## **Supporting information**

## SI 1: Application of the Langmuir-adsorption model in experiments in the presence of Citrate:

In order to prove that the citrate is merely adsorbed on the pre-nucleation cluster surface and not build into the cluster the Langmuir adsorption model (Equation SI 1) is applied. The required amounts of citrate bound  $Ca^{2+}$  (n) can be calculated easily by subtracting the amount of free  $Ca^{2+}$  from the amount of ions added. The free  $Ca^{2+}$  concentration (c) is accessible from the recorded calcium ion potential. In case of experiments in the presence of carbonate buffer, the part of the  $Ca^{2+}$  ions bound in pre-nucleation clusters is deduced from the linear part of the titration curves of the respective experiment. In all studied examples a fitting parameter  $R^2 > 0.99$  was obtained.

$$n = \frac{n_{\max} \cdot (K_{L} \cdot c)}{1 + (K_{L} \cdot c)}$$
(Equation SI 1)

From Figure SI 2.2, it is obvious that both the Langmuir-coefficient  $K_L$  and the maximum amount of calcium binding sites  $n_{max}$ , develop equally with rising citrate concentrations. The  $K_L$ -value, which is a measure of the binding affinity, is decreasing with increasing citrate concentrations and apparently features a minimum at 250 mg/L citrate. Calculations of  $n_{max}$ yield linear graphs in the presence and in the absence of carbonate buffer, respectively. Here, the number of binding sites in the presence of carbonate is decreased to 60% through cluster binding.



Figure SI 2.2: K (left) and  $n_{max}$  values (right) of the Langmuir-equation obtained at different citrate concentrations

## SI 2: Application of the multiple binding equilibrium (Experiments in the presence of citrate)

A simplified multiple binding equilibrium<sup>1</sup> (Equation 2) was applied in order to quantify the cluster formation. Here the linear part of the pre-nucleation stage was analyzed. It is obvious that the microscopic equilibrium constant K develops regularly with an increasing additive concentration while x, the averaged, dynamic coordination number of a carbonate is constant (Table 1).

$$v = 1 + \frac{n_{free}(CO_3^{2-})}{n_{bound}(Ca^{2+})} = \frac{1}{x} + \frac{1}{x \cdot K} \cdot \frac{1}{c_{free}(Ca^{2+})}$$
(Equation SI 2)

Equations SI 3 to the macroscopic equilibrium constant and the GIBBS free energy are accessible.

$$Ca_{aq.}^{2+} + CO_{3,aq.}^{2-} \xleftarrow{K} CaCO_{3}]_{cluster,aq.}$$

$$\frac{c\left(\left[CaCO_{3}\right]_{cluster,aq.}\right)}{c\left(Ca_{aq.}^{2+}\right) \cdot c\left(CO_{3,aq.}^{2-}\right)} = K' = x \cdot K$$
(Equation SI 3)
$$-RT \ln K' = \Delta_{R}G_{ion pair}^{\otimes}$$

The calculation of the microscopic equilibrium constant K and the averaged, dynamic coordination number of a single carbonate x enables the determination of the macroscopic equilibrium constant for the formation of stable pre-nucleation clusters K' (Table 1; cp. Equation SI 3). K' is, as expected, rising with increasing citrate concentrations due to the citrate binding to the clusters. The calculation of the GIBBS standard reaction energy  $\Delta_{R}G_{ion pair}$  for the formation of calcium/carbonate ion pairs (table 1; cp. Equation SI 3) shows that even at 50 mg/L citrate the energy gain of ion pair formation is higher, than at pH 9 in the absence of additives where mainly calcite is formed.<sup>1</sup> Under the assumption that this GIBBS free energy is a measure of the polymorph formed after nucleation and that structures are already preformed in the soluble equilibrium clusters it is not surprising that indeed calcite, determined by WAXS, is formed at all studied citrate concentrations instead of vaterite, which is obtained in the reference experiment (type V).

Table S1: Determined values of averaged, dynamic coordination number of a single carbonate x, the microscopic equilibrium constant K, and the macroscopic equilibrium constant K' and the Gibbs free energy of ion pair formation ( $\Delta_R G_{ion pair}$ ) (for more information see SI 2)

	0	50 mg/L	100 mg/L	150 mg/L	250 mg/L	500 mg/L
Х	1,26	1,26	1,26	1,26	1,26	1,26
K/ L·mol⁻¹	1002	1424	1711	1667	2236	2772
K' / L·mol⁻¹	1266	1798	2161	2106	2824	3500
∆ <sub>R</sub> G <sub>ion pair</sub> / KJ·mol <sup>-1</sup> ·K	-17.7	-18.6	-19.0	-19.0	-19.7	-20.2

## SI 3: Experiments in the presence of Poly(aspartic acid)



Figure SI 7.2: SEM images of CaCO<sub>3</sub> particles obtained in the presence of a) 100 mg/L PAsp ( $M_W = 27,000 \text{ g/mol}$ ) 2h after the first drop (scale bar 200 nm); b) 100 mg/L PAsp ( $M_W = 27,000 \text{ g/mol}$ ) 3h after the second drop (scale bar 200 nm) and c) 10 mg/L PAsp ( $M_W = 27,000 \text{ g/mol}$ ) 3h after the drop of the Ca<sup>2+</sup> concentration (scale bar 300 nm).