Dissolution and Solubility of the Calcite-Otavite Solutions [(Ca$_{1-x}$Cd$_x$)CO$_3$] at 25°C

Table S1. Speciation reaction in the PHREEQC simulation.

Speciation reaction	log K
$Cd^{2+} + H_2O = CdOH^+ + H^+$	-10.097
$Cd^{2+} + CO_3^{2-} = CdCO_3^0$	4.3578
$Cd^{2+} + 2CO_3^{2-} = Cd(CO_3)_2^{2-}$	7.2278
$Cd^{2+} + H^+ + CO_3^{2-} = CdHCO_3^+$	10.6863
$Ca^{2+} + H_2O = CaOH^+ + H^+$	-12.697
$Ca^{2+} + H^+ + CO_3^{2-} = CaHCO_3^+$	11.599
$CO_3^{2-} + Ca^{2+} = CaCO_3^0$	3.2
$H^+ + CO_3^{2-} = HCO_3^-$	10.329
$2H^+ + CO_3^{2-} = H_2CO_3^0$	16.681
$Cd(OH)_2 \text{ (am)} + 2H^+ = Cd^{2+} + 2H_2O$	13.73
$Cd(OH)_2 + 2H^+ = Cd^{2+} + 2H_2O$	13.644
$CdO \text{ (Monteponite)} + 2H^+ = Cd^{2+} + H_2O$	15.1034
$CdCO_3 \text{ (Otavite)} = Cd^{2+} + CO_3^{2-}$	-12
$CaO \text{ (Lime)} + 2H^+ = Ca^{2+} + H_2O$	32.6993
$Ca(OH)_2 \text{ (Portlandite)} + 2H^+ = Ca^{2+} + 2H_2O$	22.804
$CaCO_3 \text{ (Calcite)} = Ca^{2+} + CO_3^{2-}$	-8.48
$CaCO_3 \text{ (Aragonite)} = Ca^{2+} + CO_3^{2-}$	-8.3

Note: Compiled from the minteq.v4.dat database (Parkhurst and Appelo, 2013).

Table S2. Solubility constants (log K) of otavite at standard state [$CdCO_{3(s)} = Cd^{2+} + CO_3^{2-}$].

log K	Reference
-13.74	Smith, R.M.; Martell, A.E. Critical Stability Constants, Volume 4, Inorganic Complexes, Plenum Press: New York United States, 1976; pp. 1–257.
-13.6	Zhuk, N.P. Thermodynamic constants of sulfates, carbonates, chromates, bromates, iodates, oxalates, and other salts slightly soluble in water. Zhurnal Fizicheskoi Khimii 1954, 28, 1690–1697.
-11.284	Latimer, W.M. The Oxidation States of the Elements and their Potentials in Aqueous Solutions, 2nd ed.; Prentice Hall: New York, United States, 1952; pp. 1–392.
-11.209	Wagman, D.D.; Evans, W.H.; Parker, V.B.; Schumm, R.H.; Halow, I.; Bailey, S.M.; Churney, K.L.; Nuttall, R.L. The NBS tables of chemical thermodynamic properties: Selected values for inorganic and C1 and C2 organic substances in SI units. J. Phys. Chem. Ref. Data 1982, 11(supp. 2), 1–392.
-11.292	Egorov, A.M.; Titova, Z.P. Solubility products of salts with polyatomic ions as a function of the temperature. Zhurnal Neor-ganicheskoi Khimii 1962, 7, 275–278.
-12.06	Krestov, G.A.; Kobenin, V.A.; Sokolov, V.N. Method for calculating the solubility product at 273-373°K. Zhurnal Neorganicheskoi Khimii 1977, 22, 2864–3867.
-11.31 ± 0.03	Davis, J.A.; Fuller, C.C.; Cook, A.S. A model for trace metal sorption processes at the calcite surface: Adsorption of Cd^{2+} and subsequent solid solution formation. Geochim. Cosmochim. Acta 1987, 51, 1477–1490.
-12.1 ± 0.1	Stipp S.L.; Parks G.A.; Nordstrom D.K.; Leckie J.O. Solubility-product constant and thermodynamic properties for synthetic otavite, $CdCO_{3(s)}$, and aqueous association constants for the Cd(II)-CO$_2$-H$_2$O system. Geochim. Cosmochim. Acta 1993, 57, 2699–2713.

-12.03 ± 0.13	Gamsjäger, H.; Magalhães, M.C.F.; Königsberger, E.; Sawada, K.; Churagulov, B.R.; Schmidt, P. and Zeng, D. IUPAC-NIST Solubility Data Series. 92. Metal Carbonates. Part 1. Solubility and related thermodynamic quantities of cadmium (II) carbonate in aqueous systems. J. Phys. Chem. Ref. Data 2011, 40, 043104.
-12.0	(minteq.v4.dat) Allison, J.D.; Brown, D.S.; Novo-Gradac, K.J. MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Version 3.0 User's Manual. Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Athens, Georgia, United States, 1991; pp. 1–106.
-12.1	(wateq4f.dat) Parkhurst, D.L.; Appelo, C.A.J. Description of Input and Examples for PHREEQC Version 3, A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations; Techniques and Methods, Book 6, Chap. A43; U.S. Geological Survey: Denver, Colorado, United States, 2013; pp. 1–497.
-12.2288	(llnl.dat) Plummer, L.N.; Busenberg, E. The solubilities of calcite, aragonite and vaterite in CO_2-H_2O solutions between 0 and 90°C, and an evaluation of the aqueous model for the system $CaCO_3$-CO_2-H_2O. Geochim. Cosmochim. Acta 1982, 46, 1011–1040.

Table S3. Gibbs free energies of formation (ΔG_f°) of otavite at standard state.

| ΔG_f° (kJ/mol)	Reference
-683.46	Zhuk, N.P. Thermodynamic constants of sulfates, carbonates, chromates, bromates, iodates, oxalates, and other salts slightly soluble in water. Zhurnal Fizicheskoi Khimii 1954, 28, 1690–1697.
-595.07 ± 4.18	Robie, R.A. Thermodynamic properties of minerals; Open File Report TEI-816; U.S. Geological Survey: Denver, Colorado, United States, 1962; pp. 1–31.
-669.44 ± 2.64	Robie, R.A.; Hemingway, B.S.; Fisher, J.R. Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 Pa) pressure and at higher temperatures; U.S. Geological Survey Bulletin 1452; U.S. Government Printing Office: Washington D.C., United States, 1978; pp. 1–456.
-779.43	Barin, I.; Knacke, O. and Kubaschewski, O. Thermodynamic properties of inorganic substances, Supplement; Springer Verlag: Berlin, Germany, 1977; pp. 1–861.
-662.7	Sverjensky, D.A. Prediction of Gibbs free energies of calcite type carbonates and the equilibrium distribution of trace elements between carbonates and aqueous solutions. Geochim. Cosmochim. Acta 1984, 48, 1127–1134.
-670.3 ± 2.1	La Iglesia, A.; Félix, J.F. Estimation of thermodynamic properties of mineral carbonates at high and low temperatures from the sum of polyhedral contributions. Geochim. Cosmochim. Acta 1994, 58, 3983–3991.
-674.3 ± 0.6	Gamsjäger, H.; Preis, W.; Königsberger, E.; Magalhaes, M.C.; Brandao, P. Solid-solute phase equilibria in aqueous solution. XI. Aqueous solubility and standard Gibbs energy of cadmium carbonate. J. Solution Chem. 1999, 28, 711–720.
-671.1 ± 1.1	Rock, P.A.; Casey W.H.; McBeath M.K.; Walling E.M. A new method for determining Gibbs energies of formation of metal-carbonate solid solutions: 1. The $Ca_xCd_{1-x}CO_{3(s)}$ system at 298 K and 1 bar. Geochim. Cosmochim. Acta 1994, 58, 4281–4291.
-674.7±0.6	Stipp S.L.; Parks G.A.; Nordstrom D.K.; Leckie J.O. Solubility-product constant and thermodynamic properties for synthetic otavite, $CdCO_{3(s)}$, and aqueous association constants for the Cd(II)-CO_2-H_2O system. Geochim. Cosmochim. Acta 1993, 57, 2699–2713.
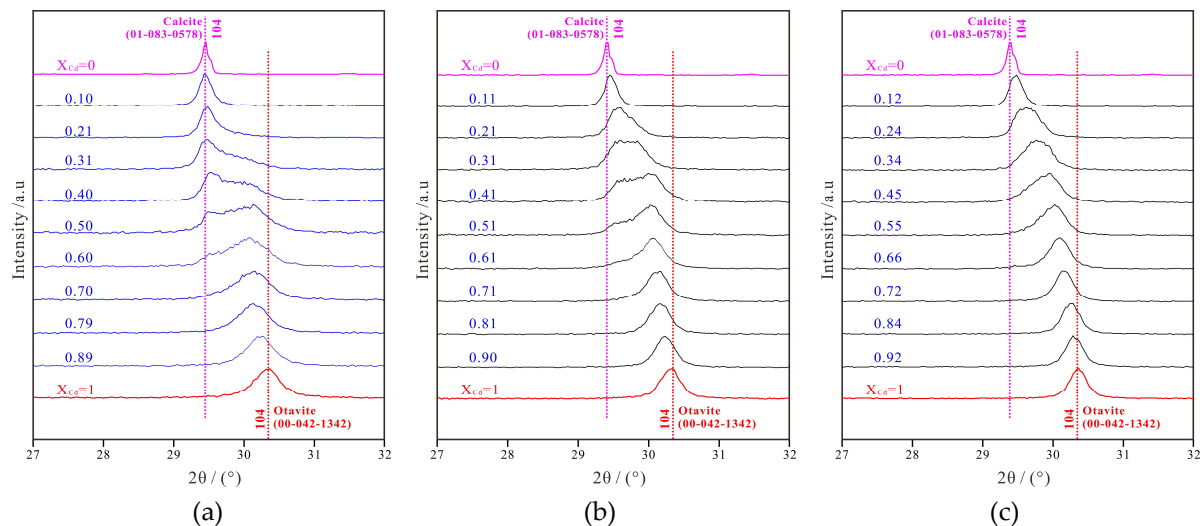
Figure S1. Position variation of the strongest peak (104) with the solid composition X_{Cd}: (**a**) before dissolution, and (**b**) after dissolution in the N_2-degassed water for 270d and (**c**) after dissolution in the CO_2-saturated water for 270d.
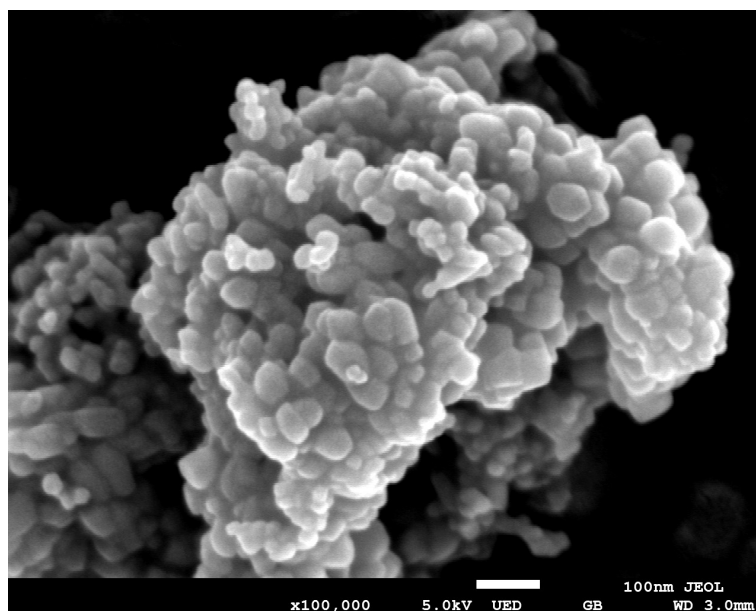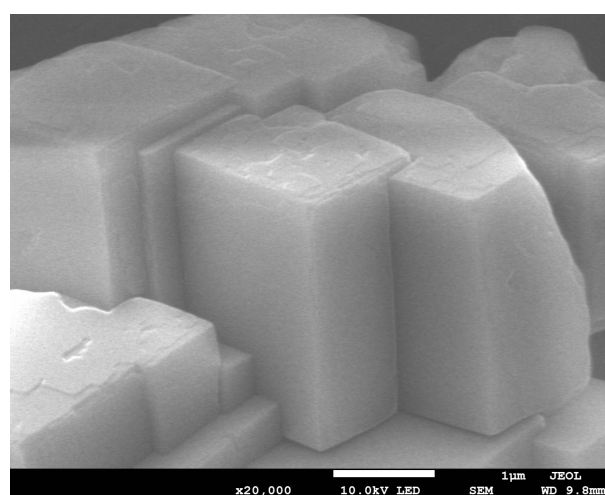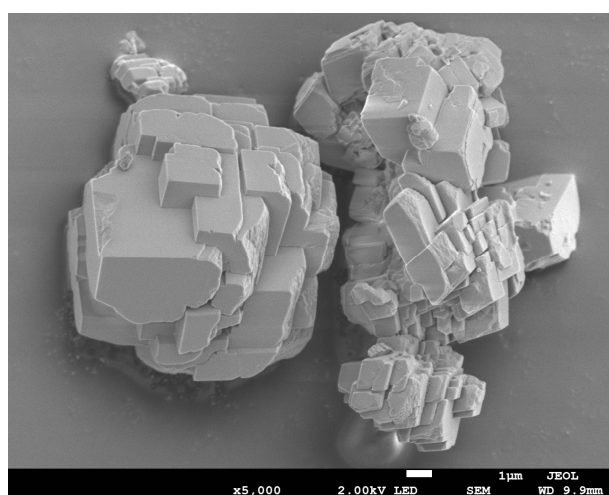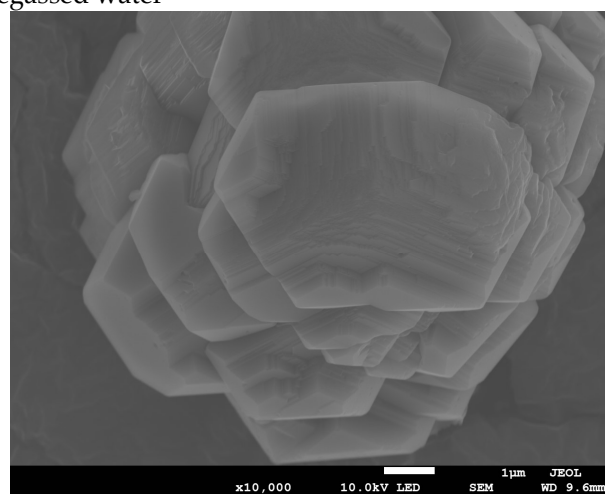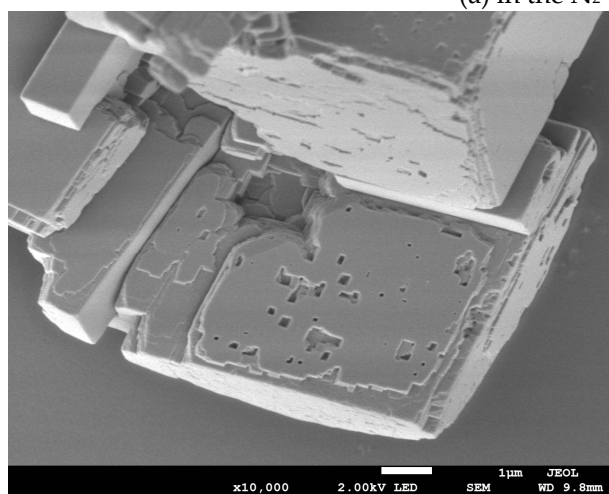

(a) Cal-Ot-07 [$(Ca_{0.30}Cd_{0.70})CO_3$]
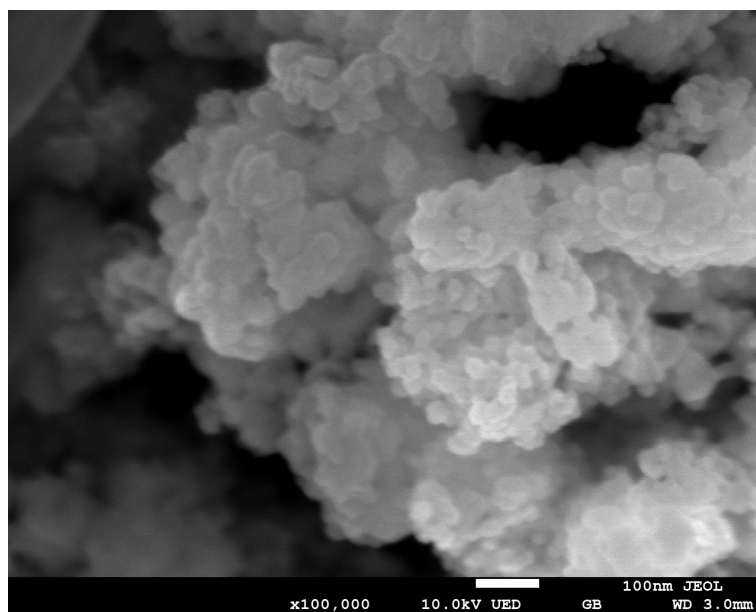
(b) Cal-Ot-10 [$(Ca_{0.00}Cd_{1.00})CO_3$]

Figure S2. SEM image of the $(Ca_{1-x}Cd_x)CO_3$ solid solutions before dissolution.

(a) in the N_2-degassed water

(b) in the CO_2-saturated water

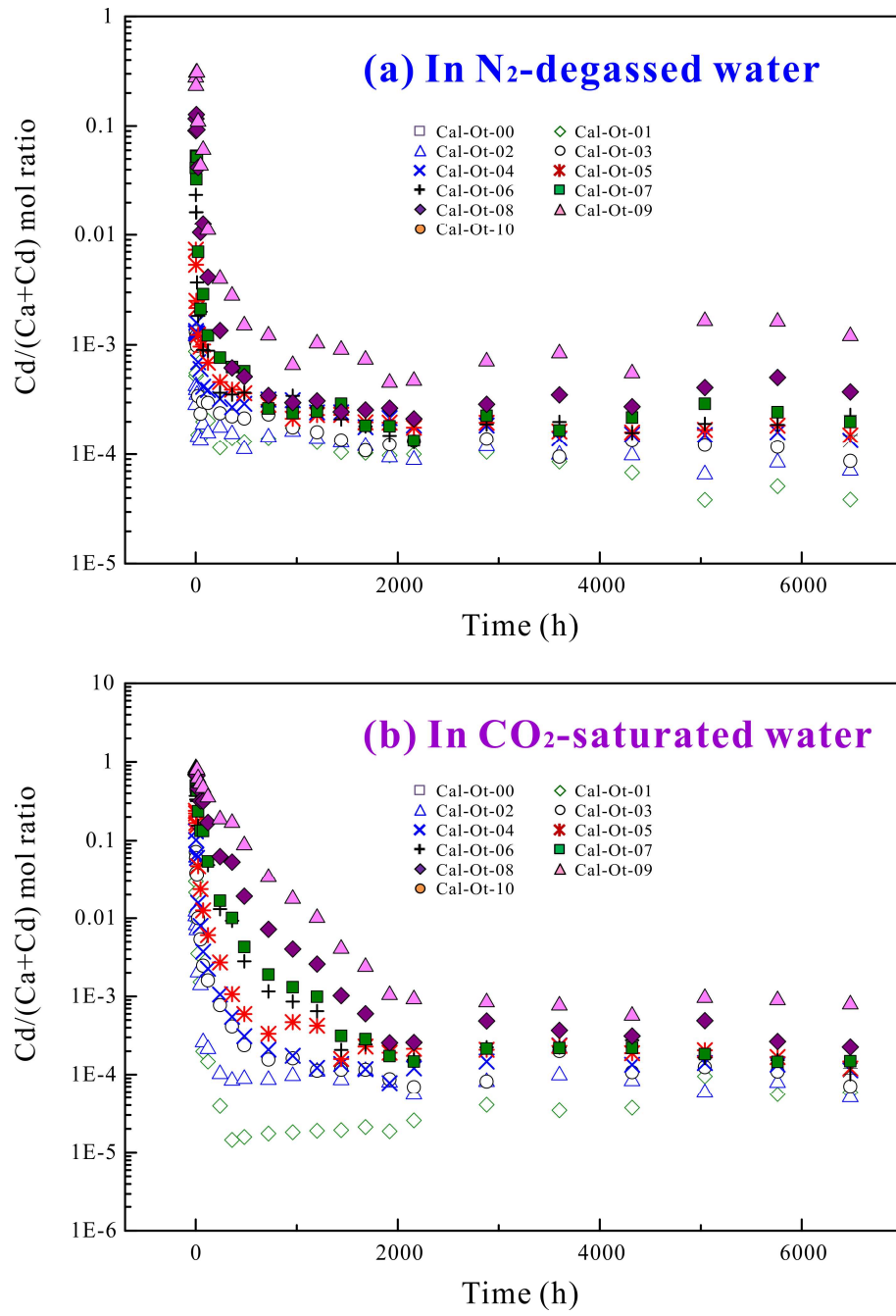**Figure S3.** SEM image of calcite (Cal-Ot-00) after dissolution for 270d.

Figure S4. Change of the Cd/(Ca+Cd) mole ratios of the aqueous phases during the dissolution of the $(Ca_{1-x}Cd_x)CO_3$ solid solution.
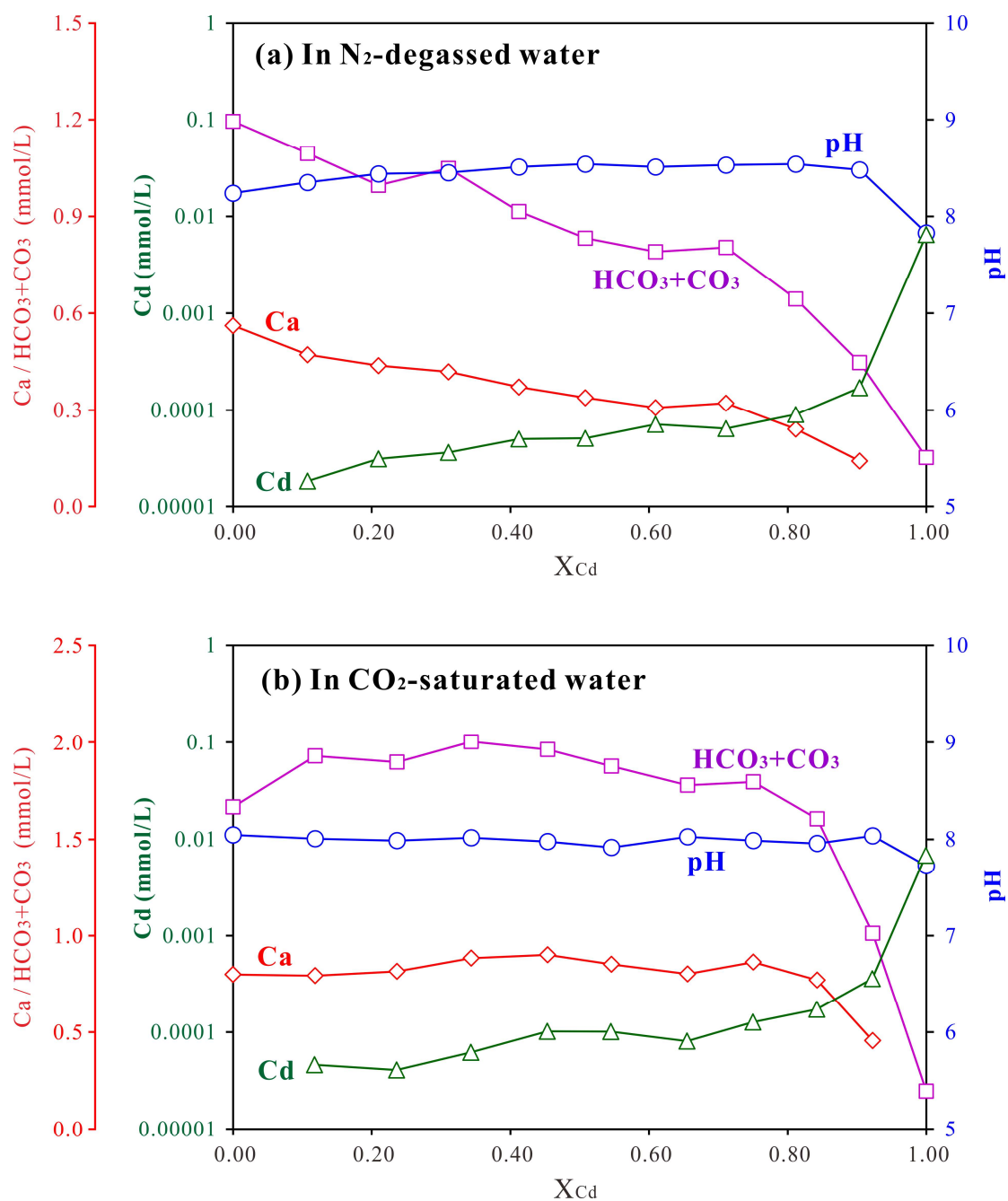
Figure S5. Variation of the final aqueous phases with the solid X_{Cd} mol ratios during the 270d dissolution of the $(Ca_{1-x}Cd_x)CO_3$ solid solutions in water.
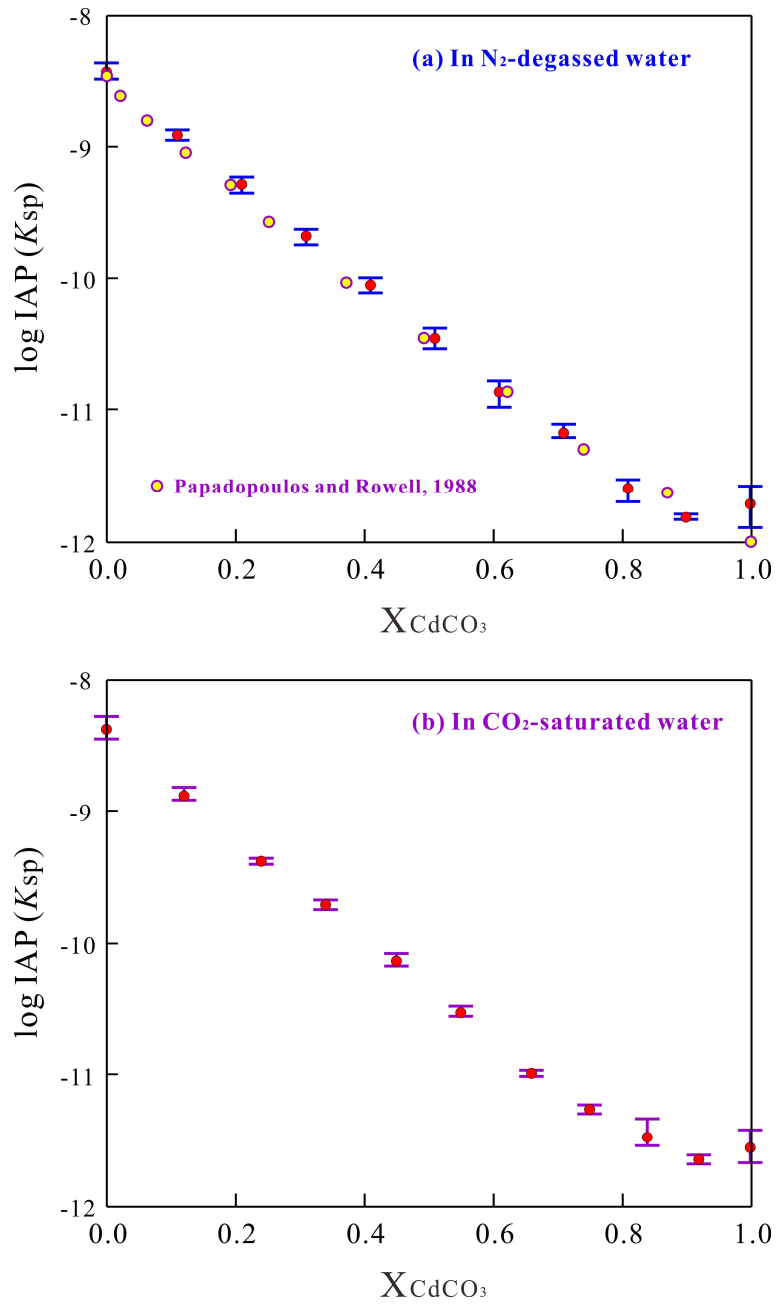
Figure S6. Change of log IAP ($\approx$log K_{sp}) for the $(Ca_{1-x}Cd_x)CO_3$ solid solution with the $CdCO_3$ mole fraction (X_{CdCO_3}).

(a) In N$_2$-degassed water

$y = 455.84x - 1130.1$
$R^2 = 0.9999$

○ Rock et al, 1994

X$_{CdCO_3}$

ΔG_f° (kJ/mol)

(b) In CO$_2$-saturated water

$y = 456.68x - 1129.8$
$R^2 = 0.9999$

X$_{CdCO_3}$

ΔG_f° (kJ/mol)
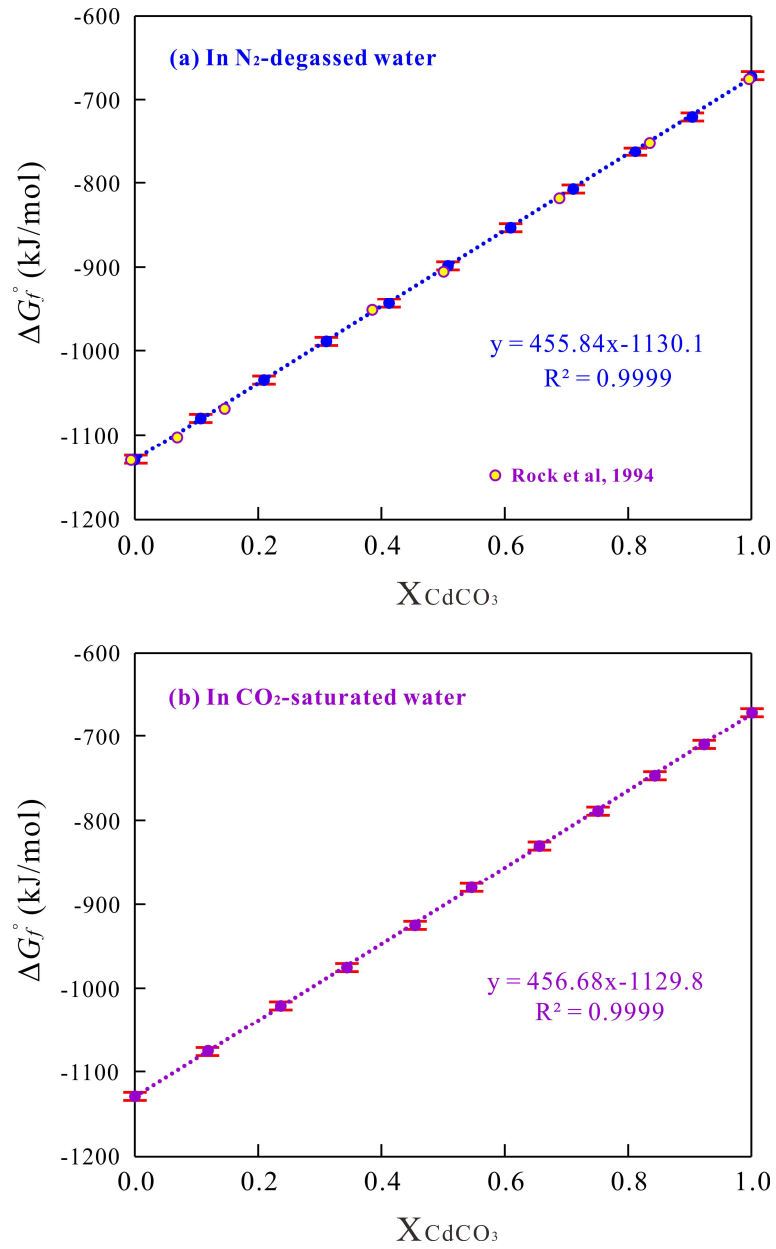
Figure S7. Change of the Gibbs free energy of formation (ΔG_f°) for the (Ca$_{1-x}$Cd$_x$)CO$_3$ solid solution with the CdCO$_3$ mole fraction (X$_{CdCO_3}$).

(a) In N_2-degassed water

Model	Guggenheim equation	
Equation	y = x*(1-x)*a0 + x*(1-x)*(x-(1-x))*a1 -19.41 *(1-x) + (1-x)*ln(1-x) -26.95*x + x*ln(x)	
Reduced Chi-Sqr	122.62359	
Adj. R-Square	-15.67357	
		Value	Standard Error
Ln Ksp	a0	-0.84098	19.17557
	a1	-3.80459	50.78646

(b) In CO_2-saturated water

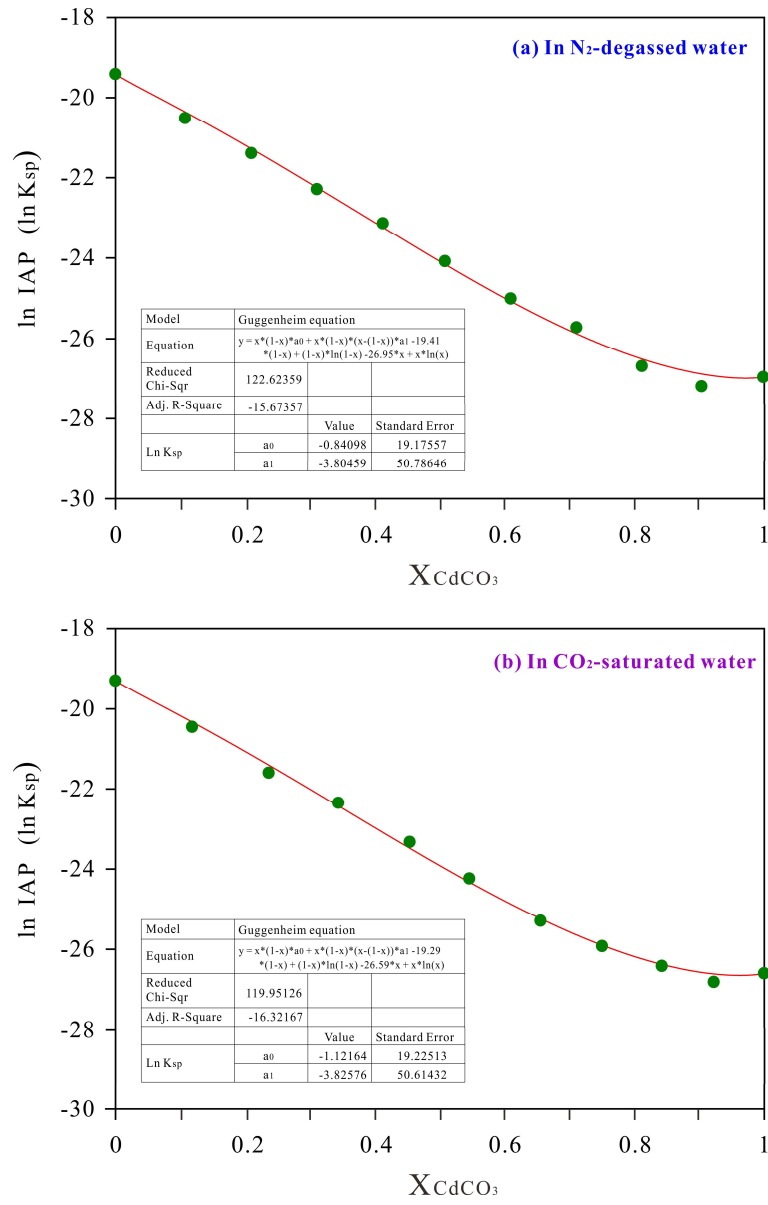| Model	Guggenheim equation	
Equation	y = x*(1-x)*a0 + x*(1-x)*(x-(1-x))*a1 -19.29 *(1-x) + (1-x)*ln(1-x) -26.59*x + x*ln(x)	
Reduced Chi-Sqr	119.95126	
Adj. R-Square	-16.32167	
		Value	Standard Error
Ln Ksp	a0	-1.12164	19.22513
	a1	-3.82576	50.61432

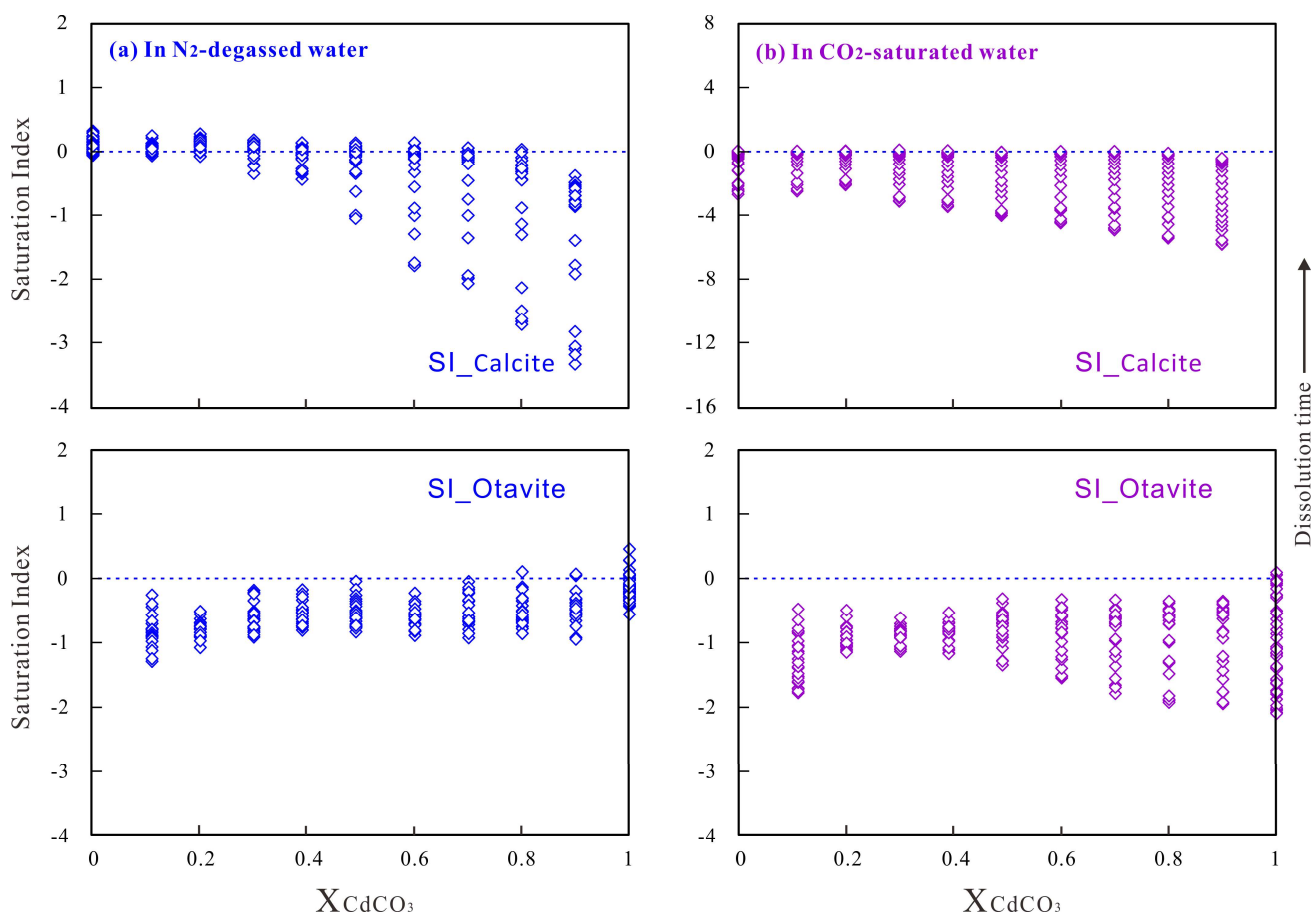**Figure S8.** Estimation of the Guggenheim coefficients (a_0 and a_1) for the non-ideal $(Ca_{1-x}Cd_x)CO_3$ solid solution.

Figure S9. Saturation Index (SI) of the aqueous solution with respect to calcite and otavite during the dissolution of the $(Ca_{1-x}Cd_x)CO_3$ solid solution for 1, 3, 6, 12, 24, 48, 72, 120, 240, 360, 480, 720, 960, 1200, 1440, 1680, 1920, 2160, 2880, 3600, 4320, 5040, 5760 and 6480 h.