## Supporting Information



Figure $\mathrm{S1}$. XRD patterns of the $\mathrm{CaCO}_{3}$ white slurry obtained during the synthesis procedure, before placing it in the autoclave, showing that the white slurry is amorphous and therefore corresponds to amorphous calcium carbonate (ACC).


Figure S2. XRD patterns of the $\mathrm{CaCO}_{3}$ powders obtained when grown without additives (blue), with 0.1 M aspartic acid (red), and with 0.2 M aspartic acid (orange), showing that aspartic acid promotes vaterite formation. The letters C, V, A indicate the reflection peaks from calcite, vaterite and aragonite phases respectively.


Figure $\mathrm{S3}$. XRD patterns of the $\mathrm{CaCO}_{3}$ powders obtained when grown with 0.2 M aspartic acid and no foreign ions (blue), $50 \% \mathrm{Mg}$ (red), and $30 \% \mathrm{Ba}$ (orange), showing that the presence of foreign ions hinders vaterite formation. The letters $\mathrm{C}, \mathrm{V}, \mathrm{A}$ indicate the reflection peaks from calcite, vaterite and aragonite phases respectively.


Figure S4. XRD patterns of the $\mathrm{CaCO}_{3}$ powders obtained when grown with $30 \% \mathrm{Mg}$ in solution and in the presence of 0.1 M aspartic acid (blue), and in the absence of aspartic acid but with the pH of $\mathrm{Na}_{2} \mathrm{CO}_{3}$ solution adjusted to 9.35 , i.e. the same pH as that of $\mathrm{Na}_{2} \mathrm{CO}_{3}+0.1 \mathrm{M}$ aspartic acid (blue). Although grown at the same pH , vaterite is present only when aspartic acid is also present. The letters V , A indicate the reflection peaks from vaterite and aragonite phases respectively.

Table S1. Goodness of fit (GOF) parameters and refinement results: weight fractions (wt\%) and lattice parameters $a, c$ of the vaterite phase obtained, before and after heating (300ㅇ, 2 h).

|  |  | Before heating |  |  |  |  | After heating |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | wR | GOF | wt\% | a (Å) | c ( $\AA$ ) | wR | GOF | wt\% | a (Å) | c ( ${ }^{\text {a }}$ ) |
| $\begin{gathered} \text { 0.1 M Asp } \\ +\mathrm{Mg} \end{gathered}$ | 0.1 M Asp | 16.1 | 6.7 | 50.8 | 4.1341(1) | 8.4752(3) | 14.6 | 3.2 | 43.8 | 4.1305(2) | 8.4689(5) |
|  | 0.1 M Asp+10\% Mg | 17.4 | 6.7 | 41.4 | 4.1271(2) | 8.4573(4) | 10.4 | 1.7 | 32.8 | 4.1238(2) | 8.4470(5) |
|  | 0.1 M Asp+20\% Mg | 16.4 | 2.8 | 27.1 | 4.1192(2) | 8.4383(5) | 14.7 | 1.9 | 25.1 | 4.1178(2) | 8.4301(5) |
|  | 0.1 M Asp+30\% Mg | 16.6 | 7.8 | 20.7 | 4.1111(4) | 8.4100(9) | 12.4 | 4.5 | 20.1 | 4.1089(4) | 8.3966(9) |
| $\begin{gathered} 0.2 \mathrm{M} \text { Asp } \\ +\mathrm{Mg} \end{gathered}$ | 0.2 M Asp | 13.6 | 6.2 | 94.6 | 4.1338(1) | 8.4741(2) | 13.9 | 4 | 93.1 | 4.1295(1) | 8.4700(3) |
|  | 0.2 M Asp+10\% Mg | 13.1 | 7.1 | 91.8 | 4.1298(1) | 8.4657(2) | 13.7 | 2.7 | 89.5 | 4.12505(7) | 8.4594(2) |
|  | 0.2 M Asp+20\% Mg | 12.2 | 2.1 | 37.9 | 4.1251(2) | 8.4566(4) | 18.1 | 1.8 | 34.8 | 4.1228(3) | 8.4458(7) |
|  | 0.2 M Asp+30\% Mg | 13.7 | 6.7 | 78.2 | 4.1199(2) | 8.4369(4) | 12.9 | 4 | 75.2 | 4.1175(2) | 8.4234(4) |
|  | 0.2 M Asp+50\% Mg | 11.0 | 6.6 | 26.3 | 4.1058(3) | 8.3942(8) | 11.9 | 4.6 | 20.3 | 4.0999(4) | 8.3919(9) |
| $\begin{gathered} \text { 0.1 M Asp } \\ +\mathrm{Ba} \end{gathered}$ | 0.1 M Asp | 16.1 | 6.7 | 50.8 | 4.1341(1) | 8.4752(3) | 14.6 | 3.2 | 43.8 | 4.1305(2) | 8.4689(5) |
|  | 0.1 M Asp+10\% Ba | 14.5 | 7.1 | 1.7 | 4.136(1) | 8.477(3) | 16.1 | 6.6 | 2.1 | 4.133(2) | 8.471(6) |
|  | 0.1 M Asp+20\% Ba | 10.9 | 3.2 | 0.3 | 4.136(2) | 8.480(4) |  |  |  |  |  |
|  | 0.1 M Asp+30\% Ba | 7.37 | 4.0 | 1.3 | 4.1385(9) | 8.480(2) | 8.34 | 3.0 | 2.2 | 4.136(2) | 8.477(5) |
| $\begin{gathered} \text { 0.2 M Asp } \\ +\mathrm{Ba} \end{gathered}$ | 0.2 M Asp | 13.6 | 6.2 | 94.6 | 4.1338(1) | 8.4741(2) | 13.9 | 4 | 93.1 | 4.1295(1) | 8.4700(3) |
|  | 0.2 M Asp+10\% Ba | 12.8 | 6.9 | 15.1 | 4.1359(3) | 8.4761(7) | 12.5 | 5.9 | 12.9 | 4.1311(3) | 8.4712(8) |
|  | 0.2 M Asp+20\% Ba | 11.6 | 3.2 | 8.5 | 4.1372(3) | 8.4768(7) | 13.9 | 2.4 | 10.3 | 4.1315(4) | 8.4705(8) |
|  | 0.2 M Asp+30\% Ba | 7.07 | 4.0 | 12 | 4.1375(2) | 8.4780(6) | 7.01 | 4.0 | 10.1 | 4.1333(3) | 8.4724(7) |
|  | 0.2 M Asp+40\% Ba | 11.2 | 3.3 | 9.4 | 4.1388(2) | 8.4785(6) | 12.0 | 2.5 | 10 | 4.1361(4) | 8.4734(8) |
|  | 0.2 M Asp+50\% Ba | 8.29 | 5.5 | 1.3 | 4.140(2) | 8.482(4) | 8.15 | 4.8 | 1.3 | 4.134(2) | 8.476(5) |

Table S2. Amounts of Mg and Ba incorporated into vaterite as determined by EDS.

| Sample |  | $\begin{aligned} & \text { \%impurity } \\ & \left(\frac{M g}{C a+M g} \text { or } \frac{B a}{C a+}\right. \end{aligned}$ | SD |
| :---: | :---: | :---: | :---: |
| 0.1 M Asp + Mg | 0.1 M Asp | 0 | 0 |
|  | 0.1 M Asp+10\% Mg | 3.33 | 0.35 |
|  | 0.1 M Asp+20\% Mg | 5.65 | 0.82 |
|  | 0.1 M Asp+30\% Mg | 10.80 | 1.39 |
| 0.2 M Asp + Mg | 0.2 M Asp | 0 | 0 |
|  | 0.2 M Asp+10\% Mg | 1.75 | 0.70 |
|  | 0.2 M Asp+20\% Mg | 4.15 | 0.20 |
|  | 0.2 M Asp+30\% Mg | 5.54 | 0.30 |
|  | 0.2 M Asp+40\% Mg | 8.64 | 0.36 |
|  | 0.2 M Asp+50\% Mg | 12.59 | 0.38 |
| 0.1 M Asp + Ba | 0.1 M Asp | 0 | 0 |
|  | 0.1 M Asp+10\% Ba | 0.47 | 0.30 |


|  | $0.1 \mathrm{M} \mathrm{Asp+30} \mathrm{\%} \mathrm{Ba}$ | 1.29 | 0.30 |
| :---: | :---: | :---: | :---: |
| $0.2 \mathrm{M} \mathrm{Asp}+\mathrm{Ba}$ | 0.2 M Asp | 0 | 0 |
|  | $0.2 \mathrm{M} \mathrm{Asp+10} \mathrm{\%} \mathrm{Ba}$ | 0.33 | 0.10 |
|  | $0.2 \mathrm{M} \mathrm{Asp+20} \mathrm{\%} \mathrm{Ba}$ | 0.59 | 0.33 |
|  | $0.2 \mathrm{M} \mathrm{Asp+30} \mathrm{\%} \mathrm{Ba}$ | 1.01 | 0.32 |
|  | $0.2 \mathrm{M} \mathrm{Asp+40} \mathrm{\%} \mathrm{Ba}$ | 1.41 | 0.42 |
|  | $0.2 \mathrm{M} \mathrm{Asp+50} \mathrm{\%} \mathrm{Ba}$ | 2.62 | 0.48 |

