

Supplementary Information to “Variations in calcite growth kinetics with surface topography: Molecular Dynamics simulations and process-based growth kinetics modelling” by M. Wolthers, D. Di Tommaso, Z. Du and N.H. de Leeuw

Superscript numbers refer to references in the main paper.

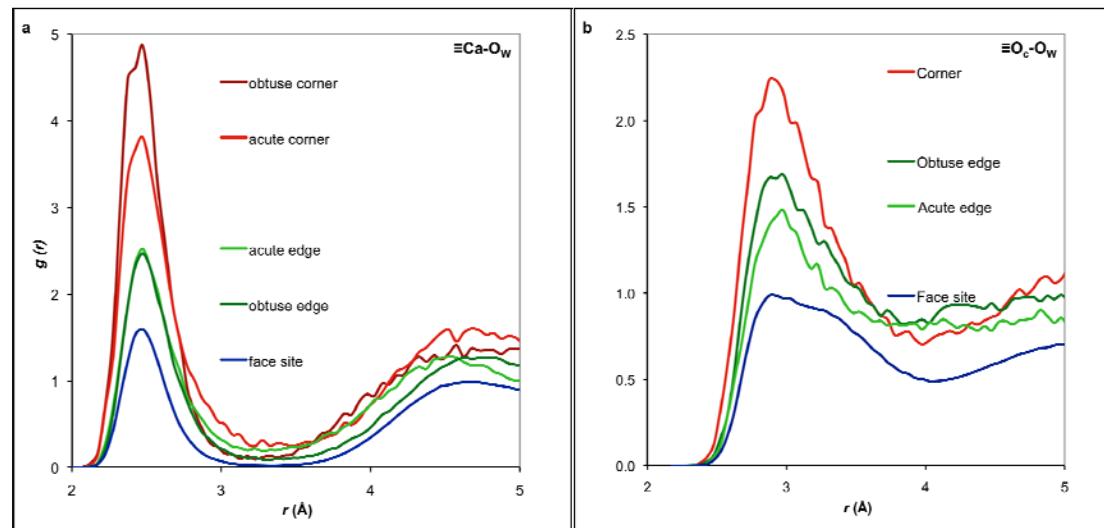


Figure S1. Radial distribution function (RDF) at 340K for (a) various surface calcium sites ($\equiv\text{Ca}$) and (b) various surface carbonate oxygen sites ($\equiv\text{O}_C$) with respect to water oxygen ($\equiv\text{O}_W$). The value for g at the first minimum of an RDF reflects the dynamics in the first coordination shell.^{e.g.³⁷ The near-zero g at the first RDF minimum for calcium face sites suggests that there is little water exchange between first and second water layers. For calcium and carbonate, this minimum g increases with decreasing surface coordination, reaching values of ~0.8 for carbonate sites, strongly indicating that there is significant movement of water molecules between the first and second water layers.}

Table S1. Summary of the key equations of the process-based growth model for calcite.⁶ See Table S4 for parameter values and Table S5 for explanation of the symbols.

PROCESS-BASED GROWTH MODEL SUMMARY	
Kink propagation rate u_c (in s⁻¹)	
$u_c = 2\chi \bar{v}_A \bar{v}_B (S^2 - 1) \frac{1}{\bar{v}_A (Sr_i^{1/2} + \theta) + \bar{v}_B (\theta Sr_i^{-1/2} + 1)}$	
Kink formation rate i_c (in s⁻¹)	
$i_c = \chi \bar{v}_A \bar{v}_B S (S^2 - 1) \exp(-\epsilon/kT) \left(\frac{1}{\bar{v}_A r_i^{1/2} + \bar{v}_B S} + \frac{1}{\bar{v}_B r_i^{-1/2} + \bar{v}_A S} \right)$	
Kink density ρ_c	
$\rho_c = S^{1/2} \exp(-\epsilon/kT) \left[\left(\frac{1}{\bar{v}_A r_i^{1/2} + \bar{v}_B S} + \frac{1}{\bar{v}_B r_i^{-1/2} + \bar{v}_A S} \right) \right] / \left(\frac{1}{\bar{v}_A (Sr_i^{1/2} + \theta) + \bar{v}_B (\theta Sr_i^{-1/2} + 1)} \right)^{1/2}$	
Growth rate R_c (in s⁻¹)	
$R_c = \chi k_{in} (K_S \bar{k}_A \bar{k}_B)^{1/2} (S^2 - 1) S^{1/2} \ln S \left[\left(\frac{1}{\bar{v}_A r_i^{1/2} + \bar{v}_B S} + \frac{1}{\bar{v}_B r_i^{-1/2} + \bar{v}_A S} \right) \right] \left(\frac{1}{\bar{v}_A (Sr_i^{1/2} + \theta) + \bar{v}_B (\theta Sr_i^{-1/2} + 1)} \right)^{1/2}$	
with	
$S = \left[\frac{\{A\} \{B_1\}}{K_S} \right]^{1/2} = \left[\frac{\bar{k}_A \bar{k}_B \{A\} \{B_1\}}{\bar{v}_A \bar{v}_B} \right]^{1/2}$	$K_S = \frac{\bar{v}_A \bar{v}_B}{\bar{k}_A \bar{k}_B}$
$r_i = \frac{\bar{k}_A \bar{v}_B \{A\}}{\bar{k}_B \bar{v}_A \{B_1\}}$	$k_{in} = \frac{2aK_S^{1/2}(\bar{k}_A \bar{k}_B)^{1/2} \exp(-\epsilon/kT)}{19\gamma/kT}$
$\chi = P_A + P_{B1} + P_{B2}$	$\theta = (1 + 10^{-pH}) K_{CaHCO_3}$

Table S2. Parameters of the process-based growth model. Values for ϵ , γ and ν_{A1} were re-optimized and for k_{B1} the normalized water exchange frequencies for the various surface calcium sites were assumed.

Parameter	Symbol	Value
Kink formation energy	$\epsilon, \epsilon_{A,B}$	$7.8 \times 10^{-21} \text{ J}$
Edge work	γ	$7.2 \times 10^{-20} \text{ J}$
Attachment frequencies	k_{A1}	$\frac{\bar{k}_B}{2(1+10^{8.6}10^{-\text{pH}})}$
	k_{A2}	$\approx k_{A1}$
	k_{B1}	From Table 1
Detachment frequencies	k_{B2}	$\approx k_{B1}$
	ν_{A1}	$2.0 \times 10^2 \text{ s}^{-1}$
	ν_{A2}	$\approx \nu_{A1}$
	ν_{B1}	$\frac{K_s \bar{k}_A \bar{k}_B}{\bar{\nu}_A (1+10^{8.6}10^{-\text{pH}})}$
	ν_{B2}	$\approx \nu_{B1}$

Table S3. Nomenclature of the process-based growth model.

A	(Index for) calcium ion
{A}	Activity of calcium ion in solution
A1, A2	Index for a calcium ion reacting with a carbonate or bicarbonate surface site, respectively
<i>a</i>	Mean ionic diameter (3.199 Å for calcite)
B	(Index for) carbonate and bicarbonate ions
B1	(Index for) carbonate ion
{B1}	Activity of carbonate ion in solution
B2	(Index for) bicarbonate ion
{B2}	Activity of bicarbonate ion in solution
<i>c</i>	Index for process-based calcite growth model
IAP	Activity product of the constituent ions, $\{\text{Ca}^{2+}\}\{\text{CO}_3^{2-}\}$ for calcite
<i>K_s</i>	Solubility product of calcite
<i>k</i>	Boltzmann constant
$\overline{k_A}, \overline{k_B}$	Overall attachment frequencies for calcium and (bi-)carbonate
<i>R</i>	Overall growth rate
<i>r_{aq}</i>	Ionic activity ratio $\{\text{Ca}^{2+}\}/\{\text{CO}_3^{2-}\}$
<i>S</i>	Saturation ratio $((\text{IAP}/K_s)^{1/2} = \Omega^{1/2})$
<i>T</i>	Temperature
<i>u</i>	Kink propagation rate
<i>V</i>	Rate of step movement
γ	Edge work
ϵ	Kink formation energy
θ	Term for speciation between carbonate and bicarbonate
$\overline{v_A}, \overline{v_B}$	Overall detachment frequencies for calcium and (bi-)carbonate
ρ	Kink density
χ	Fraction of growth sites at the surface calculated using calcite surface complexation model ³⁸
Ω	Saturation ratio (IAP/K_s)
\equiv	Surface site

Table S4. Number of accounted *water* exchange events ($N_{ex}^{H_2O}$) in the first coordination shell of the **calcium** ions with a duration of more than 0.5 ps³⁶ at 300K and 320K. The first shell has been defined by the first minimum of the Ca–OW radial distribution functions, which lays at 3.3 Å for all calcium sites. The numbers of exchange events are averaged over the number of each type of \equiv Ca site.

T	\equiv Ca site position	t_{sim} (ps)	$N_{ex}^{H_2O}$	$\log k_w$ /s
300K	Flat face	1002.8	9.3	9.97
	Pit corner	1002.8	49.5	10.69
	Obtuse pit edge	1002.8	211.3	11.32
	Acute pit edge	1002.8	209.7	11.32
	Obtuse island edge	1002.8	129.8	11.11
	Acute island edge	1002.8	267	11.43
	Obtuse island corner	1002.8	165	11.22
	Acute island corner	1002.8	379	11.58
320K	Flat face	639.2	8.6	10.00
	Pit corner	639.2	40.5	10.78
	Obtuse pit edge	639.2	135.0	11.32
	Acute pit edge	639.2	143.8	11.34
	Obtuse island edge	639.2	101.4	11.20
	Acute island edge	639.2	216.7	11.53
	Obtuse island corner	639.2	126.0	11.30
	Acute island corner	639.2	369.0	11.76

Table S5. Number of accounted water exchange events ($N_{ex}^{H_2O}$) in the first coordination shell of the **carbonate oxygen** atoms with a duration of more than 0.5 ps³⁶ at 300K and 320K. The first shell has been defined by the first minimum of the Oc–Ow radial distribution functions, which lays at 4.0 Å for all carbonate oxygen sites. The numbers of exchange events are averaged over the number of each type of $\equiv O_C$ site.

$\equiv CO_3$ site position	300K			320K			340K			
	t_{sim} (ps)	$N_{ex}^{H_2O}$	$\log k_w$ /s	t_{sim} (ps)	$N_{ex}^{H_2O}$	$\log k_w$ /s	t_{sim} (ps)	$N_{ex}^{H_2O}$	$\log k_w$ /s	
Flat face	A	1002.8	735.6	11.87	639.2	778.1	12.09	799.2	936.2	12.07
	X	1002.8	1649.6	12.22	639.2	630.1	11.99	799.2	806.5	12.00
	B	1002.8	1971.2	12.29	639.2	457.8	11.86	799.2	757.6	11.98
Pit corner	A	1002.8	2043.0	12.31	639.2	954.0	12.17	799.2	1275.0	12.20
	X	1002.8	1884.0	12.27	639.2	988.0	12.19	799.2	1299.5	12.21
	B	1002.8	1783.9	12.25	639.2	787.5	12.09	799.2	1007.0	12.10
Obtuse pit edge	A	1002.8	1666.8	12.22	639.2	1168.2	12.26	799.2	1621.5	12.31
	X	1002.8	1494.4	12.17	639.2	1337.8	12.32	799.2	1578.0	12.30
	B	1002.8	1265.0	12.10	639.2	1000.7	12.19	799.2	1459.3	12.26
Acute pit edge	A	1002.8	1861.8	12.27	639.2	1058.0	12.22	799.2	1411.7	12.25
	X	1002.8	1811.6	12.26	639.2	813.5	12.10	799.2	1648.3	12.31
	B	1002.8	1837.8	12.26	639.2	1220.7	12.28	799.2	1015.8	12.10
Obtuse island edge	A	1002.8	1686.4	12.23	639.2	1276.6	12.30	799.2	1719.8	12.33
	X	1002.8	1795.3	12.25	639.2	1300.6	12.31	799.2	1507.2	12.28
	B	1002.8	1652.0	12.22	639.2	1018.8	12.20	799.2	1634.0	12.31
Acute island edge	A	1002.8	1852.7	12.27	639.2	1265.7	12.30	799.2	1626.0	12.31
	X	1002.8	1856.0	12.27	639.2	1343.3	12.32	799.2	1669.7	12.32
	B	1002.8	2202.5	12.34	639.2	1001.7	12.20	799.2	1604.0	12.30
Island corner	A	1002.8	1543.5	12.19	639.2	1276.0	12.30	799.2	1686.0	12.32
	X	1002.8	735.6	11.87	639.2	1457.5	12.36	799.2	1998.5	12.40
	B	1002.8	1649.6	12.22	639.2	1057.5	12.22	799.2	1399.5	12.24