Carbonate Adsorption to Ferrihydrite: Competitive Interaction with Phosphate for Use in Soil Systems

SUPPORTING INFORMATION

Juan C. Mendez*, Tjisse Hiemstra
Soil Chemistry and Chemical Soil Quality Group, Wageningen University
Wageningen, The Netherlands

* E-mail address: juan.mendezfernandez@wur.nl

Table of content

1 Experimental conditions of the batch adsorption systems 2
2 Additional phosphate adsorption series in competition with carbonate 3
3 Thermodynamic databases used in the CD modeling 4
4 Evaluation of carbonate adsorption parameters at different scales 6
5 Aqueous complex formation of Fe carbonates 9
6 Normalized competitive adsorption isotherms 15
7 Adsorption isotherms: carbonate surface speciation 16
8 Adsorption data of carbonate from literature 17
9 Bond length and Brown bond valence concept 19
10 Effect of phosphate adsorption on the surface charge of ferrihydrite 21
11 References 24
1 Experimental conditions of the batch adsorption systems

Table S-1. Chemical conditions and characteristics of the ferrihydrite suspensions used in the batch experiments in binary CO$_3$-PO$_4$ competition systems and in monocomponent systems with CO$_3$.

| Fh series | Batch number | Ionic strength | Total CO$_3$ (M) | Total PO$_4$ (mM) | Total Fe (mM) | $M_{\text{nano}}$ (g mol$^{-1}$ Fe) | SSA$^1$ (m$^2$ g$^{-1}$) | Fh (g L$^{-1}$) |
|-----------|--------------|----------------|------------------|-------------------|--------------|---------------------------------|-------------------|--------------|
| A         | 1-Binary     | 0.5            | 0.030            | 0.500             | 7.20         | 96.33                           | 672               | 0.69         |
| B         | 2-Binary     | 0.5            | 0.100            | 0.500             | 7.20         | 96.33                           | 672               | 0.69         |
| C         | 3-Binary     | 0.5            | 0.200            | 0.500             | 7.20         | 96.33                           | 672               | 0.69         |
| D         | 4-Binary     | 0.5            | 0.500            | 0.500             | 7.20         | 96.33                           | 672               | 0.69         |
| E         | 5-Binary     | 0.5            | 0.100            | 0.750             | 7.31         | 96.33                           | 672               | 0.70         |
| F         | 6-Binary     | 0.5            | 0.500            | 0.750             | 7.31         | 96.33                           | 672               | 0.70         |
| G         | 7-Binary     | 0.1            | 0.030            | 0.500             | 7.46         | 96.33                           | 672               | 0.72         |
| H         | 8-Binary     | 0.1            | 0.100            | 0.500             | 7.46         | 96.33                           | 672               | 0.72         |
| I         | 9-Binary     | 0.5            | 0.004            | 0.251             | 4.88         | 98.79                           | 765               | 0.48         |
| J         | 10-Binary    | 0.5            | 0.012            | 0.251             | 4.88         | 98.79                           | 765               | 0.48         |
| J         | 11-Binary    | 0.5            | 0.030            | 0.251             | 4.88         | 98.79                           | 765               | 0.48         |
| J         | 12-Binary    | 0.5            | 0.100            | 0.251             | 4.88         | 98.79                           | 765               | 0.48         |
| J         | 13-Binary    | 0.5            | 0.500            | 0.251             | 4.88         | 98.79                           | 765               | 0.48         |
| K         | 14-Binary    | 0.05           | 0.030            | 0.251             | 4.48         | 98.79                           | 765               | 0.44         |
| K         | 15-Binary    | 0.05           | 0.030            | 0.502             | 4.48         | 98.79                           | 765               | 0.44         |
| K         | 16-Binary    | 0.5            | 0.030            | 0.502             | 4.48         | 98.79                           | 765               | 0.44         |
| L         | 17-Binary    | 0.5            | 0.500            | 0.021-1.06        | 5.20         | 97.98                           | 735               | 0.51         |
| M         | 1-Mono       | 0.1            | 0.001            | -                 | 10.4         | 95.14                           | 625               | 0.99         |
| N         | 2-Mono       | 0.1            | 0.001            | -                 | 15.3         | 95.14                           | 625               | 1.46         |
| N         | 3-Mono       | 0.1            | 0.001            | -                 | 5.10         | 95.14                           | 625               | 0.50         |

‡ Derived by interpreting the measured adsorption of PO$_4$, using the CD model with the parameter set of Hiemstra and Zhao$^1$. 

S-2
2 Additional phosphate adsorption series in competition with carbonate

Figure S-1 presents additional PO$_4$ adsorption data, collected for Fh systems with increasing concentrations of added carbonate.

![Adsorption edges of PO$_4$ to ferrihydrite in competition systems with CO$_3$. The symbols are experimental results and the lines are CD model calculations using the parameters set presented in Table 1 (main text). The specific surface area of the ferrihydrite suspensions was SSA = 672 m$^2$ g$^{-1}$ with a molar mass of $M_{nanop}$ = 96.33 g mol$^{-1}$ Fe.](image)

**Panel A:** Total PO$_4$ concentration of 0.75 mM, equivalent to 1.48 µmol m$^{-2}$. The total Fe concentration is 7.3 mM. The ionic strength was adjusted to 0.5 M using NaNO$_3$ when required.

**Panel B:** Total PO$_4$ concentration of 0.50 mM and total Fe concentrations of 7.2 mM, equivalent to 1.08 µmol m$^{-2}$. The ionic strength was adjusted to 0.1 M, using NaNO$_3$ when required.
3 Thermodynamic databases used in the CD modeling

Table S-2. Thermodynamic database used in the modeling for the aqueous speciation reactions. LogK values are given for I = 0.

| Species     | Reaction                  | logK  |
|-------------|---------------------------|-------|
| NaOH⁰       | Na⁺ + OH⁻ ↔ NaOH⁰         | -0.20 * |
| NaNO₃¹      | Na⁺ + NO₃⁻ ↔ NaNO₃⁰       | -0.60 * |
| HPO₄²⁻      | PO₄³⁻ + H⁺ ↔ HPO₄²⁻       | 12.35 * |
| H₂PO₄⁻      | PO₄³⁻ + 2H⁺ ↔ H₂PO₄⁻      | 19.55 * |
| H₃PO₄⁰      | PO₄³⁻ + 3H⁺ ↔ H₃PO₄⁰      | 21.70 * |
| HCO₃⁻       | CO₃²⁻ + H⁺ ↔ HCO₃⁻        | 10.33 * |
| H₂CO₃⁰      | CO₃²⁻ + 2H⁺ ↔ H₂CO₃⁰      | 16.69 * |
| CO₂(g)      | CO₃²⁻ + 2H⁺ ↔ CO₂(g) + H₂O(l) | 18.15 * |
| Na₂CO₃⁰     | CO₃²⁻ + 2Na⁺ ↔ Na₂CO₃⁰    | 0.01 * |
| NaCO₃⁻      | CO₃²⁻ + Na⁺ ↔ NaCO₃⁻      | 1.27 # |
| NaHCO₃⁰     | CO₃²⁻ + Na⁺ + H⁺ ↔ NaHCO₃⁰ | 10.02 # |
| NaHPO₄⁻     | PO₄³⁻ + Na⁺ + H⁺ ↔ NaHPO₄⁻ | 13.40 ‡ |
| NaPO₄²⁻     | PO₄³⁻ + Na⁺ ↔ NaPO₄²⁻      | 2.05 ‡ |

* From Lindsay (1979)
# From NIST database 46.7
‡ From Rahnemae et al. (2007).
Table S-3. Table defining formation reactions, CD coefficients and log\(K\) values for the entire set of surface species used in the CD model. The surface site densities are from Hiemstra and Zhao (2016) with \(N_s(\equiv FeOH^{0.5}(a)) = 3.0 \text{ nm}^{-2}\), \(N_s(\equiv FeOH^{0.5}(b)) = 2.8 \text{ nm}^{-2}\) and \(N_s(\equiv Fe_3O^{0.5}) = 1.4 \text{ nm}^{-2}\). The capacitance values for the extended Stern layer are size dependent. For instance, for ferrhydrite with SSA = 615 m² g⁻¹, \(C_1 = 1.15 \text{ F m}^{-2}\) and \(C_2 = 0.90 \text{ F m}^{-2}\).

| Species | \(\equiv FeOH(a)^{0.5}\) | \(\equiv FeOH(b)^{0.5}\) | \(\equiv Fe_3O^{0.5}\) | \(\Delta z_0\) | \(\Delta z_1\) | \(\Delta z_2\) | \(H^+\) | \(CO_3^{2-}\) | \(Na^+\) | \(PO_4^{3-}\) | \(NO_3^-\) | log\(K\) |
|---------|----------------|----------------|----------------|-----------|-----------|-----------|------|-------|------|--------|--------|--------|
| FeOH(a) | 0             | 0             | 0             | 0         | 0         | 0         | 0    | 0     | 0    | 0      | 0      | 0      |
| FeOH(b) | 0             | 0             | 0             | 0         | 0         | 0         | 0    | 0     | 0    | 0      | 0      | 0      |
| Fe_3O  | 0             | 0             | 0             | 0         | 0         | 0         | 0    | 0     | 0    | 0      | 0      | 0      |
| FeO(OH) | 0             | 0             | 0             | 0         | 0         | 0         | 0    | 0     | 0    | 0      | 0      | 0      |
| Fe(OH) _2 | 0             | 0             | 0             | 0         | 0         | 0         | 0    | 0     | 0    | 0      | 0      | 0      |
| Fe(OH) _3 | 0             | 0             | 0             | 0         | 0         | 0         | 0    | 0     | 0    | 0      | 0      | 0      |
| Fe(OH) _4 | 0             | 0             | 0             | 0         | 0         | 0         | 0    | 0     | 0    | 0      | 0      | 0      |

\(^a\) \(\equiv FeOH(a)^{0.5}\) form only monodentate surface complexes, whereas \(\equiv FeOH(b)^{0.5}\) can form mono- and bidentate surface complexes, according to the ion adsorption model for ferrhydrite of Hiemstra and Zhao.

\(^b\) log\(K\) (mean ± SD) are the average of the values obtained in this study using four different scales of evaluation.

\(^c\) Taken from Hiemstra and van Riemsdijk.

\(^d\) Taken from Hiemstra and Zhao.
4 Evaluation of carbonate adsorption parameters at different scales

The formation constants (log$K$) of the CO$_3$ surface complexes were derived by fitting the experimental data of PO$_4$ adsorption to ferrihydrite in the competition systems with CO$_3$. In the fitting process, four scales for evaluation were used to optimize the log$K$ values: relative PO$_4$ adsorption (%), equilibrium PO$_4$ concentration in solution (C-PO$_4$ in mol L$^{-1}$), log$_{10}$ of the equilibrium PO$_4$ concentration (log C-PO$_4$ in mol L$^{-1}$), and adsorption density of PO$_4$ (µmol m$^{-2}$). The results (log$K$ ± SD) are given in Table S-4.

Within the uncertainty of the fitting procedure, the log$K$ values presented in Table S-4 are consistent amongst the different evaluation scales (less than 1% difference). Testing for this consistency is important, as the response variable to be predicted by the model may differ from one situation to another (e.g. adsorption density vs solution concentration). The $R^2$ value and the root mean square error (RMSE) were used to evaluate the quality of the fitting and to compare the performance of the model under different alternative approaches.

In Table S-4, an alternative approach is presented (option B) to describe the competitive effect of CO$_3$ on the adsorption of PO$_4$ adsorption to ferrihydrite. In this approach, the formation of the inner-sphere monodentate complex is replaced by the formation of an outer-sphere complex with the singly (≡FeOH$^{-0.5}$) and triply (≡Fe$_3$O$^{-0.5}$) coordinated surface groups. A free fitting of the CD coefficients of this defined outer-sphere complex suggests that some negative charge is placed in the surface (0-plane) of ferrihydrite. In comparison with option A, similar quality of the fitting was obtained when the CD coefficients are set to $Δz_0 = +0.70$ v.u. and $Δz_1 = -1.70$ v.u. These charge distribution values can possibly result from a weak interaction between the CO$_3$ anions and the reactive surface groups, as for instance via H$^+$ bonding.
**Table S-4.** LogK values of the carbonate surface species, derived from the competitive effect of the CO$_3$ anion on the adsorption of PO$_4$ to ferrihydrite, fitted at four scales of evaluation: percentage of PO$_4$ adsorbed, equilibrium concentration of PO$_4$ in solution, log$_{10}$ equilibrium concentration of PO$_4$ in solution, and adsorption density of PO$_4$ in µmol m$^{-2}$. Results are presented for two different scenarios in which the formation of the monodentate inner-sphere complex (Option A) is replaced by the formation an outer-sphere complex (Option B).

| Option A | logK values |  |
| --- | --- | --- | --- | --- | --- | --- |
| Surface species | % PO$_4$ adsorbed | log C-PO$_4$ | C-PO$_4$ | µmol PO$_4$ m$^{-2}$ | Average$^\dagger$ |  |
| (≡FeO)$_2$CO | 21.85 ± 0.08 | 21.63 ± 0.10 | 21.69 ± 0.17 | 21.75 ± 0.12 | 21.73 ± 0.09 |  |
| (≡FeO)$_2$CO··Na | 22.25 ± 0.09 | 22.42 ± 0.11 | 22.45 ± 0.09 | 22.41 ± 0.08 | 22.38 ± 0.09 |  |
| ≡FeOCO$_2$ (a/b) | 11.61 ± 0.05 | 11.61 ± 0.08 | 11.59 ± 0.05 | 11.59 ± 0.05 | 11.60 ± 0.01 |  |
| R$^2$ | 0.952 | 0.941 | 0.964 | 0.974 |  |
| RMSE$^*$ | 4.12 | 0.15 | 2.09E-05 | 0.046 |  |

| Option B | logK values |  |
| --- | --- | --- | --- | --- | --- | --- |
| Surface species | % PO$_4$ adsorbed | log C-PO$_4$ | C-PO$_4$ | µmol PO$_4$ m$^{-2}$ | Average$^\dagger$ |  |
| (≡FeO)$_2$CO | 21.93 ± 0.06 | 21.63 ± 0.08 | 21.84 ± 0.08 | 21.88 ± 0.07 | 21.82 ± 0.13 |  |
| (≡FeO)$_2$CO··Na | 21.91 ± 0.10 | 22.19 ± 0.12 | 22.16 ± 0.09 | 22.16 ± 0.09 | 22.11 ± 0.13 |  |
| ≡FeOH$_2$··CO$_3$ (a/b) | 11.34 ± 0.07 | 11.52 ± 0.10 | 11.32 ± 0.06 | 11.31 ± 0.06 | 11.37 ± 0.10 |  |
| ≡Fe$_3$OH··CO$_3$ | 11.34 ± 0.07 | 11.52 ± 0.10 | 11.32 ± 0.06 | 11.31 ± 0.06 | 11.37 ± 0.10 |  |
| R$^2$ | 0.945 | 0.941 | 0.960 | 0.970 |  |
| RMSE$^*$ | 4.38 | 0.15 | 2.19E-05 | 0.049 |  |

$^\dagger$ Average logK values ± the standard deviation (SD) found by fitting the data using four evaluation scales. The values of Option A are also given in Table 1 of the main text and were used for calculating the mode lines in the various figures.

$^*$ R$^2$ and root means square error (RMSE) obtained with the FIT program express the quality of the fitting of the data set.

According to the model, there is a small contribution of an additional species (either inner-sphere monodentate or outer-sphere). It is tempting to attribute this to the formation of outer-sphere complexes, since these have been observed with *in-situ* spectroscopy at the interfaces of Fe-(hydr)oxides. These outer-sphere species are especially found at low ionic strength and low pH values. In most of our experiments, the conditions are different. Moreover, outer-sphere complexation is rather weak (low logK$_{\text{intrinsic}}$) and will only occur at favorable electrostatic conditions. These are not
present at the interface if large quantities of oxyanions (CO$_3$ and/or PO$_4$) are specifically adsorbed, strongly reducing the electrostatic potential of the Stern (1-) plane (see Figure S-7). This leads to a strong competition with any anion bound as an outer-sphere complex. As mentioned in the main text, a free search for the CD of the additional carbonate species points to monodentate complex formation (option A), however, using instead outer-sphere complexation (option B) also give a description of nearly the same quality. In the main text we have applied option A.
5 Aqueous complex formation of Fe carbonates

5.1 Open systems with constant $pCO_2$

Grivé et al.\textsuperscript{4} have recently studied the complexation of Fe by $CO_3$ ions in open systems for different partial pressures of $CO_2$ ($pCO_2 = 0, 0.98, 29.45, \text{ and } 98.15 \text{ kPa}$). Fe-(hydr)oxide in 0.5 M NaClO\textsubscript{4} solution at 25 °C was used to fix the activity of $Fe^{3+}(aq)$. A two-line (2LFh) ferrihydrite material was produced. The product was dried in a non-specified manner and then sieved to sizes between 50 and 100 µm or 50,000 and 100,000 nm, i.e. very large aggregates were used in an attempt to avoid colloidal material during the solubility experiments. The product had a BET surface area of ~200 m\textsuperscript{2} g\textsuperscript{-1} meaning that the aggregates are porous considering their very large size. X-ray diffraction confirmed the presence of 2LFh. The reported solubility product is $logQ_{so} = log (Fe^{3+}) + 3 \ log (OH^-) = -40.8 \pm 0.4$ at zero ionic strength ($I = 0$). Equilibration was relatively slow and lasted typically at least two or more weeks.

The data set of Grivé et al.\textsuperscript{4} is presented in Figure S-2. In the range of pH ~ 4.0-7.0, the solution concentration of Fe in equilibrium with the Fe-(hydr)oxide is nearly independent of the pH but clearly depends on the $pCO_2$ level. This can be explained by the formation of $FeOHCO_3^0(aq)$ according to the reaction:

$$Fe^{3+}(aq) + OH^-(aq) + CO_3^{2-}(aq) \leftrightarrow FeOHCO_3^0 (aq) \quad \log K_{FeOHCO3} (1)$$

At higher pH, the solubility increases suddenly and depends very strongly on the $pCO_2$ and pH. This behavior can be understood from the formation of $Fe(CO_3)_3^{3-}(aq)$ according to:

$$Fe^{3+}(aq) + 3 \ CO_3^{2-}(aq) \leftrightarrow Fe(CO_3)_3^{3-} (aq) \quad \log K_{Fe(CO3)3} (2)$$
Figure S-2. Concentration of Fe in solution in equilibrium with Fe-(hydr)oxide as a function of the pH and different $p\text{CO}_2$, measured in 0.5 M NaClO$_4$ at 25 °C. The experimental data (symbols) are from Grivé et al.$^4$ and the lines are results of model calculations obtained by re-evaluating the data using the reactions defined in Table S-5. The solubility of the Fe-(hydr)oxide used by Grivé et al.$^4$ is very low ($\log Q_{so} = -40.9 \pm 0.06$) pointing to the presence of a very stable mineral phase, despite the reported predominance of 2LFh. The unusual stability suggests that the surfaces of the large aggregates (50.000-100.000 nm) are covered by some rather crystalline material that determines the solubility. Importantly, for the determination of the log$K$ values of the aqueous Fe(III)-CO$_3$ complexes, the precise cause of the high stability is irrelevant. The dotted line gives the extrapolated solubility in the absence of CO$_3$. It demonstrates that the measured solubility in the presence of CO$_2$ is significantly different. It implies that the formation constants for these Fe(III)-CO$_3$ complexes can be derived rather accurately. Figure adapted from Applied Geochemistry, Vol 49, Mireia Grivé, Lara Duro, Jordi Bruno, Fe(III) mobilisation by carbonate in low temperature environments: Study of the solubility of ferrihydrite in carbonate media and the formation of Fe(III) carbonate complexes, Pages 57-67, Copyright (2014), with permission from Elsevier.

The above behavior has been re-evaluated in order to be applied in our systems. The fitted values for the formation constants of FeOHCO$_3^0$ (aq) and Fe(CO$_3$)$_3^{3−}$ (aq) are respectively $\log K_{\text{FeOHCO}_3} = 24.86 \ (± \ 0.09)$ and $\log K_{\text{Fe(CO}_3)_3} = 24.86 \ (± \ 0.09)$, using the reactions defined above. NB. The numerical value of both log$K$ values is coincidentally the same.
According to our data analysis, the hydrolysis constant of Fe(OH)\textsubscript{3}\textsuperscript{2+}(aq), Fe(OH)\textsubscript{4}\textsuperscript{2-}(aq), Fe\textsubscript{2}(OH)\textsubscript{2}\textsuperscript{4+}(aq), and Fe\textsubscript{3}(OH)\textsubscript{4}\textsuperscript{5+}(aq) are fortunately not relevant for the interpretation of these data as these values are rather uncertain. Only the values for the first and second hydrolysis constant are relevant. The intrinsic \(\log K\) values \((l = 0)\) of these species have been taken from the most recent critical review given by Lemire \textit{et al}.\textsuperscript{5}, recommending \(\log K_{\text{FeOH}^{2+}} = 11.85 \pm 0.03\) and \(\log K_{\text{Fe(OH)}^{2+}} = 23.20 \pm 0.40\). In our analysis, we used the Davis equation to account for the effect of the ionic strength, applying a value of \(D = 0.2\). The \(\log Q_{\text{so}}\) of the Fe-(hydr)oxide material used by Grivé \textit{et al}.\textsuperscript{4} was simultaneously fitted resulting in \(\log Q_{\text{so}} = \log (\text{Fe}^{3+}) + 3 \log (\text{OH}^{-}) = -40.9 \pm 0.06\). Our values are very close to the values reported by Grivé \textit{et al}.\textsuperscript{4} (Table S-5). The quality of the description was good \((R^2 = 0.93, \text{RMSE} = 0.26)\).

The solubility product fitted for the Fe-(hydr)oxide material of Grivé \textit{et al}.\textsuperscript{4} is extremely low \((\log K_{\text{so}} = -40.9)\) and difficult to attribute to 2L\textit{Fh}. Most other studies report for 2L\textit{Fh} and 6L\textit{Fh} a much higher solubility being typically about two orders of magnitude higher with \(\log K_{\text{so}}\) values that range from about -38.5 to -39.5.\textsuperscript{5,6} A recent interpretation of thermochemical data of Majzlan \textit{et al}.\textsuperscript{7} by Hiemstra\textsuperscript{6} reveals the intrinsic \(\log K_{\text{so}}\) value for the solubility of \textit{Fh} \((\log K_{\text{so}}(\text{bulk}) = -40.6 \pm 0.1)\) when virtual present as a bulk material of infinite size. This \(\log K_{\text{so}}\) (bulk) value fits well with the \(\log K_{\text{so}}\) derived by Pinney \textit{et al}.\textsuperscript{8} using MO/DFT calculations. Moreover, actual \textit{Fh} particles are nano-sized and therefore, will be significantly less stable than its virtual bulk material due to a significant surface Gibbs free energy contribution.\textsuperscript{6}

Using the recently derived surface Gibbs free energy values for goethite and hematite\textsuperscript{6} in combination with the intrinsic \(\log K_{\text{so}}\) values for both materials,\textsuperscript{9} we estimate that the observed solubility product \((\log K_{\text{so}} = -40.9)\) is equivalent to spherical particles with a size of about 14 ± 2 nm in the presence of nano-goethite or nano-
hematite. This size is beyond the critical size of 8 nm for thermodynamic stability of Fh. This is illustrated in Figure S-3. Therefore, we hypothesize that the material of Grivé et al. is likely to be 2LFh aggregated in extremely large particles (50,000 - 100,000 nm) whose surfaces have transformed into a more crystalline material, while still being a nano-size, but with a much lower solubility due to the higher crystallinity.

Figure S-3. Particle size dependency of the solubility ($\log Q_{so}$) of ferrihydrite, goethite, and hematite calculated with the thermodynamic data set provided by Hiemstra concerning the intrinsic solubility of the various bulk materials and corresponding surface Gibbs free energies. At small sizes, Fh is the most stable Fe-(hydr)oxide material. Above a diameter of about 8 nm (red arrow), it is less stable than goethite and hematite. The value of $\log Q_{so} = -40.9$ (dashed line) is equivalent the solubility of goethite or hematite with a size of about $14 \pm 2$ nm (dashed arrow). Figure adapted from Geochimica et Cosmochimica Acta, Vol 158, Tjisse Hiemstra, Formation, stability, and solubility of metal oxide nanoparticles: Surface entropy, enthalpy, and free energy of ferrihydrite, Pages 179-198, Copyright (2015), with permission from Elsevier.
5.2 Closed systems

The above-derived formation constants for the aqueous Fe(III)-CO₃ complexes reported by Grivé et al.⁴ can be used in evaluating the Fh solubility for our systems. Our closed systems have constant total CO₃ concentrations, while the pH varies. In this respect, our systems are different from the systems of Grivé et al.⁴. In closed systems the pCO₂ varies with changes in pH, whereas in the open systems of Grivé et al.⁴ the pCO₂ is constant, leading to a simultaneous increase of the total CO₃ concentrations when the pH increases.

In Figure 1 of the main text, the measured concentration of dissolved Fe is given as a function of pH for systems with different levels of added CO₃. The ionic strength in the systems has been fixed to 0.5 M by the addition of appropriate amounts of NaNO₃. The experimental data at the lowest total CO₃ concentrations are close to the detection limit of Fe (dashed line) with ICP-MS. The value of the detection limit is relatively high (log C₉Fe,total = -7 M) for our systems because dilution (50x) was needed to reduce the salt load during the analytical measurements. Therefore, we can only evaluate the solubility of our Fh in 0.1 and 0.5 M CO₃ solutions. These solutions also contain some PO₄. The Fh used has been probed with PO₄ to determine the specific surface area, yielding $A = 765 \text{ m}^2 \text{ g}^{-1}$ at a molar mass $M_{\text{nano}} = 98.79 \text{ g mol}^{-1}$. The corresponding mean diameter of the particles is ~2.2 nm as calculated with a set of equations given by Hiemstra and Zhao.¹

With the formation constants for FeOHCO₃⁰(aq) and Fe(CO₃)₃²⁻(aq), one is not able to describe the observed increase of the solubility in Figure 1 (main text) at increase of the pH. Instead, a decrease is predicted as illustrated with dotted lines in that figure. It suggests that there is an additional contribution by another Fe(III)-CO₃
species. Modeling shows that the higher pH-dependency of the solubility of Fh can be understood with the formation of Fe(CO$_3$)$_2$(OH)$_2^{3-}$(aq) according to the reaction:

$$\text{Fe}^{3+}(aq) + 2 \text{CO}_3^{2-}(aq) + 2 \text{OH}^-(aq) \leftrightarrow \text{Fe(CO}_3)_2\text{(OH)}_2^{3-}(aq) \quad \log K_{\text{Fe(CO}_3)_2\text{(OH)}_2} = 31.78 \pm 0.13$$

The fitted logK value for this reaction is $\log K_{\text{Fe(CO}_3)_2\text{(OH)}_2} = 31.78 \pm 0.13$. Simultaneously, the solubility of our Fh has been derived by fitting, resulting in $\log Q_{\text{so}} = -38.55 \pm 0.08$. The quality of the description is very good ($R^2 = 0.97$, RMSE =0.16).

The solubility obtained for our Fh is in good agreement with the particle size derived with PO$_4$ probing. For Fh with $d = 2.2$ nm, we calculate $\log Q_{\text{so}} = -38.2 \pm 0.2$ applying the Ostwald equation with a surface Gibbs free energy of $\gamma = 0.186 \pm 0.01$ J m$^{-2}$ and the intrinsic solubility of $\log Q_{\text{so}} = -40.6 \pm 0.1$ for Fh as virtual bulk material of infinite size.$^6$ An overview of the formation constants used in our modeling is given in Table S-5. These values have been used in calculating the full lines the relevant graphs.

**Table S-5.** Formation constants of aqueous Fe(III)-CO$_3$ complexes and the logK values for the solubility of Fe-(hydr)oxide materials used in this study and by Grivé et al.

| Species                     | logK      | error | Reference                |
|-----------------------------|-----------|-------|--------------------------|
| FeOHCO$_3^{0}$ (aq)         | 24.86*    | 0.09  | Grivé et al. (2014)      |
| Fe(CO$_3$)$_3^{3-}$ (aq)    | 24.86*    | 0.09  | Grivé et al. (2014)      |
| Fe(CO$_3$)$_2$(OH)$_2^{3-}$ (aq) | 31.71    | 0.13  | This study               |
| FeOH$_2^{2+}$ (aq)          | 11.85     | 0.03  | Lemire et al. (2013)     |
| Fe(OH)$_2^{+}$ (aq)         | 23.20     | 0.4   | Lemire et al. (2013)     |
| Fh(s)*                      | -38.55*   | 0.08  | This study               |
| Fe (hydr)oxide (s)          | -40.90*   | 0.06  | Grivé et al. (2014)      |

* LogK values as re-evaluated in the present study
6 Normalized competitive adsorption isotherms

Figure S-4 presents the normalized adsorption isotherms of PO₄ to ferrihydrite, in competition systems with either CO₃ (black lines) or AsO₄ (green lines). The isotherms have been calculated with the CD model. The figure illustrates the relatively high affinity of PO₄ compared to CO₃. A small fraction of PO₄ in solution gives already a high relative PO₄ adsorption. In contrast, the affinities of PO₄ and AsO₄ are very similar leading to relative isotherms that are close to the 1:1 line.

Figure S-4. Normalized adsorption isotherms of PO₄ to ferrihydrite in the presence of competing oxyanions. Black lines are for binary systems with PO₄-CO₃, whereas the green lines are for binary systems with PO₄-AsO₄. The x-axis shows the concentration of PO₄ in solution, relative to the total concentration of oxyanions in solution ([PO₄] + [AOₓz⁻]), being [AOₓz⁻] the competitor oxyanion concentration. The y-axis shows the relative adsorption of PO₄ to ferrihydrite, defined as PO₄[ads] / (PO₄[ads] + AOₓz⁻[ads]). The isotherms were calculated with the CD model. The model parameters for CO₃ were taken from Table 1 (main text), whereas the parameters for PO₄ and AsO₄ are from Hiemstra and Zhao.¹ The ionic strength was in all the systems \( l = 0.5 \) M, using NaNO₃ as background electrolyte.
7 Adsorption isotherms: carbonate surface speciation

In Figure S-5, the surface speciation of $\text{CO}_3$ in Fh systems has been modeled and presented in the form of adsorption isotherms. The chemical conditions in this modeling exercise are the same as in the systems presented in Figure 4 of the main text. At neutral pH (panel A), the bidentate complex (BC) dominates the adsorption of $\text{CO}_3$ over the entire range of solution concentrations. The relative contribution of the bidentate complex with Na (BCNa) and the monodentate complex (MC) increases with increasing the surface loading of $\text{CO}_3$. At pH 8.5 (panel B), the surface loading of $\text{CO}_3$ decreases in comparison with the systems presented in panel A. This decrease is expected, due to the analyzed pH-dependence of $\text{CO}_3$ adsorption. In addition, the surface speciation shifts toward a preferential formation of the BCNa complex. This change is mainly a result of electrostatic interactions, as explained in Section 3.4.2 of the main text.

Figure S-5. Surface speciation of carbonate as a function of the solution concentration in single-ion systems with ferrihydrite at pH 7.0 (A) and 8.5 (B). The CD model parameters set for carbonate, presented in Table 1 of the main text was used in the calculations. The ionic strength of the systems was fixed at 0.10 M by adding the corresponding amounts of NaNO$_3$. BC = Bidentate carbonate complex; BCNa = Bidentate carbonate complex with Na; MC = Monodentate carbonate complex.
8 Adsorption data of carbonate from literature

Figure S-6 presents the adsorption edges of CO$_3$ reported by Zachara et al.$^{10}$ for single-ion systems with CO$_3$[T] = 4.6 µM and two Fe[T] (0.87 and 8.7 mM). The black lines are the CD model predictions obtained with the parameters set presented in Table 1 of the main text. The specific surface area of Fh was set to SSA = 600 m$^2$ g$^{-1}$. With our modeling, we reproduced very well the observed pH dependence of the CO$_3$ adsorption in this data set. The maximum adsorption of CO$_3$ to Fh occurs at pH ~6.5. Below this pH value, the adsorption of CO$_3$ decreases markedly. The observed pH-dependency of the CO$_3$ adsorption, with a maximum in the adsorption edge, is related to the change in the solution speciation of CO$_3$.

At pH values below ~7.0, the description of the CO$_3$ adsorption to ferrihydrite slightly improves when the formation of outer-sphere complexes is considered in the modeling, instead of the monodentate inner-sphere complex (red dotted lines). The formation of outer-sphere complexes can be favored in conditions of low pH and low ionic strength levels, especially in the absence of competitor anions such as PO$_4$.

As observed in Figure S-6, overestimations of the percentage of CO$_3$ adsorption are predicted by the model at higher pH values (pH > 7.0). A lower log$K$ value than the reported in Table 1 (main text) for the formation reaction of the BC surface complex is needed to improve the description of the experimental data. However, the study of Zachara et al.$^{10}$ was performed with CO$_3$[T] at the µM level (i.e. 10$^3$ - 10$^5$ times lower than in the present study), measuring $^{14}$C scintillation and assuming no other source of CO$_3$ in the system than the added. The data are rather unreliable, as follows from the large scattering. Despite these methodological considerations and the evident uncertainty in the CO$_3$ adsorption measurements, the work of Zachara et al.$^{10}$ has been used since then as a reference to model the effect of CO$_3$ on the adsorption of other
ions to Fh (e.g. UO$_2^{2+}$ and AsO$_4^{3-}$)\textsuperscript{11–13}. The lack of reliable CO$_3$ adsorption data to Fh underlies the relevance of our present contribution.

**Figure S-6.** Adsorption edges of carbonate in single-ion systems with ferrihydrite. Data are taken from Zachara \textit{et al.}\textsuperscript{10} for systems with CO$_3$\textsuperscript{[T]}= 4.6 µM and two total Fe concentrations (0.87 and 8.7 mM). The ionic strength of the systems is $I = 0.10$ M, using NaNO$_3$ as background electrolyte. The specific surface area of the ferrihydrite suspensions was set to $A = 600$ m$^2$ g$^{-1}$ with a respective molar mass of $M_{\text{ferr}} = 94.51$ g mol$^{-1}$ Fe. The black full lines are model calculations, obtained with the set of CD model parameters set presented in Table 1 of the main text. The red dotted lines are CD model predictions considering the formation of outer-sphere complexes instead of monodentate inner-sphere complexes (See Option B in Table S-4).
9 Bond length and Brown bond valence concept

The geometries of the inner-sphere bidentate (BC and BCNa) and monodentate (MC) carbonate complexes have been optimized with Molecular Orbital (MO) calculations, applying density functional theory (DFT) with six different functional (BP86, B3LYPyp, EDF1, EDF2, BLYPyp, ωPWB97X-D) and 6-31+G** as basis set. The calculations have been done with Spartan’14 parallel software of Wavefunction, Inc.

An uncharged template composed of two Fe octahedra was used as defined previously by Rahnemaie et al.\textsuperscript{14} to optimized the geometries of the PO\textsubscript{4} surface complexes. The lower part of the template, i.e. (H\textsubscript{2}O)\textsubscript{2}Fe\textsubscript{2}(OH)\textsubscript{6}, has a fix geometry. Inner-sphere complexation of CO\textsubscript{3} was defined and the structure was hydrated with water molecules to explicitly account for hydration. The optimized geometries of (a) CO\textsubscript{3} bidentate (BC), (b) NaCO\textsubscript{3} bidentate (BCNa) and (c) CO\textsubscript{3} monodentate (MC) complex are presented in TOC graph (main text). These geometries have respectively an overall charge of respectively -2, -1, and -2. The average bond distances has been used to calculate the bond valence \( v \) (v.u.) according to the Brown bond concept\textsuperscript{15}

\[
\nu = \exp \left( - \frac{R-R_0}{B} \right)
\]

In equation (4), B is an empirical constant (B = 37 pm), \( R \) (pm) is the bond length distance and \( R_0 \) (pm) is a reference distance calibrated for each element using the sum bond valence rule. Table S-6 presents the average bond distance (pm), obtained from the six different functionals, and the respective \( \nu \) values (v.u) for the three CO\textsubscript{3} complexes used in our model: CO\textsubscript{3} bidentate (BC), NaCO\textsubscript{3} bidentate (BCNa) and CO\textsubscript{3} monodentate (MC).
From the \( \nu \) values, the bond valence coefficients (\( n_0 \) and \( n_1 \)) can be calculated, and after considering the charge contribution of the protons involved in the formation reaction (\( n_{H0} \) and \( n_{H1} \)), and a correction for the interfacial water dipole orientation, then the interfacial charge distribution coefficients (\( \Delta z_0 \) and \( \Delta z_1 \)) are derived. The \( n_0 \) and \( n_1 \) coefficients and the final \( \Delta z_0 \) and \( \Delta z_1 \) values are presented in Table 2 of the main text.

**Table S-6.** Average bond lengths in the optimized geometries of the carbonate surface complexes obtained with MO/DFT using the 6-31+G** basis set and six different functionals (BP86, B3LYP, EDF1, EDF2, BLYP, \( \omega \)P97X-D). The corresponding bond valences (\( \nu \)) are obtained with the Brown valence analysis.

| Bond  | Distance (pm) \(^a\) | \( \nu \) (v.u) | Bond  | Distance (pm) \(^a\) | \( \nu \) (v.u) | Bond  | Distance (pm) \(^a\) | \( \nu \) (v.u) |
|-------|----------------------|----------------|-------|----------------------|----------------|-------|----------------------|----------------|
| FeO-CO* | 130.8 ± 0.8 | 1.298 | FeO-CO* | 130.7 ± 1.1 | 1.296 | FeO-CO* | 130.7 ± 0.7 | 1.305 |
| FeO-CO* | 130.8 ± 0.7 | 1.301 | FeO-CO* | 130.9 ± 1.3 | 1.287 | FeOC-O | 129.7 ± 1.0 | 1.341 |
| FeOC=O | 128.0 ± 1.1 | 1.402 | FeOC=O | 127.4 ± 1.5 | 1.417 | FeOC=O | 129.4 ± 1.4 | 1.353 |
| Sum \( \nu \) | 4.000 | | Sum \( \nu \) | 4.000 | | Sum \( \nu \) | 4.000 | |
| Fe-C | 302.4 ± 2.9 | | Fe-C | 308.1 ± 1.5 | | Fe-C | 301.8 ± 3.8 | |
| Fe-C | 302.9 ± 3.1 | | Fe-C | 302.3 ± 1.4 | | \( R_0 \) | 140.5 | \( R_0 \) | 140.2 | \( R_0 \) | 140.6 |

* C-O bonds that are share with Fe at the surface of ferrihydrite

* Average (± SD) obtained from the optimized geometries applying six different DFT functionals (BP86, B3LYP, EDF1, EDF2, BLYP, \( \omega \)P97X-D)
10 Effect of phosphate adsorption on the surface charge of ferrihydrite

The interaction of PO$_4$ with CO$_3$ at the solid-solution interface of ferrihydrite affects both the total amount of CO$_3$ adsorbed and the surface speciation of this oxyanion. For instance, as shown in Figure 5 of the main text, the relative contribution of the CO$_3$ bidentate complex interacting with Na$^+$ (BCNa) increases in the presence of PO$_4$. Conversely, increase in the total PO$_4$-loading of the systems strongly reduces the formation of the inner-sphere monodentate CO$_3$ complex (MC). The electrostatic interactions between both oxyanions play a crucial role in determining the surface speciation of CO$_3$.

In the extended Stern layer approach$^2$, the net charge density of the ferrihydrite particles ($\sigma_P = \text{C m}^{-2}$) is given by the sum of the charge density in the different electrostatic planes (i.e. 0, 1, and 2) defined as: $\sigma_P = \sigma_0 + \sigma_1 + \sigma_2$. If the specific surface area (SSA in m$^2$ kg$^{-1}$) of ferrihydrite is considered, one can obtain the total net particle charge ($Q_P$ in C kg$^{-1}$). Based on the principle of overall electroneutrality, the surface charge $Q_P$ is compensated by the net counter ion charge present in the Diffuse Double Layer ($Q_{DDL}$ in C kg$^{-1}$). The charge balance can be defined as $Q_{DDL} + Q_P = 0$. Upon specific PO$_4$ adsorption to positively charged ferrihydrite, a considerable amount of negative charge is introduced to the surface and inner Stern plane. Consequently, there will be a reduction in the net charge density and the electrostatic potential of the 1-plane ($\psi_1$) of the Stern Layer will diminish. Calculations performed with the CD model show that in our binary systems with CO$_3$ and PO$_4$ particle charge ($\sigma_P$) is negative over the entire experimental pH range (Figure S-7 A,C). Likewise, for a given pH value (5-10), the electrostatic potential $\psi_1$ decreases continuously when the total PO$_4$-loading of the systems increases (Figure S-7 B,D). The more negative potential in the inner
Stern plane ($\psi_1$) is unfavorable for the formation of a CO$_3$ monodentate complex, because two of the negatively charged ligands of the CO$_3$ complex are located in the 1-plane. On the other hand, the interaction of Na$^+$ ions with the outer ligand of the bidentate CO$_3$ complex will be favored by the presence of this negative electrostatic potential ($\psi_1$).

Figure S-7. Model calculations of the net charge density ($\sigma_P$) of the ferrihydrite particles (A and C) and electrostatic potential in the 1-plane ($\psi_1$) of the Extended Stern Layer of the ferrihydrite-water interface (B and D) for a series of Fh systems with three PO$_4$-loadings (0, 0.7, and 1.5 µmol m$^{-2}$) in the presence of CO$_3$ (0.03 M). The upper panels correspond to systems with an ionic strength of $I = 0.5$ M and the lower panels are for systems with $I = 0.05$ M, using NaNO$_3$ as background electrolyte. The model calculations were performed with the parameters presented in Table 1 of the main text.

For systems with an ionic strength of $I = 0.5$ M, the decreases in the inner Stern plane potential $\psi_1$ upon specific anion adsorption is less pronounced than for the
systems with $I = 0.05$ M (Figure S-7 B,D). At higher values of the ionic strength, the counter ions (Na$^+$) present in the DDL will better screen the negative charge present in the 1-plane. This will result in a higher adsorption of PO$_4$ and CO$_3$ due to less electrostatic repulsion. This observation agrees with the experimental results presented in Figure 3b of the main text showing a lower solution concentration of PO$_4$ in binary adsorption systems with a higher ionic strength.
11 References

(1) Hiemstra, T.; Zhao, W. Reactivity of ferrihydrite and ferritin in relation to surface structure, size, and nanoparticle formation studied for phosphate and arsenate. *Environ. Sci. Nano* 2016, 3, 1265–1279.

(2) Hiemstra, T.; Van Riemsdijk, W. H. On the relationship between charge distribution, surface hydration, and the structure of the interface of metal hydroxides. *J. Colloid Interface Sci.* 2006, 301 (1), 1–18.

(3) Bargar, J. R.; Kubicki, J. D.; Reitmeyer, R.; Davis, J. A. ATR-FTIR spectroscopic characterization of coexisting carbonate surface complexes on hematite. *Geochim. Cosmochim. Acta* 2005, 69 (6), 1527–1542.

(4) Grivé, M.; Duro, L.; Bruno, J. Fe(III) mobilisation by carbonate in low temperature environments: Study of the solubility of ferrihydrite in carbonate media and the formation of Fe(III) carbonate complexes. *Appl. Geochemistry* 2014, 49, 57–67.

(5) Lemire, R. J.; Berner, U.; Musikas, C.; Palmer, D. A.; Taylor, P.; Tochiyama, O.; Perrone, J. Chemical thermodynamics of iron - Part 1 - Chemical thermodynamics volume 13a. 2013.

(6) Hiemstra, T. Formation, stability, and solubility of metal oxide nanoparticles: Surface entropy, enthalpy, and free energy of ferrihydrite. *Geochim. Cosmochim. Acta* 2015, 158, 179–198.

(7) Majzlan, J.; Navrotsky, A.; Schwertmann, U. Thermodynamics of iron oxides: Part III. Enthalpies of formation and stability of ferrihydrite (‘Fe(OH)3), schwertmannite (‘FeO(OH)3/4(SO4)1/8), and ε-Fe2O3. *Geochim. Cosmochim. Acta* 2004, 68 (5), 1049–1059.

(8) Pinney, N.; Kubicki, J. D.; Middlemiss, D. S.; Grey, C. P.; Morgan, D. Density functional theory study of ferrihydrite and related Fe-oxyhydroxides. *Chem. Mater.* 2009, 21 (24), 5727–5742.

(9) Navrotsky, A.; Mazeina, L.; Majzlan, J. Size-driven structural thermodynamic complexity in iron oxides. *Science (80-. ).* 2008, 319 (March), 1635–1639.

(10) Zachara, J. M.; Girvin, D. C.; Schmidt, R. L.; Resch, C. T. Chromate adsorption on amorphous iron oxyhydroxide in the presence of major groundwater ions. *Environ. Sci. Technol.* 1987, 21 (6), 589–594.

(11) Hiemstra, T.; Riemsdijk, W. H. Van; Rossberg, A.; Ulrich, K.-U. A surface structural model for ferrihydrite II: Adsorption of uranyl and carbonate. *Geochim. Cosmochim. Acta* 2009, 73 (15), 4437–4451.

(12) Waite, T. D.; Davis, J. A.; Payne, T. E.; Waychunas, G. A.; Xu, N. Uranium(VI) adsorption to ferrihydrite: Application of a surface complexation model. *Geochim. Cosmochim. Acta* 1994, 58 (24), 5465–5478.

(13) Appelo, C. A. J.; Van Der Weiden, M. J. J.; Tournassat, C.; Charlet, L. Surface complexation of ferrous iron and carbonate on ferrihydrite and the mobilization of arsenic. *Environ. Sci. Technol.* 2002, 36 (14), 3096–3103.

(14) Rahemaeie, R.; Hiemstra, T.; Van Riemsdijk, W. H. Geometry, charge distribution, and surface speciation of phosphate on goethite. *Langmuir* 2007, 23 (7), 3680–3689.

(15) Brown, I. D.; Altermatt, D. Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. *Acta Crystallogr. Sect. B Struct. Sci.* 1985, 41 (4), 244–247.