Table 1S. Attribution of main infrared absorption bands of EPS samples.

EPS (Exponential growth phase)	EPS (Early stationary phase)	EPS (Late stationary phase)	Band assignment
Wavenumber (cm⁻¹)			
3342	/	3351	nOH
included in OH absorption band	3281	included in OH absorption band	Amide A (nN–H)
/	3077	/	Amide B (nN–H)
2927	2959, 2922, 2851	2938	$n_{C–H}$
1730	/	1727	$n_{C=O}$
1658	1648	1650	Amide I ($n_{C=O}$)
1543	1542	1549	Amide II ($n_{C–N}$)
1376	1448, 1401	1375	$d_{C–H}$
/	1305	/	Amide III ($n_{C–N}$)
/	1242	1244	$d_{N–H}$
1136	1127		$n_{C–O–C}$
1043	1070	1038	$n_{C–O}$
867	/	811	$g_{C–H}$
582	/	/	$d_{C–X}$
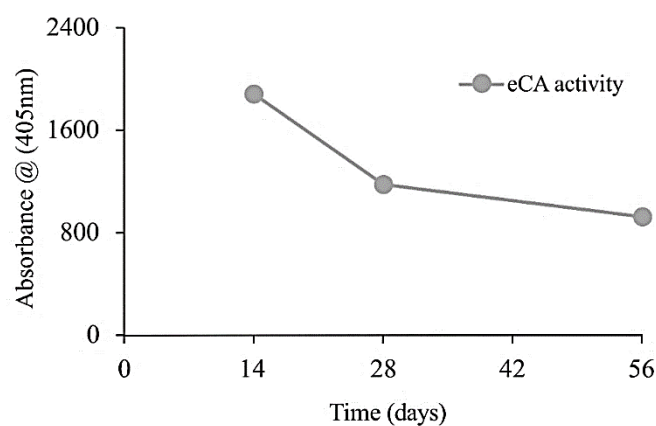
Figure 1S. Extracellular carbonic anhydrase (eCA) activity measured at days 14, 28 and 56 of *Synechococcus* PCC 7942 growth experiment.
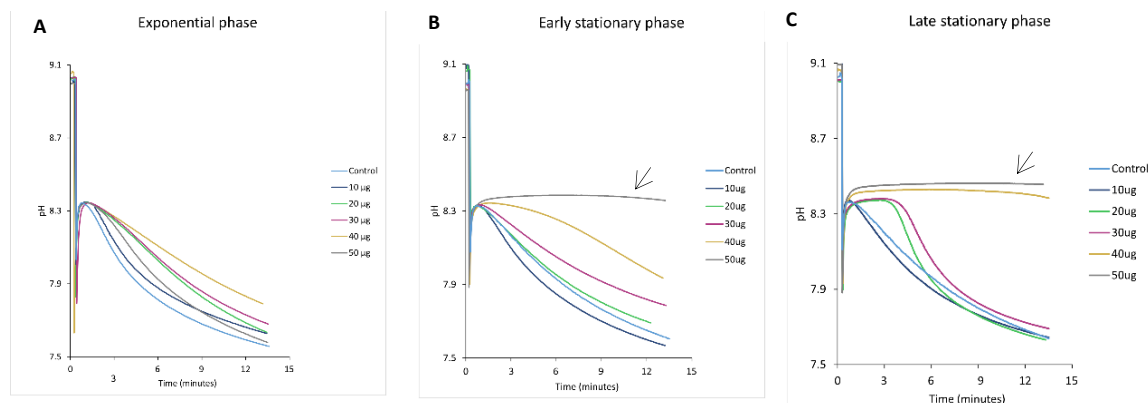
Figure 2S. Replication of the *in vitro* inhibition of calcium carbonate precipitation experiment by using EPS extracted during exponential (A), early (B) and late (C) stationary phases of Synechococcus growth experiment. A negative control (no EPS) and EPS extracts of concentrations of 10, 20, 30, 40, and 50 µg.mL^{-1} were used in the CaCO$_3$ inhibition assay. The decrease of pH indicates precipitation and a plateau inhibition of carbonate mineral precipitation. A larger plateau (> 50 µg) indicates stronger inhibition of calcium carbonate precipitation (e.g., see black arrows in panel B-C).
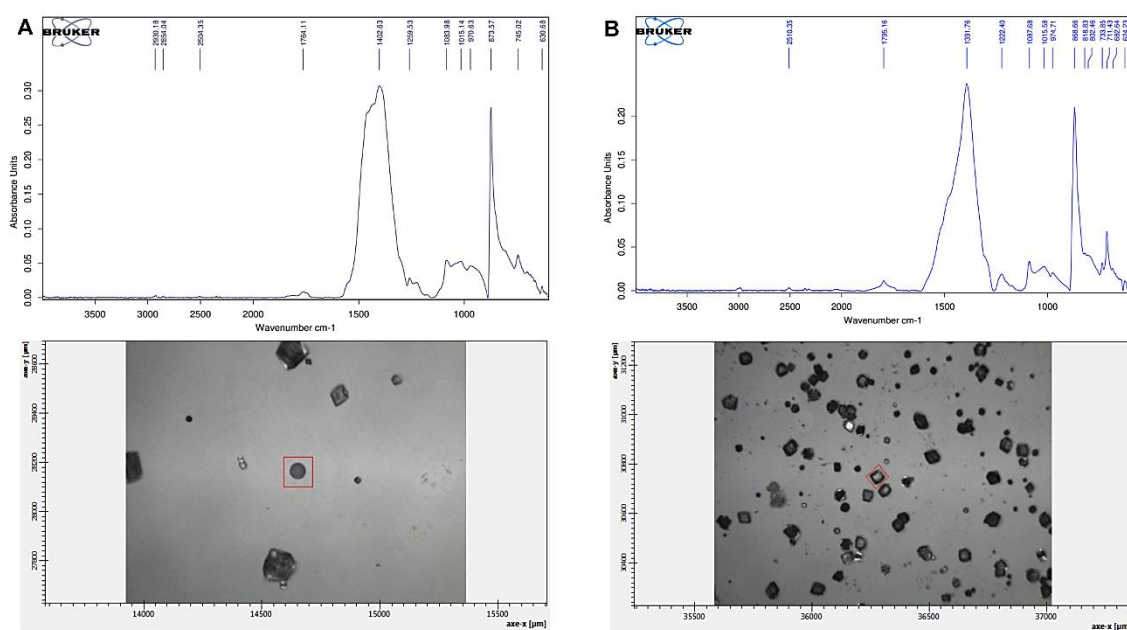
Figure 3S. FT-IR spectra of (A) vaterite and (B) calcite. The two calcium carbonate polymorphs precipitated in EPS solutions produced during two *Synechococcus* growth phases. Data shown EPS produced (A) during exponential growth phase a concentration of 3 µg·mL^{-1} and (B) during the late stationary phase with a concentration of 36 µg·mL^{-1}.