Supporting Information

Inhibition of Calcite Precipitation by Natural Organic Material: Kinetics, Mechanism, and Thermodynamics

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Table S1. Solution compositions used in this study. For each of the solution compositions, 0 – 5 mg/L of NOM was added.

Temp (^oC)	**C_T/Ca**	**(CO_3^{2-})/(Ca^{2+})**	**$NaHCO_3$ (M)**	**$CaCl_2$ (M)**	**KCl (M)**	**pH**
25	0.5	0.0022	0.004	0.008	0.0721	7.68
25	1	0.0086	0.004	0.004	0.0840	7.95
25	5	0.2312	0.004	0.0008	0.0935	8.67
25	10	0.9997	0.004	0.0004	0.0945	9.01
15	1	0.0086	0.00475	0.00475	0.0810	7.95
35	1	0.0086	0.00345	0.00345	0.0862	7.95
45	1	0.0086	0.003	0.003	0.0880	7.95

Table S2. Characteristics of the natural organic materials used in this study.

	SRFA	**WLHPOA**	**POFA**
Elemental composition (%)			
C	54.2	52.7	56.2
H	3.92	5.2	6
O	38	36.6	36.3
N	0.72	1.7	1.1
S	0.35	0.72	0.4
Ash	0.19	2.98	0.36
C/H (molar)	1.16	0.85	0.79
C/N (molar)	87.79	36.15	59.58
Chemical Properties			
M_w (g/mol)[a]	1360	772	532
SUVA254 (L/mg-m)	3.6	2.1	0.6
^{13}C NMR Analysis (% of C)			
Aliphatic I C-C (0-62 ppm)	27	50	56.9
Aliphatic II C-O, C-N, C-S (62-90 ppm)	15	15	13.4
Acetal (90-110 ppm)	5	5.8	1.2
Aromatic (110-160 ppm)	28	13.8	7.3
Carboxyl (160-190 ppm)	19	13.9	19.5
Ketone (190-230 ppm)	6	1.5	1.6

[a] Determined by high pressure size exclusion chromatography (HPSEC)

Table S3. Intrinsic stability constants for the surface complexation reactions at the calcite/water interface (I=0, 25°C) *(1)*

Surface complexation reaction	**log K^o_{int}**
$>CaOH + H^+ = >CaOH_2^{+}$ [a]	11.5
$>CaOH = >CaO^- + H^+$	-12
$>CaOH + CO_3^{2-} + 2\,H^+ = >CaHCO_3^o + H_2O$	23.5
$>CaOH + CO_3^{2-} + H^+ = >CaCO_3^- + H_2O$	17.1
$>CO_3H = >CO_3^- + H^+$	-5.1
$>CO_3H + Ca^{2+} = >CO_3Ca^+ + H^+$	-1.7

[a] > symbolizes mineral surface

Table S4. Non-conditional equilibrium constants ($K_{non\text{-}cond}$) determined for different temperatures using the K_s values determined at 25°C.

	SRFA[a]				POFA [b]				WLHPOA[c]			
T (K)	K_{cond} (L/mg)	K_{cond} (M^{-1})	[NOM]/ [NOM-Ca] (mole/eq)	$K_{non\text{-}cond}$ (L/eq)	K_{cond} (L/mg)	K_{cond} (M^{-1})	[NOM]/ [NOM-Ca] (mole/eq)	$K_{non\text{-}cond}$ (L/eq)	K_{cond} (L/mg)	K_{cond} (M^{-1})	[NOM]/ [NOM-Ca] (mole/eq)	$K_{non\text{-}cond}$ (L/eq)
288	4.97	6.76×10^{6}	0.70	4.75×10^{6}	0.35	1.86×10^{5}	0.63	1.17×10^{5}	0.26	2.04×10^{5}	0.40	8.12×10^{4}
298	8.87	1.21×10^{7}	0.81	9.77×10^{6}	0.62	3.28×10^{5}	0.67	2.21×10^{5}	0.59	4.52×10^{5}	0.43	1.92×10^{5}
308	10.16	1.38×10^{7}	0.92	1.27×10^{7}	0.64	3.43×10^{5}	0.72	2.46×10^{5}	0.90	6.91×10^{5}	0.45	3.14×10^{5}
318	13.02	1.77×10^{7}	1.03	1.83×10^{7}	0.83	4.44×10^{5}	0.77	3.41×10^{5}	1.50	1.16×10^{5}	0.48	5.61×10^{5}

[a]M_w = 1360, [b]M_w = 532, [c]M_w = 772

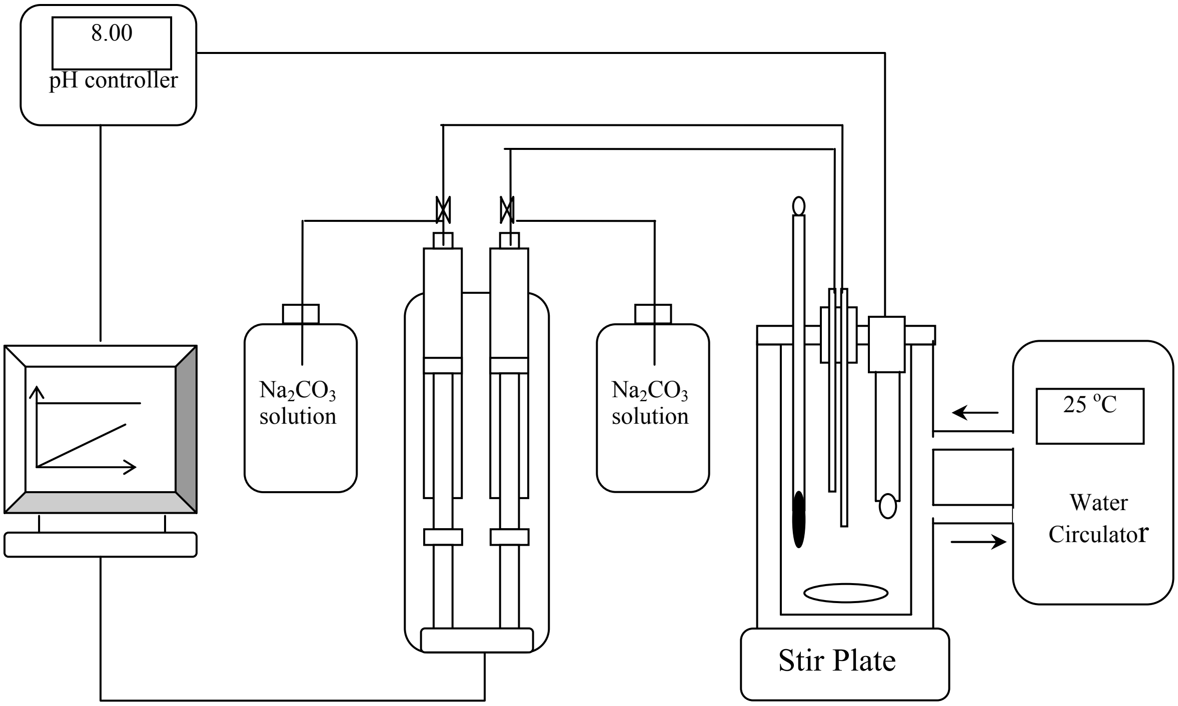

Figure S1. Schematic of pH-stat system.

A 600 mL jacketed beaker (Ace Glass Inc.) was used as the reactor. Water from a constant temperature bath was circulated through the jacket to keep a constant temperature of the working solution during the experiment. Calcite precipitates according to the reaction: $Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$. The loss of Ca^{2+} and CO_3^{2-} as calcite precipitates causes the solution pH to decrease. A microprocessor-based pH controller (Model PHCN-37, Omega Engineering, Inc.) coupled with a calomel combination pH electrode (Fisher Scientific International) was installed to monitor and control the pH value of the working solution by triggering two syringe pumps (Model 901, Harvard Apparatus) to inject equivalent volumes of equimolar $CaCl_2$ and Na_2CO_3 titrant solutions into the working solution until the pH value was restored to the initial value. The titrant solutions were added slowly to avoid local high supersaturation conditions in the working solution that can cause homogeneous calcite nucleation. The pH electrode was calibrated using pH 7.00 and 10.00 buffers before each experiment. The injection rate of the syringe pumps was calibrated weekly by comparing the injected volumes recorded by the computer against the amounts measured using a 10-mL volumetric flasks; these two measurements were within 0.5% agreement. 0.053M of $CaCl_2$ and Na_2CO_3 titrant solutions were prepared using reagent-grade $CaCl_2$ and Na_2CO_3 (Fisher Chemical Co.) and deionized water with ionic strength adjusted to 0.1 with KCl.

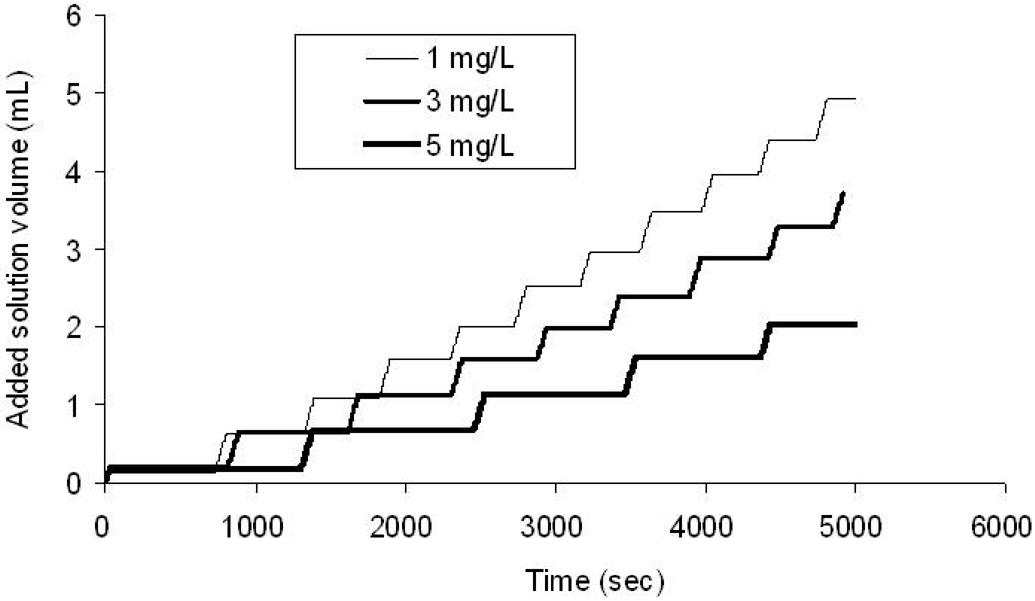

Figure S2. Typical data obtained from pH-stat system in the presence of different concentrations of NOM ($C_T/Ca^{2+} = 1$, pH=7.95, I = 0.1, $\Omega = 5.3$, 25°C, NOM: POFA)

The calcite precipitation rate normalized by the surface area of the seed is calculated by the following equation:

$$R = \frac{S \times m}{G \times SA}$$

where R is the calcite precipitation rate normalized by seed surface area (mole m^{-2} s^{-1}), S is the injection rate (L s^{-1}), m is the concentration of the $CaCl_2$ solution (M), G is the mass of added seed (g), and SA is the specific surface area of the seed (m^2/g). A quadratic regression was used to fit the stepwise titrant addition data. The quadratic trend was anticipated because of the higher precipitation rate expected as a result of the increase in seed size and surface area during the course of precipitation. Duplicate experiments were conducted for most of the experimental conditions and the normalized rate data were within 15% agreement.

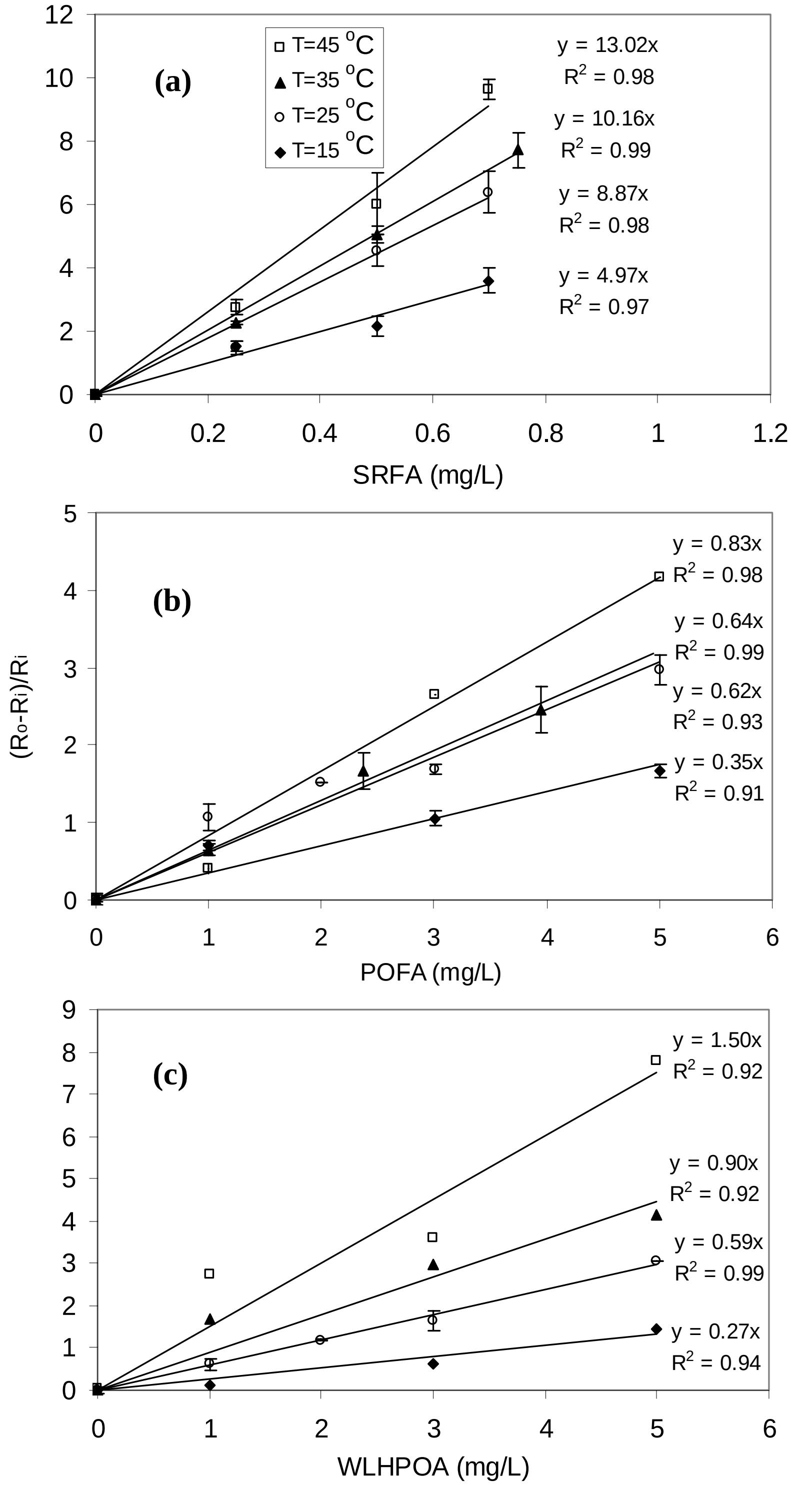

Figure S3. Inhibition of calcite precipitation by NOM at different temperatures in accordance with Equation (7). (a) SRFA (b) POFA (c) WLHPOA. The solution compositions at all temperatures were maintained at $C_T/Ca^{2+} = 1$, pH = 7.95, I = 0.1 and $\Omega = 5.3$.

Literature Cited in the Supporting Information

(1) Pokrovsky, O. S.; Mielczarski, J. A.; Barres, O.; Schott, J. Surface speciation models of calcite and dolomite/aqueous solution interfaces and their spectroscopic evaluation. *Langmuir* **2000**, *16*, 2677-2688.