Modeling the Impact of Cyanobacteria on Calcite Precipitation in an Experimental Setting

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Abstract –

Calcium carbonate and its most common polymorph calcite are vital parts of the Earth system. However, its precipitation from aqueous solutions is unfavorable at standard conditions and is usually the result of biological influence. One such organism, cyanobacteria, has well documented interactions with carbonate precipitation that lead to the creation of microbialites structures, most notably stromatolites. This study intends to explore the impact of cyanobacteria on calcium carbonate precipitation by quantifying how it affects the conditions of certain solutions in a laboratory setting.

In order to achieve this, a new model to analyze carbonate chemistry is introduced. Current carbonate models are made for complex ocean system conditions that require various and expensive measurements for accurate results. This poster presents a simple model useful for the controlled conditions of laboratory experiments. It's accuracy to current models are measured and found to be acceptable.

Photos Showing : 1 - SEM imaging showing evidence of calcium carbonate precipitation (A) on the EPS (B). 2 - A picture of the microbialite platform at FGL (D), with a bacterial mat on top of it (C). 3 - A stromatolite from South Africa dated to 3.2 Ga. (1,2) - Adapted from Murphy, 2021 (3) - adapted from Schopf, 2007

Acknowledgments

- Special thanks to Dr. Pieter Visscher for his advisement, and the CT Space grant Consortium and UConn Office of Undergraduate Research for funding.

The Model

$$SI = \log\left(\frac{\gamma[Ca^{2+}][CO_3^{2-}]}{Ksp}\right)$$

SI = Saturation index of calcium carbonate in solution. 0 is the saturation point for calcite, above 0 the solution would be supersaturated.

γ = Activity coefficient. A correction for the real activity of the calcium and carbonate ions due to the interference of other ions in solution. Calculated using the Davies equation.

Ksp = value of SI at equilibrium. Based off previous literature equations.

Model works for parameters = Salinity (ppt) = 1-50 (known ion composition), Temp (celsius) = 0-50 (measured), Ionic strength = 0-0.5 (known ion composition). Set amounts are atm = 1, pCO2 = 4.22E-4.

Model Equations

Carbonate Calculation Measurements

$$[CO_3^{2-}] = \frac{[CO_2(aq)]\cdot(1+\frac{K_1}{[H^+]}+\frac{K_1K_2}{[H^+]^2})}{(1+\frac{[H^+]}{K_2}+\frac{[H^+]^2}{K_1K_2})}$$

$$[H^+] = 10^{-pH}$$

$$K_1 = 10^{-(-126.34048+\frac{6320.813}{T}+19.568224\cdot\ln(T)+13.4191\cdot S^{0.5}+0.0331\cdot S-5.33\cdot10^{-5}\cdot S^2+\frac{-530.123\cdot S^{0.5}-6.103\cdot S}{T}-2.0695\cdot S^{0.5}\cdot\ln(T))}$$

$$K_2 = 10^{-(-90.18333+\frac{5143.692}{T}+14.613358\cdot\ln(T)+21.0894\cdot S^{0.5}+0.1248\cdot S-3.687\cdot10^{-4}\cdot S^2+\frac{-772.483\cdot S^{0.5}-20.051\cdot S}{T}-3.3336\cdot S^{0.5}\cdot\ln(T))}$$

$$[CO_2(aq)] = K_0 \cdot pCO_2$$

$$pCO_2 = 0.000422\ atm$$

$$K_0 = e^{(\frac{9345.17}{T}-60.2409+23.3585\cdot\ln(\frac{T}{100})+S\cdot[0.023517-0.00023656\cdot T+0.0047036\cdot(\frac{T}{100})^2])}$$

Solubility Product Constant Equation

$$K_{sp} = 10^{(-171.9065-0.077993\cdot T+\frac{2839.319}{T}+71.595\cdot\log(T)+(-0.77712+0.0028426\cdot T+\frac{178.34}{T})\cdot S^{0.5}-0.07711\cdot S+0.0041249\cdot S^{1.5})}$$

Activity Coefficient Equations

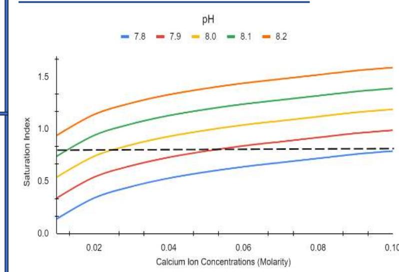
$$I = \frac{1}{2}\sum_{i=1}^{i=n} c_i z_i^2$$

Sum of molar concentration multiplied by the square of ion charge

$$\gamma = 10^{-A\cdot z^2\cdot(\frac{\sqrt{I}}{1+\sqrt{I}}-0.2\cdot I)}$$

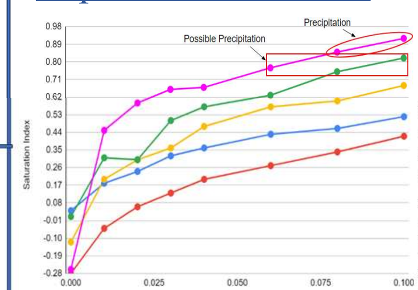
$$A = 1.82\cdot10^6\cdot(\epsilon\cdot T)^{-\frac{3}{2}}$$

Calculated Results



Graph showing the predicted change in saturation index in BG-11 with 15 grams of added NaCl with rising [Ca2+].. The dotted black line represent SI = 0.8, which in previous literature studies was found to be the value at which calcite begins to precipitate.

Experimental Results



Experimental testing of precipitation. Each dot represents the modeled of the saturation index for a single sample's specific calcium ion concentration and pH. Only samples with a SI above 0.8 showed obvious precipitation. 3 samples from a range of 0.75-0.82 show possible precipitation.

- Precipitation of calcite occurs relatively close to a saturation index (SI) value ≥ 0.8
- Accurate but highly specific to this solution

Future Work

- Run biotic trials on the same solution to quantify the effects of cyanobacteria on the SI and precipitation.
- Introduce into and correct model for other aqueous systems, with applications to astrobiology