



*Supplement of*

## **Properties of exopolymeric substances (EPSs) produced during cyanobacterial growth: potential role in whiting events**

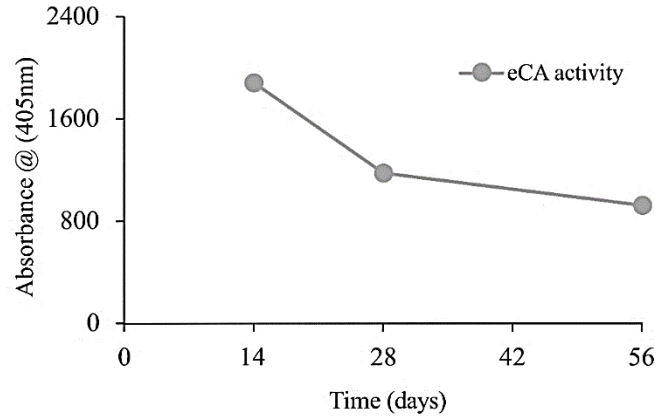
**Marlisa Martinho de Brito et al.**

*Correspondence to:* Marlisa Martinho de Brito ([marlisa\\_de-brito@etu.u-bourgogne.fr](mailto:marlisa_de-brito@etu.u-bourgogne.fr))

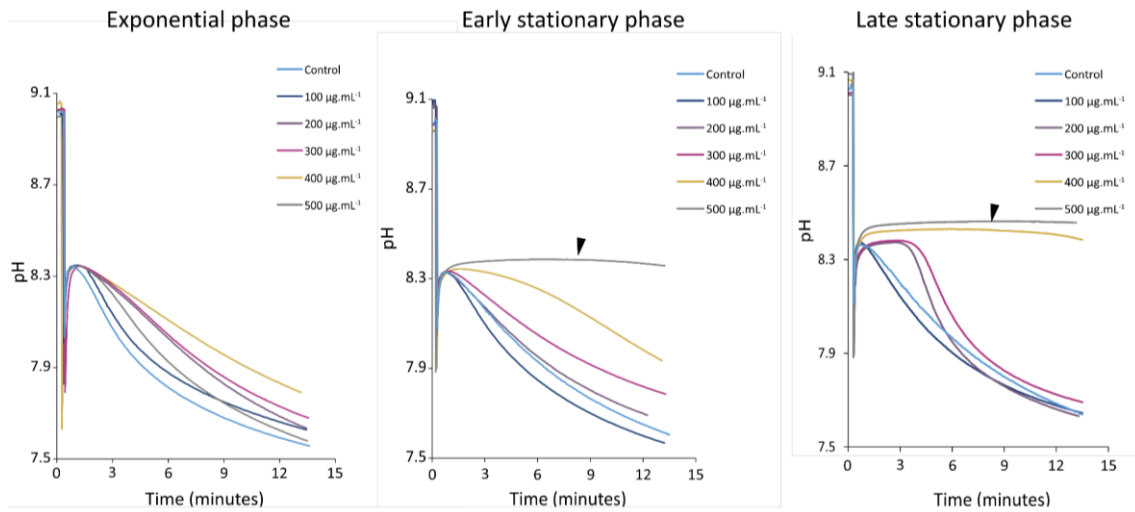
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**Table S1.** Attribution of main infrared absorption bands of EPS samples.

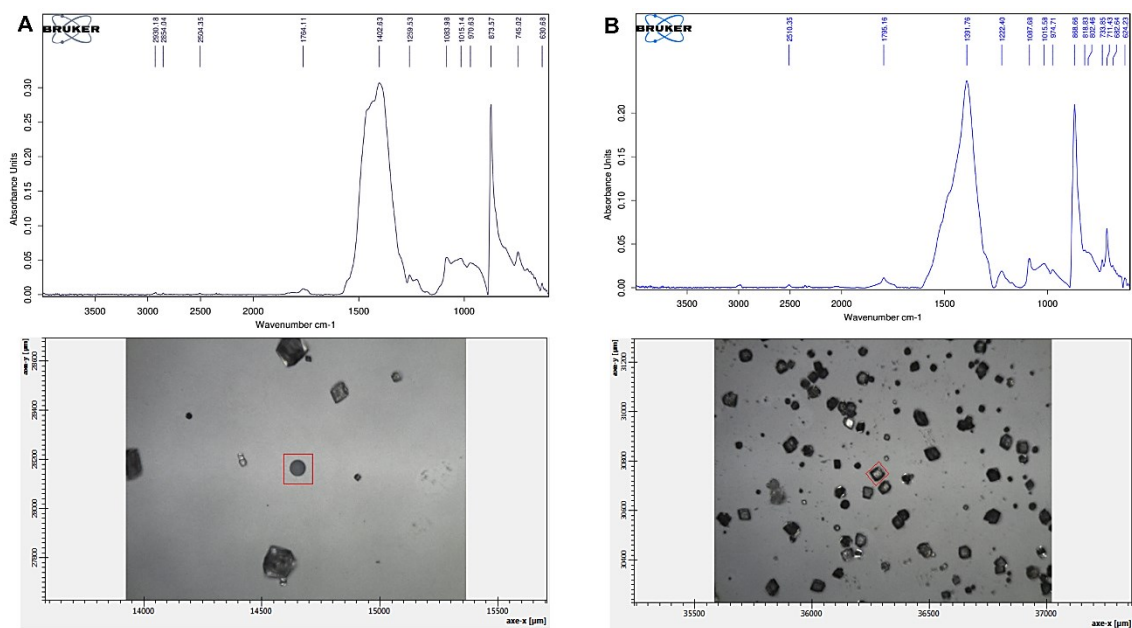
| EPS<br>(Exponential growth<br>phase) | EPS<br>(Early stationary phase) | EPS<br>(Late stationary<br>phase) | Band<br>assignment        |
|--------------------------------------|---------------------------------|-----------------------------------|---------------------------|
| <b>Wavenumber (cm<sup>-1</sup>)</b>  |                                 |                                   |                           |
| 3342                                 | /                               | 3351                              | <i>n</i> OH               |
| included in OH<br>absorption band    | 3281                            | included in OH absorption<br>band | Amide A ( <i>n</i> N–H)   |
| /                                    | 3077                            | /                                 | Amide B ( <i>n</i> N–H)   |
| 2927                                 | 2959, 2922, 2851                | 2938                              | <i>n</i> C–H              |
| 1730                                 | /                               | 1727                              | <i>n</i> C=O              |
| 1658                                 | 1648                            | 1650                              | Amide I ( <i>n</i> C=O)   |
| 1543                                 | 1542                            | 1549                              | Amide II ( <i>n</i> C–N)  |
| 1376                                 | 1448, 1401                      | 1375                              | <i>d</i> C–H              |
| /                                    | 1305                            | /                                 | Amide III ( <i>n</i> C–N) |
| /                                    | 1242                            | 1244                              | <i>ν</i> S=O              |
| 1136                                 | 1127                            | /                                 | <i>n</i> C–O–C            |
| 1043                                 | 1070                            | 1038                              | <i>n</i> C–O              |
| 867                                  | /                               | 811                               | <i>g</i> C–H              |
| 582                                  | /                               | /                                 | <i>d</i> C–X              |



**Figure S1.** Extracellular carbonic anhydrase (eCA) activity measured at days 14, 28 and 56 of *Synechococcus* PCC 7942 growth experiment.



**Figure S2.** 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  $\mu\text{g.mL}^{-1}$  were used in the  $\text{CaCO}_3$  inhibition assay. The decrease of pH indicates precipitation and a plateau inhibition of carbonate mineral precipitation. A larger plateau ( $> 50 \mu\text{g}$ ) indicates stronger inhibition of calcium carbonate precipitation (e.g., see black arrows in panel B-C).



**Figure S3.** 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  $3 \mu\text{g}\cdot\text{mL}^{-1}$  and (B) during the late stationary phase with a concentration of  $36 \mu\text{g}\cdot\text{mL}^{-1}$ .