{ mol/kg}.

The hydrolysis equilibrium reactions\(^{4,5}\) considered in the calculations are:

\[
\begin{align*}
\text{Fe}^3+ + H_2O &\leftrightarrow \text{Fe(OH)}^2+ + H^+ \\
\text{Fe}^3+ + 2H_2O &\leftrightarrow \text{Fe(OH)}_2^+ + 2H^+ \\
\text{Fe}^3+ + 3H_2O &\leftrightarrow \text{Fe(OH)}_3^0 + 3H^+ \\
\text{Fe}^3+ + 4H_2O &\leftrightarrow \text{Fe(OH)}_4^- + 4H^+
\end{align*}
\]

- **Effect of pH on the solubility of \([\text{Fe(III)}]\) of iron-(oxyhydr)oxide minerals:**

  \[\text{Figure S2: Equilibrium solubility of [Fe(III)] for the various minerals in pure water. (a-c) Particle-size dependence of [Fe(III)] solubility at pH=3, 5, and 7. The red hatched area represents the size-range of particles for which the two ferrihydrite models can potentially coexist. (d) pH-dependence of [Fe(III)] solubility of iron (oxyhydr)oxide phases considered as virtual bulk lattices, with Gibbs free energy calculated from AIT and compared to experimental values.}\]
• Supplementary References:

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