Crystallization of CaCO$_3$ in water-alcohol mixtures: Spherulitic growth, polymorph stabilization and morphology change

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Supporting Information
XRD patterns

Figure S1. XRD patterns for all the samples with 10% EtOH in the GS regime. The lower patterns are zoomed from the 24.5 to 28 degree 2θ range from the upper patterns, illustrating the disappearance of aragonite and vaterite with time.
Figure S2. XRD patterns for the samples with 10% alcohol taken after five hours, for all the alcohol types in the GS and VS regimes. The lower patterns are zoomed from the 24.5 to 27.5 degree 2θ range of the upper patterns, illustrating the lack of aragonite at high shaking speed.
Figure S3. XRD patterns of the samples using 50% alcohol taken after five hours, for all the alcohol experiments in the GS and VS regimes. The samples collected in the VS regime contain vaterite, in contrast with the samples taken in the GS regime.
Derivation of Equation 1

The computer software, Origin, was used to fit the data for the experiments with 50% isopropanol (IOH) in the GH regime and the experiments with 50% ethanol (EtOH) in the VH regime (Figures S4 and S5). We fitted the data to the equation:

\[ y = Ae^{(x/t)} + y_0 \]  

(S1)

where: \( y \) = % aragonite, \( x \) = time (in hours), \( A \) = amplitude (constant), \( t \) = growth constant and \( y_0 \) = constant.

**Figure S4.** The fit of the data from the experiment with 50% IOH in the GH regime.
We rearranged the equation to isolate time in hours \( (x) \) that an experiment would have to proceed to obtain the percentage of aragonite \( (y) \) desired:

\[
x = t \ln\left( \frac{y - y_0}{A} \right).
\]  

(S2)

From fitting the equations, we got a set of constants presented in Table S1.

<table>
<thead>
<tr>
<th>Constants</th>
<th>50% 1OH</th>
<th>50% EtOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>( y_0 )</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>( A )</td>
<td>-6.5</td>
<td>-50</td>
</tr>
<tr>
<td>( T )</td>
<td>300</td>
<td>-80</td>
</tr>
<tr>
<td>Range (% aragonite)</td>
<td>40-95</td>
<td>50-100</td>
</tr>
<tr>
<td>System</td>
<td>aragonite-calcite</td>
<td>aragonite-vaterite</td>
</tr>
<tr>
<td>Alcohol:water ratio</td>
<td>4.1</td>
<td>3.2</td>
</tr>
<tr>
<td>RPM (shaking speed)</td>
<td>80</td>
<td>140</td>
</tr>
</tbody>
</table>

We transformed the meaning of the constants: \( y_0 \), \( A \) and \( t \) into constants related to the \( \text{H}_2\text{O}:\text{alcohol} \) ratio and shaking speed (revolutions per minute, RPM) of the experiments. Figure S6 illustrates the relationship between \( A \), \( t \), \( \text{H}_2\text{O}:\text{alcohol} \) ratio and RPM for the 50% 1OH and 50% EtOH VH experiments.
In the equation from Figure S6c:

\[ y = -0.1579x + 127.47, \quad (S3) \]

\( y \) corresponds to the shaking speed (v) (RPM) and \( x \) corresponds to the growth constant (t), giving:

\[ t = \frac{127.37 - v}{0.1579}. \quad (S4) \]

After substituting this expression into Equation (S2) we derive:

\[ x = \frac{127.37 - v}{0.1579} \ln \left( \frac{y - y_0}{A} \right). \quad (S5) \]

Because \( y_0 \) has the same value (100) for both experiments, we can include it in the equation.

We eliminated the parameter \( A \), by using the equation from Figure S6b:

\[ y = 0.0207x + 4.2345, \quad (S6) \]

where \( y \) corresponds to the alcohol:water ratio and \( x \) corresponds to the amplitude (A) of the exponential function:
\[ r = 0.0207A + 4.2345. \]  
(S7)

This equation can be re-written as:

\[ A = \frac{r - 4.2345}{0.0207}. \]  
(S8)

Adding Equations S8 and S5, we derive the final equation:

\[ x = \frac{127.37 - v}{0.1579} \ln \left[ \frac{0.0207(y - 100)}{r - 4.2345} \right], \]  
(1)

where: \( x = \) time (hours), \( v = \) shaking speed, \( r = \) alcohol:water ratio and \( y = \% \) aragonite.

Equation 1 can be used within the constraints specified in Table S2.

**Table S2.** Constraints for the range and use of Equation 1 at 25 °C.

<table>
<thead>
<tr>
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<tr>
<td>RPM (shaking speed) ( (v) )</td>
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<td>140</td>
</tr>
</tbody>
</table>