Supplementary information for the manuscript:

A route for the direct crystallization of dolomite

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Calculation of proto-dolomite saturation indexes in aqueous solutions equilibrated with Mg-ACC.

Due to the lack of available data on the solubility product of Mg-ACC we have used the following method to estimate the saturation index with respect to proto-dolomite in a solutions equilibrated with Mg-ACC.

1. We analysed the composition of Mg-ACC from our experiments (nine replicates). Our experimental data showed that the composition of our Mg-ACC that was precipitated from mixing the 0.5M $CaCl_2$/0.5M $MgCl_2$ and 1M Na_2CO_3 solutions was $Ca_{0.606}Mg_{0.394}CO_3 \cdot 1.37H_2O$. We know the concentrations of aqueous Ca, Mg and CO_3 before the precipitation of the Mg-ACC (0.250 M $CaCl_2$, 0.250 M $MgCl_2$ and 0.500 M Na_2CO_3). From these data and using the calculated solubility for ACC with PHREEQC (and by inference that of Mg-ACC based on Davis et al., 2000) we can calculate the concentration of Mg in solution after the precipitation of Mg-ACC (for each 0.606 moles of Ca removed from solution, 0.394 moles of Mg and 1.000 moles of CO_3 are also removed).

2. In order to calculate the concentration of Mg in solution after the precipitation of Mg-ACC, we assumed that most of the Ca^{2+} was removed from solution during precipitation until equilibrium with respect to pure ACC was reached. This is an approximation because the solubility product of Mg-ACC is unknown, but from literature we can assume that Mg-ACC is likely a bit more soluble than ACC (as often happens in the carbonate system; Davis et al., 2000). The solubility of ACC is very low (~ 10^{-3} M) compared to the initial concentration of Ca in solution (0.250 M) prior to the formation of any solid. Taking into account that the initial composition of the aqueous solution as we prepared them (before Mg-ACC formation) was 0.250 M $CaCl_2$, 0.250 M $MgCl_2$ and 0.500 M Na_2CO_3, and also that the composition of the Mg-ACC that we analysed was $Ca_{0.606}Mg_{0.394}CO_3 \cdot 1.37H_2O$, we can confidently estimate that the approximate concentration of Mg remaining in solution after Mg-ACC precipitation was ~ 0.0885 M. The only other ions in solution were Na^+ (1M) and Cl^- (1M).

The following expression was used to calculate the concentration of Mg^{2+} in solution:

$$[Mg^{2+}]_{eq(Mg-ACC)} = [Mg^{2+}]_{t=0} - \left[\left([Ca^{2+}]_{t=0} - [Ca]_{eq(ACC)} \right) \cdot \frac{\chi_{Mg^{2+}(Mg-ACC)}}{\chi_{Ca^{2+}(Mg-ACC)}} \right] ,$$

where $[Mg^{2+}]_{eq(Mg-ACC)}$ stands for concentration of Mg^{2+} when the aqueous solution is in equilibrium with Mg-ACC. $[Mg^{2+}]_{t=0}$ and $[Ca^{2+}]_{t=0}$ correspond to the initial concentrations of Mg^{2+} and Ca^{2+} (0.250 M) before the formation of any solid. $[Ca]_{eq(ACC)}$ stands for the concentration of Ca^{2+} when the aqueous solution is in equilibrium with pure ACC ($1.60 \cdot 10^{-3}$ M, calculated with PHREEQC) and $\chi_{Ca^{2+}(Mg-ACC)}$ and $\chi_{Mg^{2+}(Mg-ACC)}$ correspond to the molar fractions of Ca^{2+} and Mg^{2+} in Mg-ACC (0.606 and 0.394, respectively).

The calculated aqueous Mg^{2+} remaining in solution after the precipitation of the Mg-ACC was 0.0885 M.

3. Then we used this solution composition we calculated to determine the SI of proto-dolomite, dolomite and hydromagnesite with PHREEQC.

In this step we used PHREEQC (Parkhurst, 1995) to equilibrate the above solution with pure ACC (using the solubility product from Brečević and Nielsen 1989) and in conjunction with the proto-dolomite solubility product (Ball and Nordstrom, 2001) we estimated the saturation index of proto-dolomite at 25˚C and 220 at pH 8.5 (pH of 8.5 was experimentally measured after Mg-ACC precipitation from the initial solutions at 25˚C). This was done using the Pitzer activity coefficient models (Pitzer, 1979) throughout the modelling process.

```
Example of model solution
PHASES
FixpH
    H+ = H+
    log_k     0
SOLUTION 1
    temp      25
    pH        8.5
    pe        4
    redox     pe
    units     mol/L
    density   1
    Mg        0.0885
    Cl        1.0
    Na        1.0
    -water    1 # kg
EQUILIBRIUM_PHASES 1
    ACC       0 10
    FixpH     -8.5 HCl       10
```

Once Mg-ACC precipitated the saturation index (SI) for proto-dolomite at 25°C is 2.46. Due to the reverse solubility of carbonates, the saturation index increases with increasing temperatures (e.g., at 220 °C the SI for proto-dolomite is 3.07). All calculated SI for the phases in the experiments are listed in Table S1. These calculations are the closest and best approach because the solubility of Mg-ACC is not known. From literature we can assume that Mg-ACC is likely a bit more soluble than ACC but within the same order of magnitude (Davis et al., 2000), yet we assert that calculated SI values would be slightly higher. Furthermore, as we have stated in the text of the main manuscript, we assert that the crystallization of proto-dolomite occurs through the dissolution of Mg-ACC and this means that the SI values that we calculated would be at some point even higher, fulfilling the condition to promote spherulitic growth (SI greater than 2-3).

Table S1. Saturation indexes calculated for the Ca-Mg-carbonate phases at the various stages in our crystallization reactions

Temp (°C)	Equilibrium with respect to:	$SI_{Mg\text{-}ACC}$	$SI_{proto\text{-}dolomite}$	$SI_{dolomite}$	$SI_{hydromagnesite}$
25	Before mixing: starting concentrations (0.5M $CaCl_2$/0.5M $MgCl_2$ + 1 M Na_2CO_3)	4.02	8.62	9.16	14.74
25	Mg-ACC	0.00	2.46	3.00	0.61
60	Mg-ACC	0.00	3.04	3.46	4.76
220	Mg-ACC	0.00	3.07	3.13	15.64
60	Proto-dolomite	-0.76	0.00	0.42	-1.80
220	Proto-dolomite	-1.03	0.00	0.06	-4.12
60	Dolomite	-0.79	-0.54	0.00	-12.74
220	Dolomite	-1.06	-0.06	0.00	-4.27

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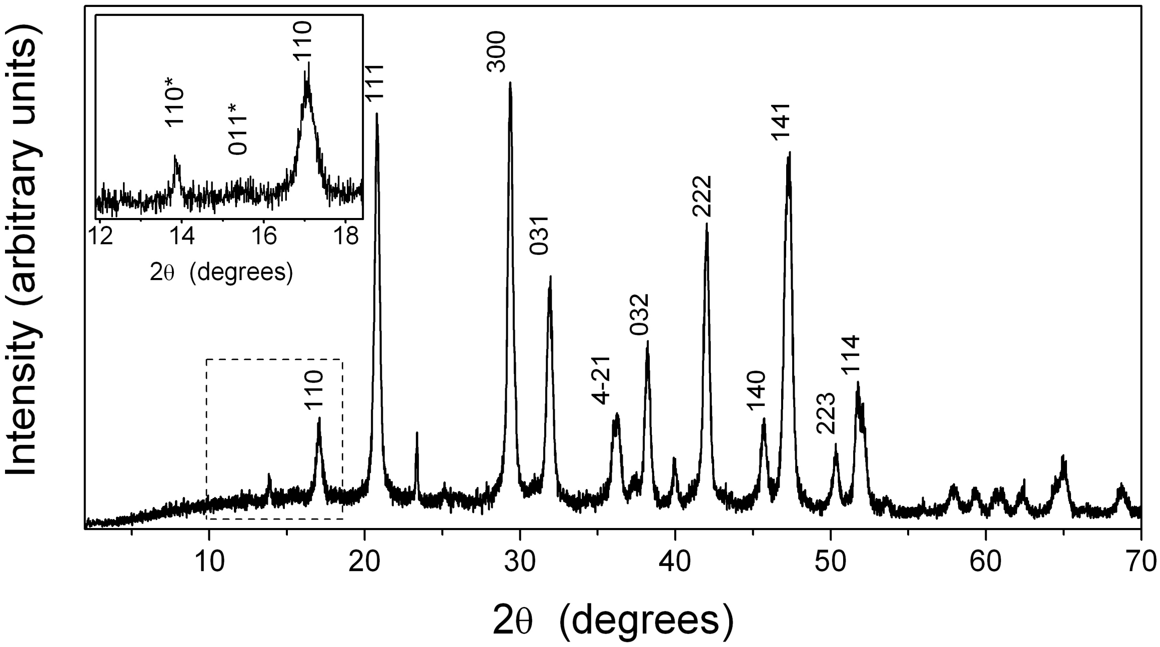

Figure S1. X-ray diffraction pattern of monohydrocalcite with the peaks of hydromagnesite marked with a * (inset).