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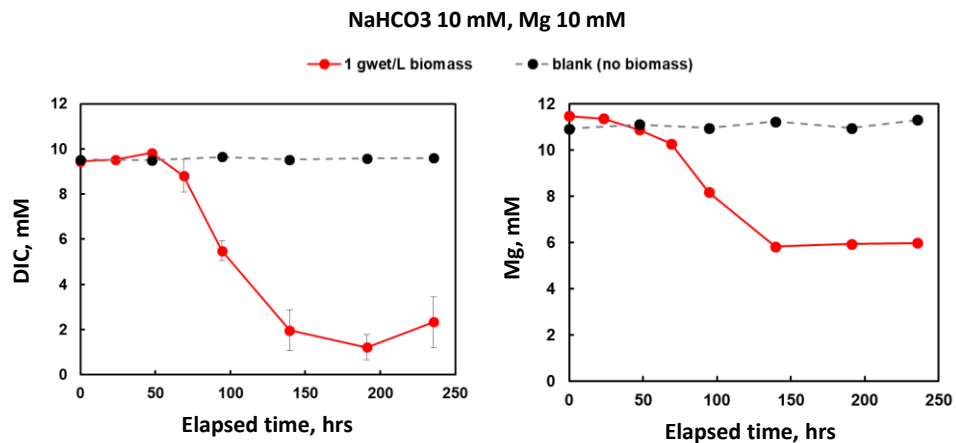


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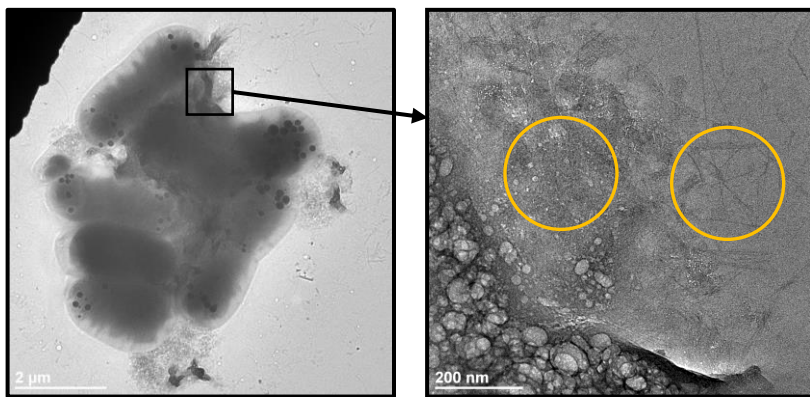
Chemical Geology

Carbon sequestration potential of Mg carbonate and silicate biomineralization in the presence of cyanobacterium *Synechococcus* --Manuscript Draft--

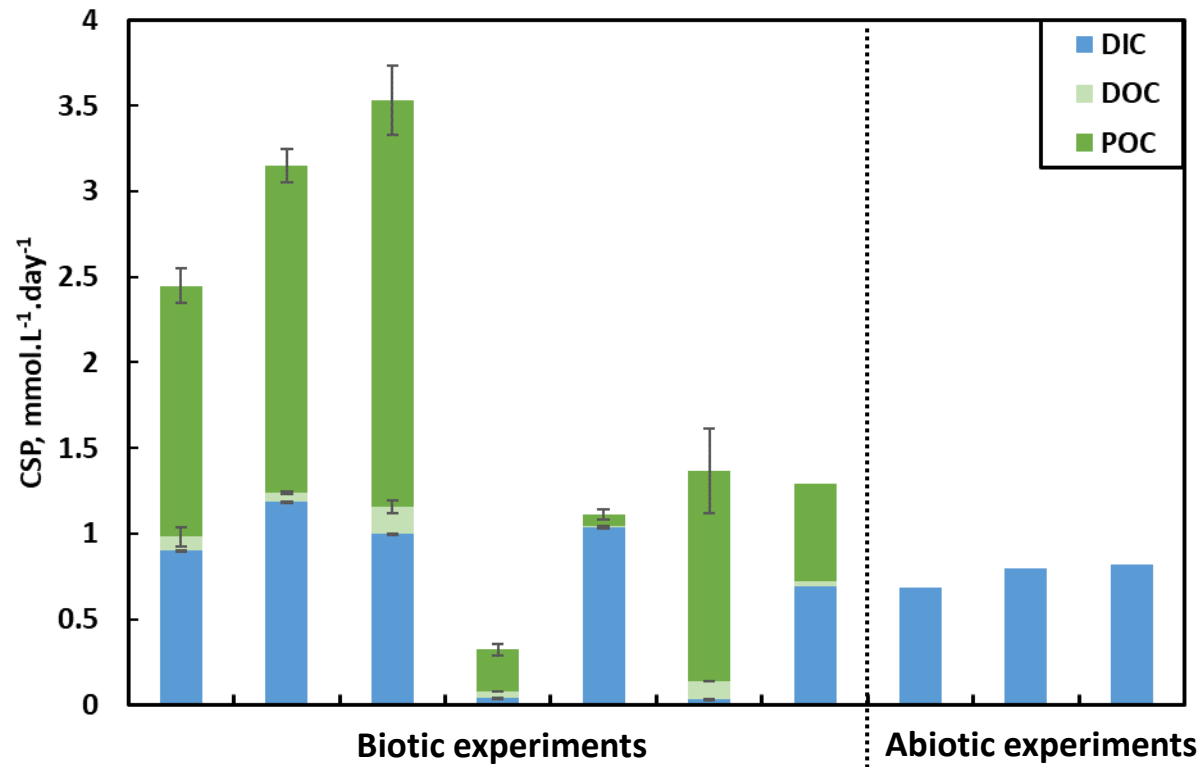
Manuscript Number:	CHEMGE14674
Article Type:	Research paper
Keywords:	carbon, sequestration, biomass, carbonates, silicates, cyanobacteria, hydromagnesite.
Abstract:	<p>Bacterially-induced sequestration of atmospheric CO₂ is at the forefront of geomicrobiological research due to high potential of this process in the mitigation of climate warming. Cyanobacteria have been known to form stromatolites for millions of years and could be used to enhance this process by sequestering carbon via the biomineralization of Mg and Ca carbonates. Currently, olivine (MgSiO₄) is considered as one of the most efficient silicate minerals suitable for CO₂ capture in the form of secondary Mg carbonates. However, the role of dissolved Si on the efficiency of biomineralization is not sufficiently well understood. The present study intended to reproduce in the laboratory the processes of biomineralization by <i>Synechococcus</i> sp. cyanobacteria extracted from modern stromatolites in a carbonate- and Mg-bearing medium containing various Si concentrations, in order to characterize the rates and stoichiometry of reactions as well as mineralogical nature of precipitates. The results demonstrated the dominant role of cyanobacterial metabolism in the precipitation of carbonate minerals by increasing the pH of the medium via photosynthesis and providing a template in the form of cell walls and their EPS for mineral nucleation. Transmission electron microscopy and other microscopic and spectroscopic observations and analyses identified magnesium carbonates and silicates, such as nesquehonite (MgCO₃ · 3H₂O) and/or hydromagnesite (Mg₅(CO₃)₄(OH)₂ · 4(H₂O) together with sepiolite (Mg₄Si₆O₁₅(OH)₂ · 6H₂O) as dominant precipitated minerals. Apparent inorganic C precipitation rates were not affected by the concentration of Mg and Si in the initial solution. However, the carbon sequestration potential was 20-40% higher in the presence of Si. Overall, the experimental approach developed in this study allows efficient reproduction of combined Mg hydroxy-carbonate and hydrous silicate precipitation under cyanobacterial activity and helps to constrain optimal conditions of cyanobacteria-induced CO₂ sequestration.</p>



Simultaneous decrease of DIC and Mg concentrations in the solution in presence of cyanobacteria



Formation of magnesian carbonates at the vicinity of cyanobacteria *Synechococcus* sp. cells



Carbon sequestered via the formation of Mg carbonate (DIC) and under organic forms in soluble organic matter (DOC) and in the cyanobacterial biomass (POC)

Strong control of the cyanobacterial activity on hydrous Mg carbonate precipitation

Increase in pH near the cells is the main driving factor of biomineralization

Cyanobacterial surfaces and their EPS act as templates for carbonate mineral precipitation

C was sequestered by particulate organic C and mineral form

Aqueous Si increased carbon sequestration potential

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1 **Carbon sequestration potential of Mg carbonate and silicate**
2 **biomineralization in the presence of cyanobacterium *Synechococcus***

3

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14

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16

17 **Key-words:** carbon, sequestration, biomass, carbonates, silicates, cyanobacteria,
18 hydromagnesite.

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39 **Abstract**

40 Bacterially-induced sequestration of atmospheric CO₂ is at the forefront of
41 geomicrobiological research due to high potential of this process in the mitigation of climate
42 warming. Cyanobacteria have been known to form stromatolites for millions of years and could
43 be used to enhance this process by sequestering carbon via the biomineralization of Mg and Ca
44 carbonates. Currently, olivine (MgSiO₄) is considered as one of the most efficient silicate
45 minerals suitable for CO₂ capture in the form of secondary Mg carbonates. However, the role
46 of dissolved Si on the efficiency of biomineralization is not sufficiently well understood. The
47 present study intended to reproduce in the laboratory the processes of biomineralization by
48 *Synechococcus* sp. cyanobacteria extracted from modern stromatolites in a carbonate- and Mg-
49 bearing medium containing various Si concentrations, in order to characterize the rates and
50 stoichiometry of reactions as well as mineralogical nature of precipitates. The results
51 demonstrated the dominant role of cyanobacterial metabolism in the precipitation of carbonate
52 minerals by increasing the pH of the medium via photosynthesis and providing a template in
53 the form of cell walls and their EPS for mineral nucleation. Transmission electron microscopy
54 and other microscopic and spectroscopic observations and analyses identified magnesium
55 carbonates and silicates, such as nesquehonite (MgCO₃·3H₂O) and/or hydromagnesite
56 (Mg₅(CO₃)₄(OH)₂·4(H₂O)) together with sepiolite (Mg₄Si₆O₁₅(OH)₂·6H₂O) as dominant
57 precipitated minerals. Apparent inorganic C precipitation rates were not affected by the
58 concentration of Mg and Si in the initial solution. However, the carbon sequestration potential
59 was 20-40% higher in the presence of Si. Overall, the experimental approach developed in this
60 study allows efficient reproduction of combined Mg hydroxy-carbonate and hydrous silicate
61 precipitation under cyanobacterial activity and helps to constrain optimal conditions of
62 cyanobacteria-induced CO₂ sequestration.

63 1. Introduction

64 One of the considered options to decrease the rising CO₂ concentration in the atmosphere
65 is to capture the CO₂ and store it into geological reservoirs (Matter *et al.*, 2009; Matter and
66 Kelemen, 2009; Sun *et al.*, 2020). An alternative and more permanent solution is the
67 mineralization of CO₂ into mafic and/or ultramafic rocks (peridotites, serpentinites) composed
68 of silicates of magnesium, iron and calcium, which allows a thermodynamic stable and safe
69 storage (Oelkers *et al.*, 2008; Matter and Kelemen, 2009; Bénézech *et al.*, 2014). Indeed, CO₂
70 can react with these minerals producing Ca, Mg and Fe cations forming carbonated minerals,
71 thus reproducing natural biogeochemical carbon (C) cycle of weathering and carbonate mineral
72 precipitation.

73 Numerous experimental and field studies are devoted to the mechanisms of serpentinization
74 and carbonatation of ultramafic rocks, all useful in the context of a possible industrial storage
75 of CO₂ and its valorization (see Kelemen *et al.*, 2011). In these studies, the forsteritic olivine
76 (Mg,Fe)₂SiO₄ is generally used as representative mineral of these rocks because it plays an
77 important role in the mechanisms of geological CO₂ sequestration via carbonatation, both in
78 abiotic (Sissman *et al.*, 2013; Peuble *et al.*, 2015) and biotic (Power *et al.*, 2009; Shirokova *et*
79 *al.*, 2013; Bundeleva *et al.*, 2014; McCutcheon *et al.*, 2014; Martinez *et al.*, 2016) systems.
80 Microorganisms are capable of C sequestration through mineral trapping via precipitation of
81 dissolved CO₂, usually in the form of carbonate minerals such as CaCO₃ (Mitchell *et al.*, 2010;
82 Dhami *et al.*, 2014; Pan *et al.*, 2018; Zhu *et al.*, 2015, 2018; Zhuang *et al.*, 2018; Saneiyani *et*
83 *al.*, 2019; Naveed *et al.*, 2020; He *et al.*, 2022) thus providing durable carbon immobilization
84 over a geological time scale (Pires *et al.*, 2012).

85 Among different microorganisms, cyanobacteria play a central role in the bio-precipitation
86 of carbonate minerals. Being modern representatives of the first living organisms on the Earth,
87 these bacteria have been forming carbonated rocks, called stromatolites, in shallow marine or

88 lacustrine environments (a few dozen meters), the oldest of which situated in south-west
89 Greenland are aged of 3.7 Ga (Nutman *et al.*, 2016). The potential of calcifying cyanobacteria
90 for geological CO₂ storage was demonstrated by Jansson and Northen (2010). Some studies
91 showed the precipitation of magnesian carbonates following the dissolution of olivine in the
92 presence of green algae (unknown consortium) (Power *et al.*, 2011), cyanobacteria
93 *Synechococcus* sp. (Martinez *et al.*, 2016) or bacterial consortium (Lamerand *et al.*, 2019). The
94 precipitation of hydrated magnesian carbonates was accelerated in the presence of
95 cyanobacteria *Gloeocapsa* sp., via the increase of pH in bicarbonate-bearing solutions under
96 conditions similar to those of the natural environment (Mavromatis *et al.*, 2012). For example,
97 in the alkaline Salda Lake (Turkey), cyanobacteria *Synechococcus* sp. form stromatolites
98 composed of hydrated magnesian carbonates such as hydromagnesite
99 (Mg₅(CO₃)₄(OH)₂·4H₂O), by locally increasing the pH and providing the nucleation sites on
100 the surface of cells, allowing the formation of minerals (Shirokova *et al.*, 2013). In this lake,
101 underground springs enriched with Mg due to dissolution of peridotites at the lake watershed,
102 form waters rich in Mg and Si (Shirokova *et al.*, 2012).

103 Most of laboratory experimental studies of the formation of Mg carbonate by cyanobacteria
104 were performed with solely aqueous Mg and carbonate in solution, yet the biomineralization of
105 Mg carbonate in the context of CO₂ storage occurs in Si-bearing environments. Therefore, a
106 possible effect of the presence of aqueous Si on Mg carbonate biomineralization should be
107 investigated. It can be anticipated that photosynthetic activity of bacteria in aqueous solutions
108 containing Si and Mg could provoke the formation of both carbonates and magnesium silicates
109 as it is reported from modern stromatolites occurrences (Pace *et al.*, 2016; 2018). In natural
110 settings, magnesian calcite and sepiolite (Mg₄Si₆O₁₅(OH)₂·6H₂O) occur in lakes, subject to
111 massive algae blooms (Barbiero *et al.*, 2002; 2008). Moreover, sepiolite was reported to form
112 under controlled laboratory environment as a precursor of protodolomite (Balan *et al.*, 2018).

113 Despite numerous studies on Mg carbonate biomineralization via cyanobacteria, the
114 processes leading to the formation of these minerals are not fully understood yet. Two main
115 mechanisms of bio-induced precipitation are currently identified: (i) the increase of pH and
116 saturation state of solution due to the photosynthetic activity of cyanobacteria (Lee *et al.*, 2004;
117 Plee *et al.*, 2010 Ludwig *et al.*, 2005) and (ii) mineral crystallization on exopolymeric
118 substances (EPS) that could decrease the activation barrier via serving as nucleation centers
119 (Dupraz *et al.*, 2009). However, assessing the relative role of each of these mechanisms has not
120 yet fully achieved.

121 The aims of this study were to 1) acquire new knowledge on the optimal conditions for
122 massive precipitation of Mg carbonate and Mg silicate minerals in the context of CO₂ storage;
123 2) quantify the rates and characterize the nature of the precipitated solid phases, and 3) identify
124 the mechanisms responsible for the biomineralization processes. For this, we conducted
125 ~~different~~ laboratory experiments with *Synechococcus* sp. cyanobacterium, obtained from
126 alkaline (pH > 9) Salda Lake (Turkey) using carbonate-bearing solution containing different
127 concentrations of Mg and/or Si under different experimental settings, designed to distinguish
128 the effect of solution supersaturation rise, cell surface sites and cell soluble exometabolites. We
129 used a combination of physico-chemical, microscopic and spectroscopic techniques to
130 characterize the formation of organo-mineral solid phases in order to produce a quantitative
131 model of mineral formation in the system Mg - HCO₃ - Si - cyanobacteria at various
132 physicochemical parameters of solution and to estimate the C sequestration potential of this
133 system.

134

135

136 **2. Material and methods**

137 *2.1 Bacterial strain*

138 Cyanobacteria *Synechococcus* sp. PCC 7942 were isolated from the surface of stromatolites
139 growing in the alkaline, $\text{Mg}(\text{HCO}_3)_2$ -dominated Salda Lake (Turkey) and used previously in
140 mineral carbonation experiments in pure culture (Shirokova *et al.*, 2013). They were cultured
141 in BG-11 (Sigma-Aldrich C3061) nutrient solution under air bubbling and continuous light to
142 insure most efficient development (Stanier *et al.*, 1979). Before the inoculation of batch
143 reactors, cells were rinsed twice in appropriate fresh culture media or sterile 0.1 M NaCl
144 solution using centrifugation (~500 mL of solution for 1 g of wet biomass) to remove, as
145 possible, the adsorbed ions and cell exudates from the surface.

146

147 2.2 Aqueous solutions

148 The precipitation of secondary Mg-carbonate and Mg-silicate minerals in the presence of
149 cyanobacteria *Synechococcus* sp. was studied in aqueous solutions of 10 mM NaHCO_3 enriched
150 or not with Mg and Si. Aqueous silica was added from a Na_2SiO_3 concentrated solution and Mg
151 was added from a MgCl_2 concentrated solution. Various control experiments were performed
152 as similar composition of aqueous solution. The composition of experimental fluids is listed in
153 **Table 1.**

154

155 2.3 Experimental setup

156 Experimental setup was aimed at testing separately the effect of Mg, HCO_3 , Si
157 concentration, pH of the aqueous solution, cell photosynthesis, EPS, and the presence of cell
158 surfaces as templates for mineral crystallization. All the experiments were run in duplicates and
159 included: *i*) cyanobacterial suspension in 500 mL polycarbonate Erlenmeyer flasks closed with
160 sterile porous caps (Bio-Silico®) which allowed free atmospheric air exchange (experiments
161 Mg_3 , SiMg_3 , SiMg), *ii*) cyanobacteria enclosed into a dialysis bag (pore size 6-8 kDa, ~2 nm)
162 placed in a glass beaker also in free exchange with atmosphere (experiment DSM, **Fig. 1A**), *iii*)

163 dialysis bags (6-8 kDa, ~2 nm) containing a solution of 10 mM NaHCO₃ and 10 mM of Mg
164 were placed into a polycarbonate jar filled up with the same solution in which 1 g_{wet} L⁻¹ of
165 cyanobacteria *Synechococcus* sp. was added (experiment SD, **Fig. 1B**), *iv*) cyanobacterial
166 suspension without BG-11 nutrient under light (experiment BSM), *v*) cyanobacterial suspension
167 in the darkness (aerated bottles wrapped in aluminum foil; experiment CSM), and *vi*) abiotic
168 experiments where NaOH was added to reproduce the increase of pH due to photosynthesis in
169 biotic experiments (experiments AMg3, ASiMg3, ASiMg). All experiments were run at
170 25±1°C with an orbital shaker (for DSM) or under magnetic stirring (all other experiments).
171 Biotic experiments were carried out under cool fluorescent lights of constant 2500 lux (~40
172 μmol.m⁻².s⁻¹, in duplicates and with abiotic controls. A 10% diluted BG-11 solution (freshwater
173 cyanobacteria nutrient solution) was used as a nutrient source for bacteria except for BSM
174 experiment. All manipulations were performed under sterile conditions in a laminar flow hood
175 class A100. .

176

177 *2.4 Sampling procedure*

178 Samples were taken daily during the first week and then every 2-3 days in order to follow
179 the evolution of different microbiologic and physicochemical parameters (biomass, pH,
180 alkalinity, concentrations in Mg, Si and dissolved organic carbon (DOC)) and to characterize
181 eventual precipitation of secondary minerals. An aliquot of 20 mL was taken during vigorous
182 stirring to maintain the homogeneity of the suspension, and subdivided into several parts. The
183 first 5 mL were used to measure the cyanobacterial concentration and the pH. The remaining
184 15 mL were centrifuged (3500 g, 30 min) and the supernatant was filtered (0.45 μm). A part of
185 this filtrate was used to analyze the alkalinity (Alk), Si and DOC concentrations. The other part
186 was acidified with HNO₃ to measure Mg²⁺ concentration. The filtrates were preserved at 4°C
187 pending analyzes.

188

189 2.5 Chemical analyzes

190 Cyanobacterial biomass was calculated from optical density of suspension at 680 nm
191 (OD_{680nm}), using a Helios Epsilon spectrophotometer. The conversion factor from OD_{680nm} to
192 dry biomass (g_{dry}/L) was equal to 0.519 and the ratio wet:dry biomass was 8 ± 0.5 . The pH was
193 measured with a combination pH-electrode (Schott Geräte H62), with an uncertainty of 0.01
194 units. NIST buffers (pH = 4.00, 6.88, 9.22 at 25°C) were used for the calibration of the
195 electrode. The total silica concentration was measured by colorimetry with the **molybdate blue**
196 **method using a colorimetric chain Technicon Autoanalyzer II**, with an uncertainty of 2% and a
197 detection limit of 3×10^{-7} M. Dissolved inorganic carbon (DIC) was calculated from pH and
198 alkalinity, which was determined by a standard HCl titration using an automatic Schott
199 TitroLine alpha plus titrator, with an uncertainty of 1% and a detection limit of 5×10^{-5} M.
200 Magnesium concentration was measured by **flame atomic absorption spectroscopy using a**
201 **Perkin Elmer AAnalyst 400** with an uncertainty of 1% and a detection limit of 1×10^{-7} M. The
202 DOC was determined using a Shimadzu TOC-V_{CSN} analyzer with an uncertainty of 5% and a
203 detection limit of 0.1 mg C_{org} L⁻¹.

204 The saturation indices were calculated using PHREEQC geochemical code (Parkhurst and
205 Appelo, 1999), with its llnl.dat database modified to consider new equilibrium constants in the
206 Ca-Mg-CO₂-H₂O system from Palmer and Wesolowski (1997), Millero *et al.* (2007), Bénézeth
207 *et al.* (2011), Stefánsson *et al.* (2013; 2014), Gautier *et al.* (2014), and Harrison *et al.* (2019).

208

209

210 2.6 Microscopic analyzes

211 For Transmission Electron Microscopy (TEM) observations, samples were prepared in
212 three different ways. The first method included aliquots of bacteria + precipitated mineral

213 suspension were centrifuged (30 min, 1000 rpm) and the organic matter was removed from the
214 solid phase by treating them in aqueous 10% H₂O₂ overnight. The remaining solids were rinsed
215 three times with MilliQ® water, freeze-dried at -50°C, and deposited on carbon-coated copper
216 grids. The second method used a drop of fresh suspension (~1 g_{wet} L⁻¹) was deposited on a
217 carbon-coated copper grid. Finally, the third method involved ultrathin slices for TEM analyses
218 which were prepared as following: freshly sampled cells and precipitated minerals were fixed
219 with 2.5% glutaraldehyde / 2% paraformaldehyde in 0.1 M cacodylate buffer (pH = 7.2) at
220 ambient temperature for 1.5 h, then washed three times with 0.1 M cacodylate, and subsequently
221 soaked in 1% osmium tetroxide at ambient temperature for 1 hour and washed three times with
222 0.1 M cacodylate. Supernatant was discarded and pellets were embedded in agarose, then
223 samples were subjected to stepwise ethanol dehydration (15 min at 25, 50, 70 and 90% ethanol
224 at ambient temperature, and 3 x 30 min at 100% dry ethanol). Samples were then embedded in
225 epon and 80 nm thick ultrathin sections were prepared with a Leica UCT ultramicrotome.
226 Ultramicrocuts were mounted on Cu formvar-carbon grids, and electron stained with uranyl
227 and lead citrate. Grids were characterized using a JEOL JEM-2100F TEM coupled with an SDD
228 Brucker EDS analyzer.

229

230 **3. Results**

231 *3.1 Aqueous solution evolution in the presence of cyanobacteria*

232 Results of experiments with a monoculture of cyanobacteria *Synechococcus* sp. in a 10
233 mM NaHCO₃ solution with various Mg and Si concentrations are presented in **Fig. 2A** (10 mM
234 Mg), **2B** (10 mM Mg and 0.4 mM Si) and **2C** (5 mM Mg and 0.3 mM Si). In experiments with
235 10 mM of Mg, the pH increased from 9 to 11.3 during the first 80 hours, then it became stable
236 until the end of experiments (**Figs. 2A-B**). Note that the pH and the concentration of DIC, Mg
237 and Si were stable in blanks. The DIC was stable at 10 mM during the first 50 hours then

238 decreased by 90-95% during the next 150 hours. The Mg concentration slightly decreased
239 (~10%) during the first 50 hours, and then further decreased two-folds during the following 100
240 hours. In the experiment without Si, the Mg concentration remained stable until the end of the
241 experiment (**Fig. 2A**), whereas it still decreased from 6 mM to 4 mM in the presence of Si (**Fig.**
242 **2B**). At 0.4 mM of initial Si, the Si concentration decreased by 99% during the first 150 hours
243 and then remained stable (**Fig. 2B**). The simultaneous sharp decrease of DIC, Mg and Si (when
244 present) concentrations at high pH values suggested the precipitation of magnesium carbonates
245 and/or silicates.

246 In experiments with 5 mM of Mg and 0.3 mM of Si, the evolution of different parameters
247 was similar to the experiments previously described, with an increase of pH from 9 to 11.3
248 during the first 100 hours, and a loss of 90% of DIC and 98% of Mg and Si between 100 and
249 240 hours (**Fig. 2C**).

250 Considering the decrease of DIC, Mg and Si concentrations and the pH evolution in the
251 course of experiments, the saturation indices (SI) calculated with PHREEQC indicated a
252 possibility of precipitation of Mg carbonate and silicate minerals: artinite, hydromagnesite,
253 brucite and sepiolite (**Figs. 2A-C**). The SI values of artinite, brucite and hydromagnesite were
254 negative at the beginning of experiments and increased to reach a maximum of 3, 2 and 5,
255 respectively, between 70 and 100 hours; subsequent decrease of SI indicated a possible
256 formation of these minerals. The SI of nesquehonite was negative in all experiments. In
257 experiments where Si was added (**Figs. 2B-C**), the SI of sepiolite was positive from the
258 beginning until the end of experiments, and a decrease of Si after about 100 hours of experiment
259 indicated a possible precipitation of this mineral.

260 In experiments without 10% BG-11 nutrient medium (BSM), the pH increased from 8.5 to
261 9.6 between 0 and 96 hours and remained stable until the end of the experiment (**Fig. 3A**). A
262 lack of nutrients in the solution did not allow the cyanobacteria to metabolize and produce

263 sufficiently high pH. Consequently, no precipitation was observed: the concentration of DIC
264 remained stable at 10 mM. The Mg concentration decreased from 12 to 9.8 mM, which could
265 be due to its uptake and adsorption by cyanobacteria for nutrient requirement.

266 During experiments in the darkness (CSM), cyanobacteria did not photosynthesize; thus,
267 their biomass and solution pH remained stable. A decrease of Mg concentrations during the
268 first 96 hours may indicate a consumption of this potential nutrient by cyanobacteria (**Fig. 3B**).
269 Increasing artificially the pH to 10 led to a decrease of DIC concentrations from 10 to 4 mM
270 between 96 and 200 hours. Further increase in pH to the value of 10.6 led to a rapid decrease
271 of Mg concentration (from 9.8 to 7.2 mM in an hour). Thus, a concomitant decrease of both
272 DIC and Mg concentrations indicated the formation of Mg carbonate in the solution.

273 During experiments with cyanobacteria which were confined within a dialysis bag (DSM),
274 the photosynthetic activity induced an increase in pH inside and outside of the dialysis bags
275 from 8.9 to 10 over the first 380 hours of the experiment (**Fig. 3C**). Magnesium concentration
276 slightly decreased from 13 to 11.5 mM during the first 24 hours and then remained stable. The
277 DIC concentration was stable at 10 mM during full duration of the experiment. Note that ion
278 concentrations inside the dialysis bag were measured at the beginning and the end of the
279 experiments and were similar to those outside of the bag (not shown). Even though pH
280 increased, no precipitation was observed in these experiments.

281 When cyanobacteria were placed outside of the dialysis bag (SD), the pH value and Mg
282 concentration were similar in and out of the bag, while the DIC was equilibrated between two
283 compartments at 10 mM after 250 hours of exposure (**Fig. 3D**). The pH increased from 8 to 11
284 in 400 hours, the Mg concentration decreased from 12 to 8 mM between 0 and 300 hours of
285 experiment, and the DIC concentration decreased from 9.8 to 4 mM between 250 and 410 hours
286 of experiment, when pH reached a value of 10.5, thus indicating the precipitation of Mg
287 carbonate. The formation of this phase was clearly observed outside the dialysis bag in the form

288 of a mixture of the mineral deposit and cyanobacterial biomass at the bottom of the reactor and
289 on its walls (**Fig. S1A**), as well as on the external surface of the dialysis bags (**Figs. S1B-C**).

290

291 *3.2 Microscopic and spectroscopic characterization of solid phases formed during the*
292 *biotic experiments*

293 In order to reveal the relationship between cyanobacterial cells and precipitated mineral
294 phase(s), the experimental suspension was examined with transmission electronic microscopy
295 (TEM) after one and two weeks of experiment with 10 mM of Mg and 0.4 mM of Si in the
296 initial solution (**Figs. 4 and 5**). After first week, a solid fibrous phase was visible around the
297 cyanobacteria cells (**Fig. 4A**, top and bottom right). Thin, hair-like needles were detectable in
298 the immediate vicinity of the cell (shown at the bottom of **Fig. 4A**). The observation in dark
299 field using a diaphragm allowed to distinguish the crystalline particles, appearing in bright
300 white on **Fig. 4B**, from the amorphous phase appearing in grey on the same figure. The Fast
301 Fourier Transform (FFT) pattern confirmed the presence of a crystalline phase (**Fig. 4C**)
302 particularly in the zone encircled in red on **Fig. 4B**, where the quantity of white particles was
303 the highest. After two weeks of experiments, cyanobacteria were surrounded by some solid
304 phase (**Fig. 5A**). Near the cells, nanometric white particles were clearly detectable (encircled in
305 the left, **Fig. 5B**). At some distance from the cells (100-200 nm), thin needles were present (**Fig.**
306 **5B**, in the right circle). At the same time, at the end of experiment, solid fibrous phase was not
307 detectable anymore. The FFT pattern indicated the presence of a crystalline phase in the spots
308 where the largest amount of white nanoparticles was concentrated (**Fig. 5C**). An energy
309 dispersive X-ray spectrometry (EDS) analysis allowed the determination of the chemical
310 composition of the crystalline phases after one and two weeks of experiment (**Figs 4D and 5D,**
311 **respectively**). These phases contained mostly magnesium (~ 40%), oxygen (~ 35%) and carbon
312 (7 to 17%). Hence the crystalized phases could be hydrous magnesian carbonates. In the sample

313 retrieved after one week of reaction, silicon was also present (12%), which could correspond to
314 a magnesian silicate such as sepiolite. No crystalline phase was detected within the needles.
315 However, the needles could be too thin (i.e., less than 10 nm wide) to reveal the nature of
316 constituent minerals.

317 The TEM observations of the experimental suspension collected outside the dialysis bags
318 (experiment SD) revealed a crystalline phase near the *Synechococcus* cells (**Figs. 6A-B**).
319 According to the EDS analysis realized in the red circle on **Fig. 6B**, this phase contained mostly
320 carbon (47%), magnesium (38%) and oxygen (13%) (**Fig. 6D**), which could indicate the
321 presence of hydrous Mg carbonate. In the sample collected from the experiment in the darkness
322 (CSM), a crystallized precipitated phase composed of Mg, C and O was also present but no
323 cells were visible, and there was only some residual organic matter from the bacterial cells
324 which were present at the beginning of the experiment (**Fig. S2**).

325 The FFT patterns obtained from the crystalline phases after one and two weeks of
326 experiments (**Figs. 4C and 5C**, respectively) and from the experiment SD in the dialysis bag
327 (**Fig. 6C**) yielded an average lattice thickness of 0.153 nm, which is similar to the major
328 reflection (d_{101} , 100% intensity) of nesquehonite, a magnesian carbonate ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$), and
329 one of the major reflection (d_{110} , 73% intensity) of hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$).

330 In order to observe the intra- and extra-cellular precipitation, a cross-sectional TEM
331 observation of organo-mineral aggregates formed in SiMg3 experiment during 2 weeks of
332 incubation was also realized (**Fig. 7**). A longitudinal section of the cyanobacteria
333 *Synechococcus* sp. (**Fig. 7A**) revealed a black photosynthetic membrane and dark spherical
334 formations corresponding to intracellular phosphate globules consistent with previous
335 observations (Lamérand *et al.*, 2020). Inside the cells, white formations a few nm in size were
336 detected (**Fig. 7B**). Some mineral solid phase was also present outside the cells (**Fig. 7C**, black
337 formations), in which an EDS analysis revealed the presence of Mg and Si. Finally, some

338 filaments were visible on the cell membrane (**Fig. 7B**); however, they were too thin to be
339 characterized by EDS analysis. These could be EPS released by the bacteria during their
340 metabolic activity.

341

342 *3.3 Abiotic experiments*

343 In abiotic experiments, we artificially increased the pH via progressive addition of NaOH
344 to approximate a temporal pattern of the pH rise due to photosynthesis in the biotic experiments.
345 The precipitation of hydrous Mg-carbonate and Mg-silicate occurred when the pH reached the
346 value of ~10.3, accompanied by a simultaneous decrease of DIC, Mg and Si (when present)
347 concentrations in solution (**Figs. S3 A-C**).

348 SEM observations of the mineral formed during the experiment showed the presence of
349 rosette-like crystals in the experiment AMg3 (**Figs. 8A-B**), similar to Mg carbonate
350 hydromagnesite and dypingite. These crystals were partially visible in the experiment ASiMg3
351 (**Figs. 8C-D**) together with a granular, probably amorphous phase, which was the only one
352 visible in the ASiMg experiment (**Figs. 8E-F**). These observations were confirmed by XRD
353 analysis, which showed a mixture of hydromagnesite and dypingite in the sample from AMg3
354 experiment (**Fig. S4**), whereas no crystalline phase was detected in the samples from Si-bearing
355 abiotic experiments (ASiMg and ASiMg3, not shown).

356

357

358

359 *3.4 Rates of precipitation*

360 Apparent rates of Mg, Si and DIC concentrations decrease ($\text{mmol L}^{-1} \text{day}^{-1}$) were
361 calculated for the stage of maximum precipitation, according to the following equations:

362
$$R_{\text{Mg}} = \frac{d[\text{Mg}]}{dt}, R_{\text{Si}} = \frac{d[\text{Si}]}{dt}, R_{\text{DIC}} = \frac{d[\text{DIC}]}{dt}$$

363 These rates are listed in **Table 2**. In most experiments, a higher initial Mg concentration led to
364 a faster decrease of Mg and DIC concentrations. Under the same initial conditions, the rate of
365 DIC decrease was similar for abiotic and biotic experiments. In the abiotic experiments, a
366 decrease of Mg concentration was slightly slower ($0.62\text{-}0.96\text{ mmol L}^{-1}\text{ day}^{-1}$ compared to 0.76-
367 $1.5\text{ mmol L}^{-1}\text{ day}^{-1}$ in the biotic experiments). This difference could be explained by intracellular
368 consumption and/or surface adsorption of Mg by cyanobacteria in biotic experiments in
369 addition of Mg precipitation, while in the abiotic experiments only the precipitation occurred.
370 The magnitude of Si concentration decrease was similar regardless the initial Si concentration
371 but the apparent rate was faster in abiotic experiments compared to biotic experiments (~ 0.2
372 $\text{mmol L}^{-1}\text{ day}^{-1}$ and $\sim 0.1\text{ mmol L}^{-1}\text{ day}^{-1}$, respectively).

373

374 **4. Discussion**

375 *4.1. Precipitation of secondary minerals: rates and identity of secondary phases*

376 Distinct precipitation of secondary minerals was observed in a biotic ($1\text{ g}_{\text{wet}}\text{ L}^{-1}$ of
377 bacterial biomass) carbonate-bearing environment with different concentrations in Mg and Si.
378 Fast and simultaneous decrease of the Mg and Si (when present) concentrations in biotic
379 experiments ($1\text{ g}_{\text{wet}}\text{ L}^{-1}$ of biomass, **Fig. 2**) indicated the precipitation of magnesian carbonates
380 and/or silicates, highlighting the governing role of cyanobacteria in the secondary phase
381 formation. Indeed, during the photosynthesis, cyanobacteria increased the pH above 10.3 (**Fig.**
382 **2**), thus rising significantly the supersaturation degree of solution with respect to artinite,
383 hydromagnesite, brucite and sepiolite. This induced the precipitation of phases which could not
384 be formed at **lower pH values.**

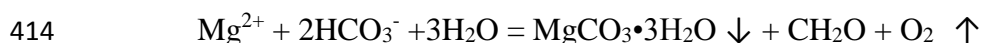
385 The observation by TEM coupled with EDS analysis highlighted the presence of
386 crystalline hydrous magnesian carbonate phases in the vicinity of bacterial cells (**Figs. 4-7**).
387 The FFT patterns allowed identifying these minerals as nesquehonite and/or hydromagnesite,

388 whereas temporal evolution of saturation indices during experiments indicated the possible
389 precipitation of hydromagnesite but not nesquehonite. However, at the surface of cells, the pH
390 is known to be much higher than that measured in the bulk solution (Revsbech *et al.*, 1983,
391 Dupraz *et al.*, 2009). Although this is generally applied to cyanobacterial biofilms, unicellular
392 photosynthesizing plankton is also likely to exhibit a sizable pH gradient suitable for
393 precipitation of carbonate minerals (Pokrovsky and Savenko, 1995). Therefore, cyanobacterial
394 photosynthesis could have induced a much higher local supersaturations leading to the
395 crystallization of nesquehonite, which could have evolved over time into hydromagnesite as it
396 is known from other biotic and abiotic experiments. Generally, nesquehonite is the first phase
397 to precipitate in the Mg-CO₂-H₂O system at 25°C, in the presence or absence of cyanobacteria
398 (Mavromatis *et al.*, 2012; Hopkinson *et al.*, 2012; Shirokova *et al.*, 2013).

399 **Variations of DIC**, Si and Mg concentrations were calculated between the beginning
400 and the end of the main precipitation stage (**Table 2**) allowed assessing the ratios of DIC to Mg
401 concentrations in the solid phase which ranged between 1.25 and 3.34. These values are higher
402 than those of hydromagnesite (0.8) and nesquehonite (1), and consistent with a mixture of
403 different magnesian carbonate phases. The apparent Mg rates during the fastest precipitation
404 stage in both abiotic and biotic experiments varied between 0.61 to 1.64 mmol Mg L⁻¹ day⁻¹. They
405 are of the same order of magnitude than those calculated from the data of Shirokova *et al.* (2013)
406 in Si-free solutions which varied from 0.31 to 2.88 mmol Mg L⁻¹ day⁻¹.

407 In biotic experiments where the formation of Mg carbonate was observed, the ratio of
408 Mg decrease to organic carbon produced ($\Delta\text{Mg}/\Delta\text{C}_{\text{org}}$) during the course of experiment was
409 calculated considering that the proportion of carbon in dry biomass is 50%. This ratio was equal
410 to 0.24, 0.45, 0.37, 0.22 and 0.73 for the experiments SiMg, Mg3, SiMg3, DSM and SD,
411 respectively (see **Table 1** for abbreviation of experimental conditions). These values are inferior

412 to the theoretical Mg/C_{org} ratio of 1 for nesquehonite as first precipitating phase during
413 cyanobacterial photosynthesis:



415 Therefore, one can assume that the efficiency of cyanobacterially-induced precipitation of
416 hydrous Mg carbonate is partially decreased due to the presence of aqueous Si, and a part of
417 Mg resides within amorphous Si-Mg compounds.

418

419 *4.2. Mechanisms of biomineralization and the role of sepiolite as a precursor of carbonate*
420 *mineral formation*

421 A solid fibrous phase observed via TEM in the experiment containing 10 mM of Mg and
422 0.4 mM of Si in presence of cyanobacteria did not show any crystalline order, however these
423 formations strongly resembled to sepiolite recently synthesized in laboratory (Baldermann *et*
424 *al.*, 2018) (**Fig. S5**). The latter study was performed under abiotic conditions at different Si/Mg
425 ratios, and reported the precipitation of sepiolite after 2 to 3 months. One of their experiments
426 (Si/Mg = 1/28) corresponded to Si:Mg ratio in our experiment (10 mM Mg and 0.4 mM Si). In
427 our case, no abiotic precipitation of sepiolite was observed; presumably, the relatively short
428 duration of the experiments (two weeks) was not sufficient to allow the abiotic formation of
429 this mineral. However, in biotic experiments, the bacterial metabolism and the associated
430 increase of pH could have induced the precipitation of sepiolite, via increasing the saturation
431 index of this mineral (**Fig. 2**). This is a notable result which demonstrates a strong power of
432 bacteria to accelerate the precipitation of minerals whose abiotic formation is
433 thermodynamically possible but delayed because of the low rate and the kinetic barriers of
434 nucleation. Presumably, cyanobacterial cells and their exopolysaccharides can act as mineral
435 nucleation centers by decreasing activation energies (Dupraz *et al.*, 2009) thus rendering
436 possible the precipitation of sepiolite already after the first week of incubation.

437 Another interesting result of this study is that the sepiolite can serve as a precursor of
438 hydrous Mg carbonate formation. According to the EDS analysis of the biotic experiment
439 reaction products (**Figs. 4D, 5D**), the sepiolite (or sepiolite-like amorphous material) decreased
440 its relative abundance between 1 and 2 weeks of incubation as reflected in a ten-fold decrease
441 of Si concentration in the solid phase. This observation is consistent with a hypothesis of
442 hydrous Mg silicate providing Mg for in-situ hydrous Mg carbonate precipitation via coupled
443 dissolution/precipitation reaction. Such an explanation was recently put forward by Pace *et al.*
444 (2016) to explain in-situ dolomite/protodolomite formation in the vicinity of natural biofilm
445 producing both Mg, Ca carbonate, protodolomite and sepiolite.

446 The dark spheric formations observed inside the cells of cyanobacteria (**Fig. 7**) were similar
447 to amorphous calcium carbonates intracellularly precipitated by several cyanobacteria, such as
448 *Synechococcus* sp. PCC 6312 or *Synechococcus* sp. PCC 6716 (Benzerara *et al.*, 2014).
449 However, according to a former study of the precipitation of secondary minerals in presence of
450 *Synechococcus* sp. PCC 7942, these were phosphate globules, initially present in the cells
451 before the beginning of the experiments (Lamérand *et al.*, 2020).

452 In abiotic experiments, the increase of pH via the addition of NaOH led to the precipitation
453 of the same minerals than those formed during biotic experiments, thus indicating that the main
454 driving factor of biomineralization is the photosynthetically-induced pH increase. However,
455 production of alkaline microenvironment is certainly necessary but not sufficient for
456 extracellular Mg silicate and carbonate formation. Indeed, separating the cyanobacteria from
457 the bulk of aqueous solution via enclosing them in the dialysis bag (< 2-3 nm pore size) yielded
458 the precipitation solely inside the dialysis compartment (**Fig. S1**), despite of identical chemical
459 composition of aqueous solution (pH, Mg, DIC, saturation state) inside and outside the dialysis
460 compartment. This strongly suggests that cyanobacterial cells and their EPS which were
461 retained by dialysis membrane, serve as nucleation centers to promote the mineralization. As

462 such, the limiting step of bio-carbonation could be the presence of bacterial cells whose surfaces
463 provided a template for nucleation. Another explanation could be that Mg-carbonate / Mg-
464 silicate nucleation clusters that were formed in the microenvironment around the cells inside
465 the dialysis bag were too large to pass through the pores of the dialysis membrane, and thus the
466 majority of precipitation occurred in the bulk of bacterial suspension.

467 The processes of precipitation of magnesian carbonates by cyanobacteria could be similar
468 to those of calcium carbonates. The latter are well studied in various phototrophic bacterial
469 systems (Aloisi, 2008; Bundeleva *et al.*, 2014; Cam *et al.*, 2018; Dittrich *et al.*, 2003; 2004; Lee
470 *et al.*, 2006). Following this path, we suggest that, first, Mg²⁺ ions accumulate at the surface of
471 the cells because of electrostatic interactions between the negatively charged groups of the cells
472 surface (carboxylates, hydroxylates, phosphorylates) and the Mg²⁺ cations (Douglas and
473 Beveridge, 1998). This is further stimulated by the presence of EPS which could act as
474 nucleation centers (Dittrich and Obst, 2004), via decreasing the interfacial energy and providing
475 sizeable amount of cation-binding moieties (Priester *et al.*, 2006; Guibaud *et al.*, 2008; Kantar
476 *et al.*, 2011). Aqueous carbonate and bicarbonate anions may interact with these cations to form
477 carbonate minerals, near the cells and in their capsules (Miller *et al.*, 1990). Another possible
478 mechanism, suggested for the first time by Douglas and Beveridge (1998) for *Synechococcus*
479 cells suspended in Fayetteville Green Lake water and producing massive gypsum or calcite
480 deposits is the continuous release of mineralized S-layer by the cells, quickly replaced by new
481 polymeric molecules. This may produce biominerals located at some distances from the cell
482 surfaces, as also seen in our TEM images. Such a pathway does not require any specific
483 protection mechanism against cell encrustation by newly formed minerals, unlike the one which
484 operates for CaCO₃ - *Synechococcus* sp. system (Martinez *et al.*, 2010; Bundeleva *et al.*, 2014).
485 Presumably, hydrous Mg carbonates formed in the vicinity of photosynthesizing cells,

486 essentially over external EPS templates, are not capable of creating full cell encrustation and
487 entombment.

488 To resume, macroscopic experiments, thermodynamic calculations and TEM observations
489 suggest the following mechanism. First, an amorphous magnesium silicate and nanocrystals of
490 Mg carbonates are formed around the cells, then these precursors are dissolved, liberating Mg
491 in the fluid. Nanocrystals of nesquehonite are formed in the vicinity of the cells, and they
492 gradually assemble themselves into thin needles. Over time, a part of these crystals could
493 transform into more stable magnesium carbonate such as hydromagnesite.

494

495 4.3. *CO₂ sequestration capacity via hydrous Mg carbonate biomineralization by* 496 *cyanobacteria*

497 During the CO₂ biomineralization by cyanobacteria, carbon can be sequestered (i.e.,
498 removed from solution) via two pathways: as organic carbon (C_{org}) during the production of
499 biomass (both the biomass and soluble exometabolites), and as inorganic carbon (C_{inorg}) during
500 the formation of carbonate minerals. The quantity of sequestered C_{inorg} was estimated via mass-
501 balance calculation from a decrease of DIC concentration between the beginning and the end
502 of the experiment. The amount of C_{org} formed in the experiment is composed of particulate
503 organic carbon (POC) which corresponds to half of the dry biomass, and DOC in the form of
504 exometabolites and EPS. Carbon sequestration potential (CSP) was calculated via dividing the
505 quantity of sequestered carbon by the time it took to be sequestered. We estimated that carbon
506 was mostly (ca 60-70%) sequestered in particulate organic form (**Fig. 9**). Soluble
507 exometabolites and EPS (DOC) contributed to only 2-10% of the total CSP. The quantity of C
508 sequestered in the mineral form (**as DIC**) was similar in biotic and abiotic experiments (0.7-1.2
509 mmol L⁻¹ day⁻¹). The presence of Si in the solution slightly increased (~20%) the quantity of
510 sequestered inorganic carbon, whereas there was no correlation between the quantity of aqueous

511 Mg in the initial solution and the CSP. Overall, biotic experiments with nutritive medium and
512 without dialysis bags (Mg3, SiMg3 and SiMg) exhibited the highest carbon sequestration
513 potential because of the large quantity of C sequestered in the biomass during the development
514 of cyanobacteria. This shows the potential of cyanobacteria to sequester carbon, by both the
515 biomass they produce and the carbonate minerals they stimulate to precipitate whereas in
516 abiotic environment, **an external addition of NaOH was necessary to form carbonate minerals.**

517

518 **5. Conclusions**

519 The biomineralization of carbon dioxide is an important process to consider in CO₂ storage
520 and sequestration techniques. During this study, the role of cyanobacteria in the precipitation
521 of carbonate phases was examined at variable biological and physicochemical parameters
522 (cyanobacterial biomass, pH, Mg, Si, DIC, DOC) over 10 to 14 days of reaction. The rates of
523 Mg carbonate precipitation were comparable to those observed in previous experiments with
524 Si-free aquatic systems of Mg carbonates and cyanobacteria and were unaffected by Mg:Si ratio
525 in the initial solution.

526 Obtained results demonstrate strong control of the cyanobacterial activity on hydrous
527 carbonate (nesquehonite and hydromagnesite) and Mg silicate mineral precipitation. The
528 dominant mechanisms include the increase in pH near the cells during the photosynthesis and
529 the release of exopolymers that can serve as nucleation centers and thus trigger carbonates and
530 silicates precipitation from supersaturation solution. The dialysis experiments demonstrated
531 incontestable role of cyanobacterial surfaces, serving as templates for both Mg silicate and
532 carbonate precipitation. The TEM observations highlighted the formation of crystalline
533 magnesian carbonated phases in the vicinity of cells. The minerals formed could be a mixture
534 of nesquehonite and hydromagnesite. A magnesium silicate such as sepiolite or its poorly
535 crystalline analogue could also be present at the beginning of biomineralization reaction. This

536 suggests its possible role as a precursor of carbonate minerals, which is consistent with recent
537 natural observations. The overall C sequestration in the organic and mineral form was
538 dominated by particulate organic C (in the form of bacterial biomass) with ca. 35% of C
539 sequestered in the form of hydrous Mg carbonates.

540

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545

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Table 1. List of conducted experiments, chemical composition of experimental solutions, bacteria status and reactor type. All the experiments were run in the diluted BG-11 (10%) nutrient medium.

Nom	NaHCO ₃ , mM	Mg, mM	Si, mM	Cyanobacteria	Experimental conditions
SiMg	10	5	0.3	1 g _{wet} /L <i>Synechococcus</i> sp.	Aerated, mixed
Mg3	10	10	-	1 g _{wet} /L <i>Synechococcus</i> sp.	Aerated, mixed
SiMg3	10	10	0.4	1 g _{wet} /L <i>Synechococcus</i> sp.	Aerated, mixed
ASiMg	10	5	0.3	Bacteria-free	Aerated, mixed
AMg3	10	10	-	Bacteria-free	Aerated, mixed
ASiMg3	10	10	0.4	Bacteria-free	Aerated, mixed
BSM	10	10	-	1 g _{wet} /L <i>Synechococcus</i> sp.	Aerated, mixed
CSM	10	10	-	1 g _{wet} /L <i>Synechococcus</i> sp.	Aerated, mixed, reactors kept in darkness
DSM	10	10	-	1 g _{wet} /L <i>Synechococcus</i> sp.	Bacteria inside the dialysis bag
SD	10	10	-	1 g _{wet} /L <i>Synechococcus</i> sp.	Bacteria outside the dialysis bag

Table 2. Variations of concentrations of DIC, Mg and Si and rates of Mg, Si and DIC concentrations decrease (respectively R_{Mg} , R_{Si} and R_{DIC} , $\text{mmol L}^{-1} \text{day}^{-1}$) during the stage of maximal concentration change (mineral precipitation).

	ΔDIC , mM	$\Delta[\text{Mg}]$, mM	$\Delta[\text{Si}]$, mM	$\Delta\text{DIC}/\Delta[\text{Mg}]$	$\Delta[\text{Mg}]/\Delta[\text{Si}]$	R_{Mg}	R_{Si}	R_{DIC}
SiMg	8.32	4.51	0.29	1.85	15.6	0.76	-0.10	1.41
Mg3	7.50	4.91	-	1.53	-	1.51	-	2.33
SiMg3	9.88	5.49	0.26	1.80	21.1	1.19	-0.12	1.66
ASiMg	5.82	2.54	0.44	2.29	5.77	0.62	-0.21	1.40
AMg3	4.83	1.81	-	2.67	-	0.69	-	2.09
ASiMg3	5.67	1.70	0.58	3.34	2.93	0.96	-0.27	1.40
BSM	-	-	-	-	-	-	-	-
CSM	8.64	6.31	-	1.37	-	1.64	-	1.43
DSM	-	-	-	-	-	-	-	-
SD	5.13	4.11	-	1.25	-	0.61	-	1.28

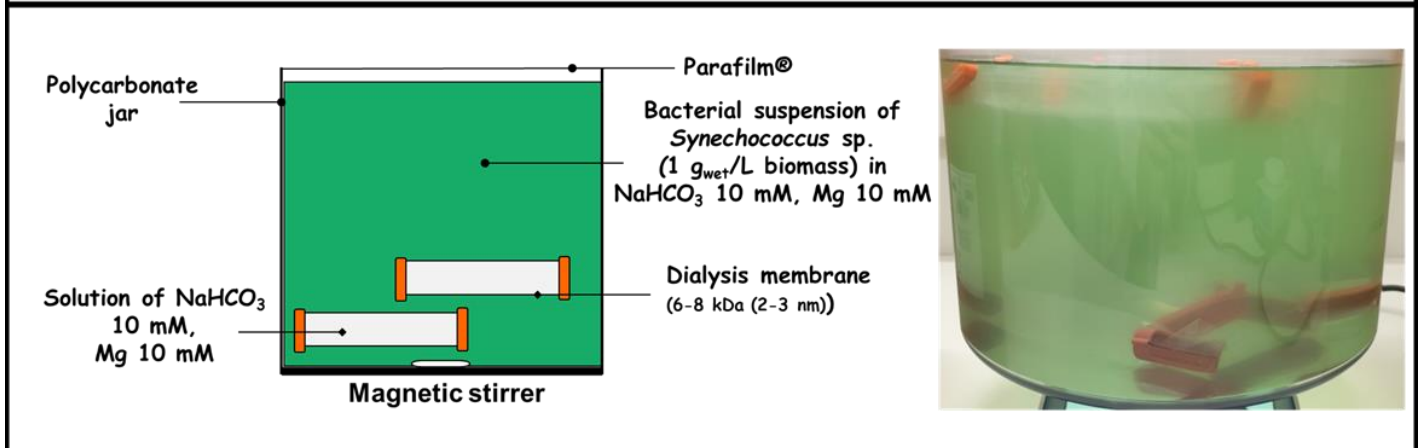
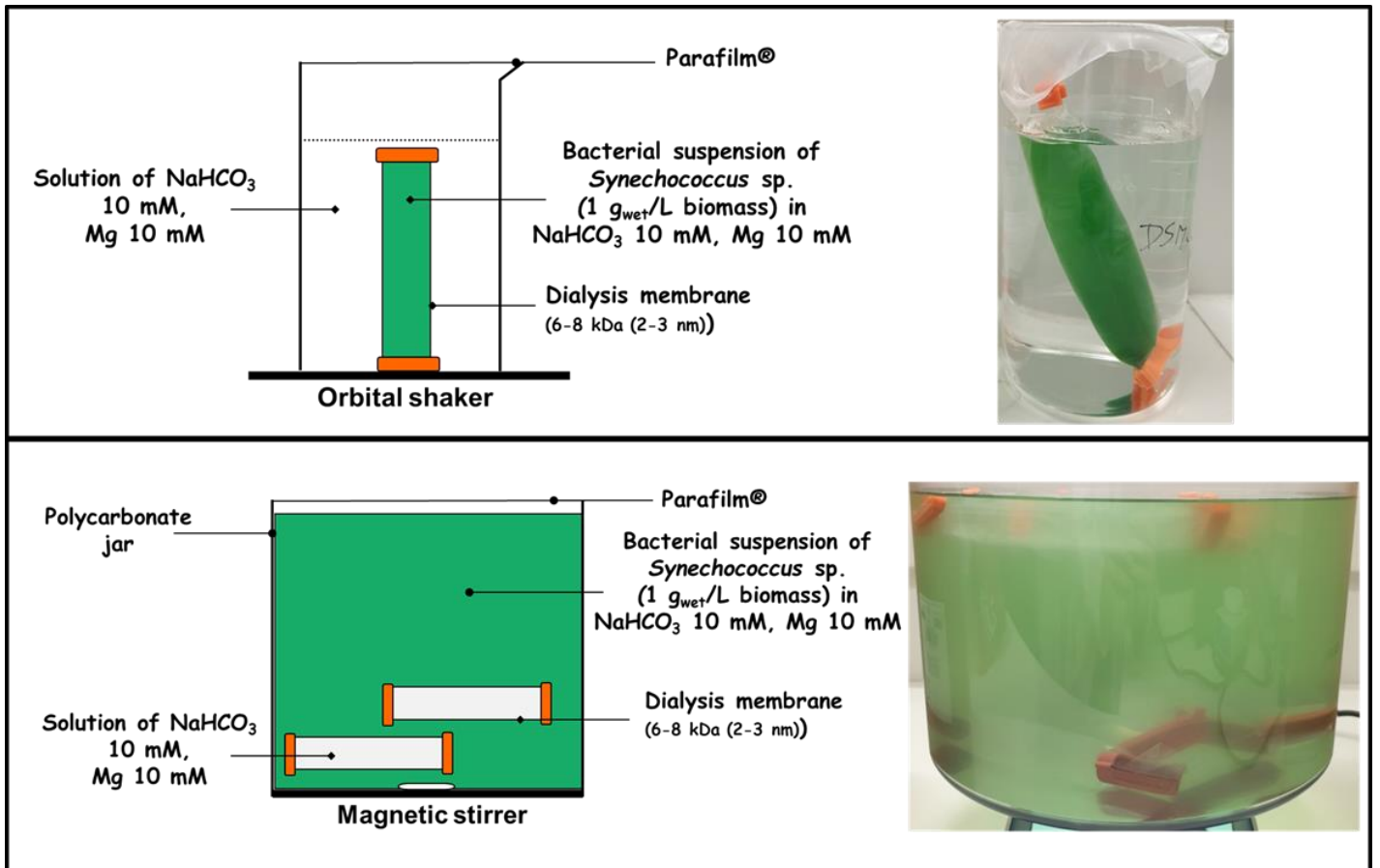


Figure 1. Schematic representations and photos of experiments with cyanobacteria *Synechococcus* sp. inside (A, experiment DSM) or outside (B, experiment SD) of the dialysis bag.

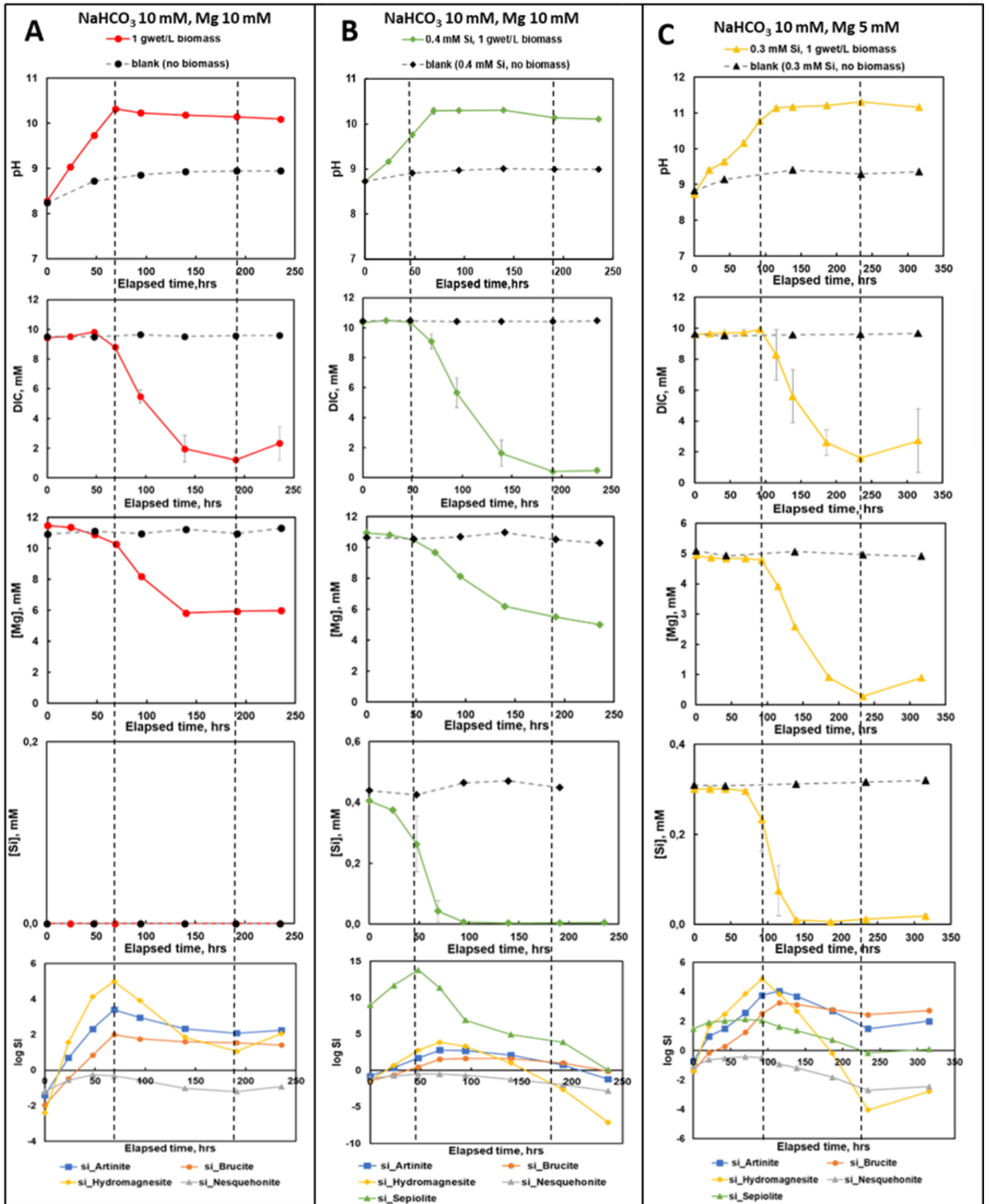


Figure 2. Evolution of pH, concentrations in DIC, Mg and Si, and saturation indices (SI) of some carbonate or silicate magnesium minerals as a function of time in experiments realized in presence of a monoculture of cyanobacteria *Synechococcus* sp. and 10% BG-11 culture medium in a solution of NaHCO₃ 10 mM with **A:** 10 mM Mg, **B:** 10 mM Mg and 0.4 mM Si, **C:** 5 mM Mg and 0.3 mM Si. Error bars represent standard deviation of experimental replicates.

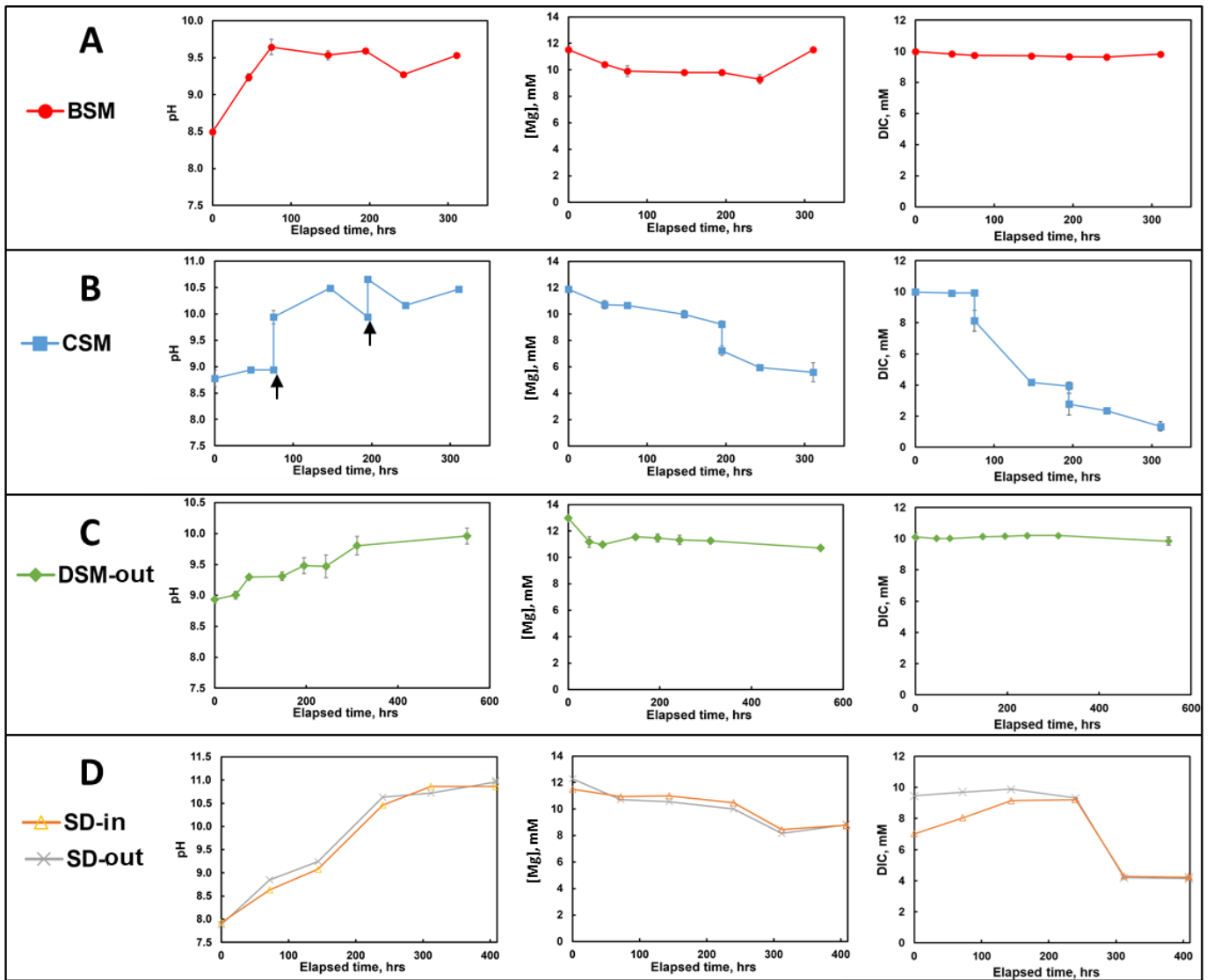


Figure 3. Evolution of pH, Mg and DIC concentrations over time for experiments without BG-11 culture media (BSM, **A**), in darkness (CSM, **B**), with cyanobacteria inside dialysis bag (DSM-out: sampling outside of the bag, **C**) and cyanobacteria outside of dialysis bag (SD-in and out: sampling respectively inside and outside of the bag, **D**). Error bars represent standard deviation of replicates.

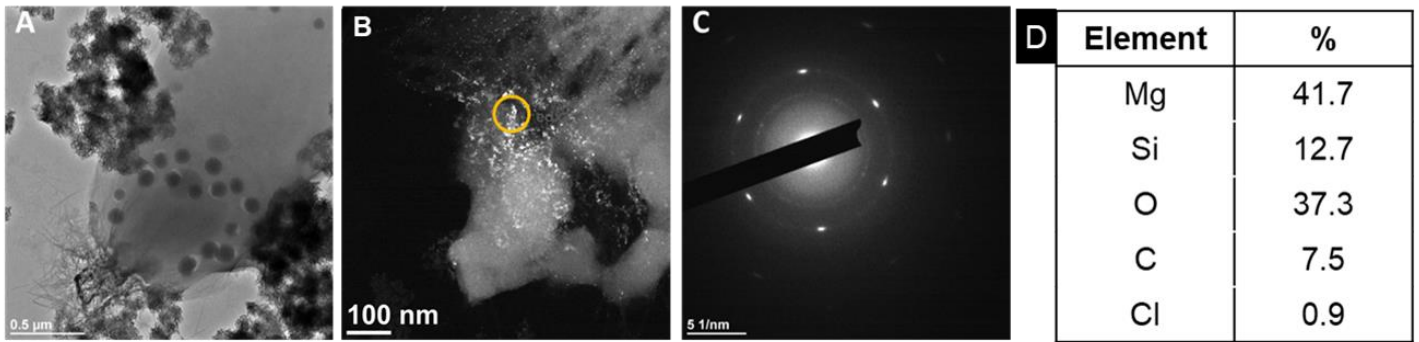


Figure 4. TEM observations of the experimental cell suspension with formed minerals in the presence of 10 mM of NaHCO_3 with 10 mM of Mg and 0.4 mM of Si after one week of experiment. **A:** cell of *Synechococcus* sp. in the center, presence of a solid fibrous phase near the cell (at the top and bottom right of the picture), and needles in the vicinity of the bacteria, **B:** picture in dark field to highlight the nanocrystals (white dots on the picture), **C:** FFT realized in the orange circle in panel B, **D:** composition of the particles in the orange circle according to the EDS analysis.

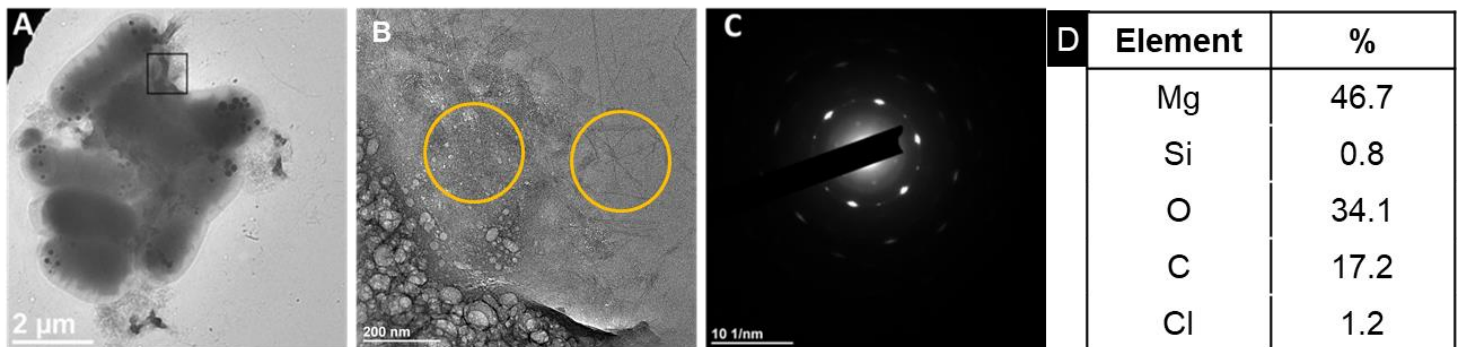


Figure 5. TEM observations of the experimental cell suspension with formed minerals in the presence of 10 mM of NaHCO_3 with 10 mM of Mg and 0.4 mM of Si after two weeks of experiments. **A:** group of cyanobacteria *Synechococcus* sp., **B:** zoom on the part framed in black on A, **C:** FFT realized on the part encircled in orange on the left on panel B, **D:** composition of the particles in the left orange circle according to the EDS analysis.

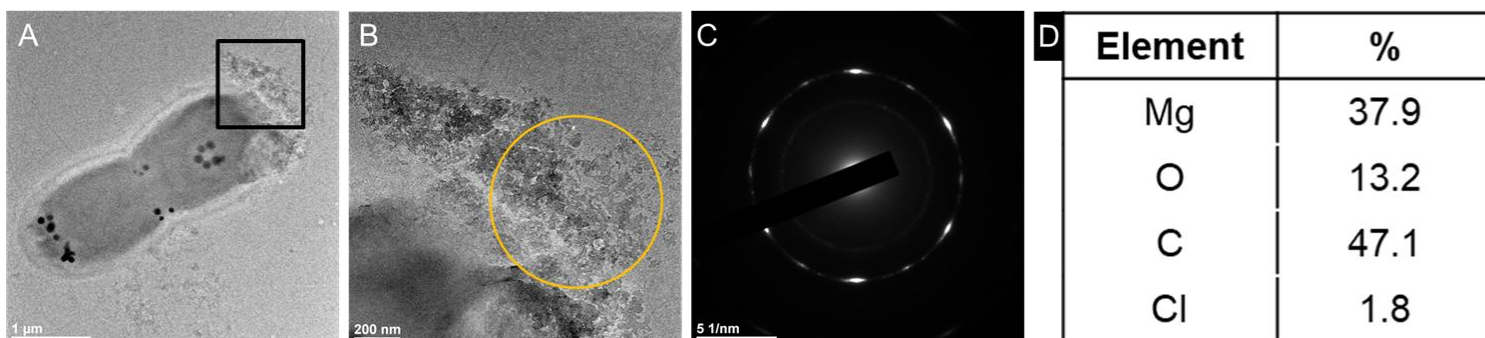


Figure 6. TEM observations of bacterial cells collected outside the dialysis bags in the experiment SD. **A:** cyanobacteria *Synechococcus* sp., **B:** zoom on the part framed in black on A, **C:** FFT realized on the part circled in orange on B, **D:** composition of the particles in the orange circle according to the EDS analysis.

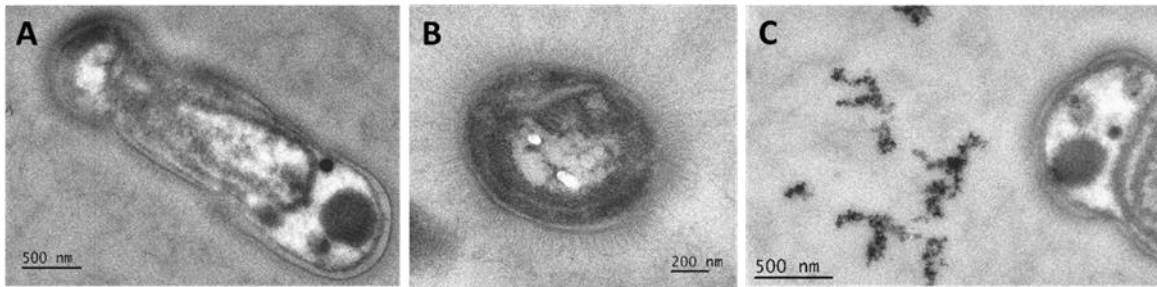


Figure 7. TEM cross-sections of *Synechococcus* sp. in a solution of 10 mM of NaHCO_3 enriched with 10 mM of Mg and 0.4 mM of Si. **A:** longitudinal section of *Synechococcus* sp., **B:** cross section of *Synechococcus* sp., **C:** solid particles on the left, cell of *Synechococcus* sp. on the right.

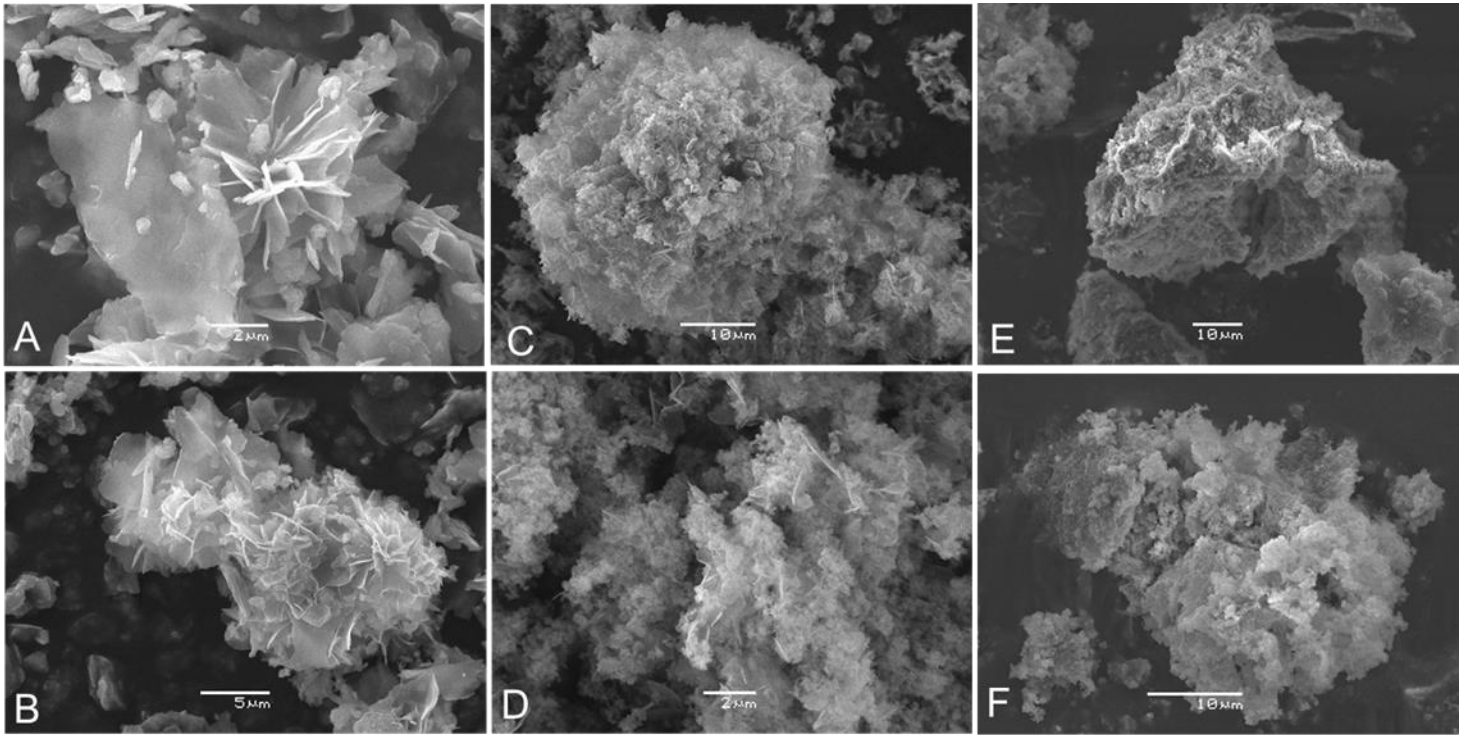


Figure 8. SEM pictures of the precipitated phases from abiotic experiments AMg3 (A and B), ASiMg3 (C and D), and ASI Mg (E and F).

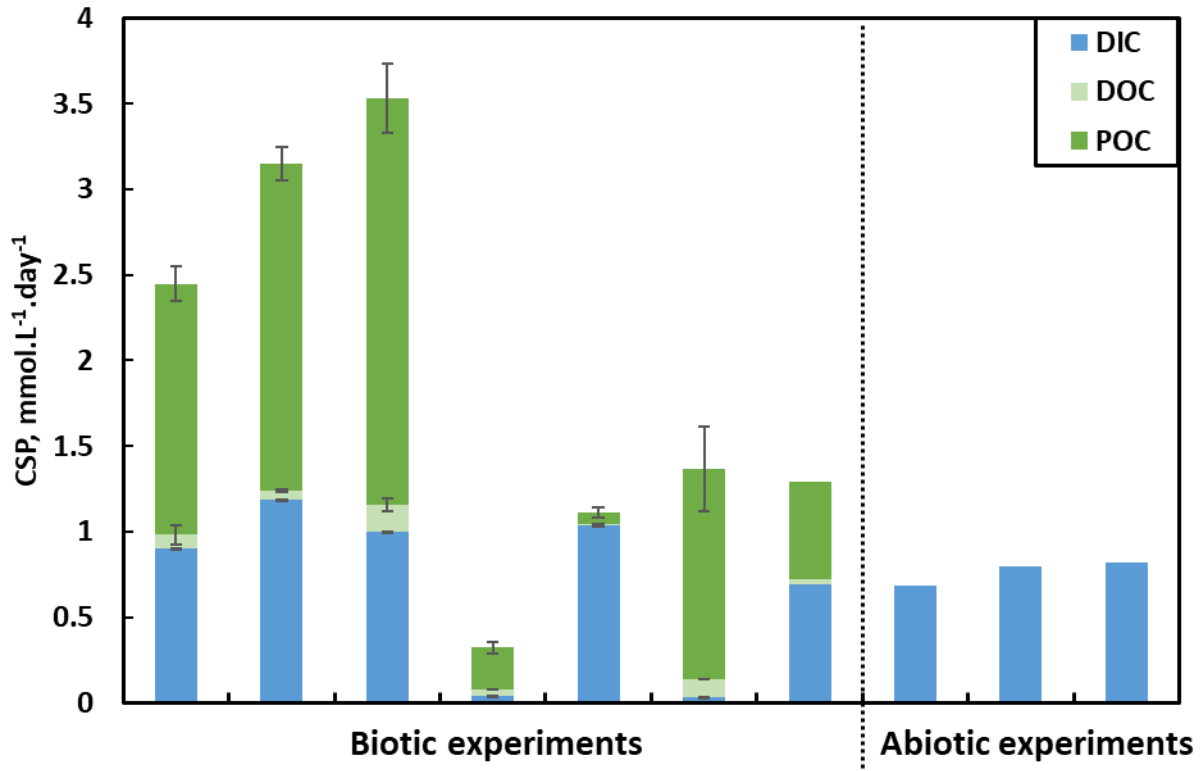
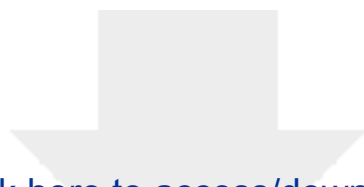


Figure 9. Comparison of carbon sequestration potential in biotic and abiotic experiments. Error bars represent standard deviation of replicates. Three forms of CO₂ sequestration – DIC, DOC and POC – represent mineral, soluble organic matter and cell biomass. See Table 1 for experimental conditions.



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Supplementary file

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