

Supporting Information for

Role of Carbonate in Thermodynamic Relationships Describing Pollutant Reduction Kinetics by Iron Oxide-Bound Fe²⁺

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Summary

20 pages, 11 figures, 4 tables

Section S1. Data compiled from the literature.

We compiled kinetic data from four studies that measured the reduction rates of substituted nitrobenzene compounds by Fe^{2+} in the presence of iron oxides:

1. Strehlau et al. reported the reduction rates of 4-chloro-nitrobenzene (4-Cl-NB, concentration: $50\ \mu\text{M}$) by Fe^{2+} associated with goethite in the presence of carbonate buffer (concentration: $10\ \text{mM}$) at pH 7.0.¹ We presented their results using a total Fe^{2+} concentration of $500\ \mu\text{M}$ and solid surface area loadings of 22.8 and $45.5\ \text{m}^2/\text{L}$.
2. Huang et al. reported the reduction rates of *p*-cyano-nitrobenzene (*p*-CN-NB, concentration: $5.5\ \mu\text{M}$) by Fe^{2+} (total concentration: $250\ \mu\text{M}$) associated with goethite in the presence of phthalic acid (concentration: $0\text{--}1000\ \mu\text{M}$) at pH 6.0.² The goethite surface area loading was $75\ \text{m}^2/\text{L}$. *The final aqueous Fe^{2+} concentrations were not present in the cited publication, but instead were received from the authors via a personal communication.*
3. Colón et al. measured the reduction rates of *p*-cyano-nitrobenzene (*p*-CN-NB, concentration: $15\ \mu\text{M}$) by Fe^{2+} (total concentration: $387\ \mu\text{M}$) associated with goethite (solid surface area: $28\ \text{m}^2/\text{L}$) in the presence of humic acid (concentration: $0\text{--}50\ \text{mg-carbon}/\text{L}$) at pH 6.6.³
4. Fu et al. reported the reduction rates of nitrobenzene reduction (NB concentration: $130\ \mu\text{M}$) by Fe^{2+} (total concentration: $4800\ \mu\text{M}$) associated with iron oxides in the presence of humic acid at pH 7.0.⁴ We represented their results for suspensions of goethite and hematite (solid surface area: $20\ \text{m}^2/\text{L}$) with a humic acid concentration of $40\ \text{mg}/\text{L}$.

The E_{H} values were calculated according to eq. 5 in the main text using the measured E_{H}^0 value from this study for goethite ($0.781\ \text{V}$) and $0.770\ \text{V}$ for hematite, the reported solution pH, the aqueous Fe^{2+} concentration (after equilibration with iron oxides prior to the addition of the aromatic compounds), and the aqueous Fe^{2+} activity coefficient calculated using the reported water matrix composition and the Davies model (Visual MINTEQ software, v3.1). We did not correct the free aqueous Fe^{2+} activities for complexation reactions with carbonate or humic acids.

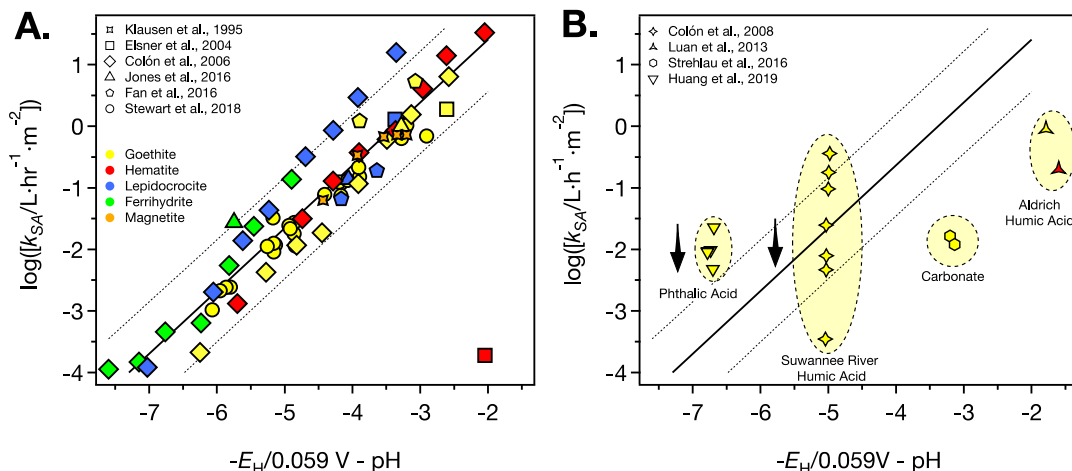


Figure S1. (A) Linear free energy relationship relating $\log(k_{SA})$ values as a function of pH and the calculated E_H values for the reduction of nitrobenzene by Fe^{2+} in the presence of different iron oxides.⁵⁻¹⁰ The derivation of the free energy relationship is provided in Stewart et al., 2018.⁵ The solid line is the least-squares linear regression for all data points excluding the one outlier, and the dashed lines encompass the 95% prediction band. This figure was adapted from Stewart et al., 2018., with permission. **(B)** Data that were collected in solutions containing an additional component commonly found in groundwater (i.e., carbonate, humic acid, or a model humic acid compound).¹⁻⁴ Note the calculated E_H values were not corrected to account for possible Fe^{2+} complexation with the additional species. Details regarding the data used to construct this figure are given in **Table S1** below. The arrows indicate the trend from low to high concentrations of the additional component.

Table S1. Kinetic data for nitroaromatic compounds reduced by goethite- and hematite-bound Fe^{2+} in the presence of an additional component compiled from the literature.

Iron Oxide	Solid SA (m ² /L) ^a	[Fe _(aq) ²⁺] (μM) ^b	α^c	Compound	Add. Comp. ^d	Comp. Conc. (mM) ^e	$-\frac{E_H}{0.059V}$	pH	log k_{SA}	Ref.
Goethite	22.8	400	0.66	4-Cl-NB	Carbonate	10	-3.96	7.0	-1.72	1
	45.5	343	0.66	4-Cl-NB	Carbonate	10	-3.96	7.0	-1.68	1
Goethite	75	103	0.70	<i>p</i> -CN-NB	Phthalic acid	0	-0.81	6.0	-1.64	2
	75	92	0.70	<i>p</i> -CN-NB	Phthalic acid	50	-0.76	6.0	-2.01	2
	75	84	0.70	<i>p</i> -CN-NB	Phthalic acid	100	-0.72	6.0	-2.03	2
	75	83	0.70	<i>p</i> -CN-NB	Phthalic acid	200	-0.71	6.0	-2.05	2
	75	100	0.70	<i>p</i> -CN-NB	Phthalic acid	1000	-0.79	6.0	-2.32	2
	28	334	0.70	<i>p</i> -CN-NB	Humic acid	2.5	-3.12	6.6	-0.44	3
Goethite	28	324	0.70	<i>p</i> -CN-NB	Humic acid	5.0	-3.10	6.6	-0.75	3
	28	318	0.70	<i>p</i> -CN-NB	Humic acid	10	-3.10	6.6	-1.02	3
	28	295	0.70	<i>p</i> -CN-NB	Humic acid	20	-3.06	6.6	-1.60	3
	28	297	0.70	<i>p</i> -CN-NB	Humic acid	30	-3.07	6.6	-2.10	3
	28	295	0.70	<i>p</i> -CN-NB	Humic acid	40	-3.06	6.6	-2.33	3
	28	288	0.70	<i>p</i> -CN-NB	Humic acid	50	-3.05	6.6	-3.46	3
Goethite	20	4000	0.70	NB	Humic acid	40	-4.89	7.0	-0.046	4
Hematite	20	4000	0.70	NB	Humic acid	40	-5.40	7.0	-0.70	4

^a Solid SA represents the surface area of iron oxide solid in suspension.

^b [Fe_(aq)²⁺] represent the concentration of aqueous Fe_(aq)²⁺ after an equilibration period with an iron oxide and before the addition of the nitroaromatic compound.

^c α represents the activity coefficient of aqueous Fe_(aq)²⁺ calculated from the Davies model (Visual MINTEQ software, v3.1).

^d Add. Comp. represents the additional component commonly found in groundwater.

^e Comp. Conc. represents the concentration of the additional component in unit of mM for carbonate, μM for phthalic acid, mg-carbon/L for humic acid at pH 6.6, and mg/L for humic acid at pH 7.0.

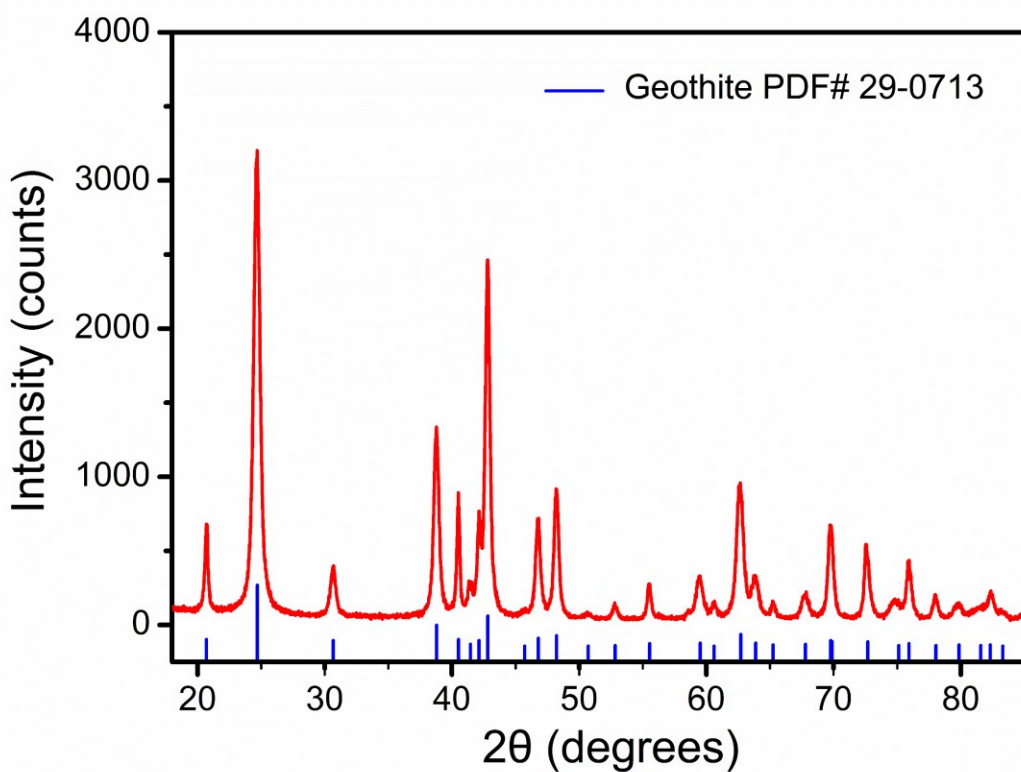


Figure S2. X-ray diffraction pattern of the synthesized goethite collected with a cobalt irradiation source ($K_{\alpha 1} = 1.7890 \text{ \AA}$, $K_{\alpha 2} = 1.7929 \text{ \AA}$).

Table S2. Chemical equilibrium and reaction constants (K) for $\text{Fe}_{(\text{aq})}^{2+}$ in the presence of carbonate

Equilibrium reactions	$\log K$	Ref.
$\text{Fe}^{2+} + \text{HCO}_3^- \leftrightarrow \text{FeHCO}_3^+$	1.10	11
$\text{Fe}^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{FeCO}_{3(\text{aq})}$	5.50	11
$\text{Fe}^{2+} + \text{CO}_3^{2-} + \text{OH}^- \leftrightarrow \text{Fe}(\text{CO}_3)(\text{OH})^-$	9.82	12
$\text{Fe}^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{Fe}(\text{CO}_3)_2^{2-}$	7.26	12
$\text{Fe}^{2+} + \text{H}_2\text{O} \leftrightarrow \text{Fe}(\text{OH})^+ + \text{H}^+$	-9.40	11
$\text{Fe}^{2+} + 2\text{H}_2\text{O} \leftrightarrow \text{Fe}(\text{OH})_{2(\text{aq})} + 2\text{H}^+$	-20.50	11
$\text{Fe}^{2+} + \text{Cl}^- \leftrightarrow \text{FeCl}^+$	-0.20	11
$\text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^-$	-6.35	11
$\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}$	-10.33	11
$\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^-$	-14.00	11

Table S3. Experimentally measured nitrobenzene reduction rate constants. The BET surface area of goethite was 36 m²/g.

pH	Goethite g/L	Carbonate (mM)	Fe _(aq) ²⁺ (μM) ^a	Fe _(soid) ²⁺ (μmol/g) ^b	<i>k</i> _{obs} (h ⁻¹) ^c	<i>k</i> _{SA} (L·h ⁻¹ ·m ⁻²)	<i>E</i> _H (mV vs. SHE)
5.97	1	0	176	36	0.33	9.0×10 ⁻³	-22.6
5.97	1	0	160	82	0.53	1.5×10 ⁻²	-20.2
5.97	1	1	181	55	0.22	6.2×10 ⁻³	-23.3
5.97	1	1	203	46	0.36	1.0×10 ⁻²	-26.2
5.99	1	10	171	51	0.13	3.6×10 ⁻³	-24.7
6.05	1	10	187	55	0.31	8.5×10 ⁻³	-37.6
6.00	2	0	163	33	0.76	1.1×10 ⁻²	-25.8
5.96	2	0	139	55	1.15	1.6×10 ⁻²	-14.8
5.99	2	1	150	41	0.37	5.1×10 ⁻²	-21.9
5.97	2	1	165	42	0.74	1.0×10 ⁻²	-20.8
6.01	2	10	138	45	0.19	2.6×10 ⁻³	-22.7
5.99	2	10	149	53	0.34	4.7×10 ⁻³	-21.2
5.99	3	0	117	45	1.34	1.2×10 ⁻²	-15.5
5.97	3	1	129	40	0.88	8.1×10 ⁻³	-14.5
6.05	3	10	106	43	0.41	3.8×10 ⁻³	-22.8
5.94	3	0	1168	59	30.42	2.8×10 ⁻¹	-65.2
5.94	3	0	1168	77	24.60	2.3×10 ⁻¹	-65.2
5.94	3	1	1156	82	12.72	1.2×10 ⁻¹	-64.9
5.95	3	1	1140	83	9.60	8.9×10 ⁻²	-66.3
6.01	3	10	1108	90	5.57	5.2×10 ⁻²	-75.5
6.00	3	10	1102	96	4.24	3.9×10 ⁻²	-73.6
6.49	1	0	145	82	3.20	8.9×10 ⁻²	-108.3
6.40	1	0	150	57	2.68	7.5×10 ⁻²	-93.4
6.49	1	1	154	72	2.37	6.6×10 ⁻²	-109.7
6.44	1	1	144	75	1.57	4.4×10 ⁻²	-99.3
6.50	1	10	140	72	1.41	3.9×10 ⁻²	-108.0
6.49	1	10	118	84	1.06	2.9×10 ⁻²	-102.0
6.95	0.25	0	182	135	6.84	7.6×10 ⁻¹	-196.6

pH	Goethite g/L	Carbonate (mM)	Fe _(aq) ²⁺ (μM) ^a	Fe _(solid) ²⁺ (μmol/g) ^b	<i>k</i> _{obs} (h ⁻¹) ^c	<i>k</i> _{SA} (L·h ⁻¹ ·m ⁻²)	<i>E</i> _H (mV vs. SHE)
6.94	0.25	0	187	240	9.66	1.1×10 ⁰	-195.7
6.94	0.25	1	182	139	4.85	5.4×10 ⁻¹	-194.7
6.93	0.25	1	205	150	7.56	8.4×10 ⁻¹	-196.0
6.97	0.25	10	125	152	3.56	4.0×10 ⁻¹	-189.0
6.96	0.25	10	142	193	4.57	5.1×10 ⁻¹	-190.6
6.93	0.5	0	178	93	25.14	1.4×10 ⁰	-192.6
6.95	0.5	0	196	109	26.70	1.5×10 ⁰	-198.5
6.93	0.5	1	160	122	12.12	6.7×10 ⁻¹	-189.7
6.95	0.5	1	175	139	14.34	8.0×10 ⁻¹	-195.5
6.98	0.5	10	108	128	6.66	3.7×10 ⁻¹	-187.0
6.97	0.5	10	124	133	7.38	4.1×10 ⁻¹	-188.8
6.92	1	0	126	116	40.92	1.1×10 ⁰	-182.0
6.95	1	0	148	106	96.72	2.7×10 ⁰	-191.4
6.93	1	1	112	116	15.84	4.4×10 ⁻¹	-180.6
6.96	1	1	135	112	28.56	7.9×10 ⁻¹	-190.8
6.93	1	10	83	111	7.62	2.1×10 ⁻¹	-171.5
6.99	1	10	84	124	14.76	4.1×10 ⁻¹	-182.4
6.92	1	10	62	87	6.48	1.8×10 ⁻¹	-171.9

^a Fe_(aq)²⁺ is the aqueous Fe²⁺ concentration after 24-hour equilibrium with goethite prior to the addition of nitrobenzene.

^b Fe_(solid)²⁺ is the quantity of Fe²⁺ taken by goethite, which was calculated from the difference between the initial and final aqueous Fe²⁺ concentrations and mass loading of goethite.

^c *k*_{obs} is the pseudo-first-order reaction rate constant.

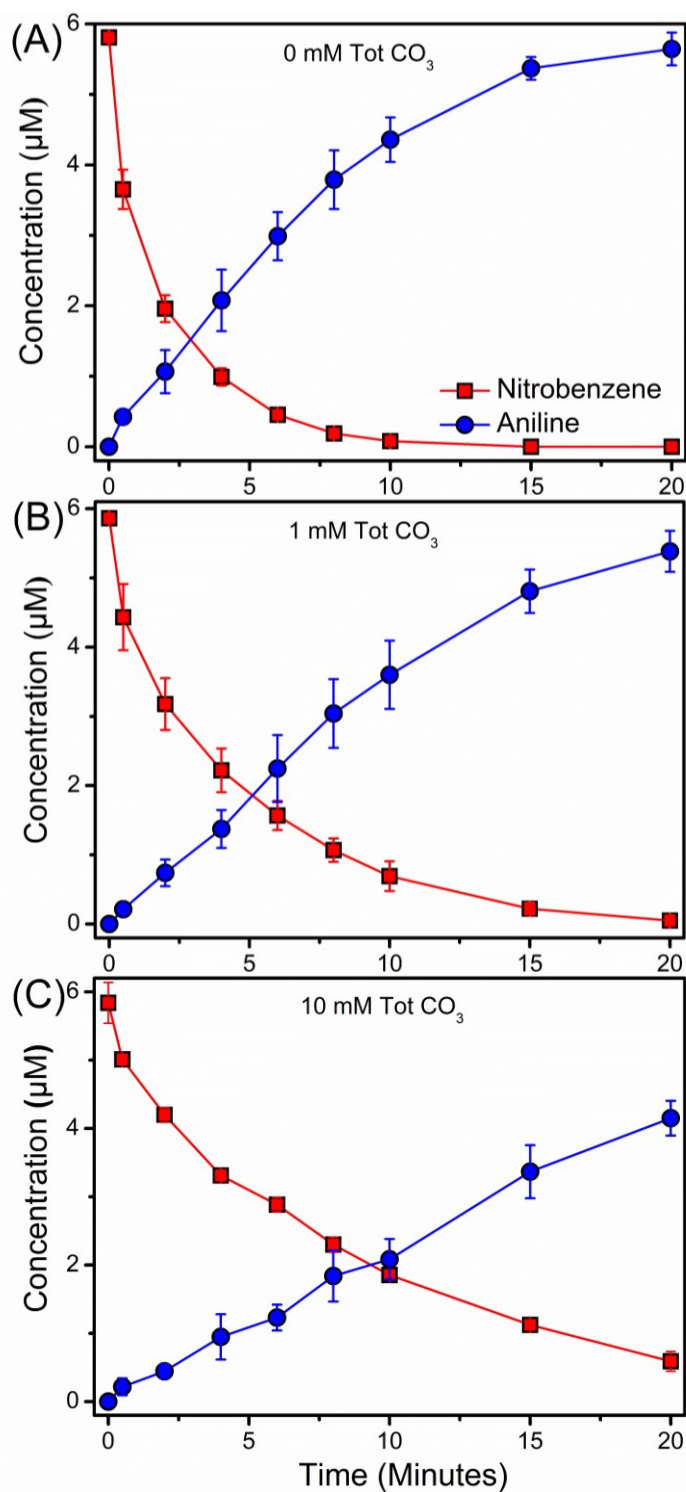


Figure S3. Impact of carbonate on nitrobenzene reduction and aniline production in $\text{Fe}_{(\text{aq})}^{2+}$ -goethite suspension: (A) 0 mM (B) 1 mM, and (C) 10 mM. Experimental conditions: 0.2 mM $\text{Fe}_{(\text{aq})}^{2+}$, 0.5 g/L goethite, 25 mM KCl, 25 mM MOPS buffer, pH = 7.0, and a 24-h equilibration time before adding nitrobenzene.

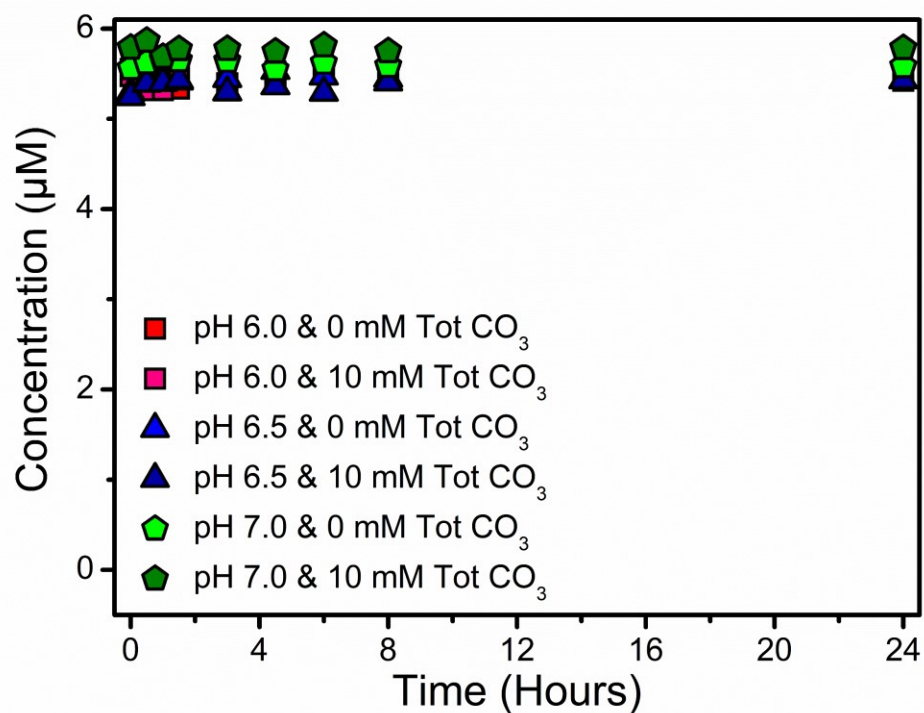


Figure S4. Nitrobenzene reduction by $\text{Fe}_{(\text{aq})}^{2+}$ in the absence of goethite at different pH values and carbonate loadings. The concentration of aniline was below the detection limit for all measurements. Experimental conditions: 0.2 mM $\text{Fe}_{(\text{aq})}^{2+}$, 25 mM KCl, and 25 mM MOPS/MES buffer.

Table S4. Comparison of experimental conditions for the reduction of nitroaromatic compounds between this study and the Strehlau et al., 2016 study.¹

	This work	Strehlau et al., 2016
Nitroaromatic used	Nitrobenzene	4-chloro-nitrobenzene
One-electron reduction potential, $E_H^{1'}$	-0.45 V ¹³	-0.486 V ¹³
pH	7.0	7.0
pH buffer	25 mM MOPS 10 mM carbonate	10 mM carbonate
Goethite loading	0.5 g/L	0.325 g/L
BET specific surface area	36 m ² /g	137 m ² /g
Total Fe _(aq) ²⁺	0.2 mM	0.5 mM
Final Fe _(aq) ²⁺ after uptake	0.13 mM	0.34 mM
Initial nitroaromatic concentration	6 μM	50 μM
k_{obs}	7.1 ± 0.4 h ⁻¹	0.96 ± 0.09 h ⁻¹

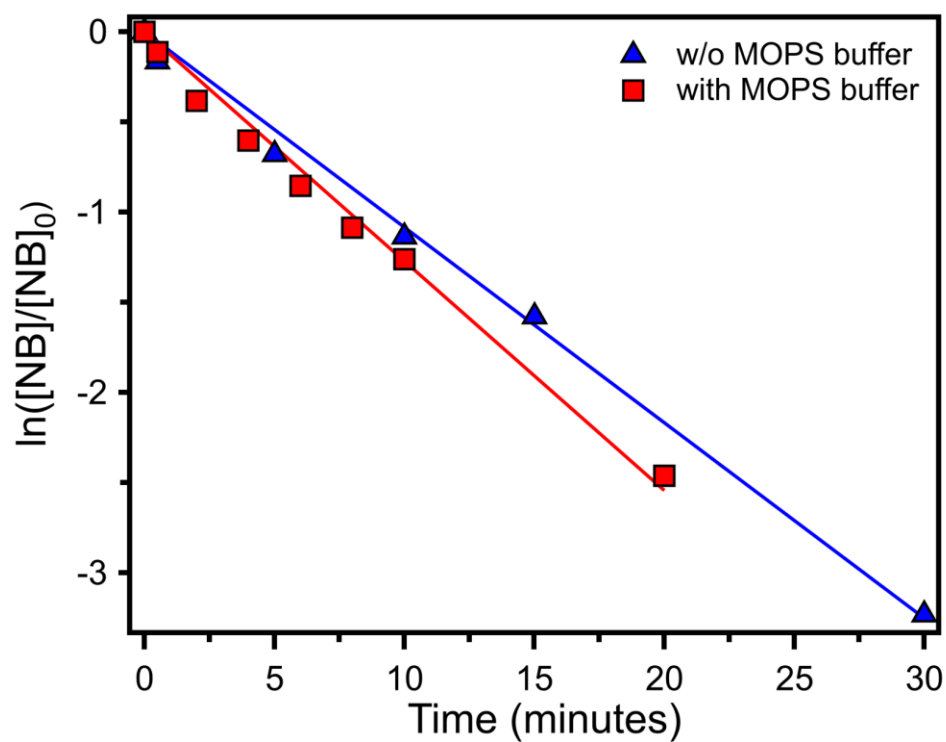


Figure S5. Impact of MOPS buffer on nitrobenzene reduction in $\text{Fe}_{(\text{aq})}^{2+}$ -goethite suspension. Experimental conditions: 0.2 mM $\text{Fe}_{(\text{aq})}^{2+}$, 1 g/L goethite, 10 mM carbonate, 25 mM KCl, 25 mM MOPS buffer, pH = 7.0, and a 24-h equilibration time before adding nitrobenzene.

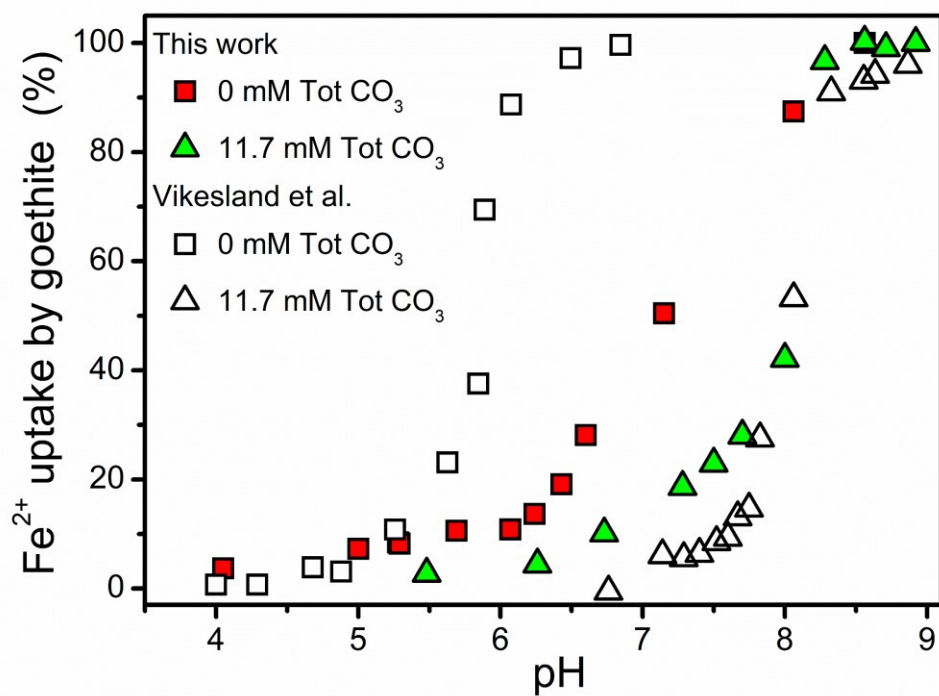


Figure S6. Impact of carbonate on Fe(II) uptake by goethite from this study and Vikesland et al.¹⁴ Experimental conditions: 0.185 mM Fe(II), 10.65 m²/L goethite, 100 mM NaClO₄, and a 24-h equilibration time.

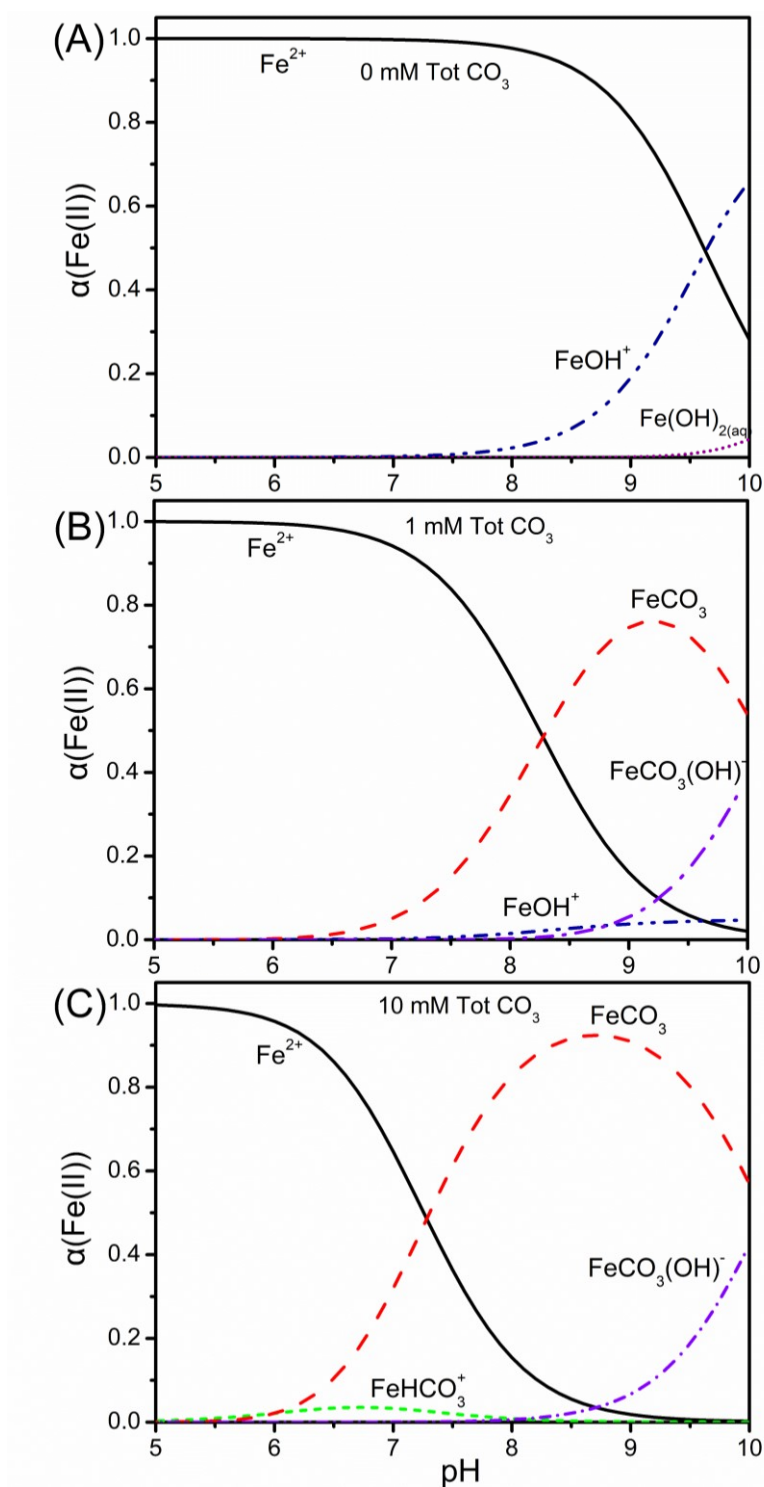


Figure S7. The speciation diagrams of aqueous Fe^{2+} at different carbonate concentrations: (A) 0 mM, (B) 1 mM, and (C) 10 mM. Solution conditions: 0.2 mM total dissolved Fe(II), 25 mM MOPS buffer, and 25 mM KCl.

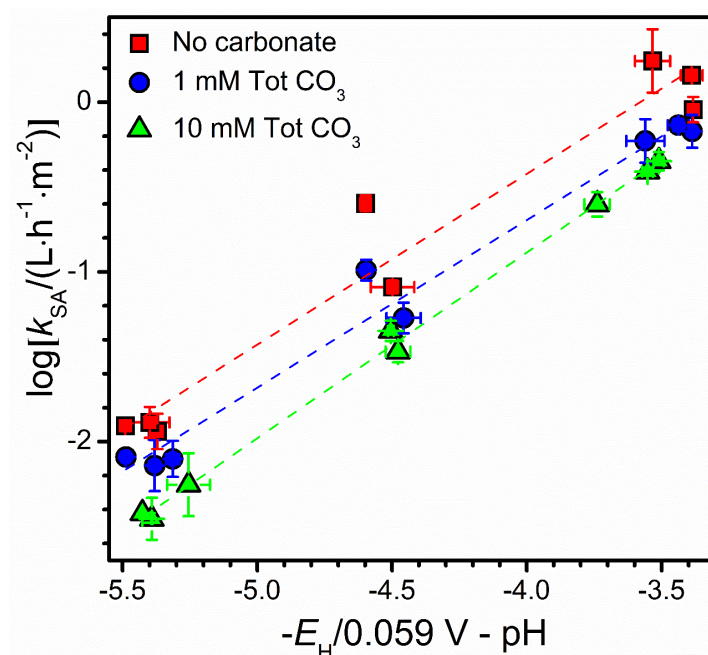


Figure S8. Linear free energy relationship between $\log(k_{SA})$ values and E_H and pH values. The slopes and y-intercepts were allowed to float during the least-squares linear regression (no carbonate: slope = 1.00 ± 0.10 , y-intercept = 3.60 ± 0.46 ; 1 mM total carbonate: slope = 0.99 ± 0.06 , y-intercept = 3.26 ± 0.28 ; 10 mM total carbonate: slope = 1.09 ± 0.02 , y-intercept = 3.49 ± 0.11). Error bars represent the two values measured from duplicate reactors, and points represent the average. The dash lines represent the linear fits: $r^2 = 0.94$ (red), 0.97 (blue), and 1.00 (green).

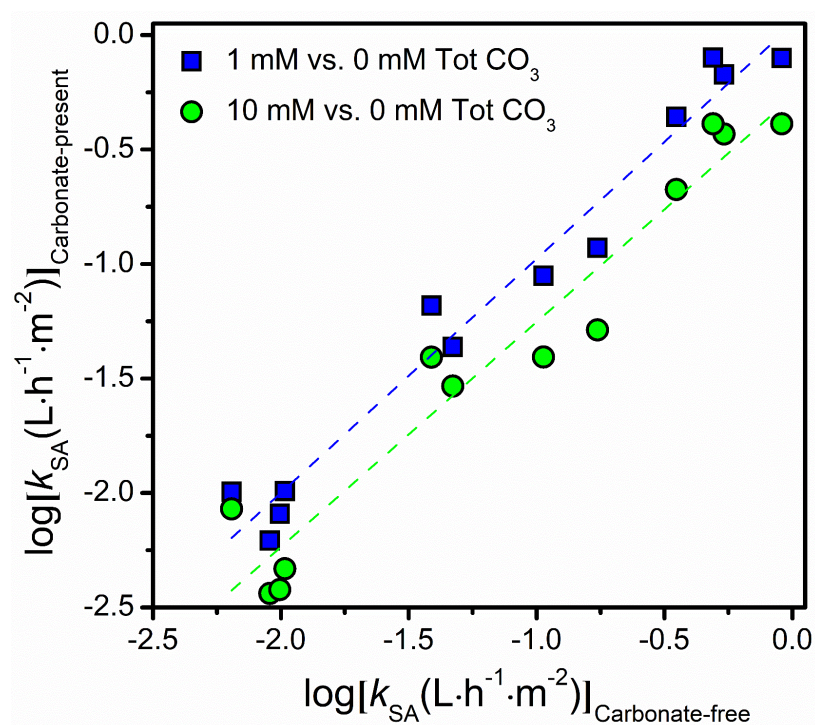


Figure S9. Cross correlation of logarithms of surface-area normalized nitrobenzene reduction rate constants in carbonate-present systems vs. carbonate-free system. The slope and r^2 of the linear fits: 1.02 ± 0.06 and 0.97 for 1 mM vs. 0 mM carbonate; 0.98 ± 0.08 and 0.93 for 10 mM vs. 0 mM carbonate.

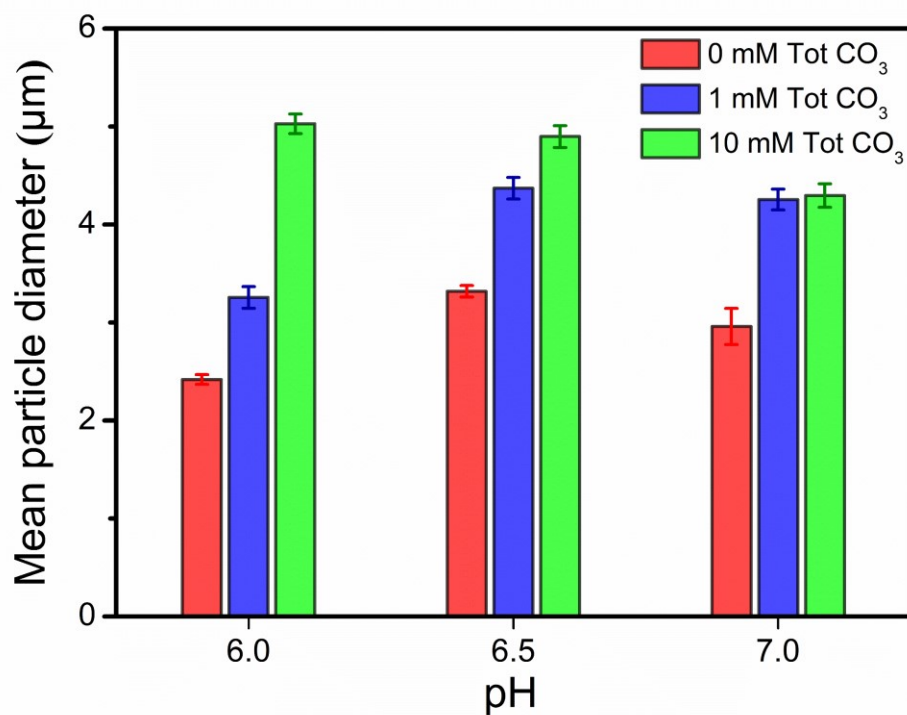


Figure S10. Impact of carbonate on the mean particle size of goethite measured by laser diffraction in $\text{Fe}_{(\text{aq})}^{2+}$ -goethite suspensions at different pH values. Experimental conditions: 0.2 mM $\text{Fe}_{(\text{aq})}^{2+}$, 25 mM KCl, 25 mM MES /MOPS buffer, and 0.05 g/L goethite.

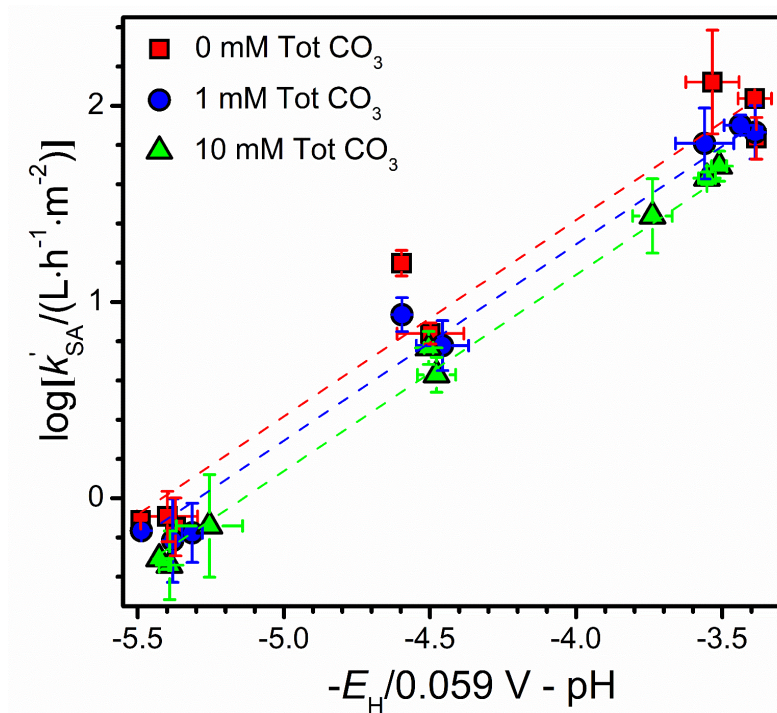


Figure S11. Impact of carbonate on the logarithms of the calibrated surface-area-normalized reaction rate constants (k'_{SA}) based on laser diffraction results as a function of E_H and pH values of $\text{Fe}_{(aq)}^{2+}$ -goethite suspension for nitrobenzene reduction. The dash lines represent the linear fits: $r^2 = 0.96$ (red), 0.98 (blue), and 0.99 (green). The slopes were held at 1 in the linear regressions.

REFERENCES

1. Strehlau, J. H.; Stemig, M. S.; Penn, R. L.; Arnold, W. A., Facet-dependent oxidative goethite growth as a function of aqueous solution conditions. *Environ. Sci. Technol.* **2016**, *50*, 10406-10412.
2. Huang, J.; Wang, Q.; Wang, Z.; Zhang, H. J., Interactions and Reductive Reactivity in Ternary Mixtures of Fe (II), Goethite, and Phthalic Acid based on a Combined Experimental and Modeling Approach. *Langmuir* **2019**, *35*, 8220-8227.
3. Colón, D.; Weber, E. J.; Anderson, J. L., Effect of natural organic matter on the reduction of nitroaromatics by Fe (II) species. *Environ. Sci. Technol.* **2008**, *42*, 6538-6543.
4. Luan, F.; Xie, L.; Li, J.; Zhou, Q., Abiotic reduction of nitroaromatic compounds by Fe (II) associated with iron oxides and humic acid. *Chemosphere* **2013**, *91*, 1035-1041.
5. Stewart, S. M.; Hofstetter, T. B.; Joshi, P.; Gorski, C. A., Linking thermodynamics to pollutant reduction kinetics by Fe²⁺ bound to iron oxides. *Environ. Sci. Technol.* **2018**, *52*, 5600-5609.
6. Jones, A. M.; Kinsela, A. S.; Collins, R. N.; Waite, T. D., The reduction of 4-chloronitrobenzene by Fe (II)-Fe (III) oxide systems-correlations with reduction potential and inhibition by silicate. *J. Hazard. Mater.* **2016**, *320*, 143-149.
7. Fan, D.; Bradley, M. J.; Hinkle, A. W.; Johnson, R. L.; Tratnyek, P. G., Chemical reactivity probes for assessing abiotic natural attenuation by reducing iron minerals. *Environ. Sci. Technol.* **2016**, *50*, 1868-1876.
8. Colón, D.; Weber, E. J.; Anderson, J. L., QSAR study of the reduction of nitroaromatics by Fe (II) species. *Environ. Sci. Technol.* **2006**, *40*, 4976-4982.
9. Elsner, M.; Schwarzenbach, R. P.; Haderlein, S. B., Reactivity of Fe (II)-bearing minerals toward reductive transformation of organic contaminants. *Environ. Sci. Technol.* **2004**, *38*, 799-807.

10. Klausen, J.; Troeber, S. P.; Haderlein, S. B.; Schwarzenbach, R. P., Reduction of substituted nitrobenzenes by Fe (II) in aqueous mineral suspensions. *Environ. Sci. Technol.* **1995**, 29, 2396-2404.
11. Smith, R. M., NIST Critically Selected Stability Constant of metal complexes database. *Version 4* **1997**.
12. King, D. W., Role of carbonate speciation on the oxidation rate of Fe (II) in aquatic systems. *Environ. Sci. Technol.* **1998**, 32, 2997-3003.
13. Hofstetter, T. B.; Heijman, C. G.; Haderlein, S. B.; Holliger, C.; Schwarzenbach, R. P., Complete reduction of TNT and other (poly) nitroaromatic compounds under iron-reducing subsurface conditions. *Environ. Sci. Technol.* **1999**, 33, 1479-1487.
14. Vikesland, P. J.; Valentine, R. L., Iron oxide surface-catalyzed oxidation of ferrous iron by monochloramine: Implications of oxide type and carbonate on reactivity. *Environ. Sci. Technol.* **2002**, 36, 512-519.