Supplementary Information

Synthesis and adsorbing properties of thin plate-like {001} calcite crystals

Nives Matijaković, Giulia Magnabosco, Francesco Scarpino, Giuseppe Falini, Damir Kralj

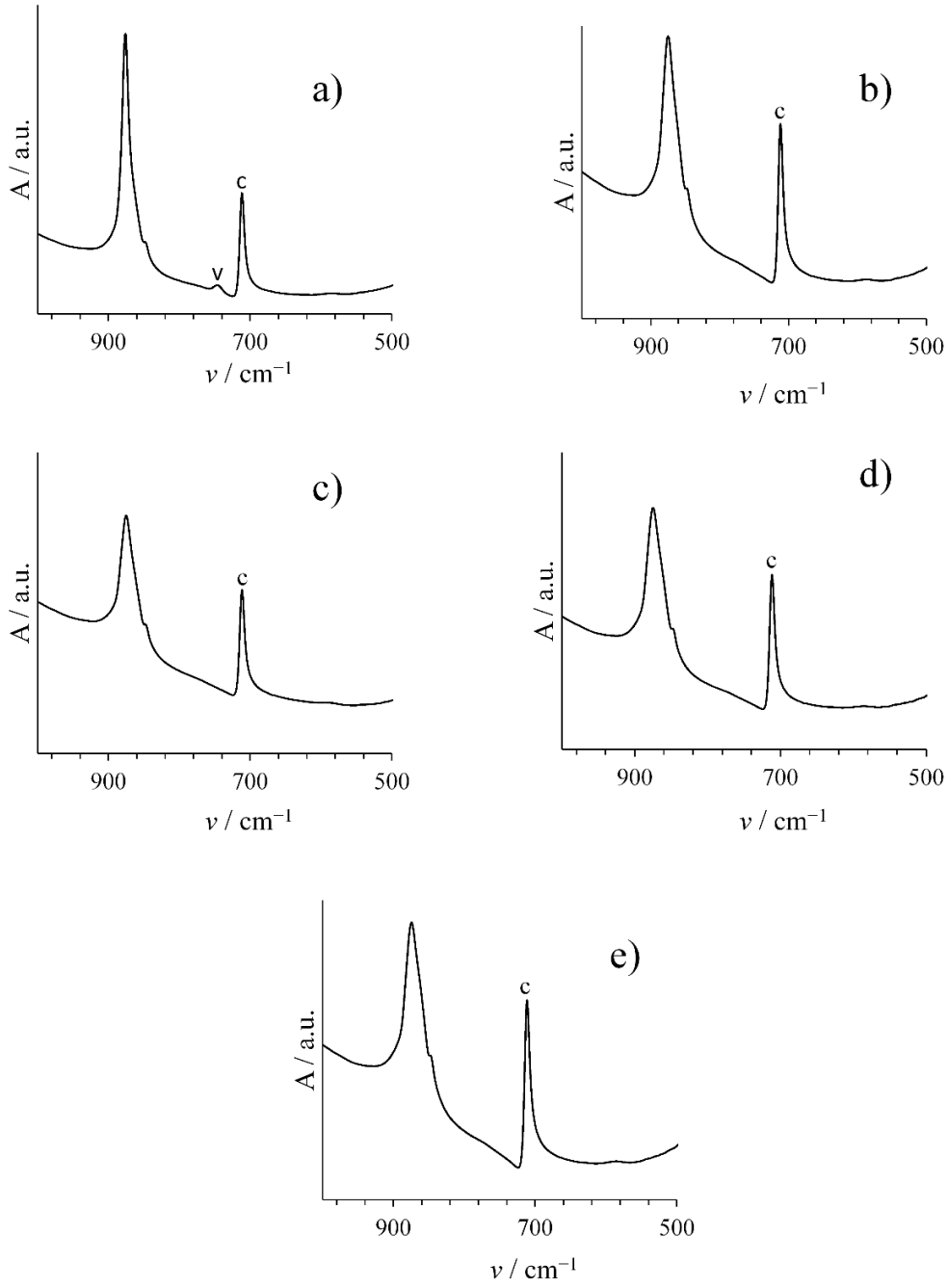


Figure SI1. FTIR spectra of the precipitates obtained in the system with $c(Li^+)$ = 0.0 mol dm^{-3} trough transformation time; a) 10 min of ultrasonic irradiation, b) 48 h, c) 72 h and d) 96 h. * v indicates vaterite. # c indicates calcite.

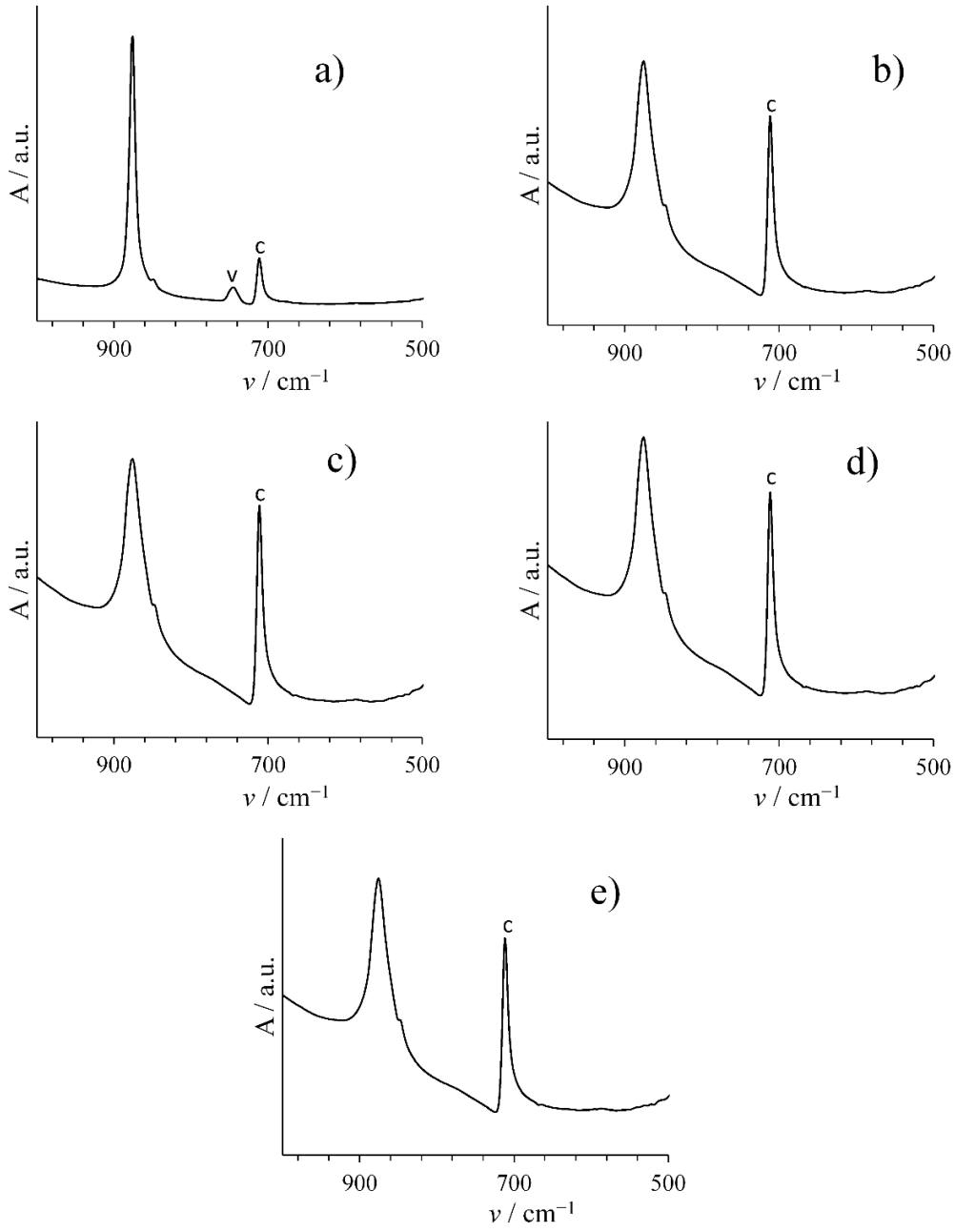


Figure SI2. FTIR spectra of the precipitates obtained in the system with $c(Li^+)$ = 0.1 mol dm^{-3} trough transformation time; a) 10 min of ultrasonic irradiation, b) 48 h, c) 72 h and d) 96 h. * v indicates vaterite. # c indicates calcite.

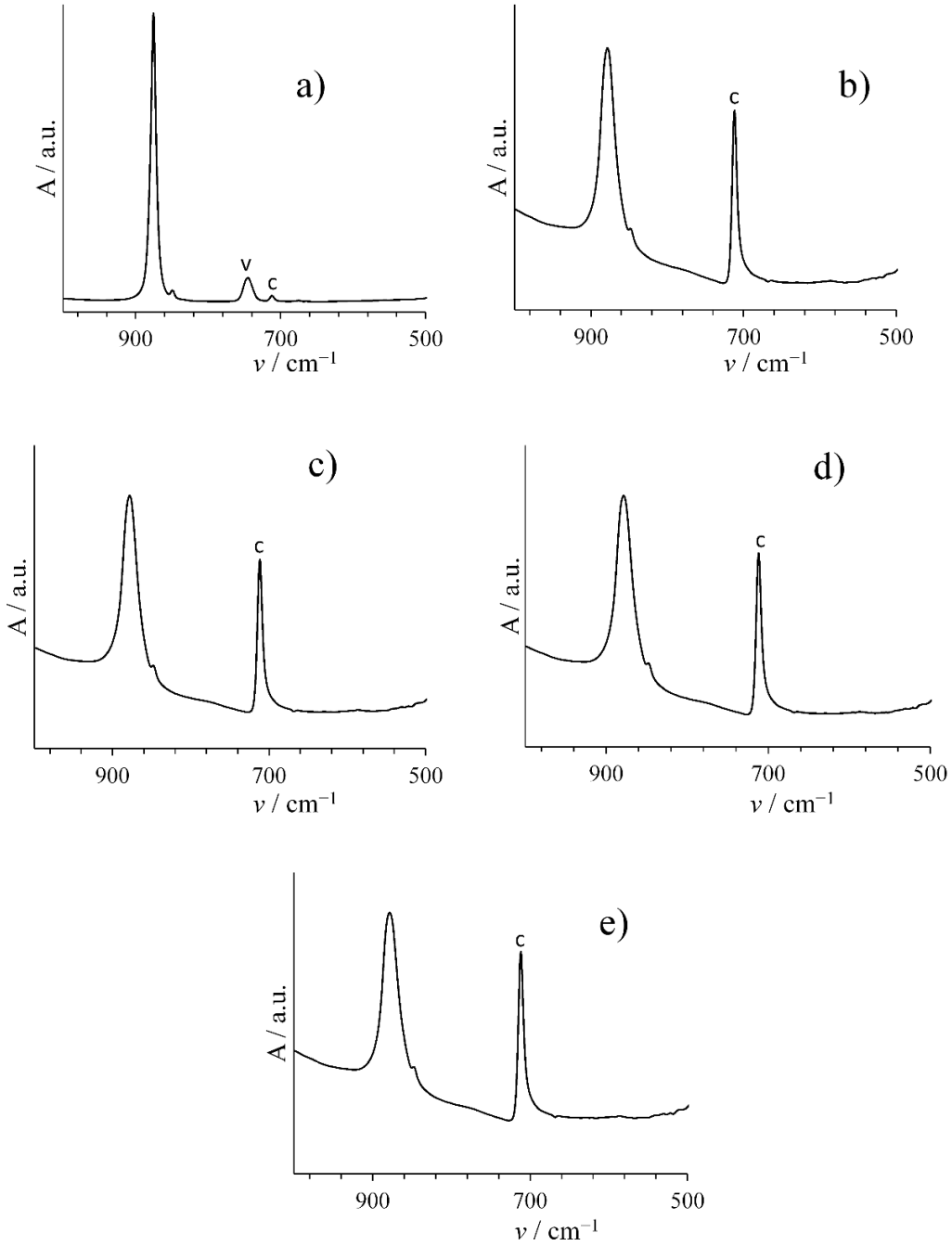


Figure SI3. FTIR spectra of the precipitates obtained in the system with $c(Li^+)$ = 0.3 mol dm^{-3} trough transformation time; a) 10 min of ultrasonic irradiation, b) 48 h, c) 72 h and d) 96 h. * v indicates vaterite. # c indicates calcite.

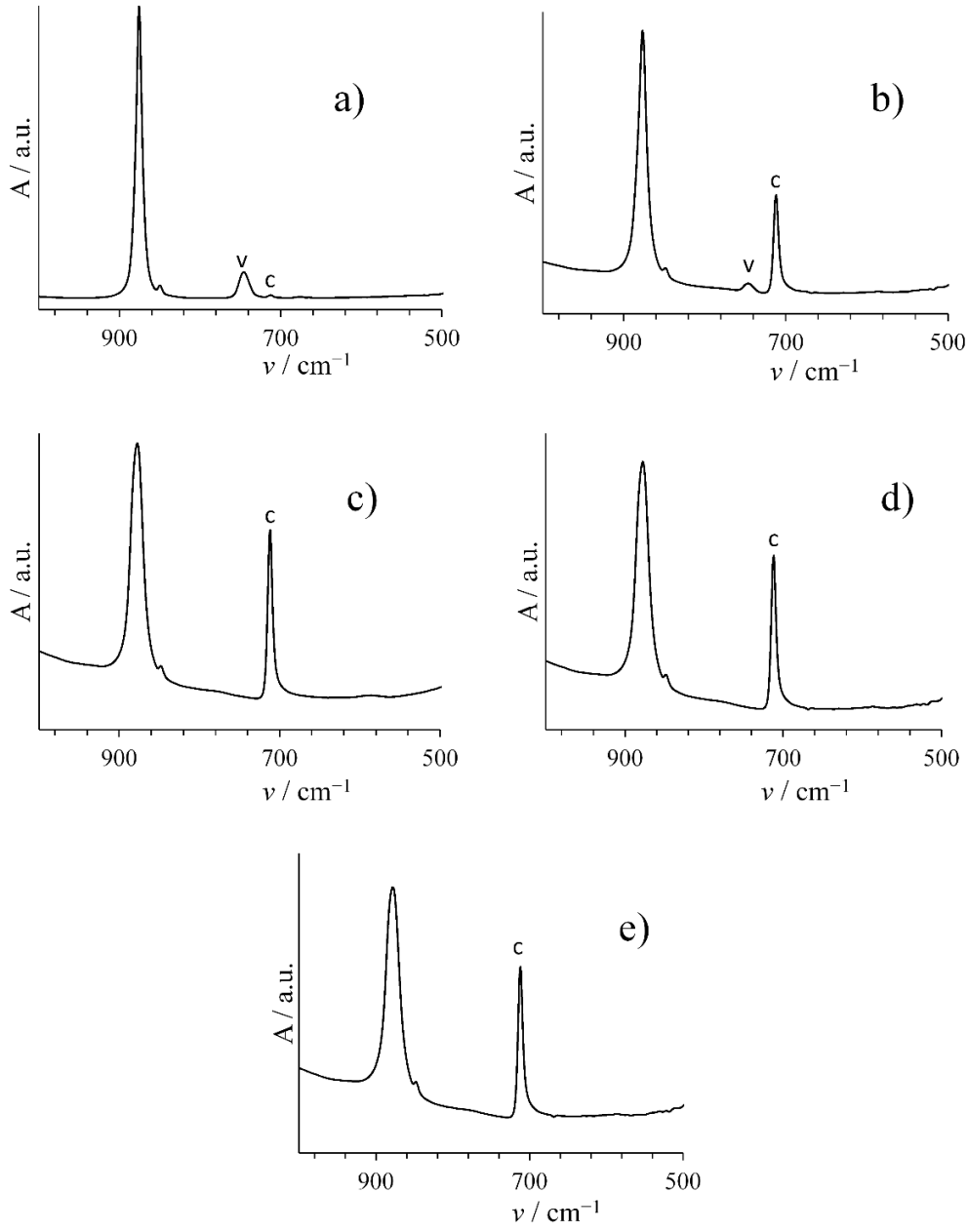


Figure SI4. FTIR spectra of the precipitates obtained in the system with $c(Li^+)$ = 0.5 mol dm^{-3} trough transformation time; a) 10 min of ultrasonic irradiation, b) 48 h, c) 72 h and d) 96 h. * v indicates vaterite. # c indicates calcite.

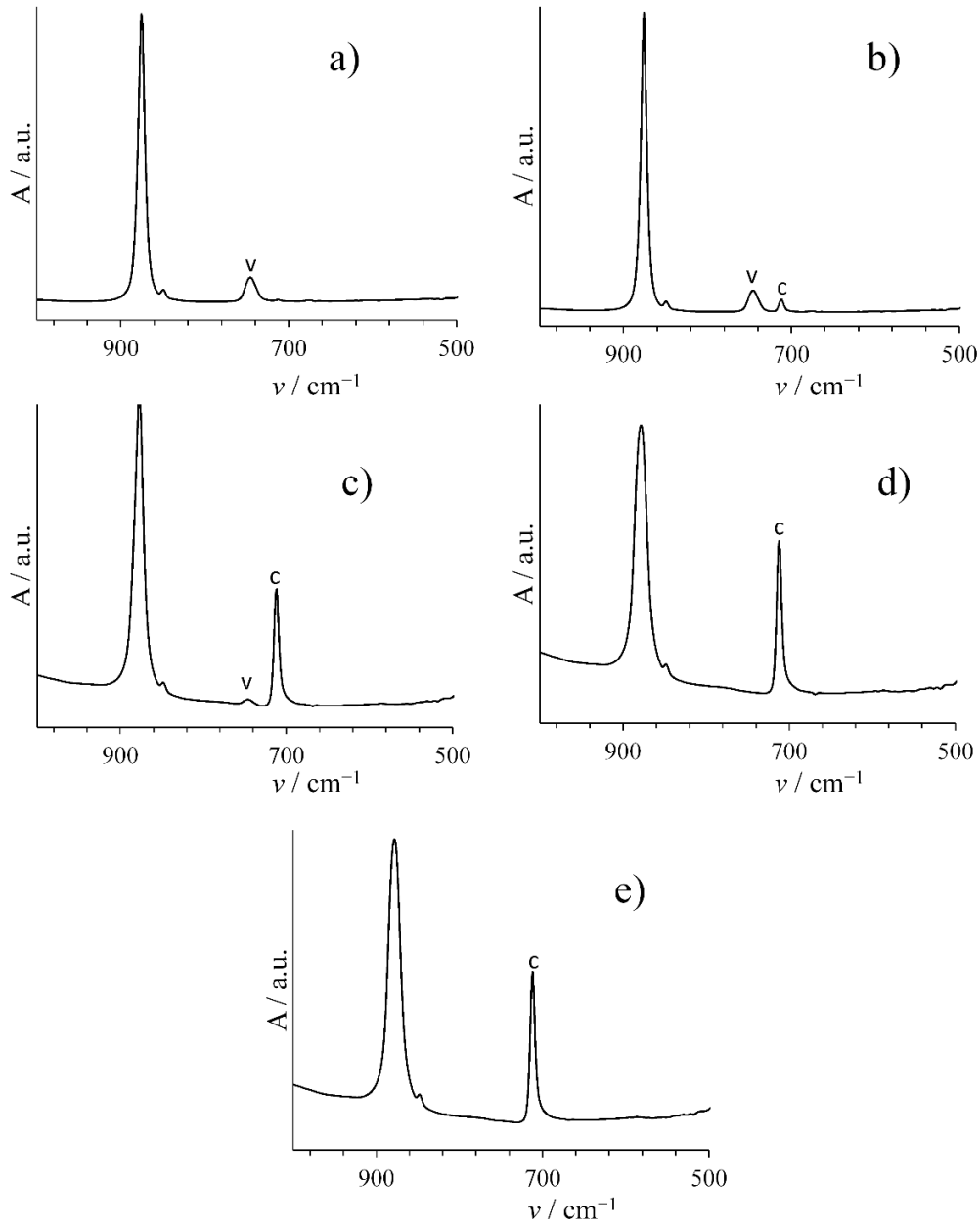


Figure SI5. FTIR spectra of the precipitates obtained in the system with $c(Li^+)$ = 0.7 mol dm^{-3} trough transformation time; a) 10 min of ultrasonic irradiation, b) 48 h, c) 72 h and d) 96 h. * v indicates vaterite. # c indicates calcite.

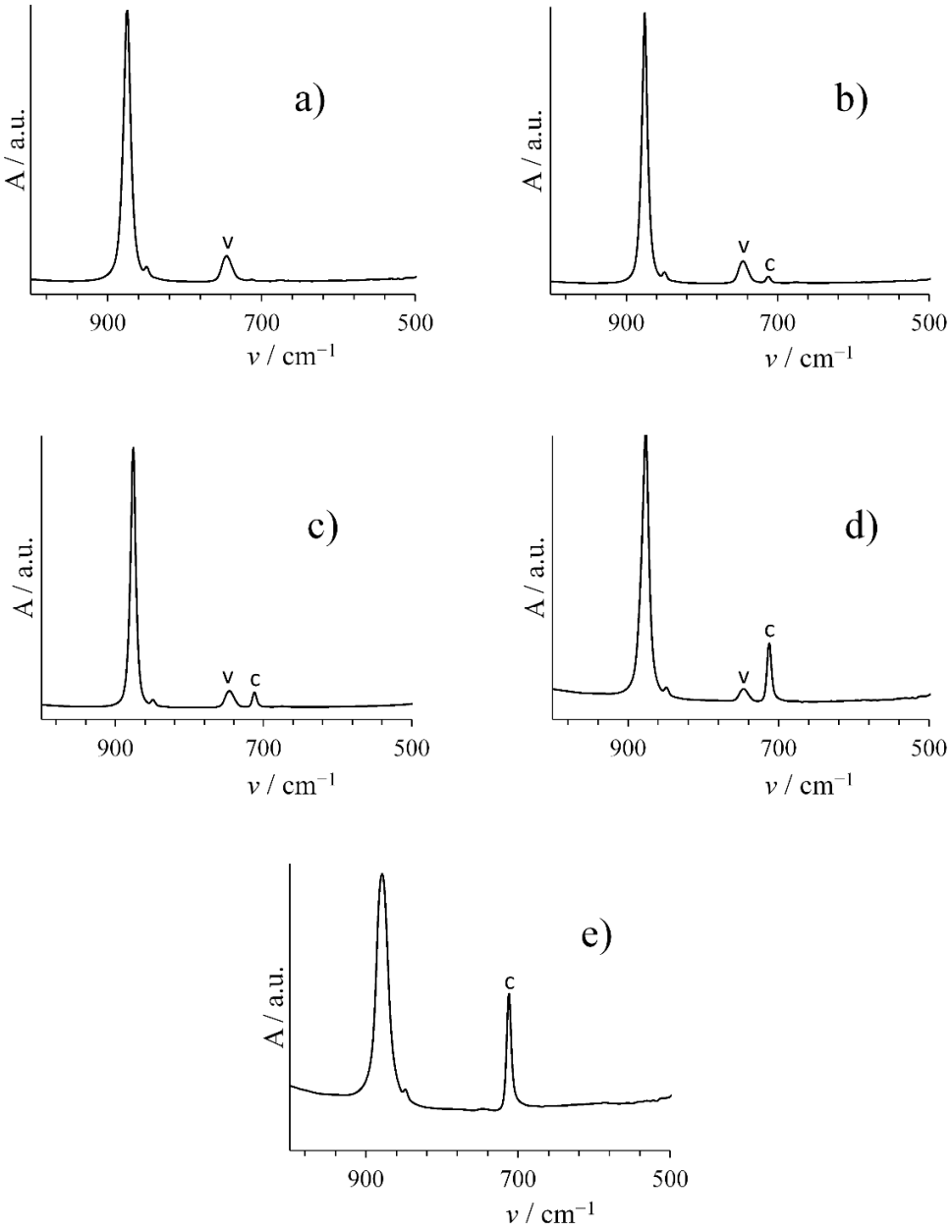


Figure SI6. FTIR spectra of the precipitates obtained in the system with $c(Li^+)$ = 1.0 mol dm^{-3} trough transformation time; a) 10 min of ultrasonic irradiation, b) 48 h, c) 72 h and d) 96 h. * v indicates vaterite. # c indicates calcite.

Table SI1. Assignment of IR bands in FTIR spectra in all systems through transformation time.

Wavenumber/ cm^{-1}	**Band assignment***
	Calcite
1425	ν_3, asymmetric C−O stretching mode
876	ν_2, CO_3 out of plane deformation mode
713	ν_4, O−C−O bending (in plane deformation) mode
	Calcite and vaterite mixture
1485	ν_3, asymmetric C−O stretching mode
1423	ν_3, asymmetric C−O stretching mode
1088	ν_1, symmetric C−O stretching mode
876	ν_2, CO_3 out of plane deformation mode
746	ν_4, O−C−O bending (in plane deformation) mode
713	ν_4, O−C−O bending (in plane deformation) mode

*Band assignment were done according to F.A. Andersen, Lj. Brečević: Infrared spectra of amorphous and crystalline calcium carbonate, *Acta Chim. Scand.* **45** (1991) 1018-1024.

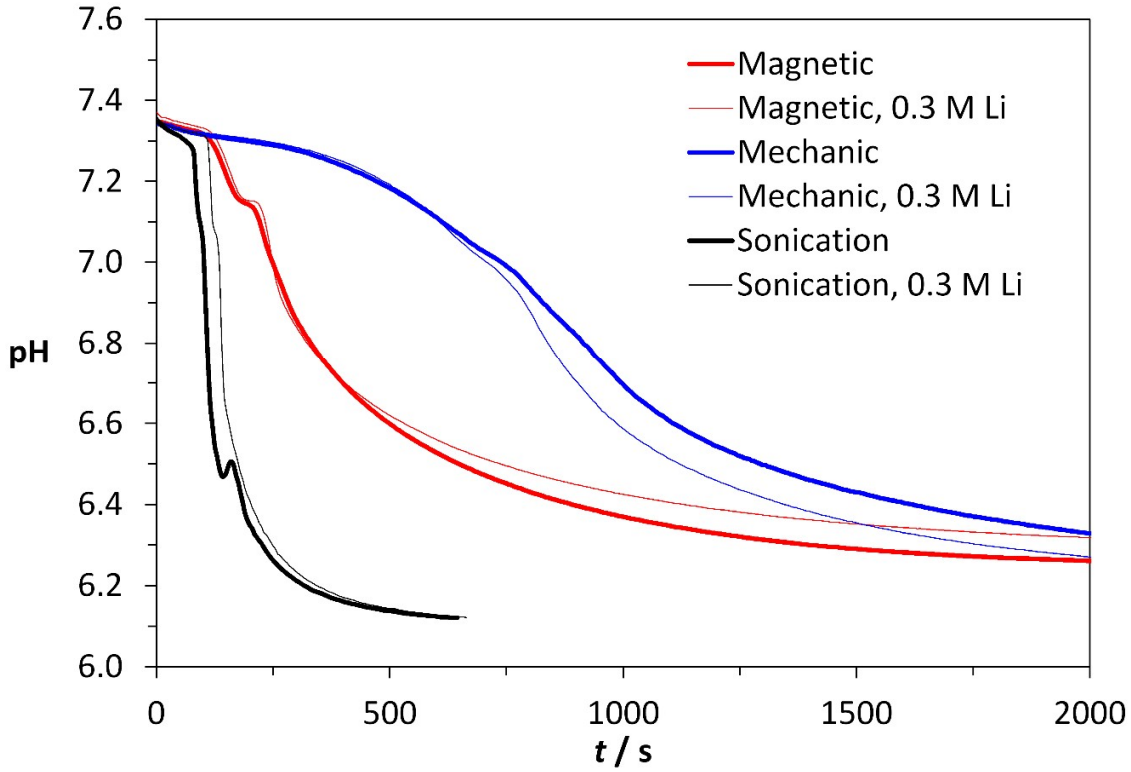
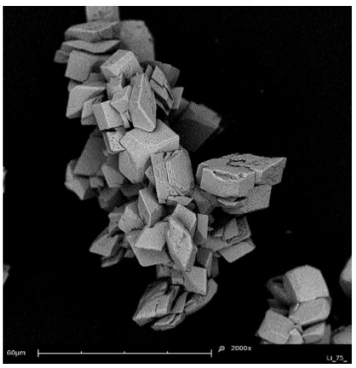
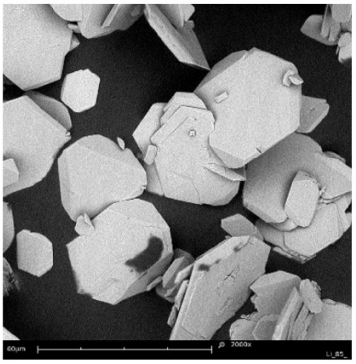


Figure SI7. The progress curves, pH vs time, of the precipitation systems ($c_i(CaCl_2) = c_i(NaHCO_3)$ = 0.1 mol dm^{-3}; $c(Li^+)$ = 0.3 mol dm^{-3} (thin lines) and no Li^+ addition (thicks lines), stirred by different devices (mechanic - blue, magnetic – red, sonication – black).

Mechanical, 60 minutes, $c(Li^+)$ = 0.3 mol dm^{-3}



Magnetic, 60 minutes, $c(Li^+)$ = 0.3 mol dm^{-3}



Sonication, 10 minutes, $c(Li^+)$ = 0.3 mol dm^{-3}

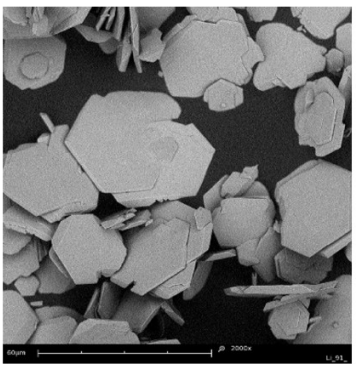


Figure SI8. Scanning electron images of calcite samples obtained after 5 days of aging, in the precipitation systems ($c_i(CaCl_2) = c_i(NaHCO_3)$ = 0.1 mol dm^{-3}; $c(Li^+)$ = 0.3 mol dm^{-3}). The systems were initially agitated for 60 minutes by means of mechanical or magnetical stirrer, or for 10 minutes by applying ultrasonic irradiation. Scale bars: 60 μm.

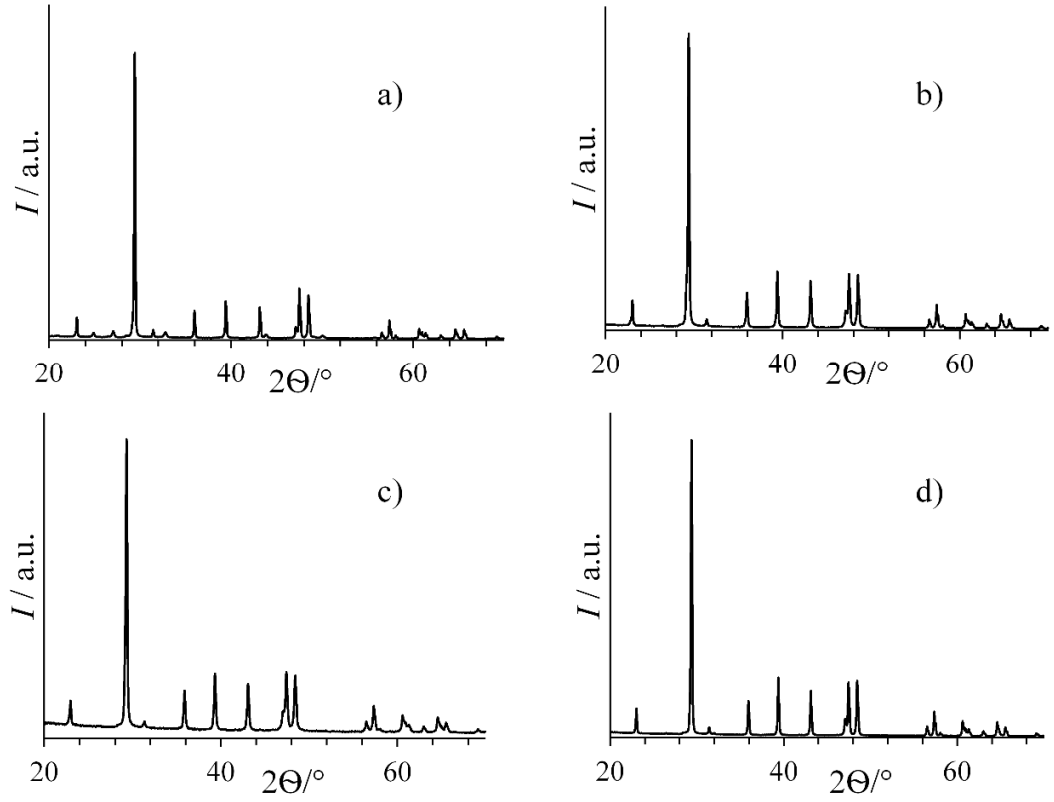


Figure SI9. PXRD patterns of the precipitates obtained in the system with $c(Li^+)$ = 0 mol dm^{-3} trough transformation time; a) 10 min of ultrasonic irradiation, b) 48 h, c) 72 h and d) 96 h.

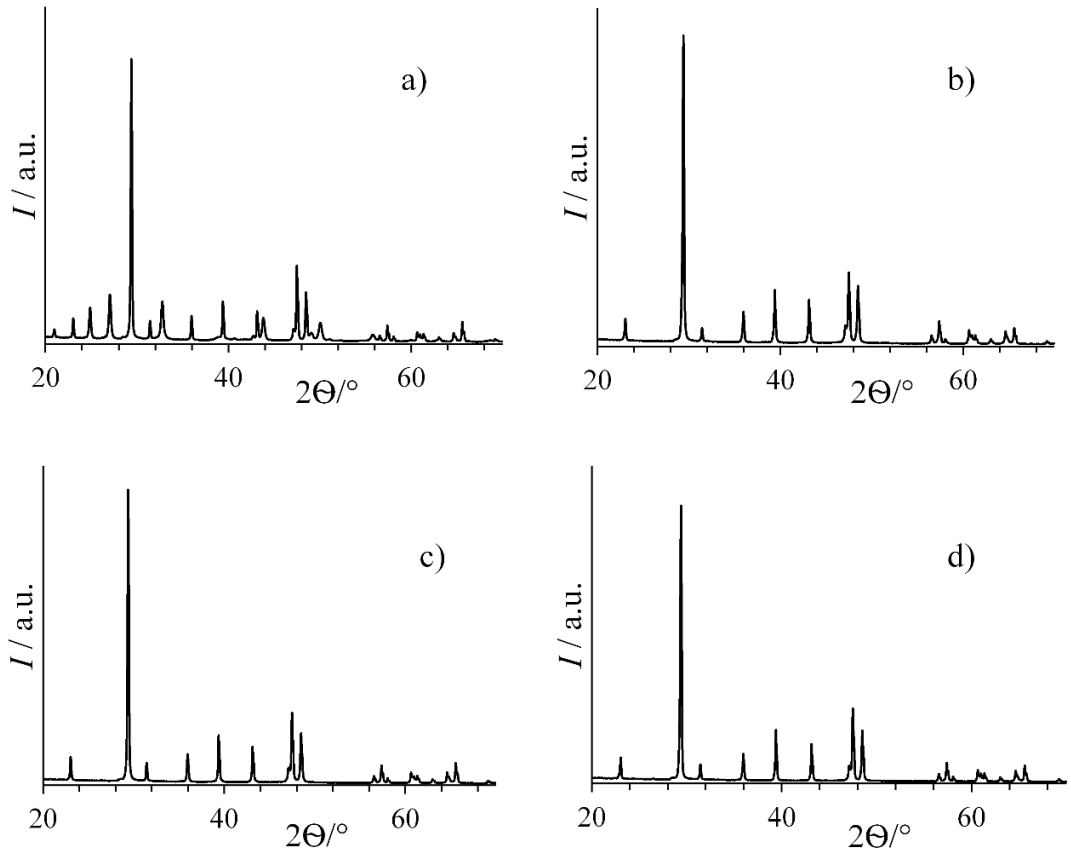


Figure SI10. PXRD patterns of the precipitates obtained in the system with $c(Li^+)$ = 0.1 mol dm^{-3} trough transformation time; a) 10 min of ultrasonic irradiation, b) 48 h, c) 72 h and d) 96 h.

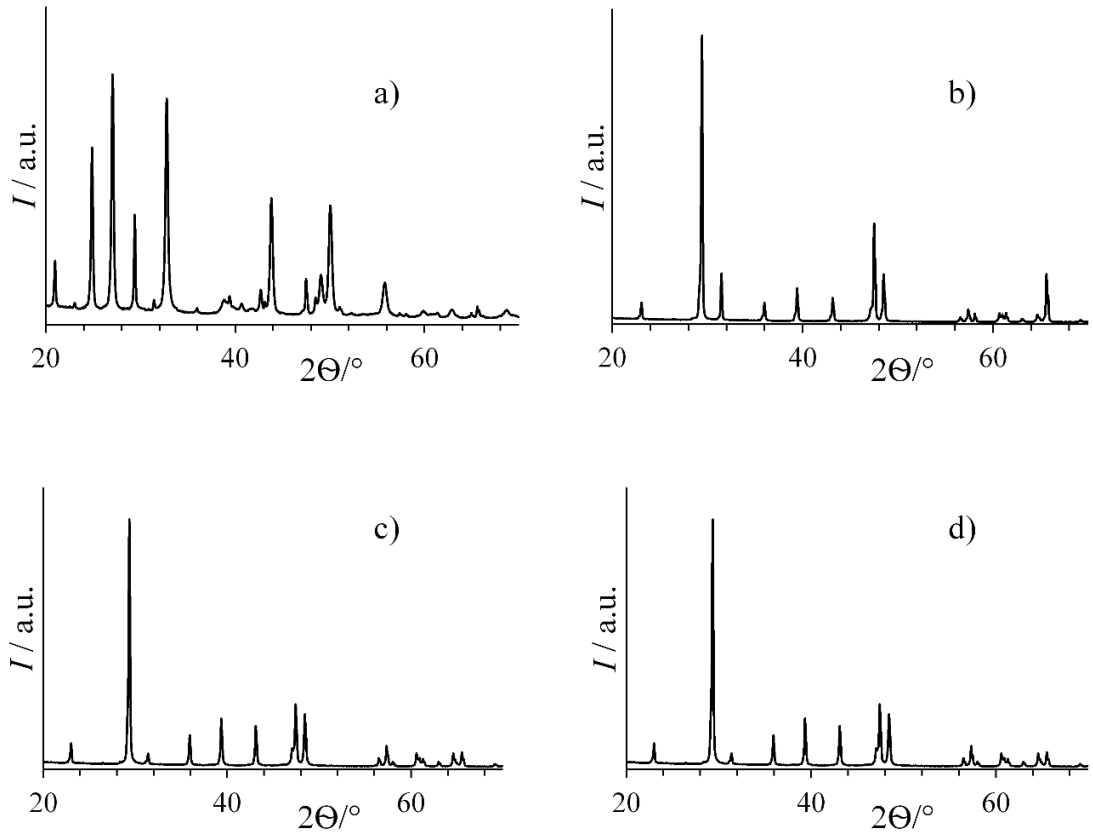


Figure SI11. PXRD patterns of the precipitates obtained in the system with $c(Li^+)$ = 0.3 mol dm^{-3} trough transformation time; a) 10 min of ultrasonic irradiation, b) 48 h, c) 72 h and d) 96 h

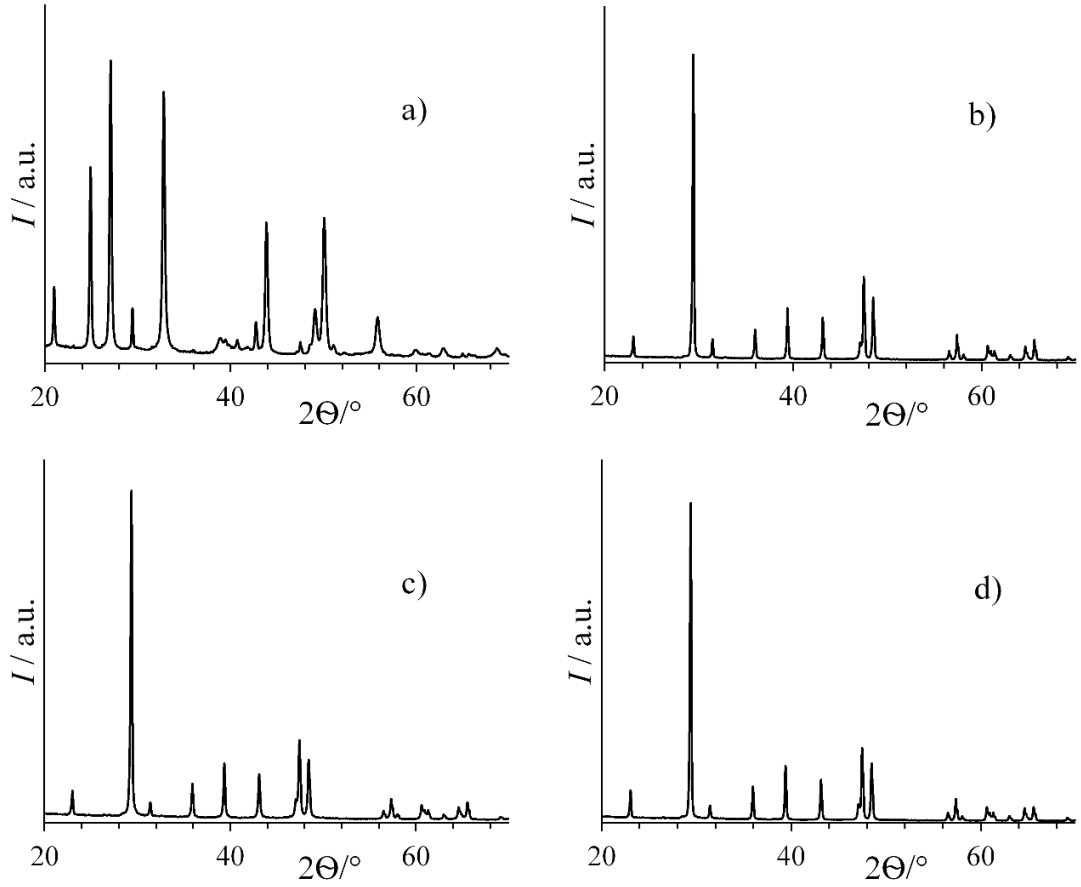


Figure SI12. PXRD patterns of the precipitates obtained in the system with $c(Li^+)$ = 0.5 mol dm^{-3} trough transformation time; a) 10 min of ultrasonic irradiation, b) 48 h, c) 72 h and d) 96 h.

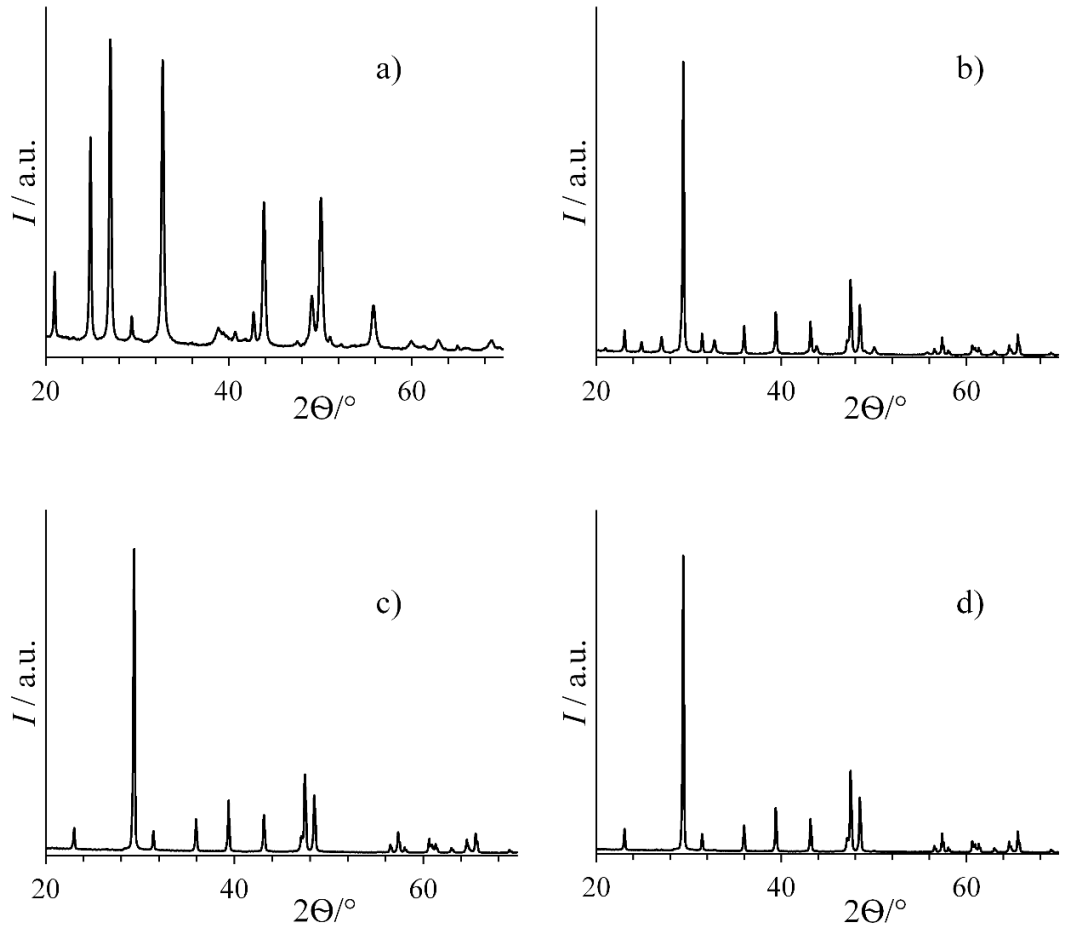


Figure SI13. PXRD patterns of the precipitates obtained in the system with $c(Li^+)$ = 0.7 mol dm^{-3} trough transformation time; a) 10 min of ultrasonic irradiation, b) 48 h, c) 72 h and d) 96 h.

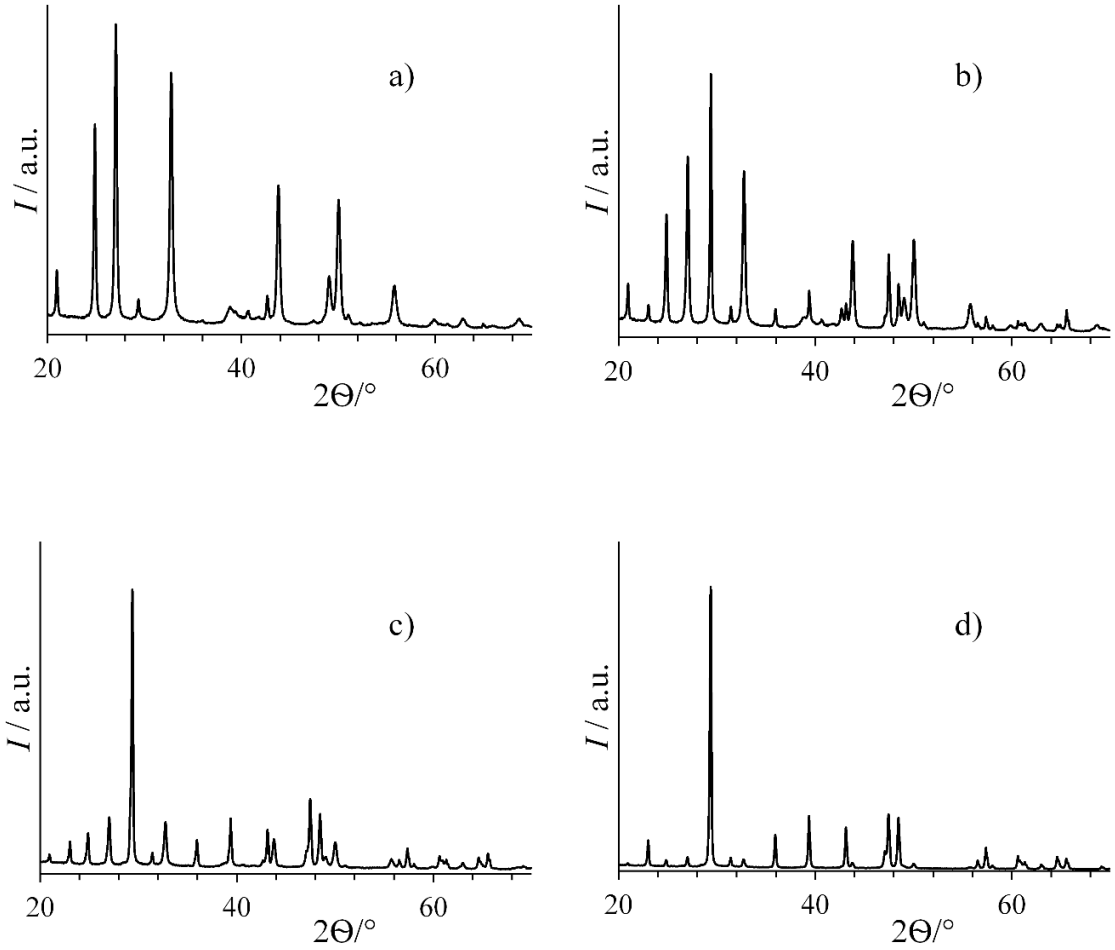


Figure SI14. PXRD patterns of the precipitates obtained in the system with $c(Li^+)$ = 1.0 mol dm^{-3} trough transformation time; a) 10 min of ultrasonic irradiation, b) 48 h, c) 72 h and d) 96 h.

Table SI2. Assignment of peaks in PXRD patterns in all systems through transformation time.

2θ / º	(hkl)
Calcite	
29.4	104
35.9	110
39.4	113
43.1	202
47.5	018
48.5	116
Calcite and vaterite mixture	
24.9	020
27.1	021
29.4	104
32.7	022
35.9	110
39.4	113
40.7	023
43.8	130
50.0	114
55.8	222

*PXRD pattern was indexed according to JCPDS card No. 05-0586 (calcite) and JCPDS card No: 33-0268 (vaterite)

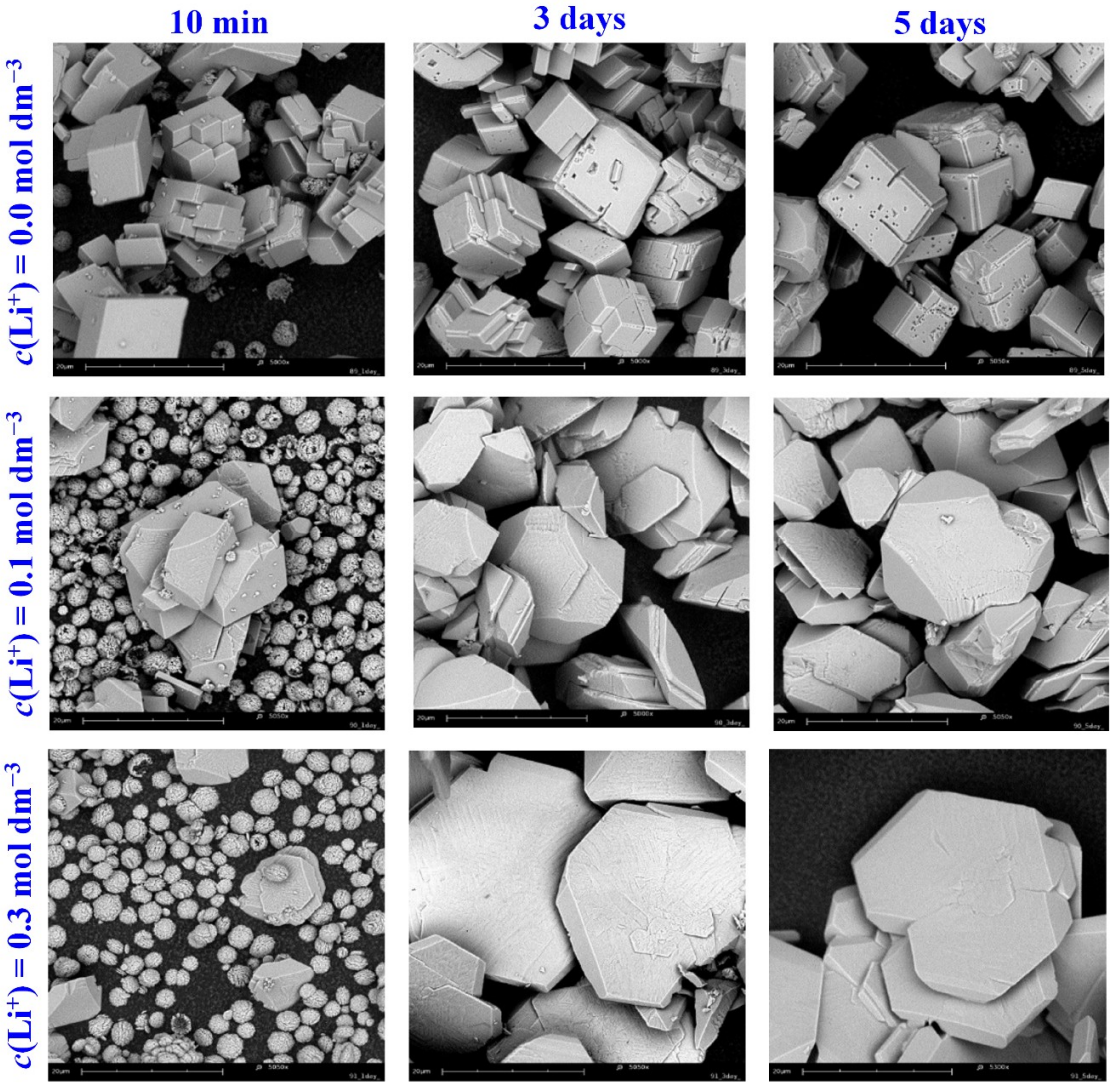


Figure SI15. Scanning electron micrographs of calcite samples obtained in the reference system, $c(Li^+)$ = 0, after 10 min of ultrasonic irradiation, tree and five days: a), b) and c) respectively; and in the systems with lithium addition in the same period for: d), e) and f) at $c(Li^+)/c(Ca^{2+})$ = 1 respectively and g), h) and i) at $c(Li^+)/c(Ca^{2+})$= 3 respectively, at P = 40 W, ts = 10 min and room temperature. Scale bar is 20 µm.

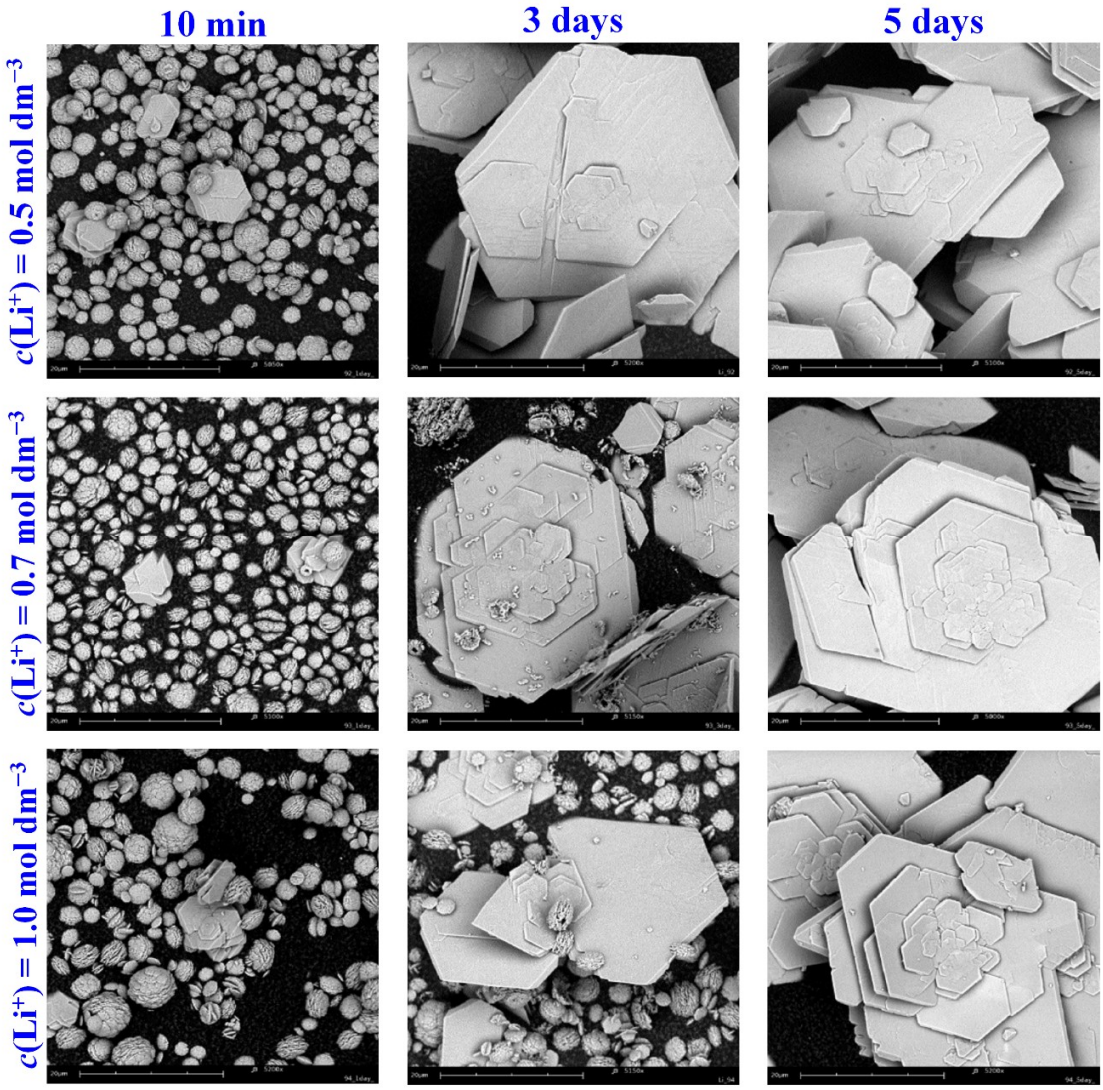
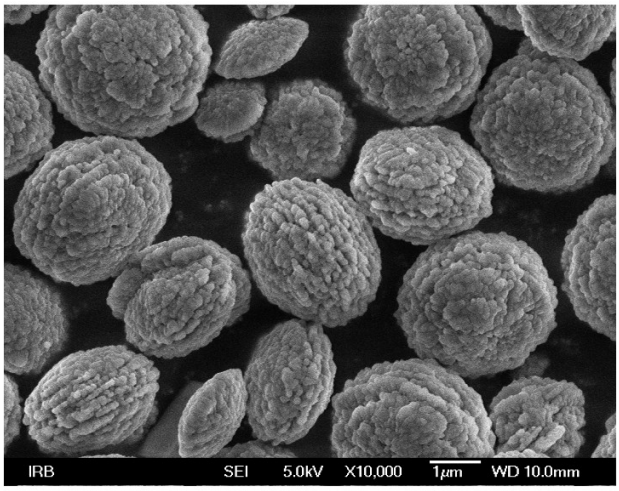


Figure SI16. Scanning electron micrographs of calcite samples obtained in the systems with lithium addition after 10 min of ultrasonic irradiation, tree and five days: a), b) and c) at $c(Li^+)/c(Ca^{2+}) = 5$; d), e) and f) at $c(Li^+)/c(Ca^{2+}) = 7$; and g), h) and i) at $c(Li^+)/c(Ca^{2+}) = 10$ respectively, at P = 40 W, ts = 10 min and room temperature. Scale bar corresponds for 20 μm.

Sonication, 10 minutes, $c(Li^+)$ = 0 mol dm^{-3}



Sonication, 10 minutes, $c(Li^+)$ = 0.3 mol dm^{-3}

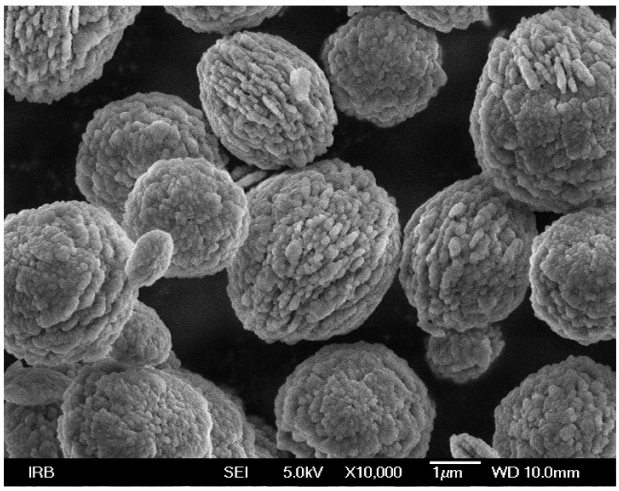


Figure SI17. Vaterite samples prepared in the systems ($c_i(CaCl_2) = c_i(NaHCO_3)$ = 0.1 mol dm^{-3}; $c(Li^+)$ = 0.3 mol dm^{-3} and no Li^+ addition, sonicated for 10 minutes. The scale bar is 1 μm.

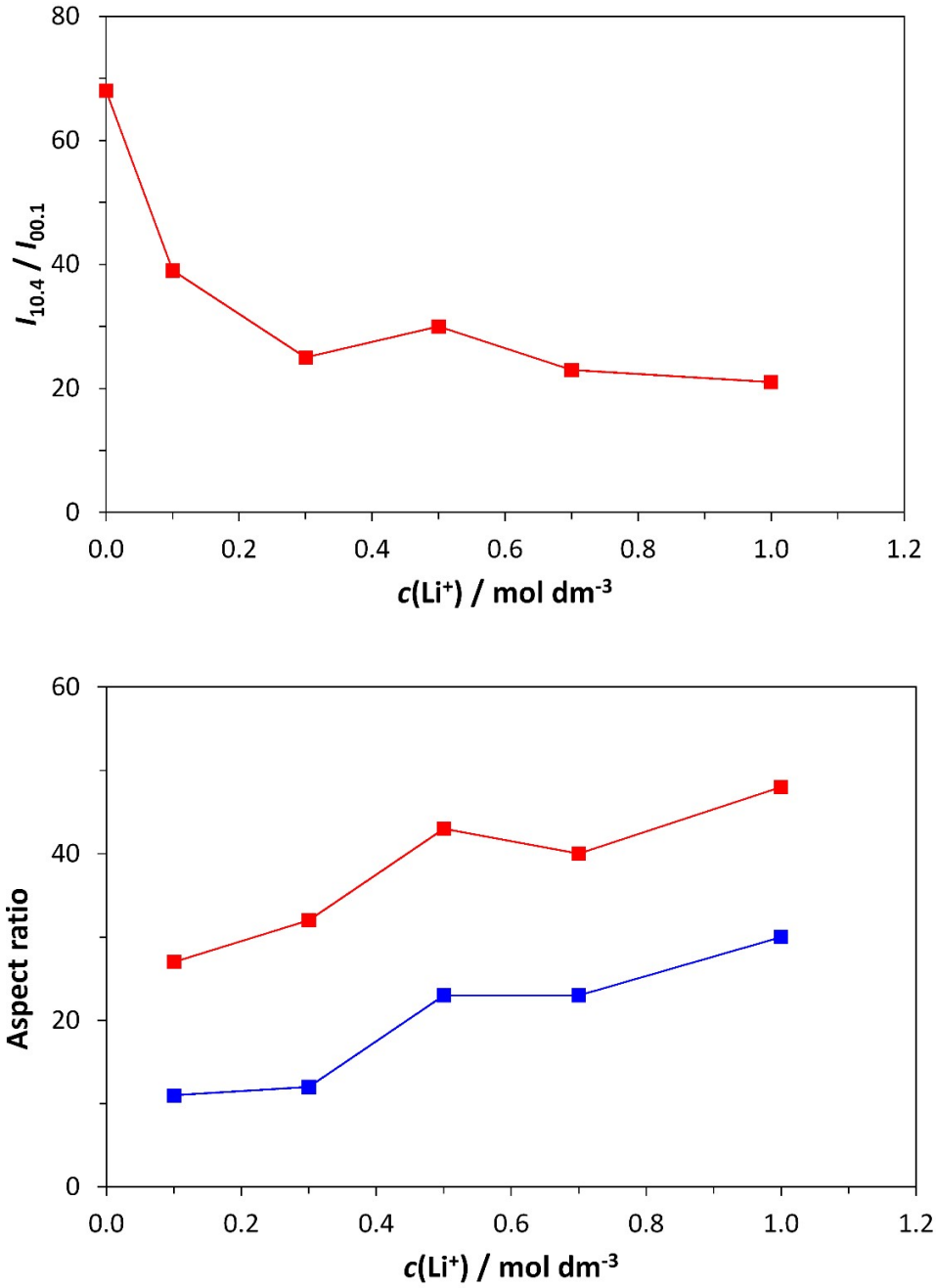


Figure SI18. (Top) Relative intensities of {00.1} with respect to the {10.4} calcite diffraction peaks shown as a function of solution concentration of Li^+ in the samples aged for 5 days. (Bottom) The aspect ratios of the plate-like calcite crystals shown as a function of solution concentration of Li^+ in the samples aged for 5 days. The ratios are shown for two size classes of crystals, indicated in the Table 1.

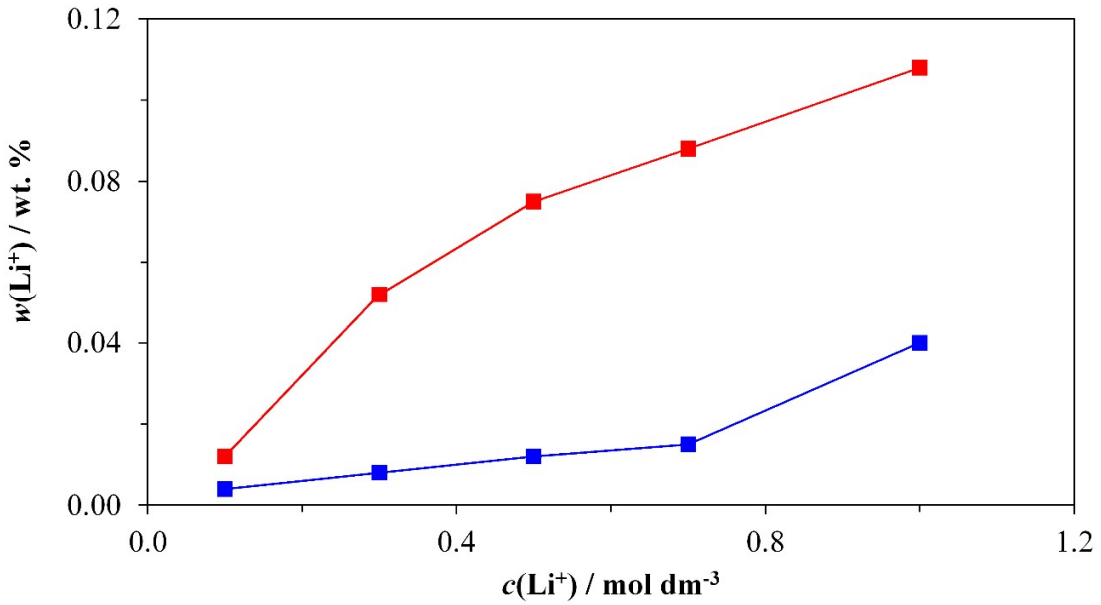


Figure SI19. Amount of lithium in precipitate separated from the solution after 10 minutes of sonication (red symbols) and after 5 days of aging of precipitate (blue), shown as a function of the initial concentration of lithium.

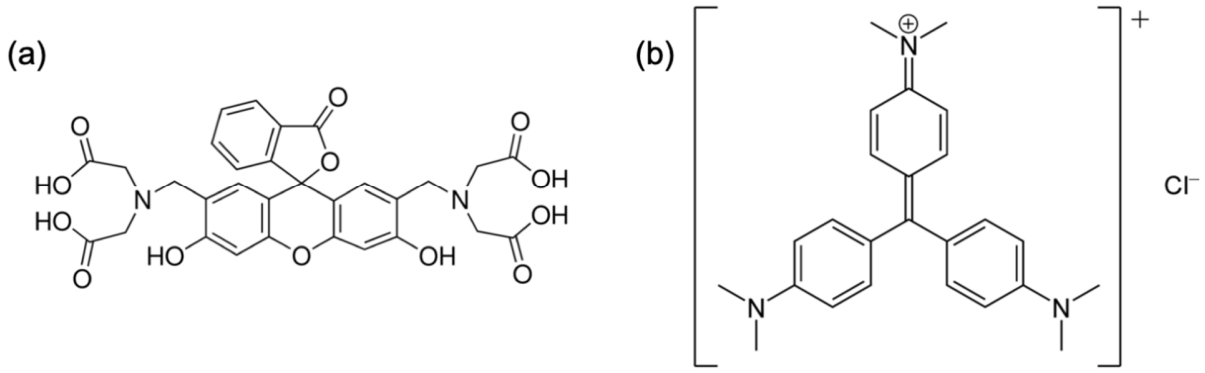


Figure SI20. Molecular structure of (a)calcein and (b) crystal violet.

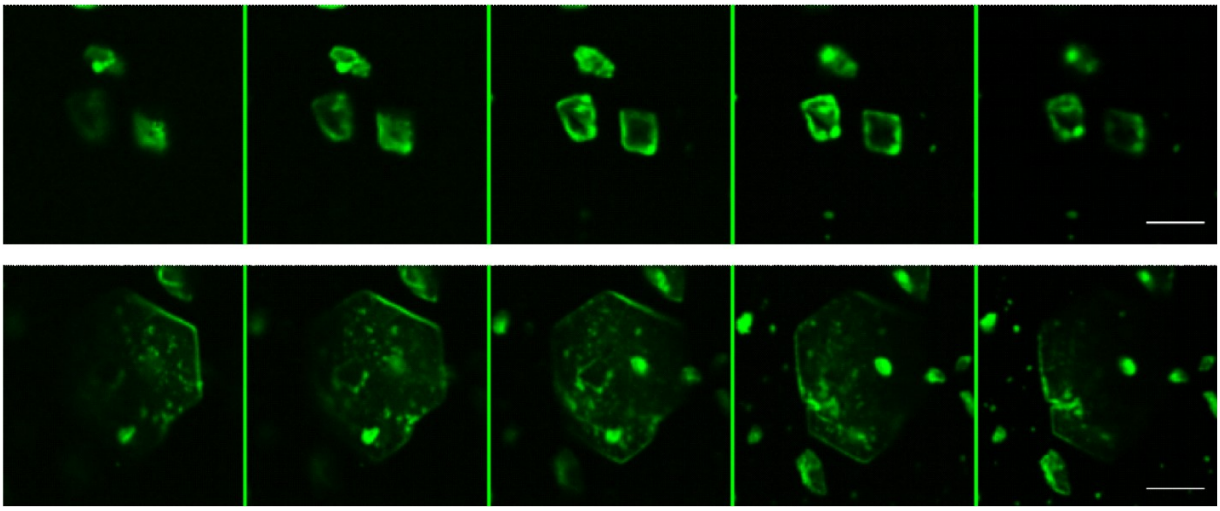


Figure SI21. Confocal microscopy images showing consecutive crystal section of the samples shown in Fig. 4. Top row: {10.4} crystals, bottom row, {00.1} crystals. The scale bar is 10 μm

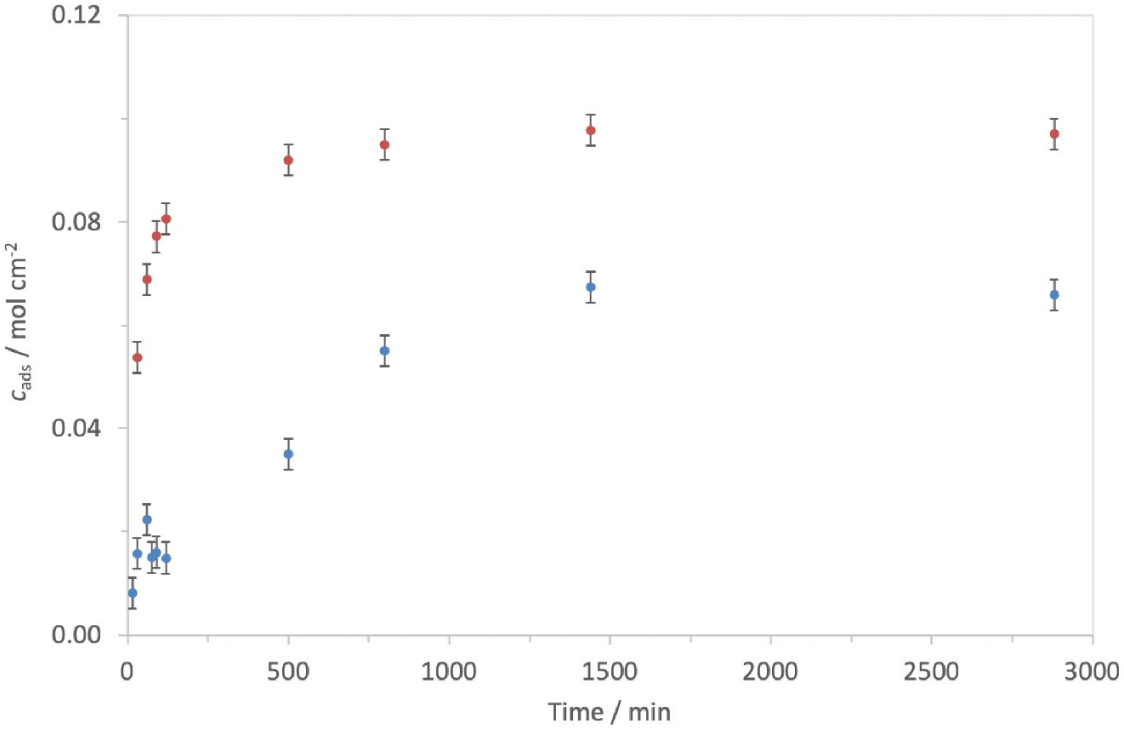


Figure SI22. The kinetics of adsorption of respective dye molecules on the {10.4} calcite crystals. The red dots indicate crystal violet and the blue dots indicate calcein. The standard errors are reported.

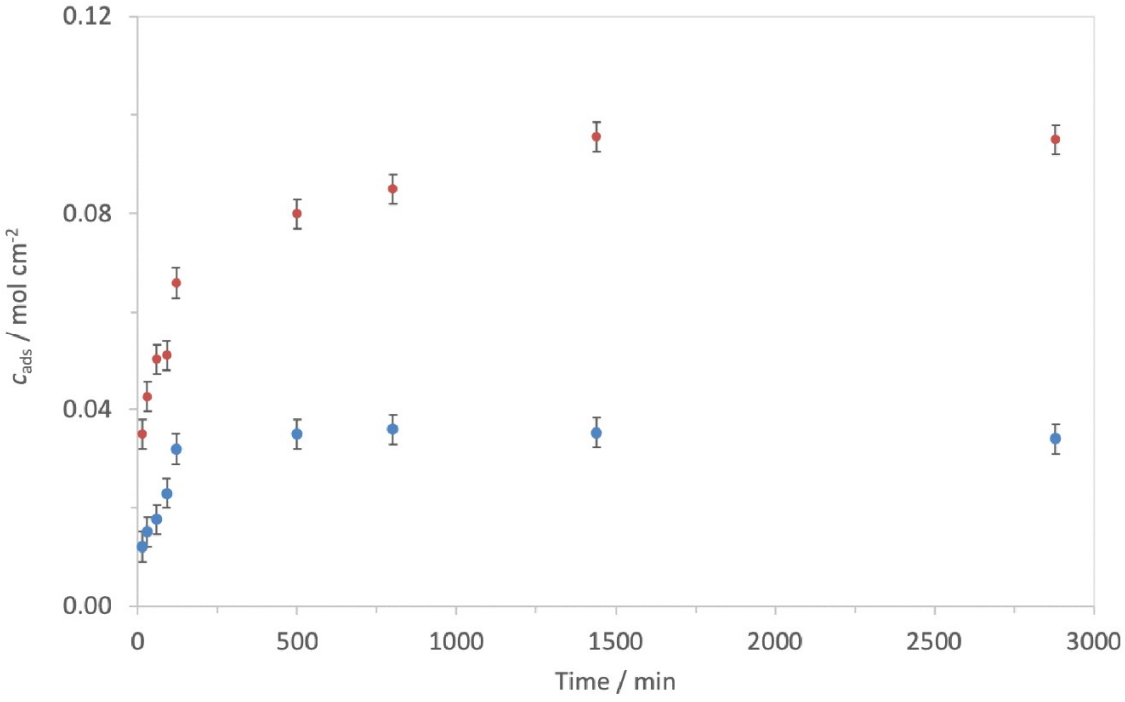


Figure SI23. The kinetics of adsorption of respective dye molecules on the {00.1} calcite crystals. The red dots indicate crystal violet and the blue dots indicate calcein. The standard errors are reported.