Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supporting information

What are the effects of environmental factors on Co speciation at magnetite surface?

Laura Fablet[1,2], Fadi Choueikani[2], Mathieu Pédrot[1], and Rémi Marsac[1,3]*

[1] Univ Rennes, CNRS, Géosciences Rennes – UMR 6118, F-35000 Rennes, France

[2] Synchrotron SOLEIL, l’Orme des Merisiers, Départementale 128, 91190 Saint-Aubin, France

[3] Université Paris Cité, Institut de physique du globe de Paris, CNRS, F-75005 Paris, France

(*corresponding author: remi.marsac@cnrs.fr)

The supporting information section contains 15 pages, 3 references, 12 figures and 2 tables.

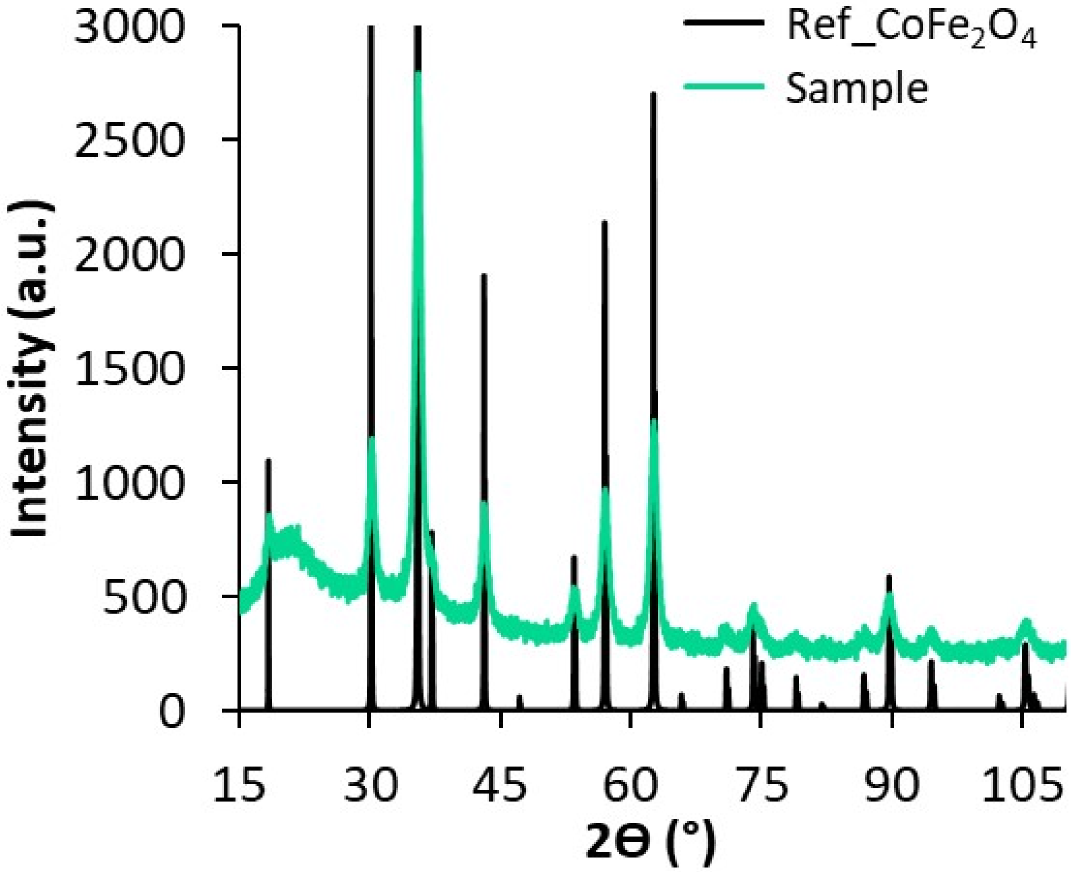

Fig. S1 *X-ray diffraction (XRD) patter of the $CoFe_2O_4$ sample (green), and theoretical pattern of $CoFe_2O_4$ (black).*

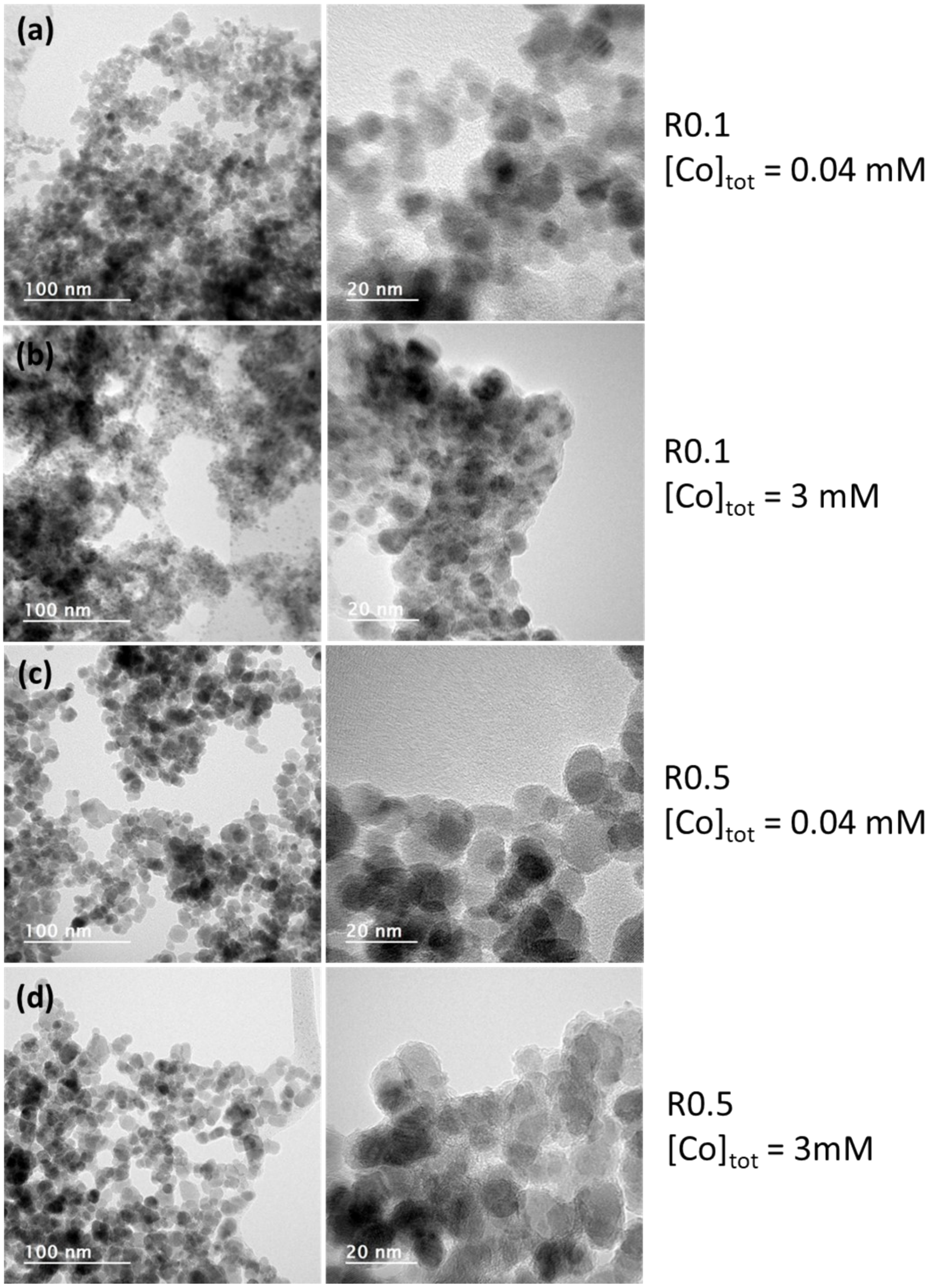

Fig. S2 TEM images of nanoparticles with (a) magnetite R0.1 and $[Co]_{tot}$ = 0.04 mM ($[Co]_s$ = 0.5 atom nm^{-2}), (b) R0.1 and $[Co]_{tot}$ = 3 mM ($[Co]_s$ = 18.9 atom nm^{-2}), (c) R0.5 and $[Co]_{tot}$ = 0.04 mM ($[Co]_s$ = 0.5 atom nm^{-2}), (d) R0.5 and $[Co]_{tot}$ = 3 mM ($[Co]_s$ = 25.7 atom nm^{-2}). (Left) scale of 100 nm and (Right) scale of 20 nm.

Table S1 Corresponding total ($[Co]_{tot}$), aqueous ($[Co]_{as}$) and solid ($[Co]_{s}$) concentration cobalt for R0.1 and R0.3. Data of R0.5 from Fablet *et al.*, 2023 are included for comparison.[1]

$[Co]_{tot}$ (mM)	**$[Co]_{aq}$ (mM)**			**$[Co]_{s}$ (mM)**			**$[Co]_{s}$ (atom nm^{-2})**		
	R0.1	**R0.3**	**R0.5**	**R0.1**	**R0.3**	**R0.5**	**R0.1**	**R0.3**	**R0.5**
0.003	3x10^{-6}	4x10^{-6}	2x10^{-6}	0.003	0.003	0.003	0.036	0.036	0.036
0.005	7x10^{-6}	1x10^{-5}	3x10^{-6}	0.005	0.005	0.005	0.060	0.060	0.060
0.01	2x10^{-5}	4x10^{-5}	6x10^{-6}	0.010	0.010	0.010	0.121	0.119	0.120
0.02	5x10^{-5}	8x10^{-5}	5x10^{-5}	0.020	0.020	0.020	0.244	0.239	0.240
0.04	1x10^{-4}	6x10^{-4}	2x10^{-4}	0.040	0.039	0.040	0.497	0.471	0.478
0.08	0.005	0.003		0.078	0.075		1.022	0.899	
0.1	0.009	0.02	0.001	0.090	0.08	0.01	1.087	0.960	1.190
0.16	0.015	0.002	0.002	0.141	0.155	0.013	1.696	1.868	1.904
0.2	0.029	0.005	0.153	0.168	0.193	0.185	2.022	2.327	2.224
0.32	0.063	0.012	0.017	0.252	0.298	0.303	3.041	3.589	3.646
0.4	0.057	0.102		0.341	0.296		4.106	3.560	
0.48	0.144			0.331			3.985		
0.64	0.274		0.052	0.359		0.588	4.319		7.084
0.8	0.434	0.132	0.110	0.346	0.654	0.689	4.162	7.876	8.304
0.94	0.561	0.250		0.383	0.695		4.617	8.373	
1.12	0.629			0.476			5.734		
1.26	0.744	0.320	0.367	0.513	0.938	0.913	6.182	11.299	11.000
1.42	0.861	0.391		0.557	1.043		6.706	12.571	
1.6		0.500			1.097			13.216	
1.74	0.914	0.568		0.821	1.175		9.887	14.155	
1.92		0.613			1.298			15.631	
2.04		0.694			1.350			16.262	
2.24		0.689			1.549			18.658	
2.4	1.220	0.747		1.255	1.647		15.116	19.842	
2.56		0.779	0.740		1.781	1.820		21.455	21.915
2.67		0.850			1.819			21.911	
2.78	1.269	0.9066		1.468	1.873		17.677	22.564	
2.89	1.273	0.920		1.851	1.969		19.039	23.714	
3	1.384	1.034	0.863	1.570	1.963	2.137	18.914	23.638	25.735

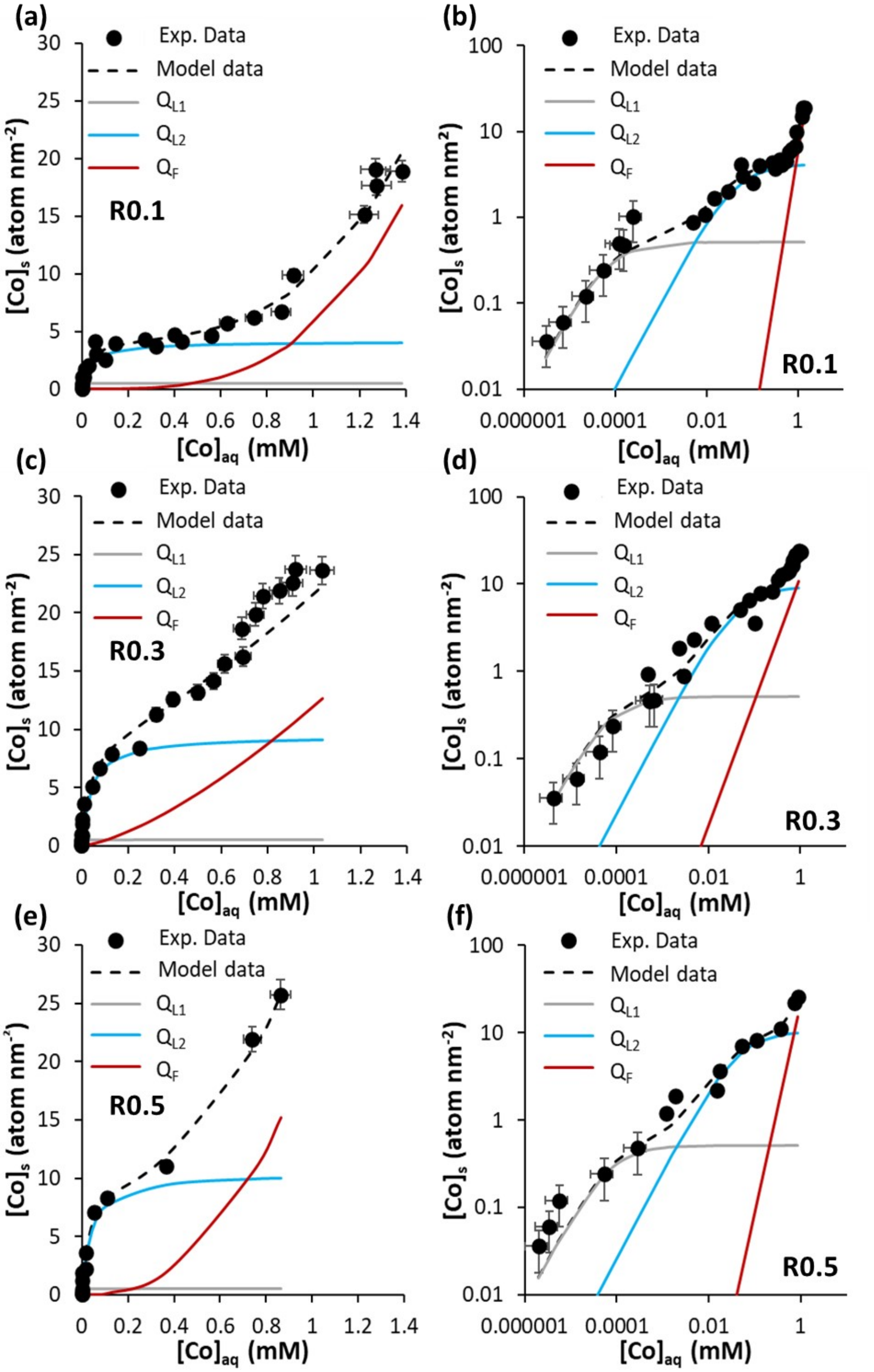

Fig. S3 *Cobalt adsorption isotherms at different stoichiometries : R0.1 (a,b), R0.3 (c,d) and R0.5 (e,f) (data of R0.5 from Fablet et al., 2023)*[1] *presented either as linear (a,c,e) and logarithmic scale (b,d,f) at pH 8 in 10 mM NaCl solution. Dashed black lines are model results using a combination of two Langmuir (Q_{L1} and Q_{L2} as grey and blue lines, respectively) and one Freundlich isotherm equations (Q_F, red lines). Analytical error bars of 5% are plotted, althought not visible for some data and at logarithmic scale. Error was set to 50% for data with $[Co]_{aq}$ < 0.001 mM on the logarithmic scale (i.e. ± 0.2 log unit)*[2] *to acknowledge the fact that larger error may be encountered at low concentrations.*

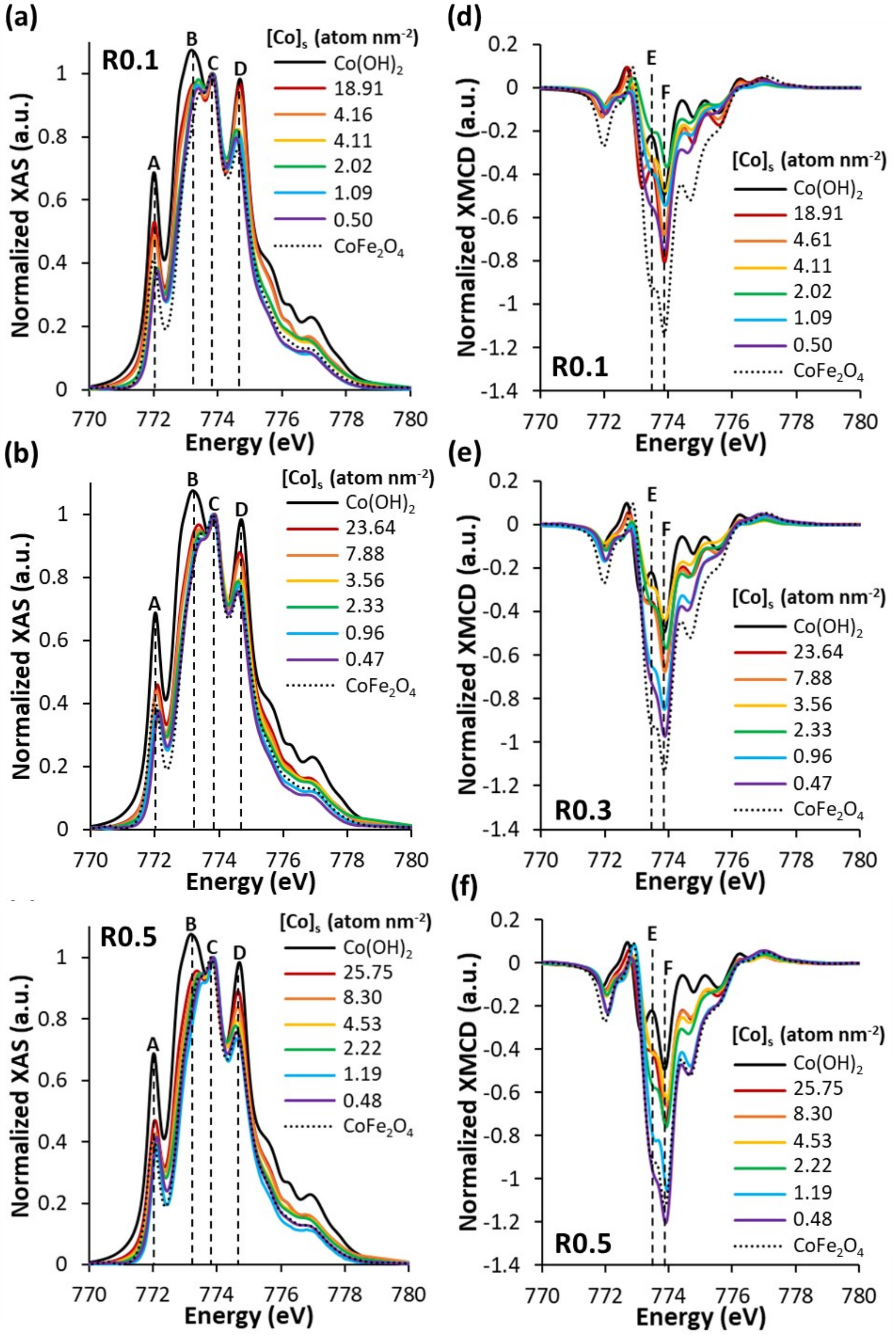

Fig. S4 *Normalized XAS of (a) R0.1, (b) R0.3 and (c) R0.5, and XMCD for (d) R0.1, (e) R0.3 and (f) R0.5 spectra at the Co* L_3*-edge, with different solid Co concentrations (*$0.48 \leq [Co]_{tot} \leq 25.74$ *atom nm*$^{-2}$*) and two references:* $CoFe_2O_4$ *(dotted line) and* $Co(OH)_2$ *(full black line). XAS and XMCD signals are normalized by dividing the raw signal by the edge jump of XAS, and XAS spectra are also normalized to the C peak. Data of R0.5 from Fablet et al. (2023).*[1]

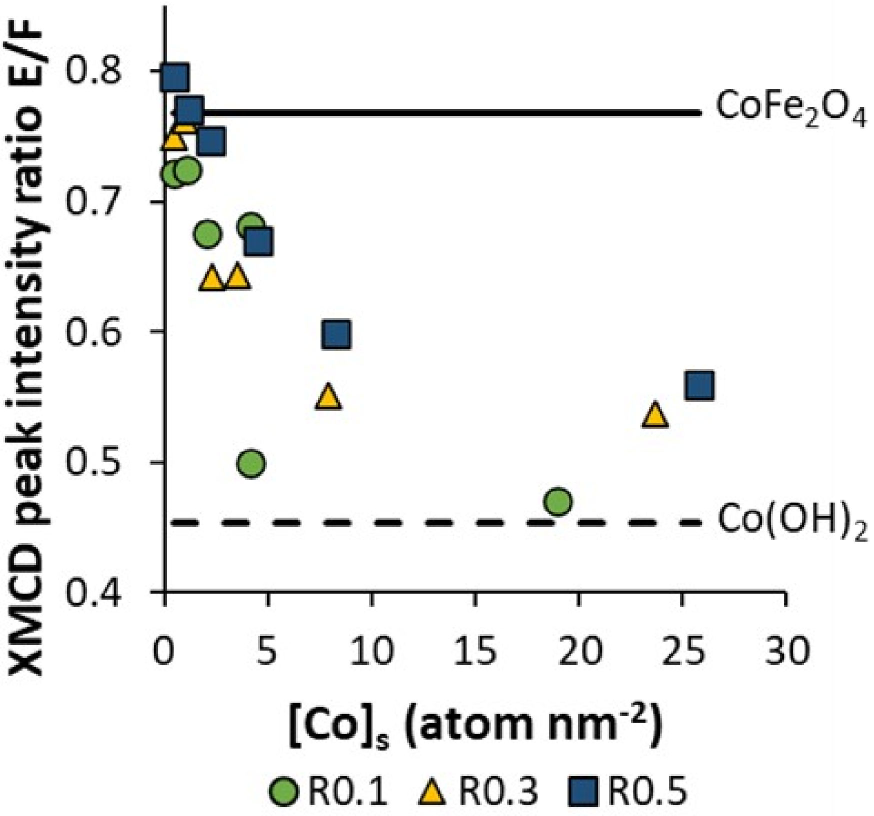

Fig. S5 *XMCD intensity ratio of E and F peaks, as a function of $[Co]_s$ (atom nm^{-2}) for R0.1 (green circles), R0.3 (yellow triangles), R0.5 (blue squares). The dashed line corresponds to the XMCD intensity of $Co(OH)_{2(s)}$ and the solid line to $CoFe_2O_4$ references. Data of R0.5 from Fablet et al. (2023).*[1]

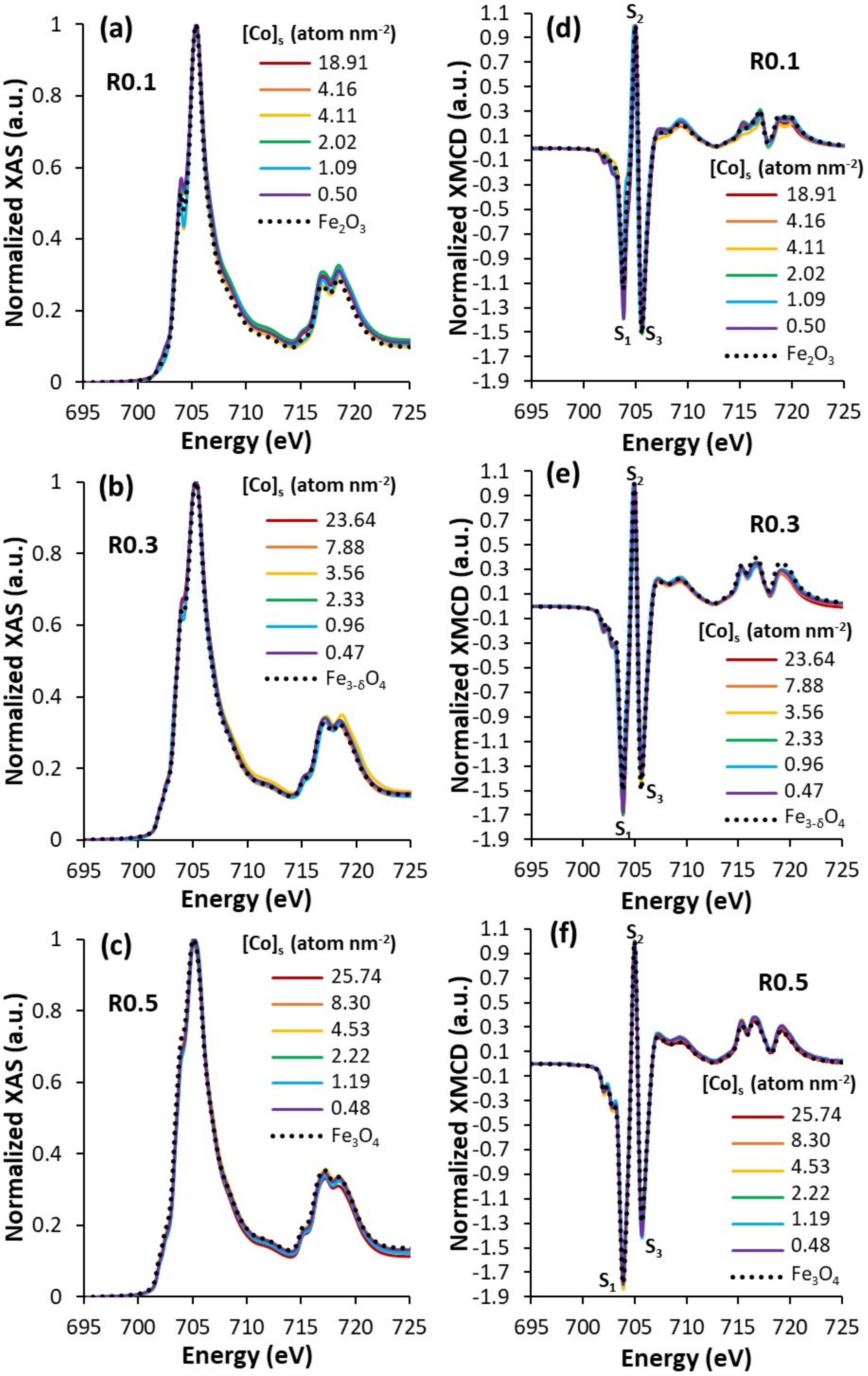

Fig. S6 *Normalized XAS spectra for (a) R0.1, (b) R0.3 and (c) R0.5 magnetites (from Fablet et al., 2023),*[1] *and normalized XMCD spectra for (d) R0.1, (e) R0.3 and (f) R0.5 magnetites, at the Fe* $L_{2,3}$*-edge, with different total Co concentrations* ($0.48 \leq [Co]_{tot} \leq 25.74$ *atom* nm^{-2}) *and three references: maghemite* (Fe_2O_3)*, non-stoichiometric magnetite* ($Fe_{3-\delta}O_4$) *and stoichiometric magnetite* (Fe_3O_4)*, represented by dotted line (data from Jungchaoren et al., 2021).*[3] *XAS signals are normalized by dividing the raw signal by the edge jump of XAS. XMCD signal was normalized to the* $Fe^{3+}_{(Td)}$ *peak (positive one).*

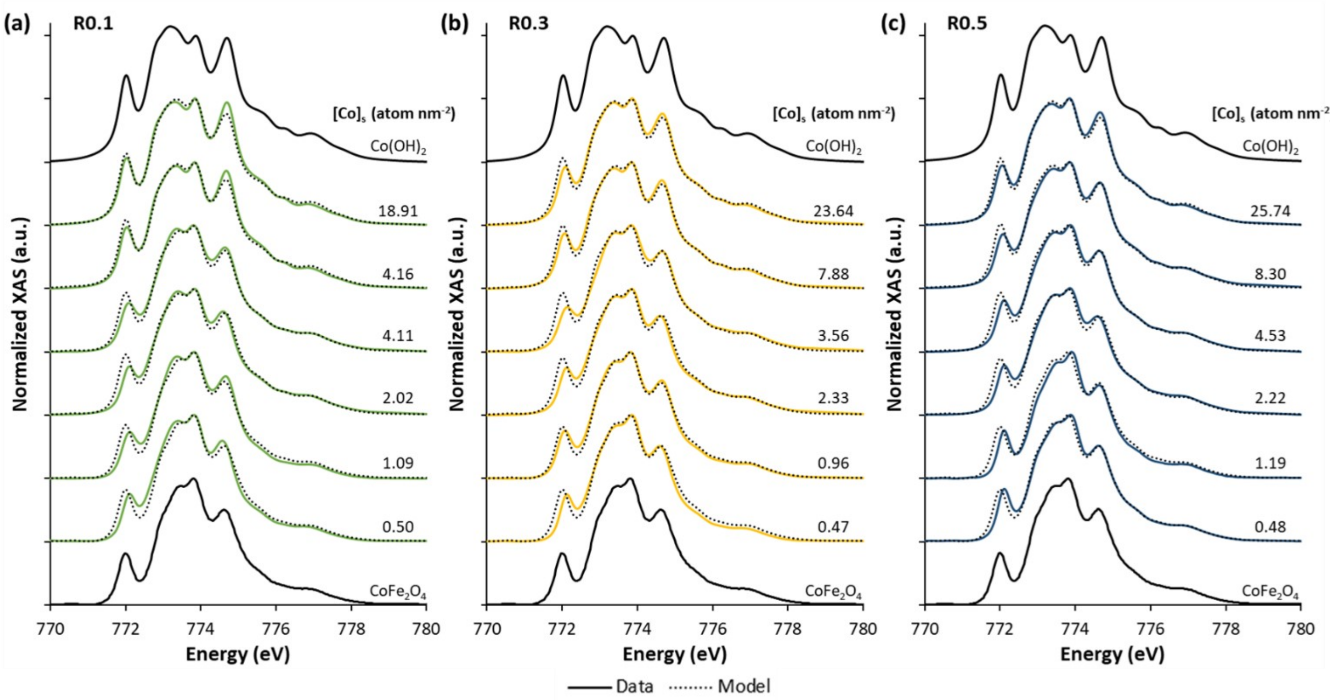

Fig. S7 *Fits of linear combination analysis of normalized XAS spectra at Co L_3 edge for different $[Co]_s$, with (a) R0.1, (b) R0.3 and (c) R0.5 magnetite, using $Co(OH)_2$ and $CoFe_2O_4$ references. Data are represented by a solid line and models by a dotted line.*

Table S2 *Results of the chi-squares test (χ^2) on the fits of linear combination analysis.*

Stoichiometry	**$[Co]_s$ (atom nm^{-2})**	**χ^2**
R0.1	0.50	**0.015**
	1.09	**0.004**
	2.02	**0.004**
	4.11	**0.003**
	4.16	**0.001**
	18.91	**0.001**
R0.3	0.47	**0.011**
	0.96	**0.003**
	2.33	**0.006**
	3.56	**0.006**
	7.88	**0.002**
	23.64	**0.002**
R0.5	0.48	**0.003**
	1.19	**0.017**
	2.22	**0.004**
	4.53	**0.003**
	8.30	**0.003**
	25.74	**0.002**

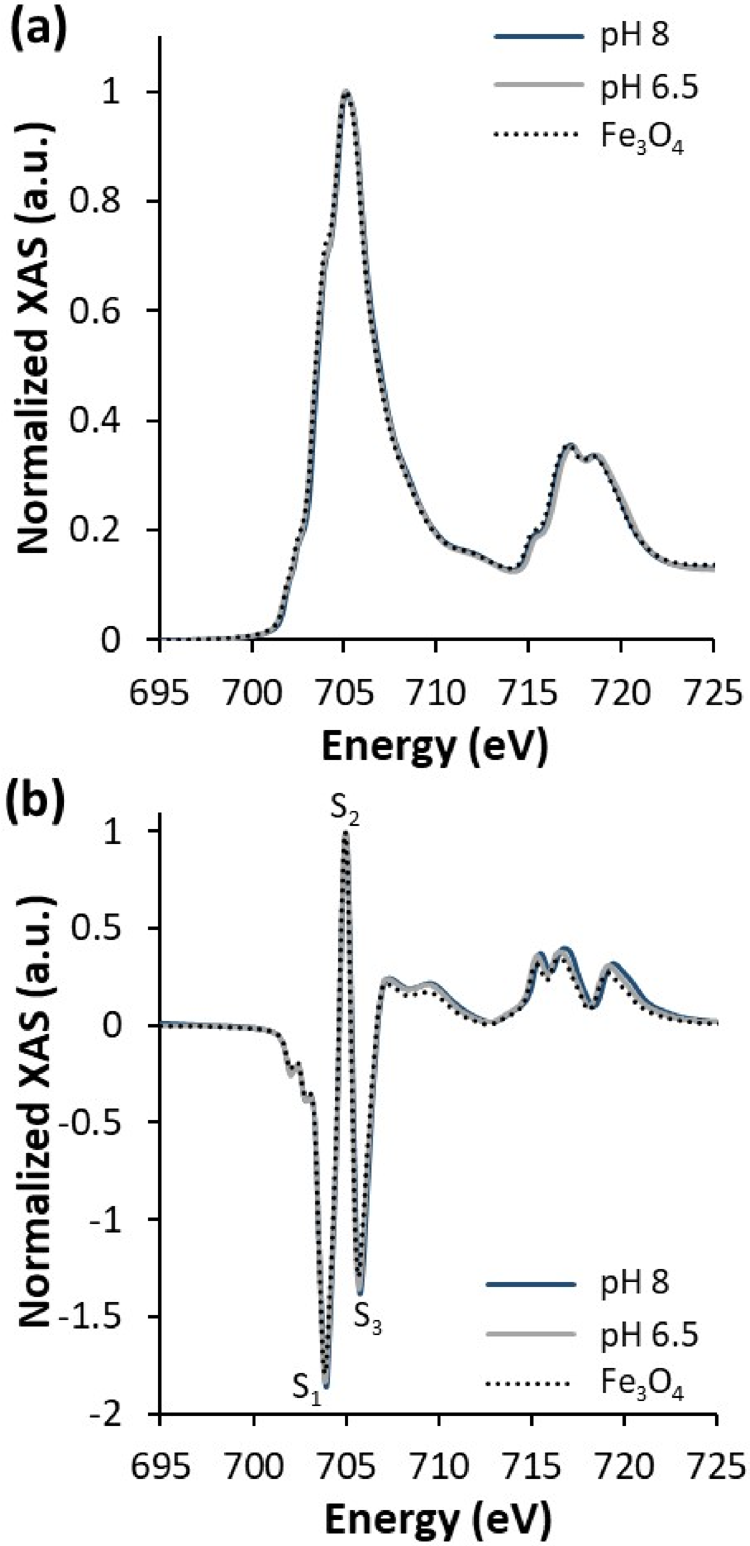

Fig. S8 *Normalized (a) XAS and (b) XMCD spectra at the Fe $L_{2,3}$-edge at pH 6.5 (gray line) and pH 8 (blue line) for $[Co]_{tot}$ = 0.4 mM, for stoichiometric magnetite (R0.5). The dotted line corresponds to the XAS of Fe_3O_4 (data from Jungchaoren et al., 2021). XAS signals are normalized by dividing the raw signal by the edge jump of XAS. XMCD signals are normalized to the $Fe^{3+}_{(Td)}$ peak (positive one).*

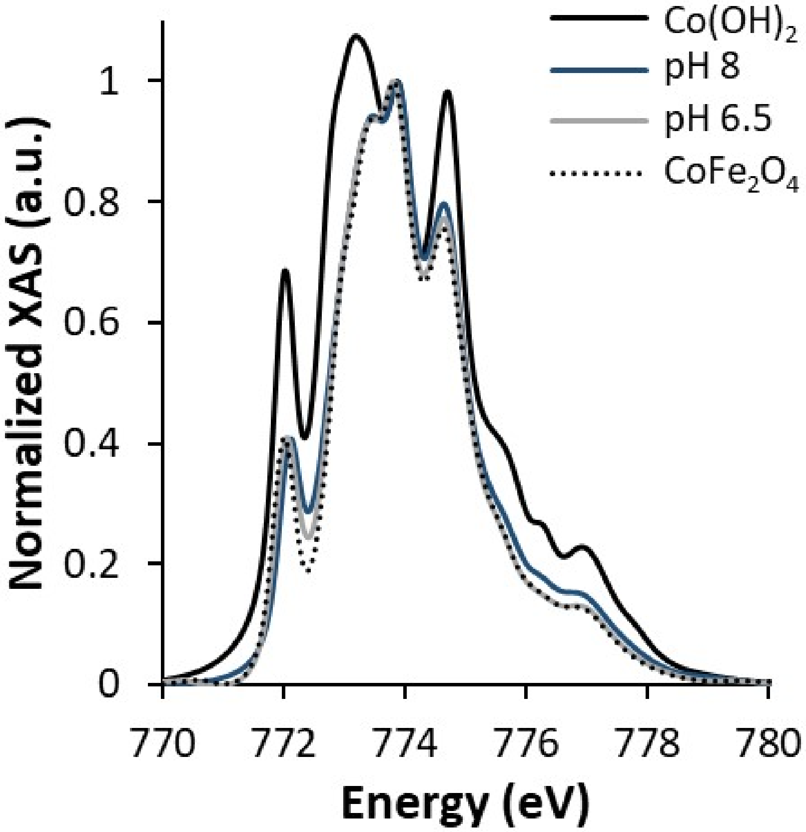

Fig. S9 *Normalized XAS spectra at the Co L_3-edge at pH 6.5 (gray line) and pH 8 (blue line) for $[Co]_{tot}$ = 0.4 mM, for stoichiometric magnetite (R0.5). The dotted line corresponds to the XAS of $CoFe_2O_4$ and the solid line $Co(OH)_2$ references. XAS signals are normalized by dividing the raw signal by the maximum XAS peak and also normalized to the C peak*

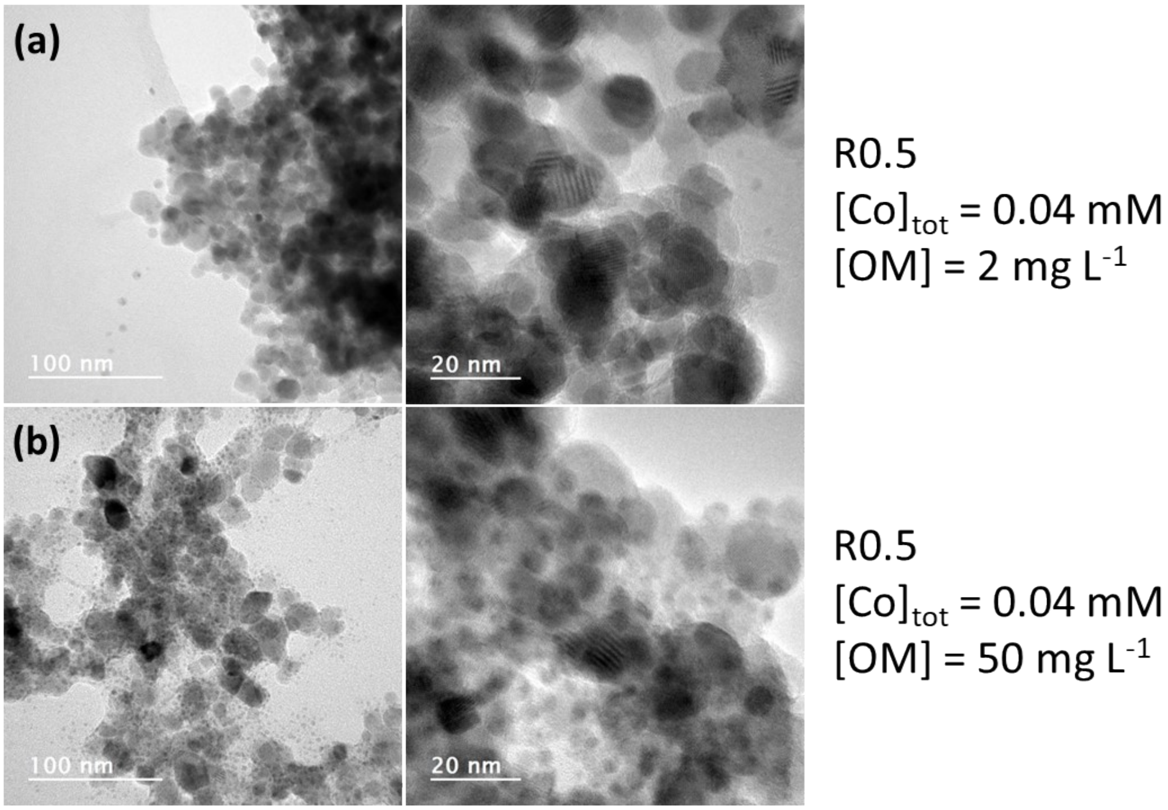

Fig. S10 *TEM images of stoichiometric magnetite with (a) [OM] = 2 mg* L^{-1} *and (b) [OM] = 50 mg* L^{-1} *and* $[Co]_{tot}$ *= 0.04 mM. (Left) scale of 100 nm and (right) 20 nm.*

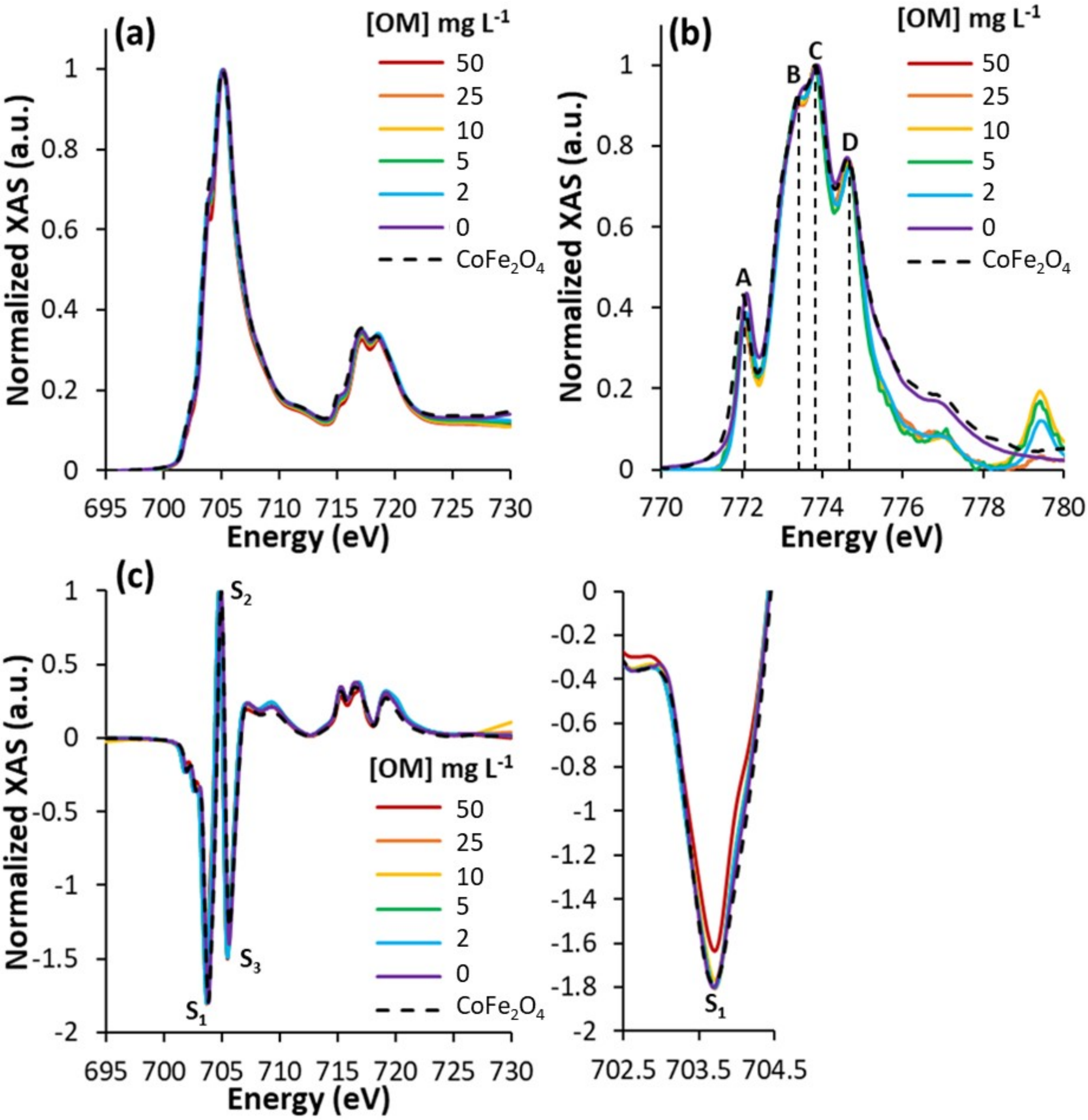

Fig. S11 *Normalized XAS (a) and XMCD (c) at the Fe $L_{2,3}$-edge and normalized XAS (b) at the Co L_3-edge of stoichiometric magnetite (R0.5) with $[Co]_{tot}$ = 0.04 mM for different OM concentrations (from 0 to 50 mg L^{-1}). XAS signals of Fe are normalized by dividing the raw signals by the edge jump of XAS, and XMCD signals are normalized to the $Fe^{3+}_{(Td)}$ peak (positive one). XAS of Co signals are normalized by dividing the raw signal by the maximum XAS peak, and are also normalized to the C peak. The apparent peak around 779.3 eV on (b) is very likely due to contamination by the substrate (barium).*

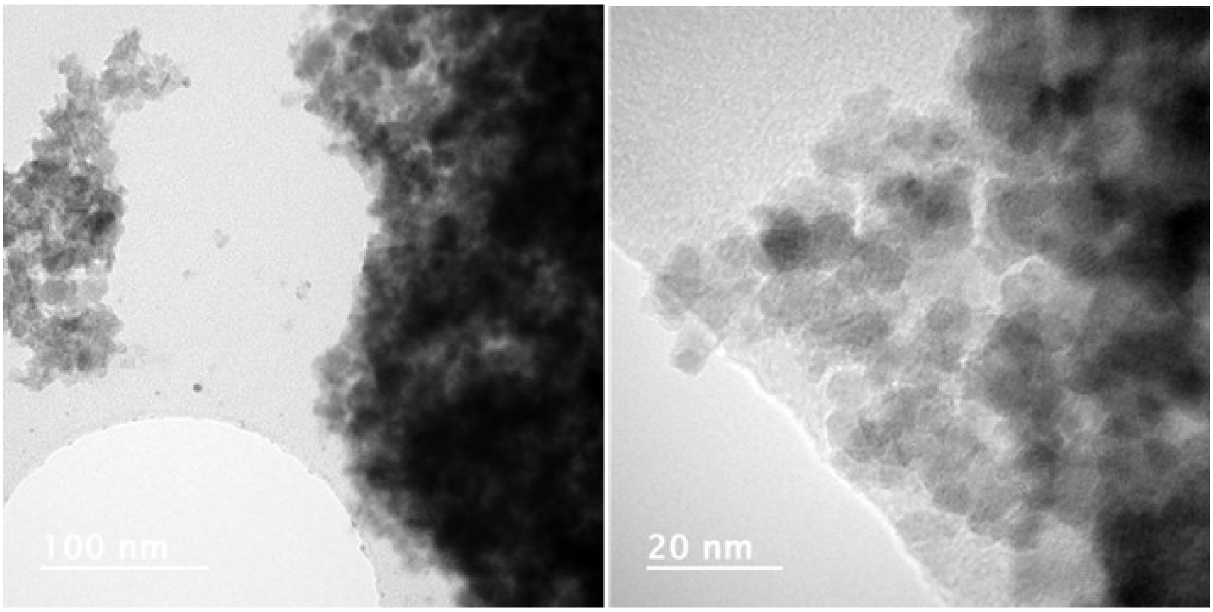

Fig. S12 *TEM images of magnetite R0.1 with* $[Co]_{tot}$ *= 3 mM, in aerobic conditions. (Left) scale of 100 nm and (right) 20 nm.*

References

1 L. Fablet, F. Choueikani, M. Pédrot, M. Kerdiles, M. Pasturel and R. Marsac, Investigation of magnetite–Co interactions: from environmentally relevant trace Co levels to core–shell Fe3O4@Co(OH)2 nanoparticles with magnetic applications, *Environ. Sci.: Nano*, , DOI:10.1039/D3EN00379E.
2 M. H. Bradbury and B. Baeyens, Sorption modelling on illite. Part II: Actinide sorption and linear free energy relationships, *Geochimica et Cosmochimica Acta*, 2009, **73**, 1004–1013.
3 P. Jungcharoen, M. Pédrot, F. Choueikani, M. Pasturel, K. Hanna, F. Heberling, M. Tesfa and R. Marsac, Probing the effects of redox conditions and dissolved Fe 2+ on nanomagnetite stoichiometry by wet chemistry, XRD, XAS and XMCD, *Environ. Sci.: Nano*, 2021, **8**, 2098–2107.