Effects of carbonate on the ferrihydrite transformation in alkaline media

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Table S1. Linear combination fitting (LCF) of Fe K-edge extended X-ray absorption fine structure (EXAFS) spectra of ferrihydrite as a function of aging time at different carbonate or nitrate concentration. The results are shown in Figs. 2 and S7.

Samples	Ferrihydrite	Goethite	Hematite	*R*-factor [a]
$[CO_3]_0$ = 0 mM [b]				
0d	1.00 (0) [c]	--	--	0.012
4d	0.43 (2)	0.52 (1)	0.04 (1)	0.006
7d	0.12 (2)	0.81 (2)	0.08 (1)	0.008
10d	--	0.91 (1)	0.09 (1)	0.008
14d	--	0.90 (1)	0.10 (1)	0.009
21d	--	0.90 (1)	0.10 (1)	0.009
$[CO_3]_0$ = 11.42 mM				
0d	1.00 (0)	--	--	0.013
4d	0.59 (2)	0.14 (1)	0.27 (0)	0.005
7d	0.39 (2)	0.18 (1)	0.43 (1)	0.004
10d	0.29 (2)	0.19 (2)	0.52 (1)	0.006
14d	0.24 (2)	0.20 (2)	0.56 (1)	0.006
21d	0.20 (3)	0.21 (2)	0.59 (1)	0.007
$[CO_3]_0$ = 80 mM				
0d	1.00 (0)	--	--	0.016
2d	0.78 (2)	0.14 (1)	0.08 (0)	0.006
4d	0.61 (2)	0.19 (1)	0.19 (0)	0.005
7d	0.44 (2)	0.23 (1)	0.33 (1)	0.005
10d	0.32 (2)	0.28 (1)	0.40 (1)	0.004
14d	0.25 (2)	0.29 (2)	0.46 (1)	0.005
21d	0.21 (2)	0.29 (2)	0.50 (1)	0.006
$[CO_3]_0$ = 180 mM				
0d	1.00 (0)	--	--	0.012

2d	0.79 (2)	0.17 (1)	0.04 (0)	0.007
4d	0.60 (2)	0.27 (1)	0.13 (0)	0.005
7d	0.45 (2)	0.33 (1)	0.23 (0)	0.004
10d	0.30 (2)	0.41 (1)	0.29 (0)	0.003
14d	0.22 (2)	0.45 (1)	0.33 (1)	0.004
21d	0.14 (2)	0.50 (1)	0.36 (1)	0.004
$[CO_3]_0$ = 286 mM				
0d	1.00 (0)	--	--	0.010
4d	0.62 (2)	0.27 (1)	0.11 (0)	0.005
7d	0.46 (1)	0.34 (1)	0.20 (0)	0.003
10d	0.34 (2)	0.41 (1)	0.25 (0)	0.004
14d	0.25 (2)	0.46 (1)	0.29 (0)	0.004
21d	0.15 (2)	0.52 (1)	0.33 (1)	0.004
$[NO_3]_0$ = 0.32 mM [d]				
0d	1.00 (0)	--	--	0.015
2d	0.67 (2)	0.33 (1)	--	0.007
4d	0.38 (2)	0.57 (1)	0.06 (0)	0.006
7d	0.10 (2)	0.81 (2)	0.09 (1)	0.008
10d	--	0.90 (1)	0.10 (1)	0.008
14d	--	0.89 (1)	0.11 (1)	0.009
21d	--	0.89 (1)	0.11 (1)	0.009
$[NO_3]_0$ = 268 mM				
0d	1.00 (0)	--	--	0.011
2d	0.68 (2)	0.32 (1)	--	0.007
4d	0.36 (2)	0.59 (2)	0.05 (1)	0.007
7d	0.06 (3)	0.86 (2)	0.07 (1)	0.009
10d	--	0.93 (1)	0.07 (1)	0.009
14d	--	0.92 (1)	0.08 (1)	0.010
21d	--	0.91 (1)	0.09 (1)	0.011

[a] *R*-factor is an indicator of the goodness for the LCF of Fe K-edge EXAFS spectra.

[b] Carbonate is abbreviated as CO_3.

[c] Standard errors of the LCF of Fe K-edge EXAFS spectra are included in the parentheses.

[d] Nitrate is abbreviated as NO_3.

Table S2. First-order reaction rate constant (k_{obs}) for ferrihydrite transformation, goethite formation, and hematite formation in the presence of carbonate (CO_3) within 10d. The results are shown in Fig. 3.

System	Ferrihydrite		Goethite		Hematite	
	k_{obs} (d^{-1})	R^2	k_{obs} (d^{-1})	R^2	k_{obs} (d^{-1})	R^2
$[CO_3]_0$ = 0 mM	0.259 ± 0.034	0.978	0.213 ± 0.016	0.990	0.010 ± 0.001	0.966
$[CO_3]_0$ = 11.42 mM	0.130 ± 0.003	0.998	0.025 ± 0.003	0.855	0.077 ± 0.002	0.997
$[CO_3]_0$ = 80 mM	0.118 ± 0.002	0.998	0.038 ± 0.005	0.822	0.053 ± 0.002	0.991
$[CO_3]_0$ = 180 mM	0.120 ± 0.003	0.998	0.060 ± 0.006	0.917	0.035 ± 0.002	0.984
$[CO_3]_0$ = 286 mM	0.112 ± 0.003	0.998	0.059 ± 0.005	0.950	0.030 ± 0.001	0.994

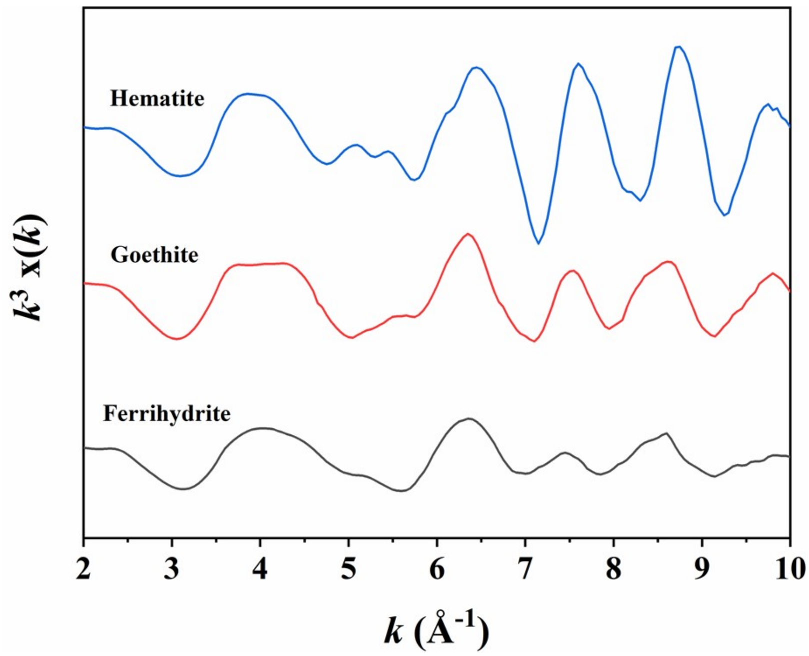

Fig. S1. XAS spectra of references (ferrihydrite, goethite, and hematite) used in LCF analysis of transformation samples.

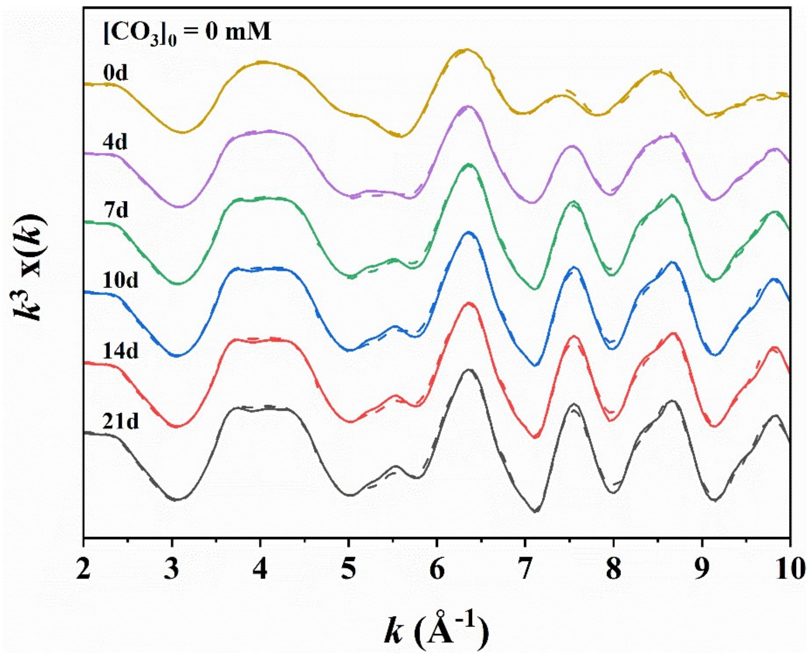

Fig. S2. Linear combination fitting (LCF) of Fe K-edge EXAFS spectra of ferrihydrite as a function of aging time at carbonate concentration ($[CO_3]_0$) of 0 mM. Solid lines and dashed lines represent the normalized k^3 weighted EXAFS spectra and their LC fits, respectively (k range for modeling = 2-10 Å^{-1}).

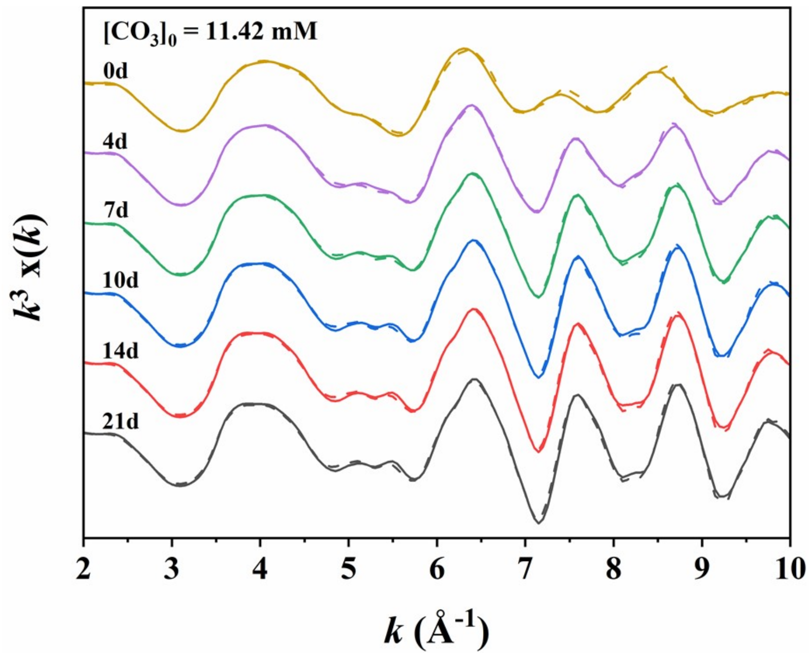

Fig. S3. Linear combination fitting (LCF) of Fe K-edge EXAFS spectra of ferrihydrite as a function of aging time at carbonate concentration ($[CO_3]_0$) of 11.42 mM. Solid lines and dashed lines represent the normalized k^3 weighted EXAFS spectra and their LC fits, respectively (k range for modeling = 2-10 $Å^{-1}$).

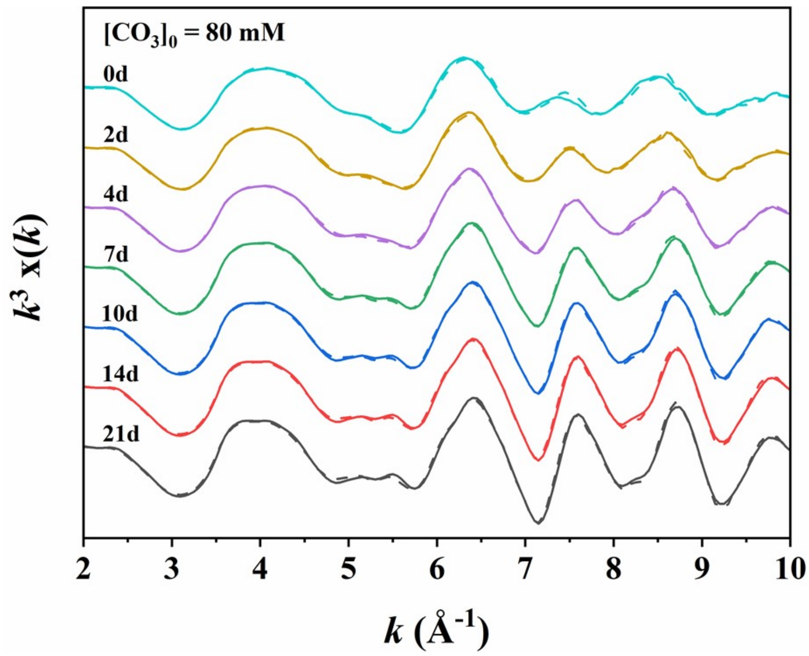

Fig. S4. Linear combination fitting (LCF) of Fe K-edge EXAFS spectra of ferrihydrite as a function of aging time at carbonate concentration ($[CO_3]_0$) of 80 mM. Solid lines and dashed lines represent the normalized k^3 weighted EXAFS spectra and their LC fits, respectively (k range for modeling = 2-10 Å^{-1}).

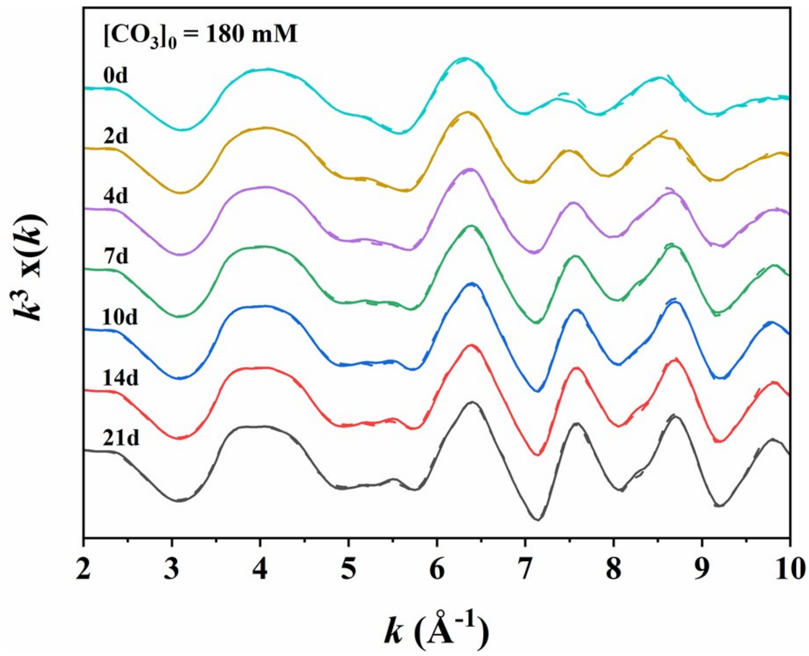

Fig. S5. Linear combination fitting (LCF) of Fe K-edge EXAFS spectra of ferrihydrite as a function of aging time at carbonate concentration ($[CO_3]_0$) of 180 mM. Solid lines and dashed lines represent the normalized k^3 weighted EXAFS spectra and their LC fits, respectively (k range for modeling = 2-10 Å^{-1}).

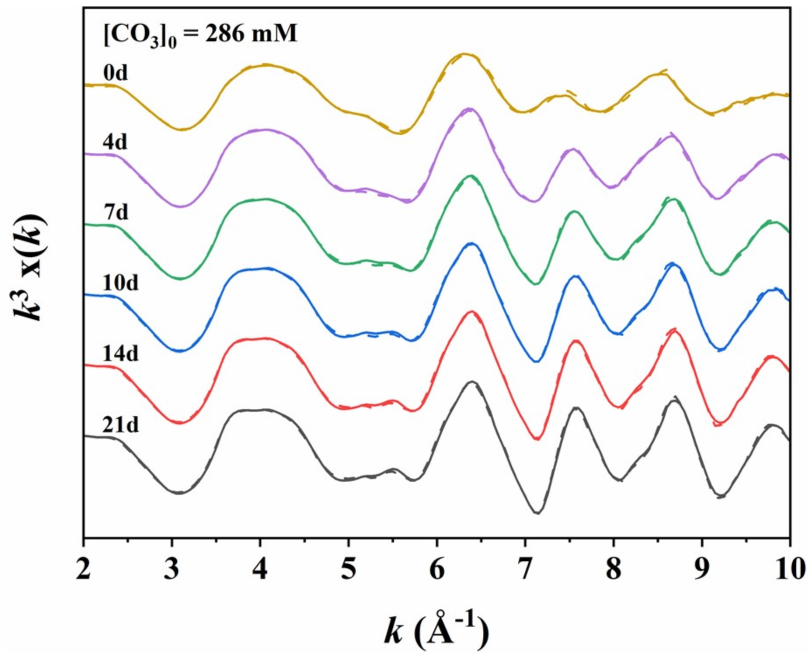

Fig. S6. Linear combination fitting (LCF) of Fe K-edge EXAFS spectra of ferrihydrite as a function of aging time at carbonate concentration ($[CO_3]_0$) of 286 mM. Solid lines and dashed lines represent the normalized k^3 weighted EXAFS spectra and their LC fits, respectively (k range for modeling = 2-10 Å^{-1}).

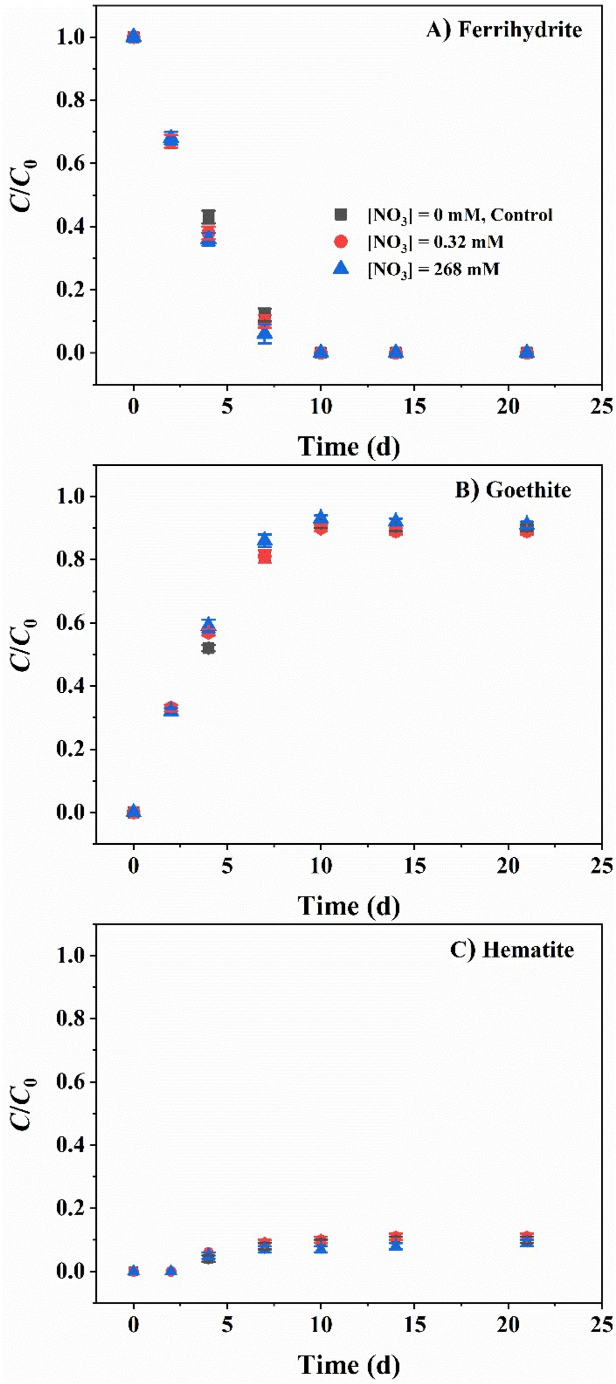

Fig. S7. Effects of nitrate concentration on A) ferrihydrite transformation, B) goethite formation, and C) hematite formation at pH 10. C_0 is the percent ferrihydrite before phase transformation (100%), and C is the relative amount of iron (oxyhydr)oxides remaining or generating at aging time t (d) calculated using the LCF of Fe K-edge EXAFS spectra. Nitrate is abbreviated as NO_3. Meaning of symbols in panels B) and C) are the same with panel A).

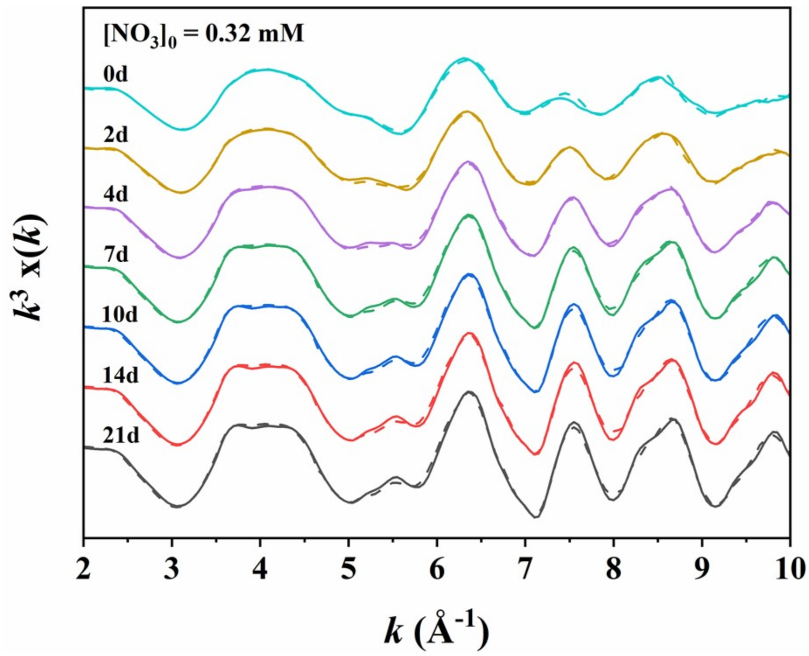

Fig. S8. Linear combination fitting (LCF) of Fe K-edge EXAFS spectra of ferrihydrite as a function of aging time at nitrate concentration ($[NO_3]_0$) of 0.32 mM. Solid lines and dashed lines represent the normalized k^3 weighted EXAFS spectra and their LC fits, respectively (k range for modeling = 2-10 Å^{-1}).

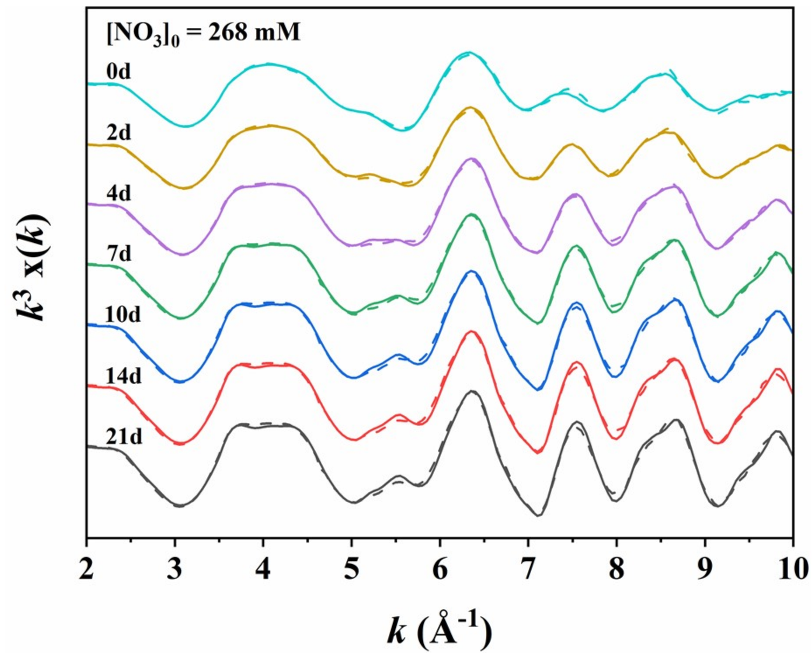

Fig. S9. Linear combination fitting (LCF) of Fe K-edge EXAFS spectra of ferrihydrite as a function of aging time at nitrate concentration ($[NO_3]_0$) of 268 mM. Solid lines and dashed lines represent the normalized k^3 weighted EXAFS spectra and their LC fits, respectively (k range for modeling = 2-10 $Å^{-1}$).

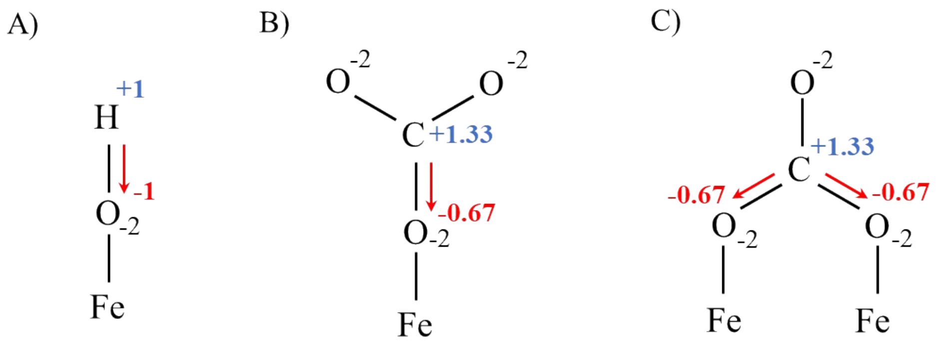

Fig. S10. Schematic diagram of charge sharing by a H^+ atom or a C^{4+} atom by oxygen in A) a hydroxyl ion and B) a carbonate ion. A bidentate binuclear surface species of carbonate is shown in C). Shared charge of the central atom (H or C) is shown in blue. The effective negative charge residing on an O atom is shown in red.