

Supplementary material

Dissolution of mixed amorphous–crystalline Cd-containing Fe coprecipitates in the presence of common organic ligands

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Table S1. Stability constants (*K*) for Cd–, Fe–, and Zn–ligand complexes

All constants obtained from Smith and Martell^[1] except where otherwise noted. All constants listed were determined at an ionic strength of 0.1 and 25 °C unless otherwise noted

Metal–ligand complex	log <i>K</i>		
	Cd ^{II}	Fe ^{III}	Zn ^{II}
Nitrate ^A			
M ⁿ⁺ + NO ₃ ⁻ = MNO ₃ ⁽ⁿ⁻¹⁾	0.31	1	0.4
M ⁿ⁺ + 2NO ₃ ⁻ = M(NO ₃) ₂	0	–	–0.3
Oxalate (p <i>K</i> _{a1} = 1.25, p <i>K</i> _{a2} = 4.27)			
M ⁿ⁺ + ⁻ OOC–COO ⁻ = M(oxalate)	3.89 ^B	7.53	4.87
Citrate (p <i>K</i> _{a1} = 3.13, p <i>K</i> _{a2} = 4.76, p <i>K</i> _{a3} = 6.40)			
M ⁿ⁺ + citrate = M(citrate)	3.75	11.5	4.98
M ⁿ⁺ + 2citrate = M(citrate) ₂	4.54	–	5.9
Cysteine ^B (p <i>K</i> _{a(COOH)} = 2.05, p <i>K</i> _{a(thiol side chain)} = 8.0, p <i>K</i> _{a(amino)} = 10.25)			
M ⁿ⁺ + cysteine = M(cysteine)	10.3 ^C	10.85 ^D	9.04
M ⁿ⁺ + 2cysteine = M(cysteine) ₂	16.92 ^C	14.49 ^D	17.54
M ⁿ⁺ + 3cysteine = M(cysteine) ₃	19.78 ^C	–	–
Histidine (p <i>K</i> _{a(COOH)} = 1.77, p <i>K</i> _{a(imidazole side chain)} = 6.10, p <i>K</i> _{a(amino)} = 9.10)			
M ⁿ⁺ + histidine = M(histidine)	5.39	4.7	6.55
M ⁿ⁺ + 2histidine = M(histidine) ₂	9.66	–	12.06
EDTA (p <i>K</i> _{a1} = 2.29, p <i>K</i> _{a2} = 3.23, p <i>K</i> _{a3} = 6.94, p <i>K</i> _{a4} = 11.28)			
M ⁿ⁺ + EDTA = MEDTA	16.36	25	16.44

^AObtained from Lindsay.^[2]

^BObtained from Berthon.^[3]

^CCd–cysteine formation constants were determined at 0.15 ionic strength and 37 °C.

^DFe–cysteine formation constants were determined at 0.15 ionic strength and 20 °C.

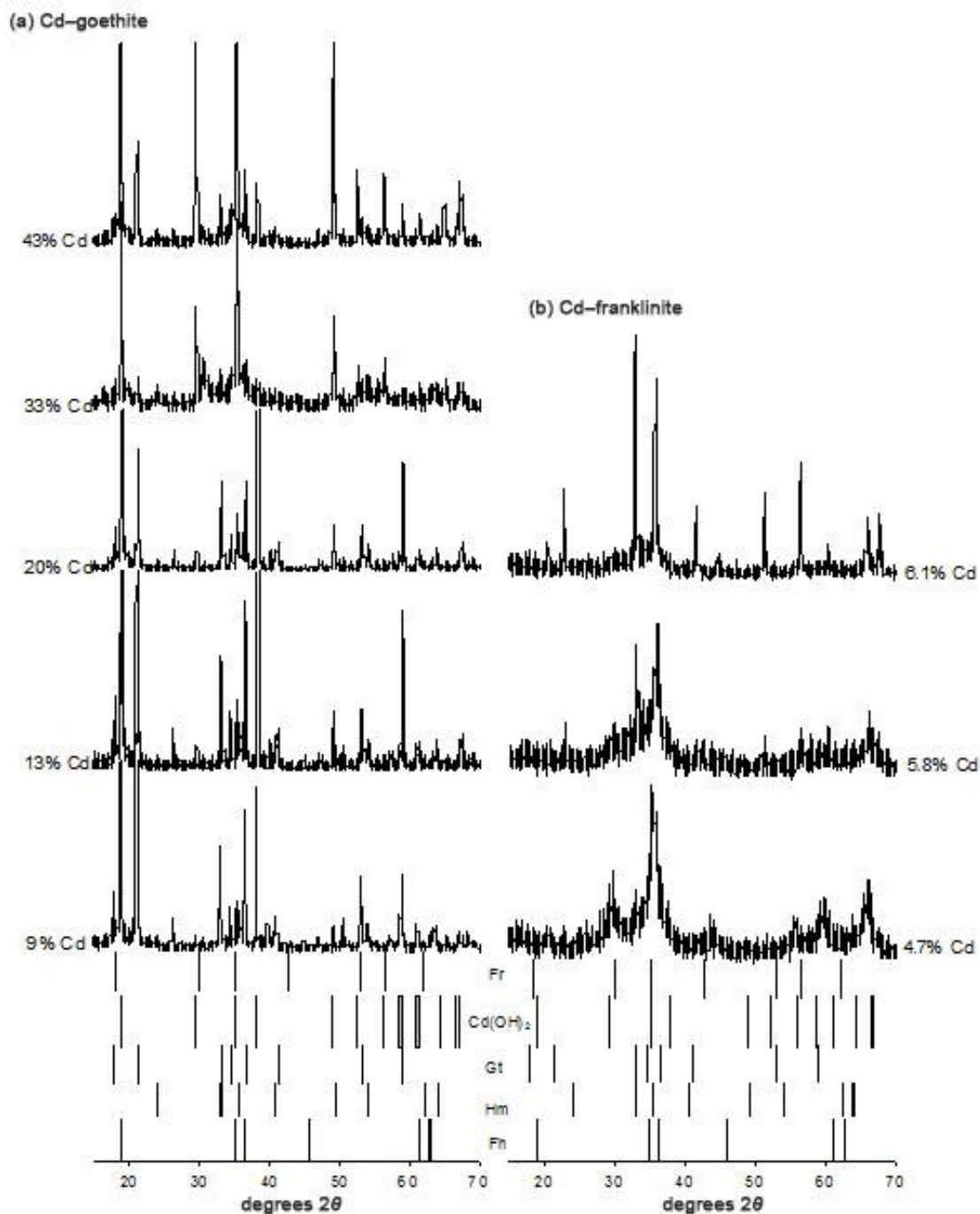


Fig. S1. X-Ray diffraction (XRD) patterns for Cd-goethite (a) and Cd-franklinite (b) minerals not used in dissolution experiments. XRD lines (degrees 2θ) of selected minerals are plotted for reference below (a) and (b). Mineral abbreviations: Fr, franklinite; Cd(OH)₂, cadmium hydroxide; Gt, goethite; Hm, hematite; Fh, ferrihydrite.

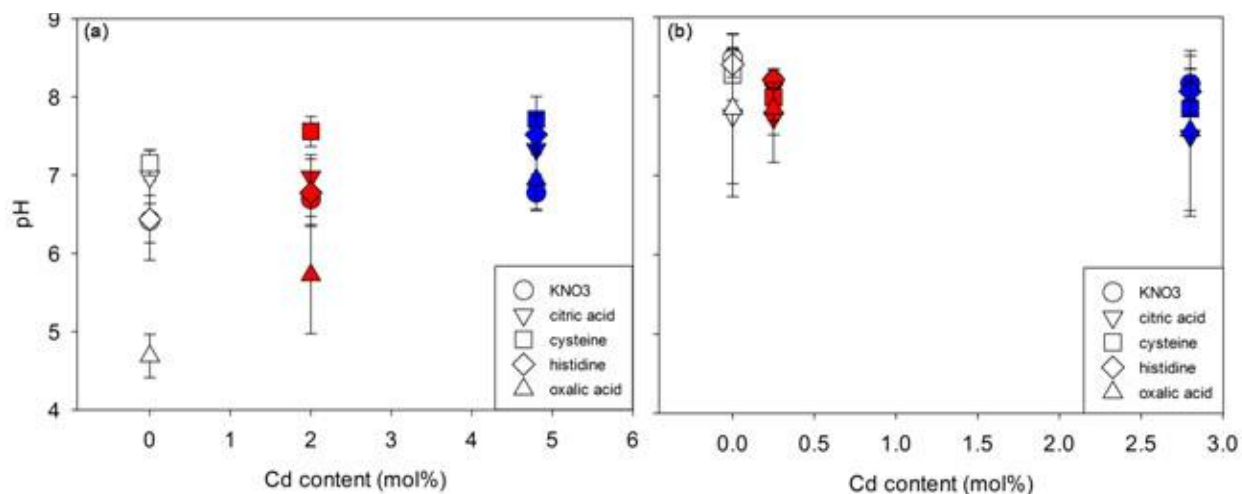


Fig. S2. Average pH measured over the course of the experiment for each of the Cd-goethite minerals (a) and Cd-franklinite minerals (b) for all ligands used for mineral dissolution.

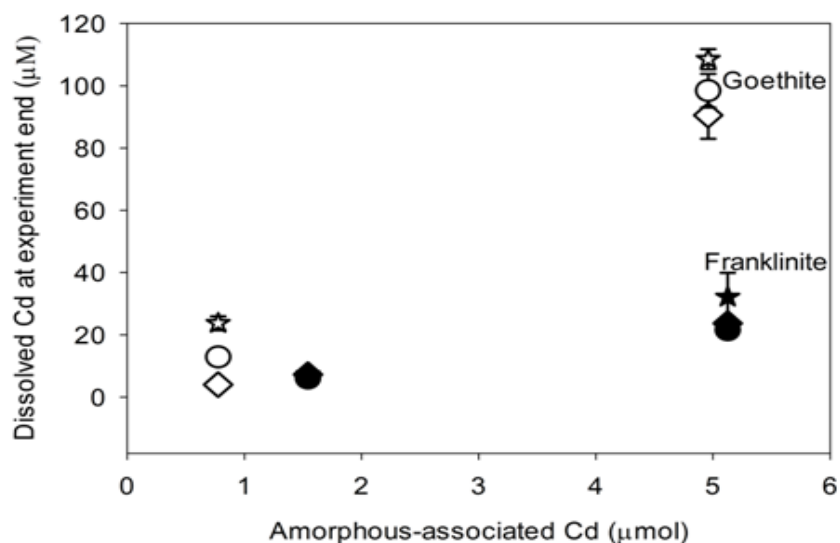


Fig. S3. Dissolved Cd concentrations measured in solution at experiment end as a function of amorphous-associated Cd for oxalic acid (stars), citric acid (diamonds) and histidine (circles) (i.e. dissolution enhancing ligands) in Cd-goethite coprecipitates (open symbols) and Cd-franklinite coprecipitates (filled symbols). Error bars represent 1 standard deviation from the mean of duplicate samples.

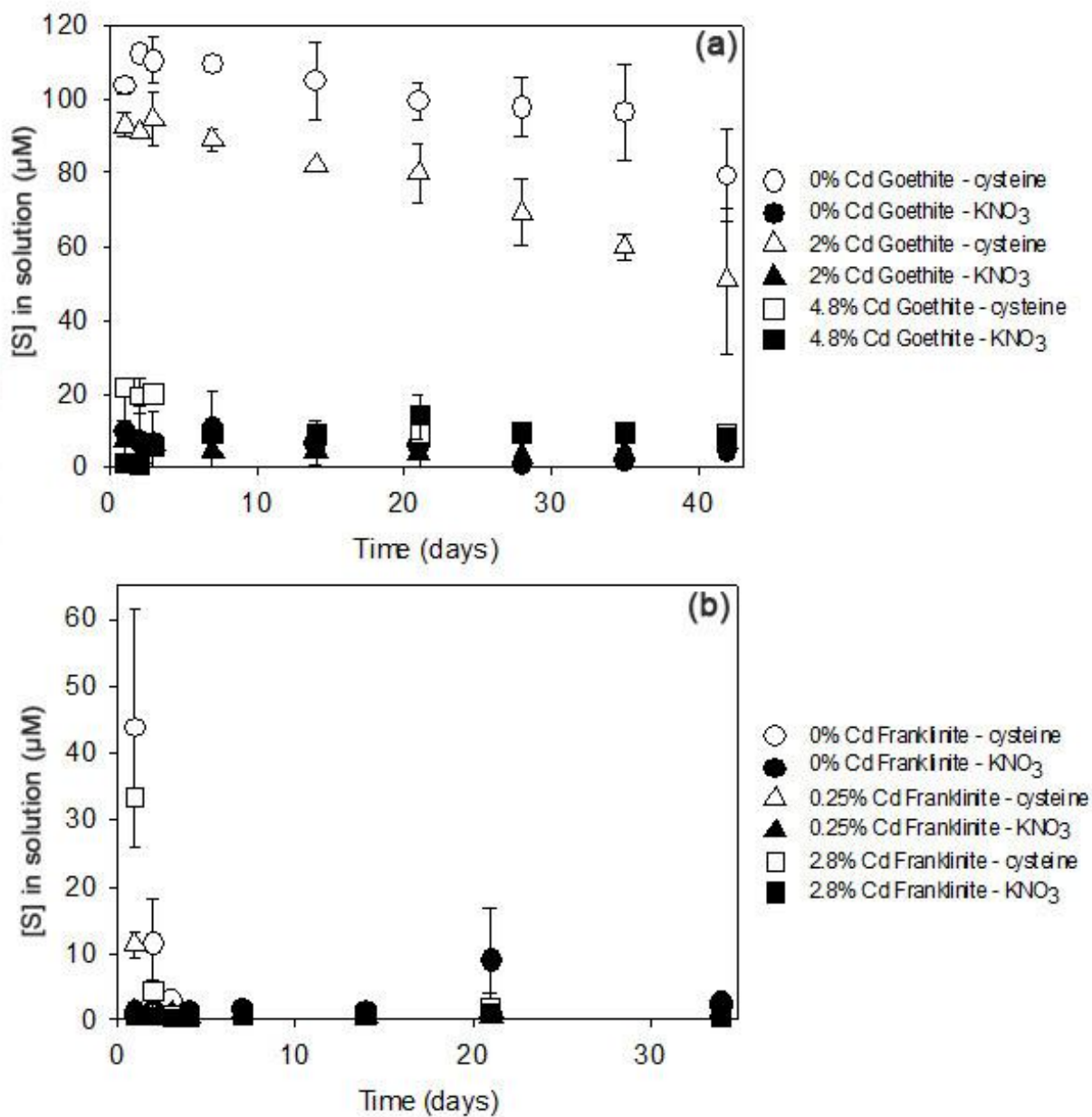


Fig. S4. Sulfur concentrations measured in solution overlying Cd-goethite (a) and Cd-franklinite (b) minerals. Error bars represent 1 standard deviation from the mean of duplicate samples.

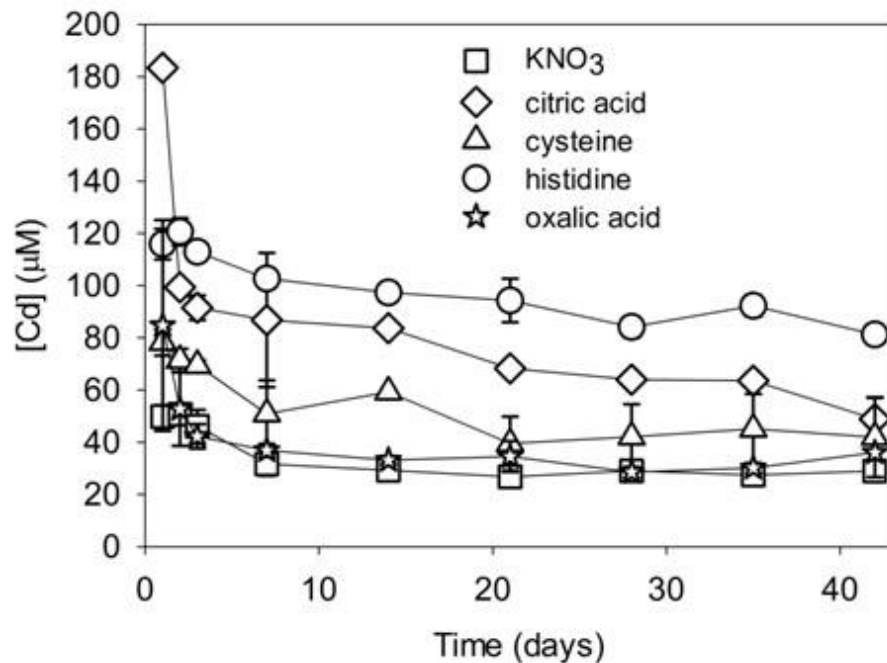


Fig. S5. Cadmium concentrations measured in solution overlying 100 % Cd–mineral. Error bars represent 1 standard deviation from the mean of duplicate samples.

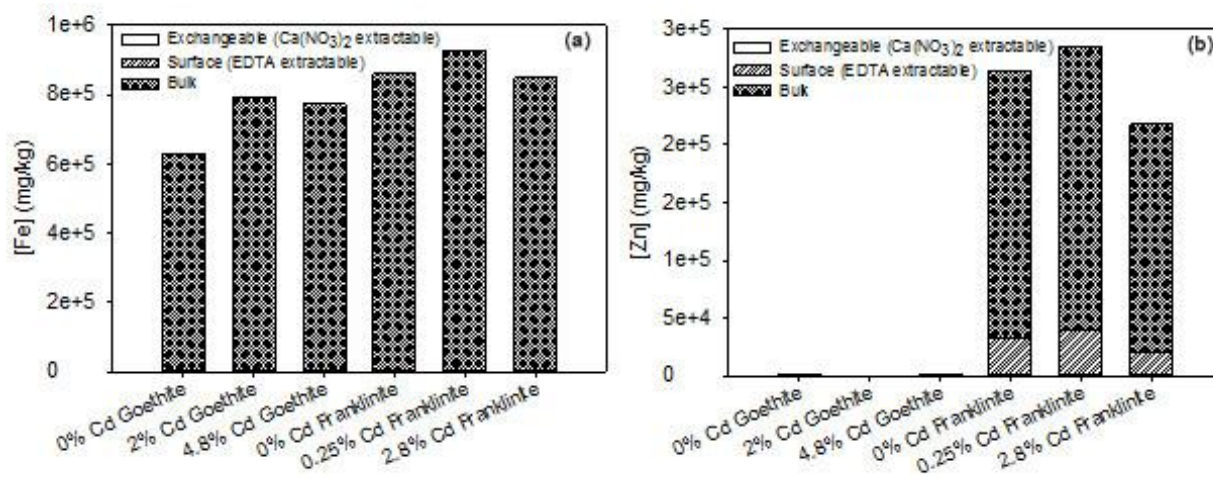


Fig. S6. Distribution of Fe (a) and Zn (b) among exchangeable, surface and bulk pools of the Cd–minerals used in the dissolution experiments.

References

- [1] R. M. Smith and A. E. Martell, *Critical Stability Constants: Inorganic Complexes* **1976** (Springer: Boston, MA).
- [2] W. L. Lindsay, *Chemical Equilibria in Soils* **1979** (Wiley: New York).
- [3] G. Berthon, Critical evaluation of the stability constants of metal complexes of amino acids with polar side chains. *Pure Appl. Chem.* **1995**, *67*, 1117.