Supplementary Information (SI)

Submitted to *RSC Advances*

Uptake of $H^{14}CO_3^-$ / $^{14}CO_3^{2-}$ by calcite: impact of ISA and chloride

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1 Determination of the absolute activity

To determine the absolute sample activity (DPM), the measured activity (CPM) has been corrected by the appropriate counting efficiency, as shown in (1):

$$DPM = \frac{CPM_{sample}}{Efficiency} \quad (1)$$

The counting efficiency is determined through quench curve. The latest consists of a measurement of a series of 10 standards (^{14}C low level quenched, Perkin Elmer) with a constant absolute activity and in which the number of quenching increases from standard to standard. Since the DPM of each standard is known and the CPM is measured, the counting efficiency is determined as follows (2):

$$Efficiency = \frac{CPM_{standard}}{DPM_{standard}} \quad (2)$$

The quench curve, plotted against the quench indicating parameter t-SIE (transformed-spectral index of an external standard), is then fitted to the standard points. More details are reported in.[1]

2 Calcite characterization

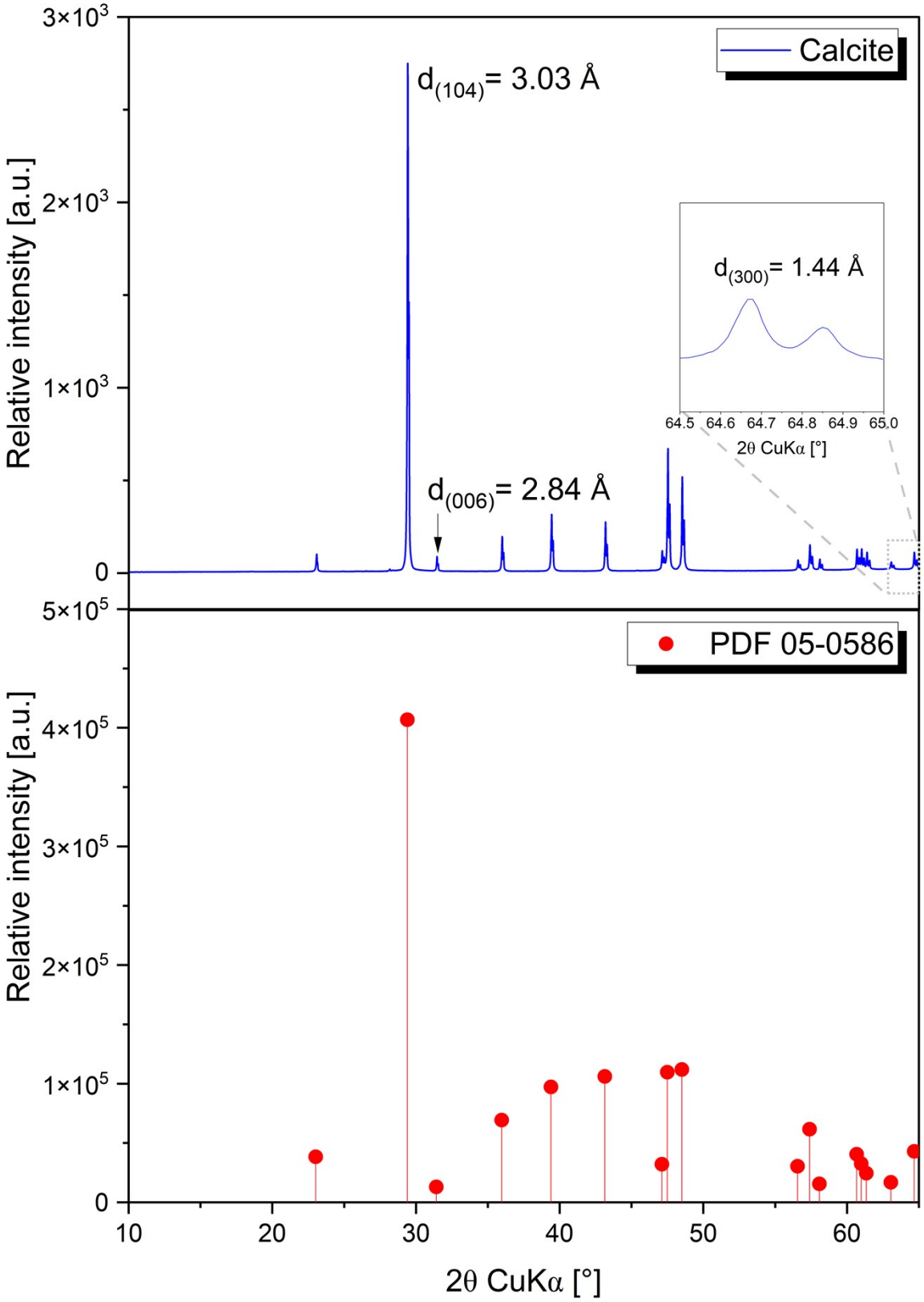

Figure S1. Diffractogram obtained for the calcite material used for sorption and recrystallization experiments before equilibration. Bottom figure corresponds to the calcite reference diffractogram PDF 05-0586.

3 Calcite recrystallization: chloride-free system

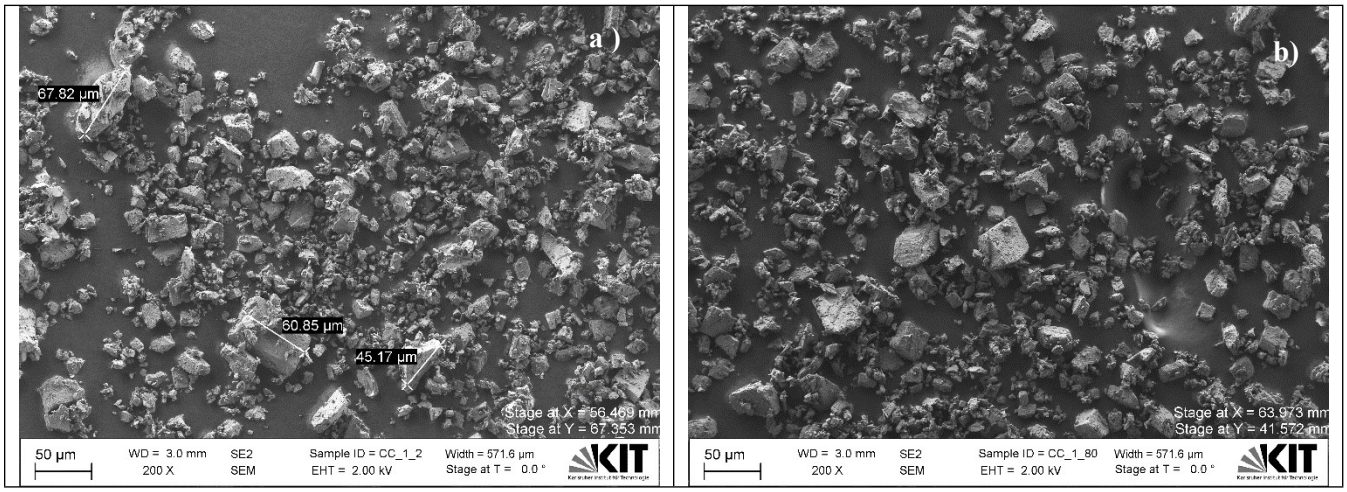

Figure S2. Heterogeneity of calcite particles (a) after 2 days and (b) after 82 days of equilibration time. SEM images are reported with a magnification of X 200.

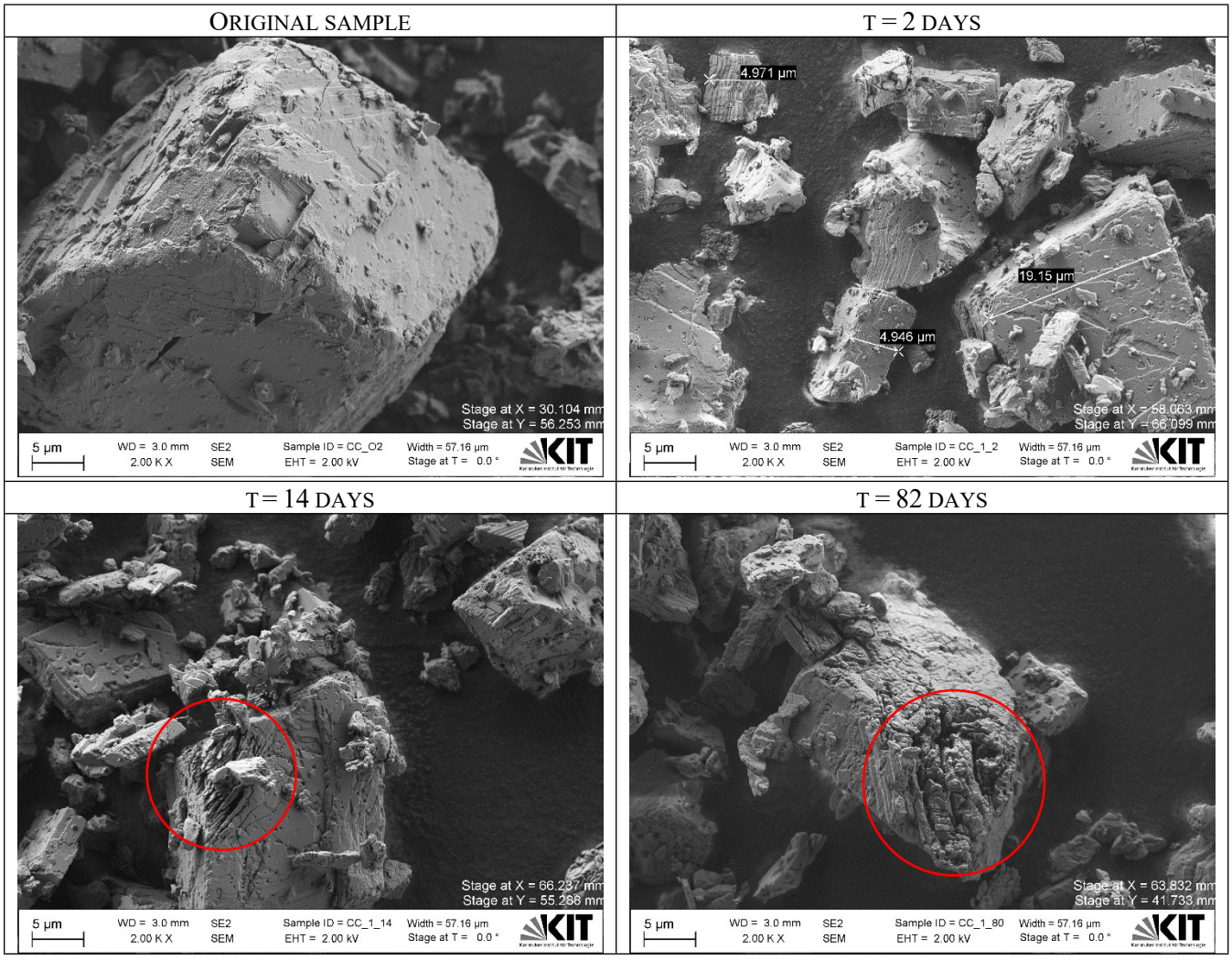

Figure S3. Surface evolution of calcite particles in recrystallization experiments carried out for contacting times 2 < t (days) < 82. SEM images with a magnification of X 2000 are reported.

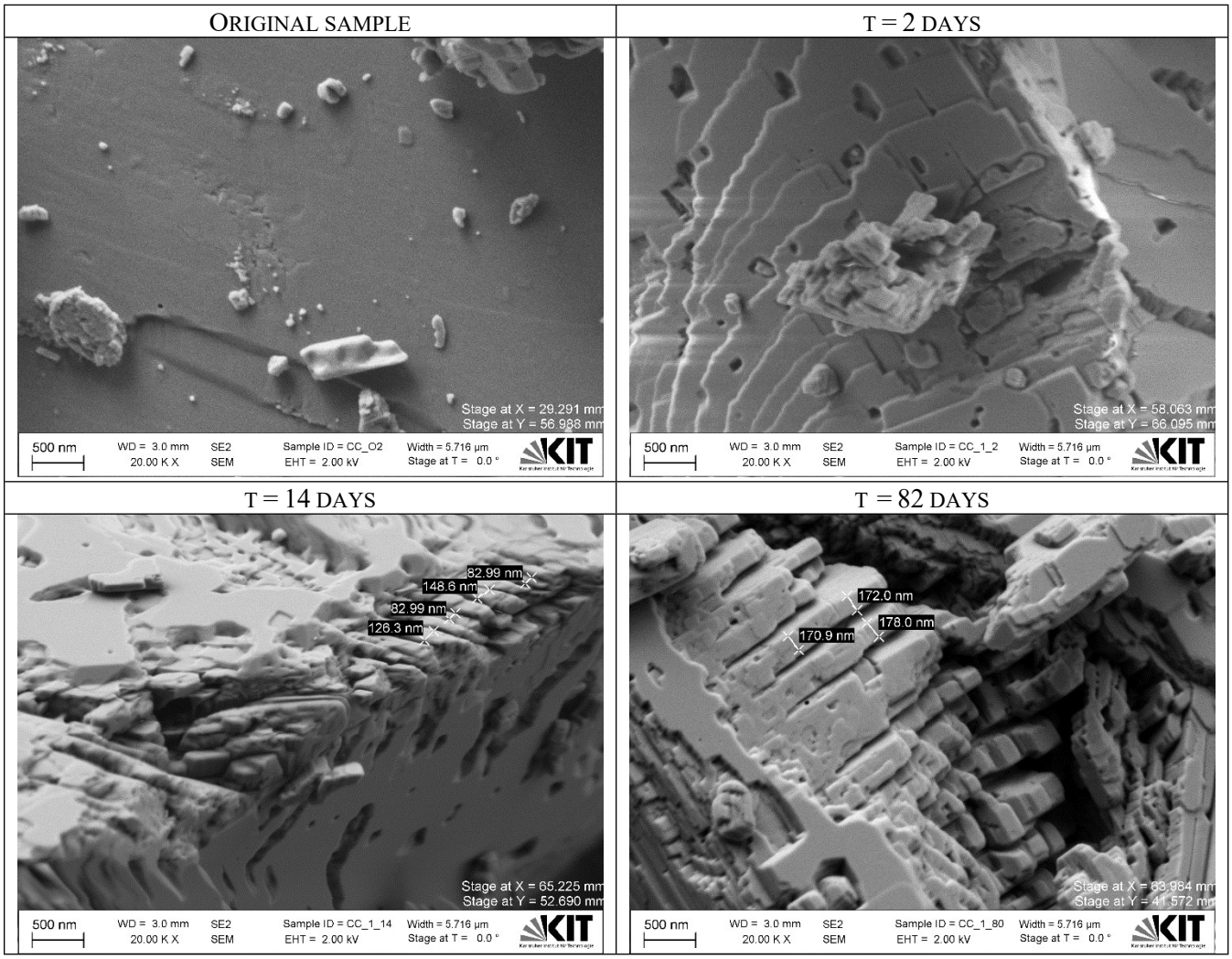

Figure S4. Surface evolution of calcite particles in recrystallization experiments carried out for contacting times 2 < t (days) < 82. SEM images with a magnification of X 20000 are reported.

4 Calcite recrystallization in the presence of chloride (NaCl)

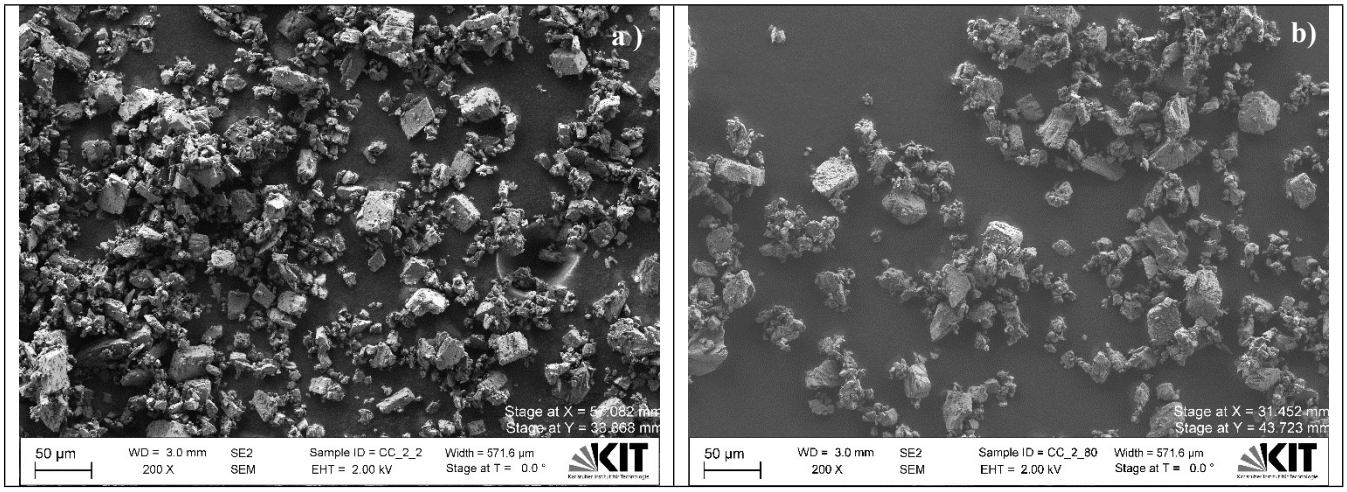

Figure S5. Heterogeneity of calcite particles in presence of $[NaCl]_{tot}$= 2 M (a) after 2 and (b) after 82 days of equilibration. SEM images are reported with a magnification of X 200.

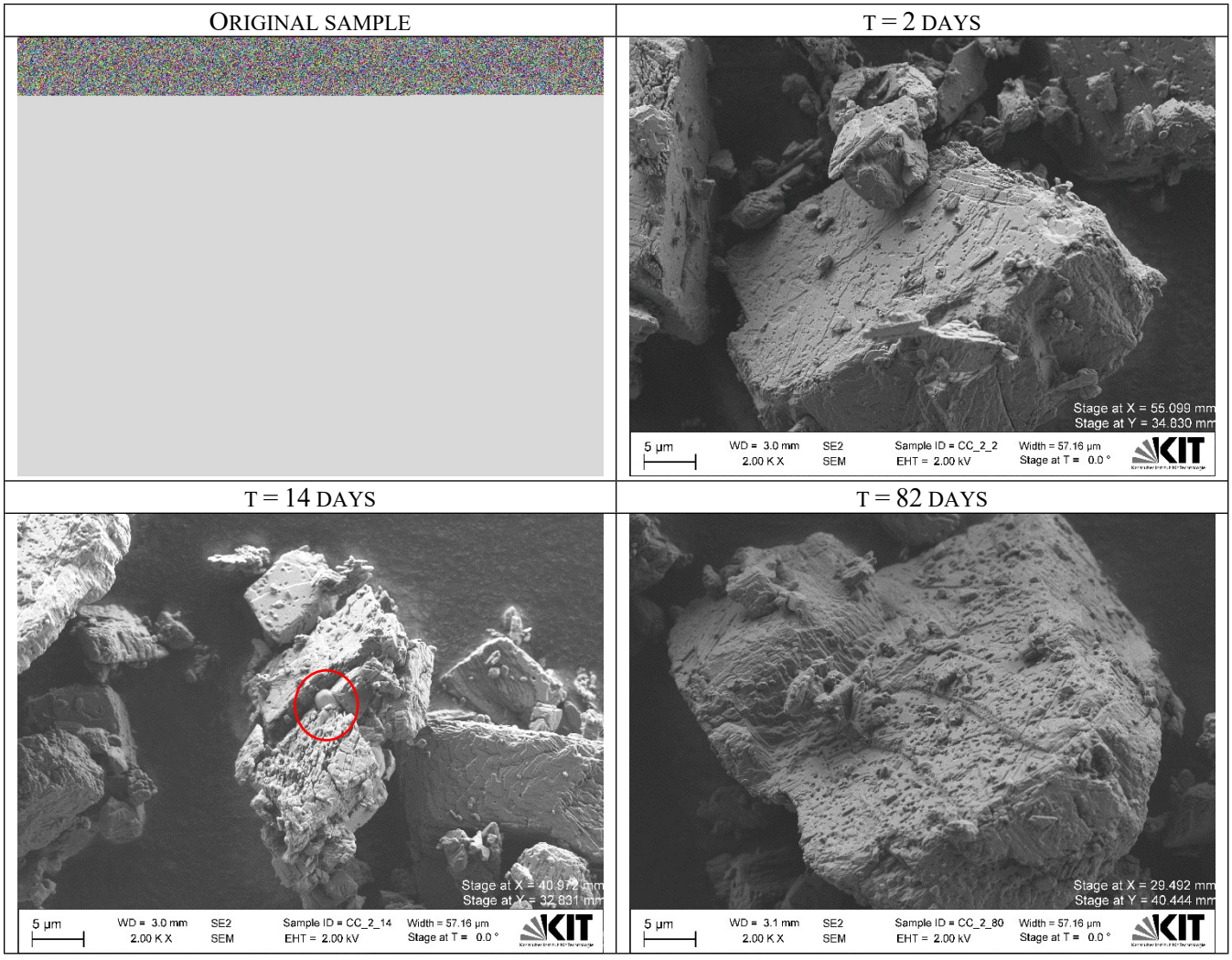

Figure S6. Surface evolution of calcite particles in presence of NaCl in recrystallization experiments carried out for contacting times 2 < t (days) < 82 experiments and $[NaCl]_{tot}$= 2M. SEM images with a magnification of X 2000 are reported.

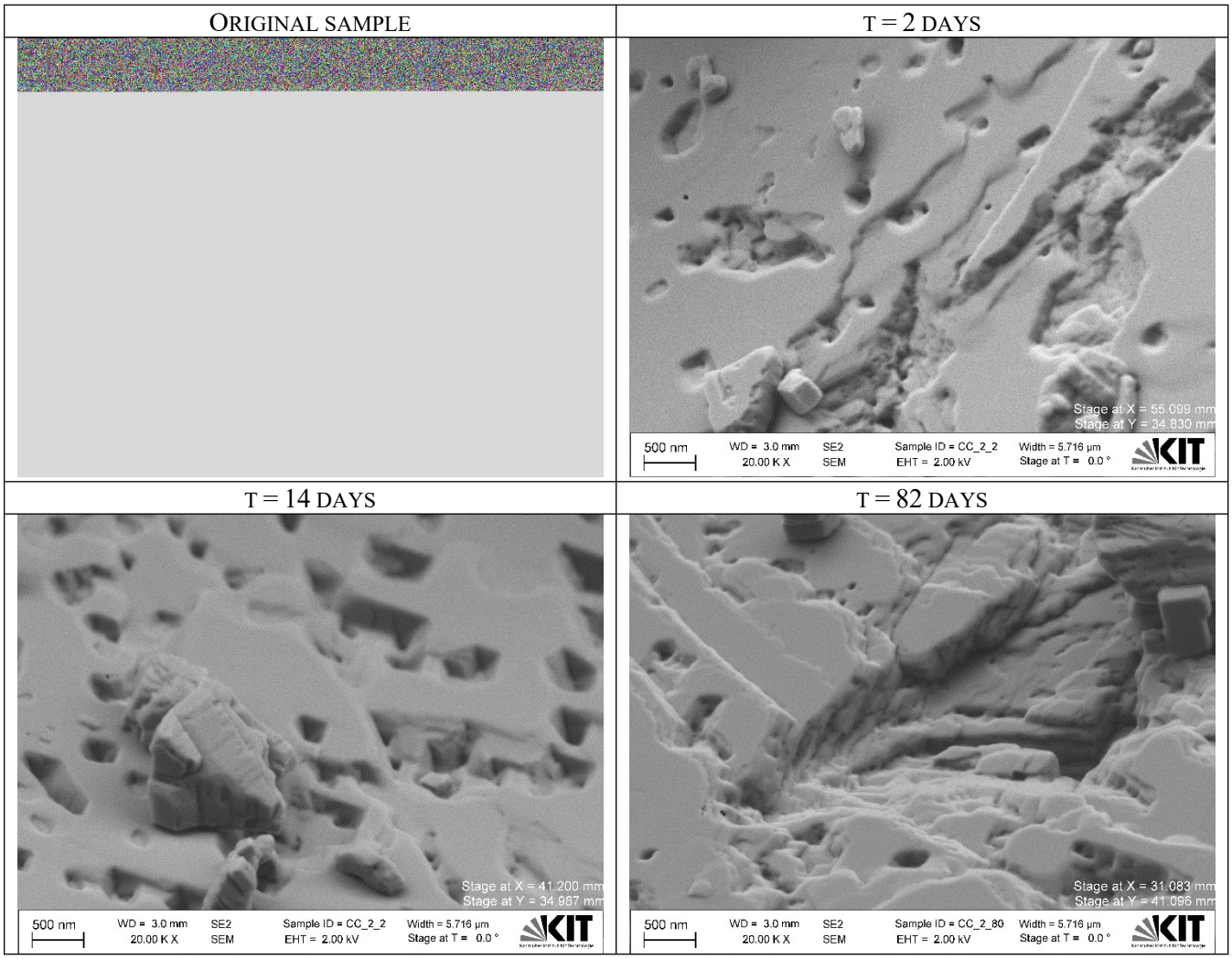

Figure S7. Surface evolution of calcite particles in presence of NaCl in recrystallization experiments carried out for contacting times 2 < t (days) < 82 experiments and $[NaCl]_{tot}$= 2M. SEM images with a magnification of X 20000 are reported.

5 Modelling and mechanistic understanding of calcite recrystallization

5.1 Calcite system

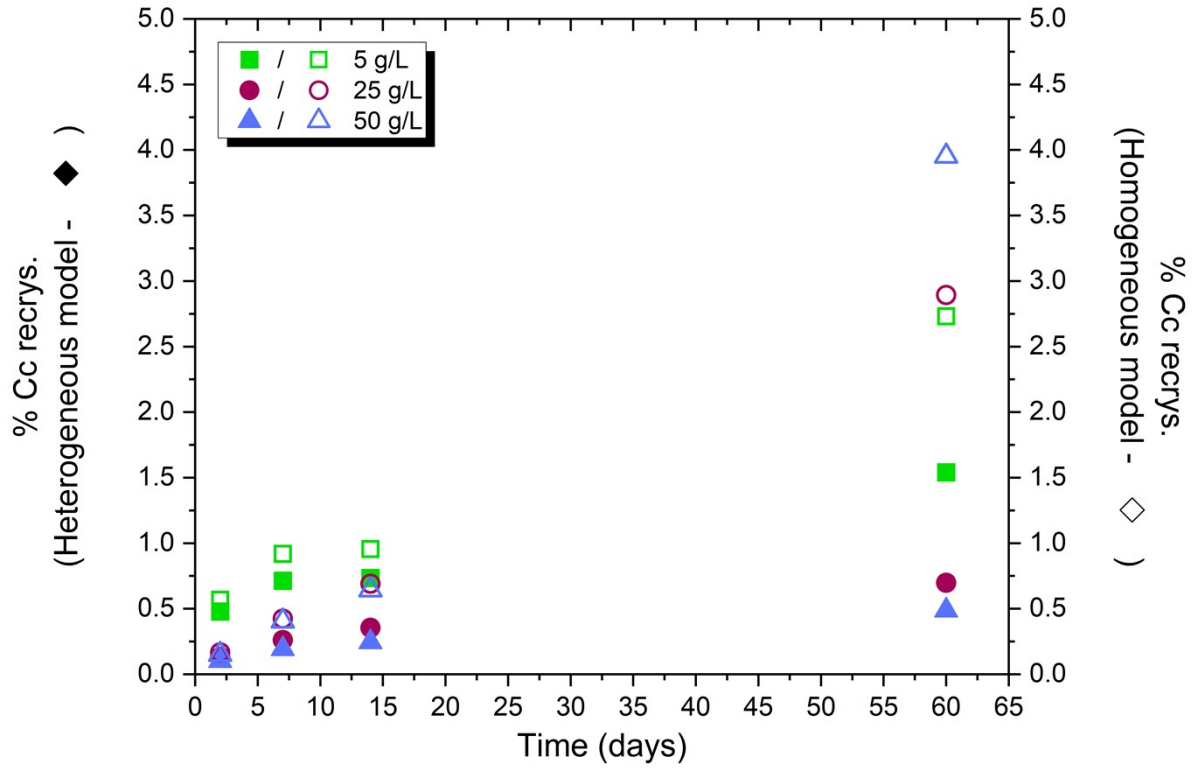

Figure S8. Fraction of recrystallized calcite (%Cc) determined for the sorption series (Calcite-^{14}C) carried out with a S/L ratio = 5, 25 and 50 g·L^{-1}. Full and empty symbols represent the %Cc for the heterogeneous and the homogeneous model respectively.

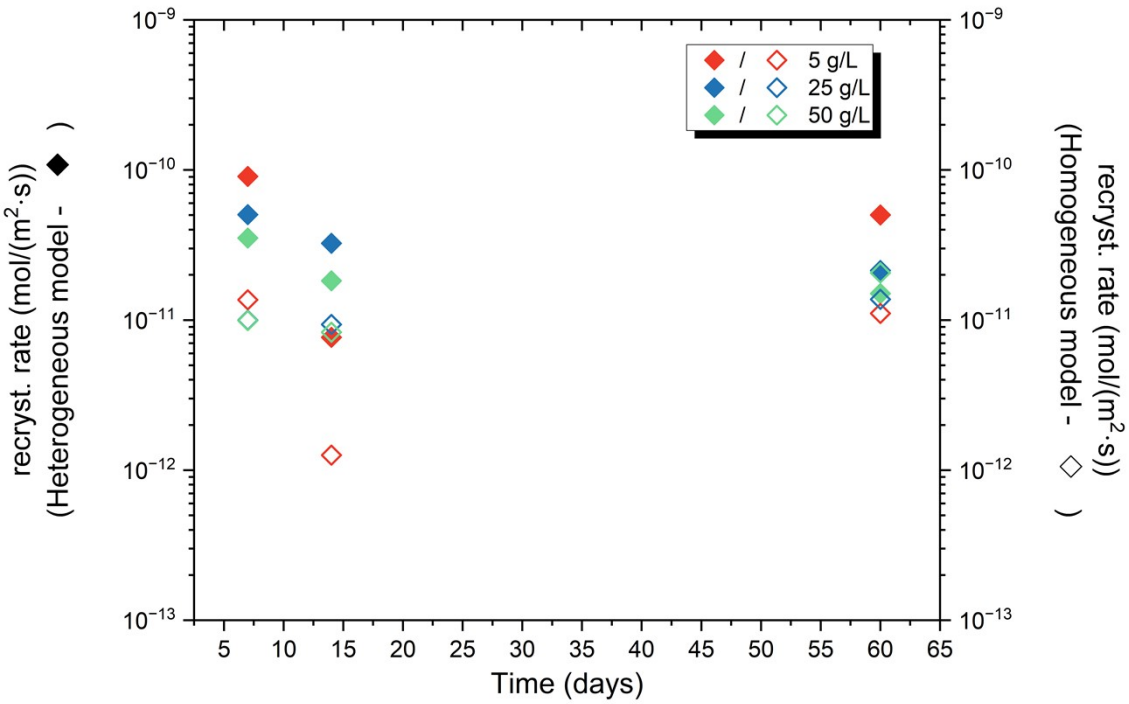

Figure S9. Calcite recrystallization rates determined for the sorption series (Calcite-^{14}C) carried out with a S/L ratio = 5, 25 and 50 g·L^{-1}. Full and empty symbols represent the recrystallization rates for the heterogeneous and the homogeneous model respectively.

6 Impact of ISA on ^{14}C retention by calcite

Table S1. Equilibrium constants in the reference state considered in this work for thermodynamic calculations (speciation, solubility) of the Ca-ISA system. ISA stands for isosaccharinic acid.

Species	Log K_0^S	Reaction	Reference
Aqueous species			
$CaCO_3$(aq)	3.22±0.14	$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3(aq)$	ThermoChimie database [2]
$CaHCO_3^+$	11.43±0.30	$Ca^{2+} + H^+ + CO_3^{2-} \leftrightarrow CaHCO_3^+$	ThermoChimie database [2]
$CaOH^+$	-12.78±0.30	$Ca^{2+} + H_2O \leftrightarrow Ca(OH)^+ + H^+$	ThermoChimie database [2]
HCO_3^-	10.33±0.08	$H^+ + CO_3^{2-} \leftrightarrow HCO_3^-$	ThermoChimie database [2]
$Ca(ISA)^+$	1.70±0.30	$Ca^{2+} + ISA^- \leftrightarrow Ca(ISA)^+$	ThermoChimie database [2]
Ca(ISA)	-10.4±0.50	$Ca^{2+} + ISA^- \leftrightarrow Ca(ISA) + H^+$	ThermoChimie database [2]
ISA	4.00±0.50	$H^+ + ISA^- \leftrightarrow ISA$	ThermoChimie database [2]
Solid species			
$Ca(ISA)_2$(cr)	6.40±0.20	$Ca^{2+} + 2ISA^- \leftrightarrow Ca(ISA)_2(cr)$	ThermoChimie database [2]
Calcite	8.48±0.02	$Ca^{2+} + CO_3^{2-} \leftrightarrow$ Calcite	ThermoChimie database [2]
Portlandite	-22.81±0.05	$Ca^{2+} + 2H_2O \leftrightarrow$ Portlandite $+ 2H^+$	ThermoChimie database [2]

6.1 NMR characterization of ISA in calcite saturated pore water

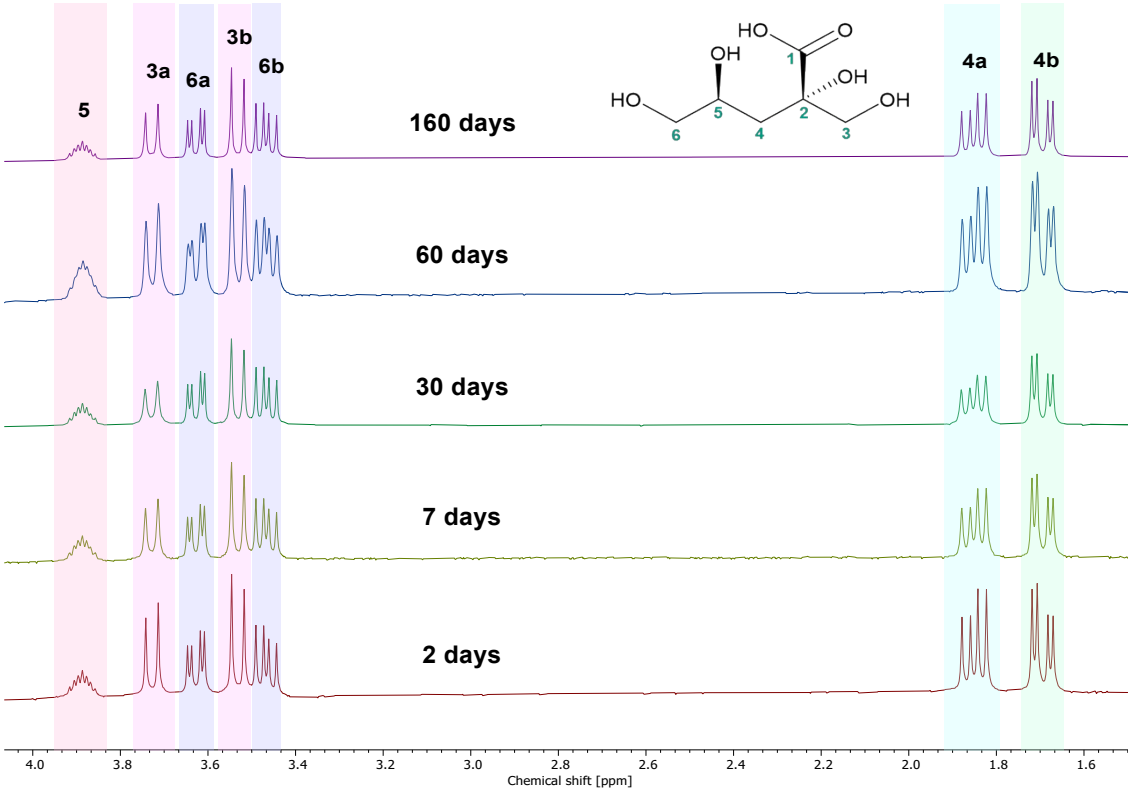

Figure S10. [1]H NMR spectra of ISA equilibrated in calcite pore water (pH=8.3) for equilibration times t = 2–160 days.

6.2 ^{14}C uptake in presence of α-ISA

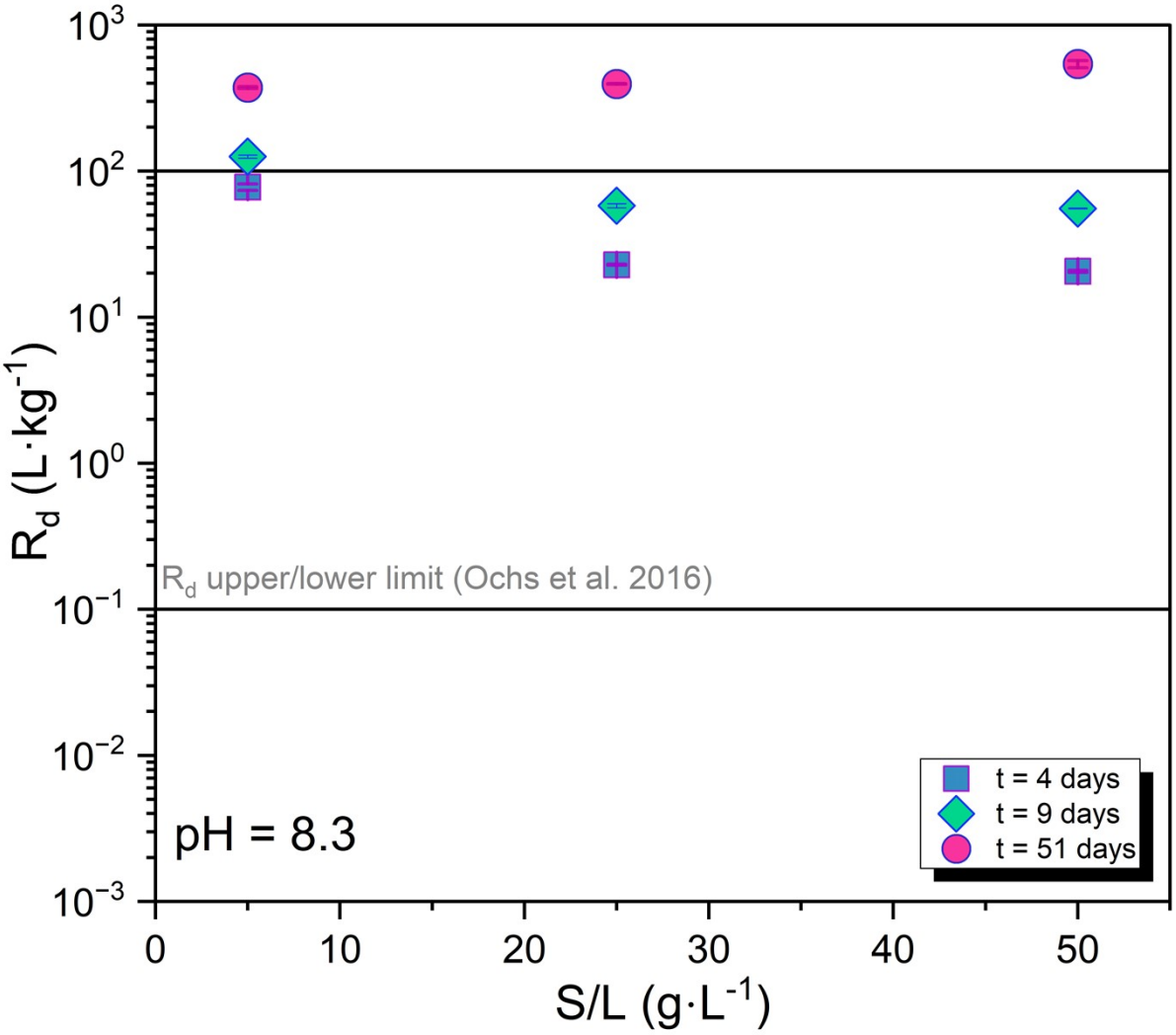

Figure S11. Distribution ratios R_d determined in the presence of $[ISA]_{tot} = 10^{-2}$ M for the uptake of ^{14}C by calcite as a function of S/L ratio. Solid lines represent the upper and lower R_d limits reported by Ochs et al.[3]

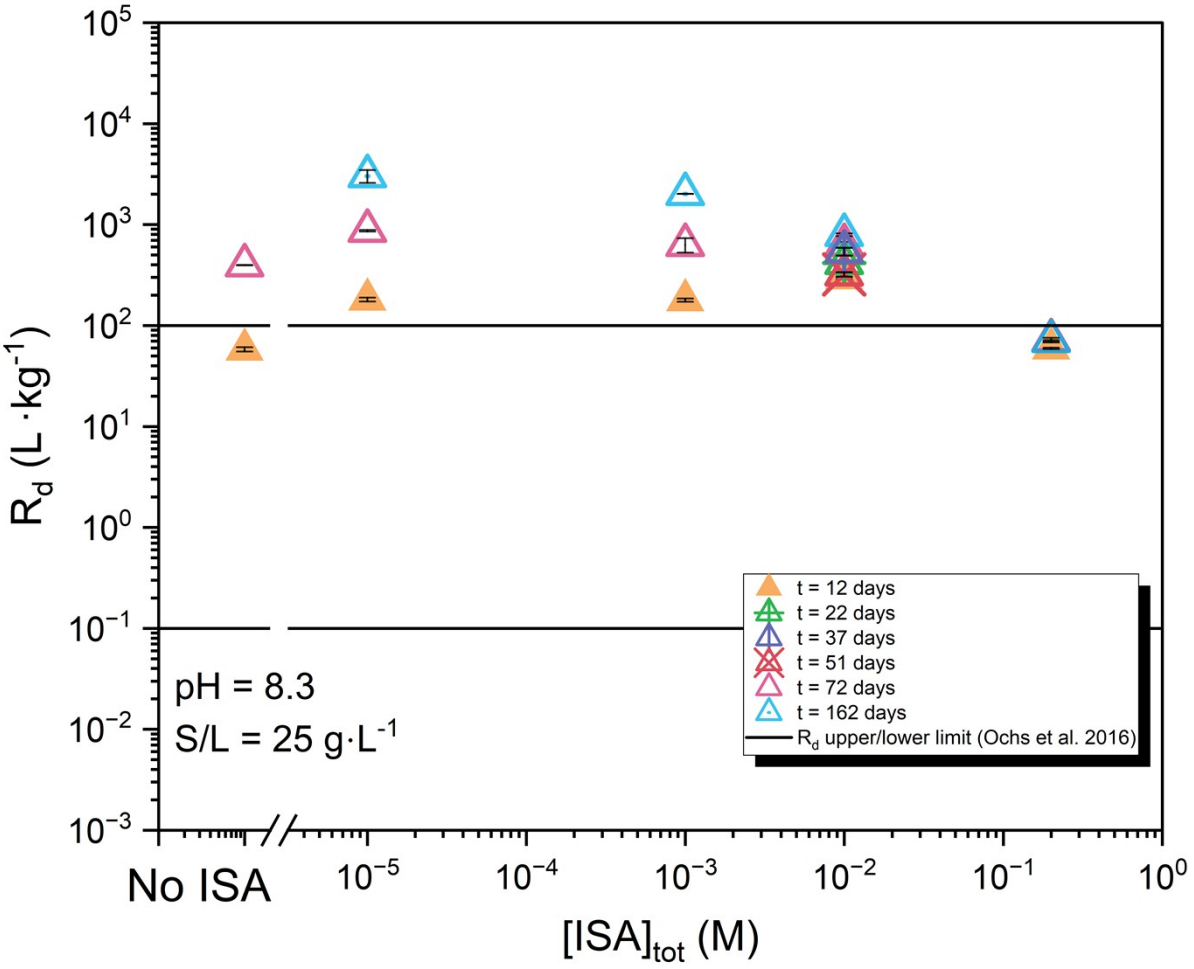

Figure S12. Distribution ratios (R_d) determined for the uptake of ^{14}C by calcite in presence of ISA ($[ISA]_{tot}$ =10^{-5}–0.2 M, S/L = 25 g·L^{-1}). Sorption batch experiments monitored for contact times of 10 ≤ t (days) ≤ 160. Solid lines represent the upper and lower R_d limits reported by Ochs et al.[3]

7 Distribution coefficients determined in the sorption experiments

Table S2. Distribution coefficients, R_d, determined in the sorption experiments for the ^{14}C-calcite system.

Initial activity, (Bq·mL^{-1})	S/L, (g·L^{-1})	Time, (days)	R_D, (L kg^{-1})	Error[A]	Experiment purpose
38.5	5	2	77.7	3.9	Sorption kinetics (variation of S/L ratio)
38.5	5	7	125.7	2.9	
38.5	5	14	130.6	2.3	
38.5	5	60	373.5	5.9	
38.5	25	2	22.87	0.21	
38.5	25	7	57.9	1.9	
38.5	25	14	94.57	0.75	
38.5	25	60	395.7	2.2	
38.5	50	2	20.62	0.36	
38.5	50	7	55.53	0.35	
38.5	50	14	88.0	1.1	
38.5	50	60	541	31	
0.20	5	2	47	55	Sorption isotherm (variation of ^{14}C initial activity)
0.20	25	2	19.1	7.8	
2	5	2	63	12	
2	25	2	29.2	3.0	
5	5	2	60.9	1.0	
5	25	2	29.57	0.82	
10	5	2	78.2	1.4	
10	25	2	32.2	3.4	
20	5	2	62.9	4.9	
20	25	2	34.20	0.44	
0.20	5	30	144	91	
0.20	25	30	[B]	-	
2	5	30	238	37	
2	25	30	348	34	
5	5	30	263	10	
5	25	30	479	90	
10	5	30	1960	72	
10	25	30	284	12	
20	5	30	417	15	
20	25	30	322.5	5.0	
0.20	5	60	[B]	-	
0.20	25	60	[B]	-	

2	5	60	414	28	
2	25	60	[b]	-	
5	5	60	439	20	
5	25	60	[b]	-	
10	5	60	854	10	
10	25	60	1111	205	
20	5	60	652	17	
20	25	60	1154	54	
0.20	5	160	[b]	-	
0.20	25	160	[b]	-	
2	5	160	[b]	-	
2	25	160	[b]	-	
5	5	160	[b]	-	
5	25	160	[b]	-	
10	5	160	3642	523	
10	25	160	[b]	-	
20	5	160	[b]	-	
20	25	160	106192	34630	
5	5	40	2073	163	
20	5	40	1180	153	
20	5	160	2584	102	

[a] Uncertainties are reported as two times the standard deviation (2σ) of mean values.
[b] Measured value below the detection limit.

Table S3. Distribution coefficients, R_d, determined in the sorption experiments for the calcite-^{14}C-ISA system carried out with $[ISA]_{tot}$ = 10^{-5}-0.2 M.

INITIAL ACTIVITY, (BQ·ML^{-1})	S/L, (G·L^{-1})	TIME, (DAYS)	$[ISA]_{TOT}$, (M)	R_D, (L KG^{-1})	ERROR[A]	EXPERIMENT PURPOSE
38.5	5	2	10^{-2}	130.5	3.2	SORPTION KINETICS (VARIATION OF S/L RATIO)
38.5	5	7	10^{-2}	179.3	4.4	
38.5	5	49	10^{-2}	326.9	2.9	
38.5	25	2	10^{-2}	40.76	0.76	
38.5	25	7	10^{-2}	79.5	1.5	
38.5	25	49	10^{-2}	321	10	
38.5	50	2	10^{-2}	42.20	0.82	
38.5	50	7	10^{-2}	72.4	1.7	
38.5	50	49	10^{-2}	386.9	6.6	
20	5	10	10^{-5}	246.0	5.4	SORPTION KINETICS (VARIATION OF S/L RATIO AND ISA CONCENTRATION)
20	5	10	10^{-3}	887.3	43.7	
20	5	10	10^{-2}	1155	34	
20	5	10	0.2	91.2	1.3	
20	25	10	10^{-5}	180.7	8.2	
20	25	10	10^{-3}	178.4	6.6	
20	25	10	10^{-2}	294.7	6.6	
20	25	10	0.2	59.21	0.94	
20	5	20	10^{-2}	349.0	9.1	
20	25	20	10^{-2}	417	30	
20	5	35	10^{-2}	1441	58	
20	25	35	10^{-2}	541	48	
20	5	70	10^{-5}	1036	32	
20	5	70	10^{-3}	913	15	
20	5	70	10^{-2}	2093	142	
20	5	70	0.2	45.5	2.5	
20	25	70	10^{-5}	868	17	
20	25	70	10^{-3}	631	103	
20	25	70	10^{-2}	631	43	
20	25	70	0.2	71.6	3.7	
20	5	160	10^{-5}	1155	40	
20	5	160	10^{-3}	1975	37	
20	5	160	10^{-2}	1774	31	
20	5	160	0.2	85.8	1.4	
20	25	160	10^{-5}	3020	438	
20	25	160	10^{-3}	2013	4	
20	25	160	10^{-2}	792	26	
20	25	160	0.2	70.3	1.3	

[a] Uncertainties are reported as two times the standard deviation (2σ) of mean values.

Table S4. Distribution coefficients, R_d, determined in the sorption experiments for the calcite-NaCl-^{14}C system carried out with $[NaCl]_{tot}$ = 10^{-4}-2 M.

Initial activity, (Bq·mL^{-1})	S/L, (g·L^{-1})	Time, (days)	$[NaCl]_{tot}$, (M)	R_D, (L kg^{-1})	Error[a]
20	5	2	10^{-4}	1868	87
20	5	2	$3.2\cdot10^{-3}$	1957	48
20	5	2	$3.2\cdot10^{-2}$	2025	60
20	5	2	0.32	1989	67
20	5	2	2	2181	101
20	25	2	10^{-4}	851	30
20	25	2	$3.2\cdot10^{-3}$	956	33
20	25	2	$3.2\cdot10^{-2}$	906	36
20	25	2	0.32	896	17
20	25	2	2	5393	251
20	5	30	10^{-4}	826.0	3.9
20	5	30	$3.2\cdot10^{-3}$	550	18
20	5	30	$3.2\cdot10^{-2}$	356.2	5.2
20	5	30	0.32	196.2	6.2
20	5	30	2	180.1	2.2
20	25	30	10^{-4}	2968	474
20	25	30	$3.2\cdot10^{-3}$	593	16
20	25	30	$3.2\cdot10^{-2}$	279.6	1.9
20	25	30	0.32	166.2	8.0
20	25	30	2	939	12
20	5	60	10^{-4}	748	16
20	5	60	$3.2\cdot10^{-3}$	686	12
20	5	60	$3.2\cdot10^{-2}$	1104	29
20	5	60	0.32	262.5	7.8
20	5	60	2	239.4	2.9
20	25	60	10^{-4}	630	24
20	25	60	$3.2\cdot10^{-3}$	952	37
20	25	60	$3.2\cdot10^{-2}$	443	12
20	25	60	0.32	265	11
20	25	60	2	342.5	9.0

[a] Uncertainties are reported as two times the standard deviation (2σ) of mean values.

Table S5. Distribution coefficients, R_d, determined in the sorption experiments for the calcite-NaCl-^{14}C-ISA system carried out with $[NaCl]_{tot}$ = 10^{-4}-2 M and $[ISA]_{tot}$ =10^{-2} M.

INITIAL ACTIVITY, (BQ·ML$^{-1)}$	S/L, (G·L^{-1})	TIME, (DAYS)	$[NACL]_{TOT}$, (M)	$[ISA]_{TOT}$, (M)	R_D, (L·KG^{-1})	ERROR[A]
20	5	5	10^{-4}	10^{-2}	1045	19
20	5	5	$3.2\cdot10^{-3}$	10^{-2}	1138	14
20	5	5	$3.2\cdot10^{-2}$	10^{-2}	1061	32
20	5	5	0.32	10^{-2}	1040	25
20	5	5	2	10^{-2}	1121	24
20	25	5	10^{-4}	10^{-2}	385	11
20	25	5	$3.2\cdot10^{-3}$	10^{-2}	347	11
20	25	5	$3.2\cdot10^{-2}$	10^{-2}	342.3	8.9
20	25	5	0.32	10^{-2}	338.8	6.7
20	25	5	2	10^{-2}	486	33
20	5	17	10^{-4}	10^{-2}	1379	12
20	5	17	$3.2\cdot10^{-3}$	10^{-2}	1323	29
20	5	17	$3.2\cdot10^{-2}$	10^{-2}	1273	31
20	5	17	0.32	10^{-2}	1178	31
20	5	17	2	10^{-2}	1309.92	0.22
20	25	17	10^{-4}	10^{-2}	760	16
20	25	17	$3.2\cdot10^{-3}$	10^{-2}	509	13
20	25	17	$3.2\cdot10^{-2}$	10^{-2}	484	12
20	25	17	0.32	10^{-2}	481	12
20	25	17	2	10^{-2}	556	14
20	5	93	10^{-4}	10^{-2}	511	27
20	5	93	$3.2\cdot10^{-3}$	10^{-2}	5428	144
20	5	93	$3.2\cdot10^{-2}$	10^{-2}	428.6	4.6
20	5	93	0.32	10^{-2}	438	18
20	5	93	2	10^{-2}	479	11
20	25	93	10^{-4}	10^{-2}	1125	53
20	25	93	$3.2\cdot10^{-3}$	10^{-2}	581.4	7.3
20	25	93	$3.2\cdot10^{-2}$	10^{-2}	363	12
20	25	93	0.32	10^{-2}	245.9	5.0
20	25	93	2	10^{-2}	396	30

[a] Uncertainties are reported as two times the standard deviation (2σ) of mean values.

8 References

1. M. F. L'Annunziata, *Handbook of radioactivity analysis*, Academic press, 2012.
2. B. Madé, W. Bower, S. Brassinnes, E. Colàs, L. Duro, P. Blanc, A. Lassin, L. Harvey and J. Begg, *Applied Geochemistry*, 2025, **180**, 106273.
3. M. Ochs, D. Mallants and L. Wang, *Radionuclide and metal sorption on cement and concrete*, Springer, 2016.