

# Does carbon dioxide storage by cyanobacteria induce biomineralization in presence of basaltic glass?

Thomas Ferrini, Olivier Grandjouan, Olivier Pourret, Raul E Martinez

# ▶ To cite this version:

Thomas Ferrini, Olivier Grandjouan, Olivier Pourret, Raul E Martinez. Does carbon dioxide storage by cyanobacteria induce biomineralization in presence of basaltic glass?. Geochemical Journal -Japan-, 2021, 55 (2), pp.51-58. 10.2343/geochemj.2.0617. hal-03085925

# HAL Id: hal-03085925 https://hal.science/hal-03085925

Submitted on 22 Dec 2020

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1	Does carbon dioxide storage by cyanobacteria induce
2	biomineralization in presence of basaltic glass?
3	
4	
5	Thomas Ferrini <sup>1</sup> , Olivier Grandjouan <sup>1</sup> , Olivier Pourret <sup>1,#</sup> , Raul E. Martinez <sup>2,*</sup>
6 7	<sup>1</sup> UniLaSalle, AGHYLE, 19 rue Pierre Waguet, 60026 Beauvais cedex, France
8	
9	<sup>2</sup> Institut für Geowissenschaten, Universität Freiburg, Alberstraße 23b, 79104 Freiburg,
10	Germany
11	
12	
13	
14	
15	
16	*Present address: Max Planck Institute for Biogeochemistry
17	#Corresponding author: olivier.pourret@unilasalle.fr.
18	
19	
20	
21	
22	
23	

## 25 Abstract

Cyanobacteria induced biomineralization of atmospheric CO<sub>2</sub> is a natural process leading to the 26 27 formation of carbonates by spontaneous precipitation or through the presence of nucleation 28 sites, under supersaturated conditions. As importance of basaltic rocks in the carbon cycle has already been highlighted, basaltic glass was chosen to test its ability to release cations needed 29 for carbonate formation in presence of Synechococcus sp. cyanobacteria. Active cyanobacteria 30 were expected to generate a local alkaline environment through photosynthetic metabolism. 31 32 This process produces oxygen and hydroxide ions as waste products, raising the pH of the immediate cell surface vicinity and indirectly enhancing the carbonate  $CO_3^{2-}$  concentration and 33 34 providing the a degree of saturation that can lead to the formation of calcite CaCO<sub>3</sub> or magnesite 35 MgCO<sub>3</sub>. In the presence of active cells, the saturation index (SI) increased from -10.56 to -9.48 for calcite and from -13.6 to -12.5 for magnesite, however they remained negative due to the 36 low  $Ca^{2+}$  and  $Mg^{2+}$  activities. Dead cells were expected to act as nucleation sites by the stepwise 37 binding of carbonate with Ca<sup>2+</sup> and Mg<sup>2+</sup> on their surface. In the presence of inactive cells, SI 38 values were closer to 0 but still negative due to the low pH and cation concentrations. Our 39 results highlight that our current understanding of the carbon cycle suggests that Earth's climate 40 is stabilized by a negative feedback involving CO<sub>2</sub> consumption and especially during chemical 41 weathering of silicate minerals. 42

43

Keywords: biomineralization, cyanobacteria, basaltic glass, carbonate, saturation index,
critical zone

### 46 **1. Introduction**

47

The rise of  $CO_2$  concentrations in the atmosphere is one of the most important 48 environmental problems on Earth today arising from anthropic activity (Gerlach, 2011). Carbon 49 storage methods, or carbon concentration mechanisms (CCM), need to be developed urgently 50 51 in order to reduce the  $CO_2$  impact on Earth's terrestrial and aquatic environments. The ability 52 of cyanobacteria to induce the biomineralization of CO<sub>2</sub> is an option which is still in its infancy and could possibly be used in the near-future to decrease atmospheric CO<sub>2</sub> levels (Martinez et 53 al., 2016). Previous studies have proven the link between cyanobacteria photosynthesis and the 54 55 presence of metallic cations could lead to carbonate precipitation in the presence of atmospheric CO<sub>2</sub> and under suitable solution conditions (Jansson and Northen, 2010; Martinez et al., 2016; 56 57 Obst et al., 2009).

58

Photosynthesis and CCM are the first steps to biomineralization of CO<sub>2</sub>. Cyanobacteria 59 are autophototrophic microorganisms. They are primary producers, which generate their own 60 nutrients by carrying out the oxygenic photosynthesis (Martinez et al., 2016). This metabolism 61 needs carbon as a source of inorganic carbon in the form of dissolved CO<sub>2</sub>, natural light as 62 63 source of energy and water to provide electrons needed in the redox transformation of carbon (Schubert et al., 1997). The Calvin-Benson cycle permits the assimilation of the inorganic 64 carbon thanks to the initial CO<sub>2</sub>-fixing-enzyme of photosynthesis: RuBisCO (Ribulose 65 Biphosphate Carbolxylase Oxygenase) (Fridlyand and Scheibe, 1999; Spreitzer and Salvucci, 66 2002). Chemical and photochemical reactions take place in photosystems located on the 67 thylakoid membrane of the cyanobacteria cell. ATP (Adenosine triphosphate) and NADPH 68 (Nicotinamide adenine dinucleotide phosphate) are chemical substances which permit  $CO_2$ 69 assimilation. A constant supply of inorganic carbon (IC) is required to carry out photosynthesis. 70

Dissolved CO<sub>2</sub>, in the form of bicarbonate  $HCO_3^-$  is the inorganic form of carbon used by 71 cyanobacteria as an IC source. A metabolic system is used to attain inorganic carbon from the 72 aqueous environment. The CCM corresponds to an environmental adaptation of cyanobacteria, 73 it allows IC incorporation inside the cell in the form of HCO<sub>3</sub><sup>-</sup> and convert it to CO<sub>2</sub> (Price et 74 al., 2008). Molecules are attracted and stocked inside the cell with the help of IC transporters 75 located in both plasma and outer membranes. HCO<sub>3</sub><sup>-</sup> transport is enhanced by the extra-ATP 76 77 generated during photosynthesis. The inorganic carbon is transported into the bacterial microcompartment where the bicarbonate molecules are transformed into CO<sub>2</sub> by the enzyme 78 carbonic anhydrase. The remaining CO<sub>2</sub> is then assimilated by the enzyme RuBisCO for 79 80 photosynthesis (Figure 1). A proton H<sup>+</sup> is consumed by each of these reactions, leading to the release of a hydroxide ion (OH<sup>-</sup>) outside the cell as a waste product along with O<sub>2</sub>. This allows 81 the generation of an alkaline pH within the micro-environment around the cyanobacteria cell. 82 83 This alkaline pH permits the deprotonation of the external bicarbonate HCO<sub>3</sub><sup>-</sup> to carbonate ions  $CO_3^2$ . The presence of both metal cations (e.g.  $Ca^{2+}/Mg^{2+}$ ) and carbonate ( $CO_3^{2-}$ ) allows the 84 85 nucleation of carbonates in the form of calcite (CaCO<sub>3</sub>) and magnesite (MgCO<sub>3</sub>) (Martinez et al., 2016; Riding, 2006). However, the amount of metal cations and carbonate must be high 86 enough to reach supersaturation with respect to these carbonate minerals. 87

In this study, basaltic glass was chosen as a source of metallic cations due to its 88 composition and abundance on the Earth's surface. Its importance in the carbon cycle has been 89 proven on several previous studies (Dessert et al., 2003; Grimm et al., 2019; Schlesinger and 90 Bernhardt, 2013; Schott et al., 2012). A high rate of dissolution of basaltic glass would be 91 92 required to release significant metallic cation concentrations to achieve supersaturation with respect to carbonate phases. Varying an electrolyte NaNO<sub>3</sub> background concentration has been 93 shown to affect the process of simple silicate mineral dissolution and the rate of release of 94 95 metallic cations as well as their activity (Martinez et al., 2014; Martinez et al., 2016). An

optimal concentration is needed in order to reach Ca<sup>2+</sup> and Mg<sup>2+</sup> activities, which together with 96 carbonate ion activities would lead to precipitation of carbonates. The Synechococcus 97 cyanobacteria species chosen for this study is representative of seawater cyanobacteria as along 98 with *Prochloroccocculs* sp., it is responsible for approximately 30% of the photosynthesis on 99 Earth. Synechococcus sp. is a unicellular coccoid cyanobacteria containing outermost surface 100 101 layers but no cell covering sheath (Martinez et al., 2010; Martinez et al., 2008). The goal of this 102 study is to determine whether basaltic glass is an efficient source of metal cations needed for 103 CO<sub>2</sub> mineralization and then to quantify the rates of carbonate precipitation in presence of this primary silicate and Synechococcus cyanobacteria species so that optimal conditions in terms 104 105 of basaltic glass dissolution and cyanobacteria biomass can be found.

106

## 107 2. Material and methods

108

A 20 mL aliquot of active Synechococcus sp. cyanobacteria stock at the stationary phase was 109 placed in a 5 L Schott® bottle. Synechococcus sp. cultures were grown in Cyanobacteria BG-110 11 Freshwater Medium (Sigma-Aldrich C3061) for three weeks to stationary growth phase 111 (Martinez et al., 2010). Active cyanobacteria stocks were prepared in order to achieve 112 photosynthesis in presence of basaltic glass (see bulk composition in Table 1), in order to 113 114 quantify the influence of cyanobacteria on the dissolution of the mineral could be observed and 115 the supersaturation conditions reached (see discussion on choice of experimental conditions in 116 Martinez et al., 2010). Stock cultures of cyanobacteria were kept at room temperature (23±1°C) under constant cool white fluorescent light illumination (5000 lx) and a constant filtered air 117 118 injection (3 L/min at around 400 ppm) in order to provide cyanobacteria with needed inorganic carbon. The air inflow was used to keep the culture in a constant movement needed for optimal 119 growth. For each experiment, 5 L of 1/500 diluted cyanobacteria growth medium inoculated 120

with a 20 mL aliquot of regular 1/50 BG-11 (Table 2) cyanobacteria stock was placed on a
rotary shaker at 250 rpm (Martinez *et al.*, 2008). Dead cyanobacteria were prepared by
autoclaving an aliquot of active stock at 121°C for 20 min. To measure the exact cyanobacteria
mass, a 25 mL sample was collected. Vacuum filtration was used to filter the sample through a
0.2 µm pore size cellulose nitrate filter (Whatman®). The filtered sample was placed in an oven
at 60°C for 30 min and then weighed.

127

## 128 2.1. Flow through open reactors system experimental design

129

Basaltic glass dissolution experiments were performed at 23±1°C by mixing two different stock
solutions in flow through reactors with a peristaltic pump with a fixed inflow rate of 1.4 µL/min.
The active cyanobacteria and inorganic stocks solutions used are described in Tables 2 and 3.

To quantify the rates of basaltic glass and carbonate precipitation in presence of *Synechococcus sp.* cyanobacteria, duplicate flow through reactors were used, each connected to the inorganic
and active cyanobacteria stocks by a peristaltic pump (Active cyanobacteria Flow Through open
reactor, AFT; **Table 2 and Figure 2**).

To assess the role of bio-mineralization by dead cells, a calcium chloride stock solution was used instead of basaltic glass as the source of metal cations (e.g. Ca<sup>2+</sup>). For these experiments, a flow through reactor was connected through the peristaltic pump to both the calcium chloride and dead cyanobacteria stocks previously washed by centrifuging at 10,000 rpm for 20 min (Calcium Flow Through reactor, CFT; **Table 3 and Figure 3**). Preliminary results and tests are available in Ferrini and Grandjouan (2015). These dead cells act as nucleation sites. They decrease the activation energy for precipitation, but saturation index (SI) values are notinfluenced by the existence of nucleation sites (Martinez *et al.*, 2008).

For all experiments, Tygon R 3603 tubes were used to link both stocks to 200 mL flow through reactors with the help of a 4 channel peristaltic pump with a low flow rate of  $1.4 \,\mu$ L/min.

147

# 148 **2.2. Sample analysis**

149

In order to monitor the chemical evolution and the cyanobacteria biomass concentration of the 150 solution inside the flow through reactor, the pH, conductivity, alkalinity, optical density, and 151 Ca<sup>2+</sup> and Mg<sup>2+</sup> concentrations were measured from samples collected in 50 mL polypropylene 152 Falcon® tubes from the output of the flow through reactors, once daily. Time zero was taken 153 154 to be the time of this first sampling of the flow through reactor solution (Martinez et al., 2016). Reactors were placed in a water bath at 22°C in order to keep their contents solutions at a 155 constant temperature. A 20 mL sample was taken from each reactor for all experiments. An 156 aliquot of 7 mL of sample was used to measure the optical density of the solution at 750 nm 157 wavelength, to approximate the concentration of cyanobacteria biomass over time. The 158 remaining 13 mL were used to measure pH, total alkalinity and conductivity. The pH and 159 alkalinity were measured with an automatic titration system (Metrohm® 719 Titrino automatic 160 titrator). In this study, dominated by the presence of dissolved CO<sub>2</sub>, the total alkalinity (TA) 161 provides an estimate of the concentrations of bicarbonate and carbonate species in solution. The 162 TA is determined through an acid titration (alkalinity titration) where the final concentration of 163 the acid, at the second end-point of the carbonate system, pH = 4.3, represents the total alkalinity 164 of the solution. Carbonate alkalinity (CA) is determined by driving the alkalinity titration to the 165

first end-point for the carbonate system at pH = 8.3. From the carbonate alkalinity, the  $CO_3^{2^-}$ concentration in solution, which is part of total alkalinity, can be determined:

168 
$$TA = [HCO_3^-] + 2 [CO_3^2] + [OH^-] - [H^+]$$
 (1a)

169

$$CA = 2 [CO_3^{2-}] + [OH^{-}] (1b)$$

As [CO<sub>3</sub><sup>2-</sup>], [H<sup>+</sup>] and [OH<sup>-</sup>] are negligible for neutral to alkaline pH conditions (between 6 and
11), total alkalinity can be re-defined to:

$$TA = [HCO_3]$$
 (2)

174

175 Ca<sup>2+</sup> and Mg<sup>2+</sup> concentrations were measured by flame atomic adsorption spectroscopy (F-176 AAS) with an Analytik Jena Vario 6 flame atomic adsorption spectrometer. The conductivity 177 of sample aliquots was measured using a WTW LF 325 conductivity meter where conductivity 178 is measured in mS/cm (Harris, 2010). Conductivity measurements for a particular solution 179 allow calculation of the ionic strength (IS). The IS is proportional to the concentration of all 180 dissolved salts in a solution. The ionic strength is required to calculate cation activity (ac) as 181 shown below:

$$a_{\rm C} = [{\rm C}] \gamma_{\rm C} \tag{3}$$

183 where [C] is the species concentration and  $\gamma_{\rm C}$  is the activity coefficient. The  $\log_{10}$  of  $\gamma_{\rm C}$  can be 184 calculated as per the Debye-Hückel equation Eq. 4 as a function of the solution IS determined 185 from conductivity measurements:

186 
$$\log \gamma_C = (-0.51 * z^2 * \sqrt{IS})/(1 + (\alpha * \sqrt{IS/305}))$$
 (4)

187 where z represents the charge of the ion (e.g. for  $Mg^{2+}$ , z=2),  $\alpha$  the radius of the ion in picometers 188 (e.g. for Ca<sup>2+</sup>,  $\alpha$  Ca<sup>2+</sup> = 600 pm) (Harris, 2010; Stumm and Morgan, 1996). To predict the formation of carbonate phases in this study, it is first necessary to quantify the degree of solution supersaturation with respect to Ca or Mg carbonates. This requires knowledge of the saturation index for each of these mineral phases. However, calculation of saturation state is first necessary. The saturation state ( $\Omega$ ) represents the degree of saturation of a solution with respect to a particular mineral phase (Langdon *et al.*, 2000) and is defined as follows:

195 
$$\Omega = (aCa^{2+}*aCO_{3}^{2-})/Ksp$$
(5)

Where Ksp is the solubility product of the mineral phase that can potentially form in solution (e.g. for calcite, Ksp= $10^{-8.48}$ ) and, aCa<sup>2+</sup> and aCO<sub>3</sub><sup>2-</sup> are the activities of Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> respectively. The SI is then defined as:

$$SI = log_{10}(\Omega) \tag{6}$$

A positive value of SI indicates supersaturation with respect to a mineral phase and suggests that precipitation of the mineral would occur. However this depends further on solution conditions (e.g. mineral nucleation, spontaneous nucleation/precipitation) (Langdon *et al.*, 203 2000).

3. Results 205

206

Temporal evolution of the pH, the total alkalinity and the cations concentrations has been 207 208 measured. These values were used to calculate saturation index with respect to calcite and magnesite. Related values for AFT and CFT are presented in Figures 4 and 5 and Figures 6 and 209 7, respectively. For all conditions, experiments were carried out in duplicates. 210

211

#### 212 3.1. Active cyanobacteria Flow Through open reactor results

213

214 In this experiments, the pH remained alkaline, starting at  $10.9 \pm 1$  and declining until a pH of 10.1 at 150 h (Figure 4). Total alkalinity increased from 1 mmol/L to 1.8 mmol/L in 242 h for 215 both reactors (Figure 4).  $[Ca^{2+}]$  and  $[Mg^{2+}]$  remained constant for the duration of the 216 experiments at an average of 3.37 + 1.00 mg/L for [Ca<sup>2+</sup>] and 3.28 + 0.44 mg/L for [Mg<sup>2</sup>]. 217 A slight decrease in these concentrations was observed for the experiment in the first reactor. 218 SI values for both calcite and magnesite remained negative for the time of the experiment. The 219 220 SI<sub>(calcite)</sub> increased from -10.6 to -9.4 over a period of 145 h whereas the SI<sub>(magnesite)</sub> raised from -13.6 to -12.5 (Figure 5). Both SI curves reached a constant threshold at 150 h. 221

222

#### **3.2.** Calcium Flow Through reactor results 223

224

The pH and the total alkalinity increased through the 300 h of the experiments. A total alkalinity 225 226 of 0.2 mmol/L was recorded at the start of experiments to reach a final value of 0.75 mmol/L (Figure 6). The pH was for the most part neutral but raised from 6.3 to a last value of 6.75 227

(Figure 6). The calcium chloride used permitted to obtain a rather constant [Ca<sup>2+</sup>] concentration
at an average of 280 mg/L. The calculated SI<sub>(calcite)</sub> is negative but close to the solution
supersaturation with respect to calcite. These values are remained within the range of -4.6 to 4.9 for the duration of the experiment (Figure 7).

None of both experiments could achieve supersaturation state with respect to calcite or 235 236 magnesite. The SI remain negative but fluctuate as a function of the pH, the cation concentration and the total alkalinity. This confirms that saturation index depends on metal cations and  $\text{CO}_3^{2-}$ 237 activities and further suggests the inability of basaltic glass dissolution to provide the necessary 238 amount of cations required for solution supersaturation with respect to carbonates. The AFT 239 experiment shows constant  $[Ca^{2+}]$  and  $[Mg^2]$  concentrations (see details in Ferrini and 240 Grandjouan (2015) ). In this case an increase in the  $CO_3^{2-}$  activity would be required to achieve 241 242 supersaturated conditions with respect to carbonate, this would be reflected in a positive value of the SI for these mineral phases. As the concentration of cations remained constant, a higher 243 concentration of carbonate or a higher degree of bicarbonate deprotonation from a higher pH 244 would be required. This means an enhanced deprotonation of bicarbonate HCO<sub>3</sub><sup>-</sup> and the 245 consumption of hydroxide ion (OH<sup>-</sup>). This then explains the decreasing pH and the increasing 246 247 total alkalinity as per eq.1. According to the previously mentioned definition of the carbonate alkalinity a pH higher than 8.3 would be required in order to induce bicarbonate ion 248 deprotonation for production of  $CO_3^{2-}$  in significant concentrations (Stumm and Morgan, 1996). 249 250 A higher pH could be reached by active cyanobacteria. Indeed, cyanobacteria consume bicarbonate ions by photosynthesis which leads to the higher pH values, the formation of 251 carbonate ( $CO_3^{2-}$ ) and a raising SI in the presence of sufficient metal cations for supersaturation 252 In the CFT case, increasing pH rates can be explained by the presence of dead cyanobacteria 253 mass and their interaction of their deprotonated cell surface groups with dissolving CO<sub>2</sub> from 254 255 air injection (Weber and Martinez, 2017). However, SI remains negative because of the nearneutral pH which prevents calcite precipitation as bio-mineralization needs a pH higher than 256 8.3 to commence the generation of carbonate ions. 257

It has been shown that active cyanobacteria have a protective mechanism against carbonate 258 259 precipitation on their surface, which is missing for dead cyanobacteria implying that this is the consequence of the metabolic activity of these primary producers (Martinez et al., 2010; 260 Martinez et al., 2008). Dead cyanobacteria cells or cellular debris may act as nucleation sites 261 by binding Ca<sup>2+</sup> and Mg<sup>2+</sup> cations on their surface. This could explain why the SI results become 262 less negative in the CFT experiment in presence of dead cells. There are two mechanisms of 263 264 mineral precipitation which are favored depending on the degree of solution supersaturation with respect to a particular mineral. In our study, we did not observe supersaturation with 265 respect to carbonate minerals, nor the conditions for spontaneous nucleation of these minerals, 266 267 a process that takes place saturation state values equal or in excess of 3 to 4. However, the existence of nucleation sites, does decrease the activation energy for precipitation, therefore 268 affecting the saturation index for a particular mineral, not in the bulk solution, but in the 269 270 microenvironment of dead cell surfaces, for example, where the value of the SI for a specific carbonate mineral may be enhanced due to the higher concentration of metal cations and 271 272 carbonate, near the negatively charged reactive solid surface. Therefore, the presence of both active and dead cyanobacteria, as in the natural environment, contributes to controlling the 273 mode of carbonate mineral precipitation, through the generation of an alkaline pH or due to the 274 275 efficient sorption of metal cations leading to the nucleation of mineral phases (Martinez et al., 2010; Martinez et al., 2016; Weber and Martinez, 2017). 276

Another important factor which is needed for supersaturation is the metal cations concentrations. CFT results proved that high metal cation concentrations from an efficiently dissolving source, such as calcium chloride, lead to SI values which are closer to solution supersaturation with respect to carbonates. AFT  $[Ca^{2+}]$  and  $[Mg^{2+}]$  concentrations from basaltic glass dissolution were insufficient to achieve carbonate precipitation. Indeed, a solution needs to be supersaturated with respect to a particular mineral in order for it to precipitate. Therefore,

the precipitation of carbonate minerals will depend not only on the metal cation activity but 283 284 also on the carbonate activity. In our results the pH of the solutions was low, therefore we observed a low carbonate activity and a slight release of metal cations from the basaltic glass. 285 Therefore, both of these aspects did not allow the ion activity product of metal cation and 286 carbonate in solution, to exceed the solubility product for carbonate minerals. This implies that 287 the use of basaltic glass for carbonation and CO<sub>2</sub> mineralization would be inefficient if 288 289 employed at large scale, requiring the use of faster dissolving simple silicate minerals such as 290 olivine, or finding a way to enhance the release of metal cations from simple and more complicated alumino-silicate minerals. The slight decrease in metal cation concentrations in 291 292 these experiments, occasionally observed, can be explained by the need for more testing and development of the flow through reactor used, where a fast flow rate would cause dilution of 293 294 metal cations. A slower pump rate would have to be used. Moreover, higher metal cation 295 dissolution rates would have to be reached, however, another silicate mineral would need to be tested which can release metal cations at a faster rate. The background electrolyte concentration 296 297 of 0.04 mol/L NaNO<sub>3</sub> could be modified in order to find the optimal concentration and optimize the dissolution rate and the metal cation activities. Smaller basaltic glass particles can be used, 298 this would produce and increase mineral surface area which would lead to an increase in the 299 300 basaltic glass dissolution rate.

As proposed on Figure 1, parameters which could contribute to achieving supersaturation state with respect to carbonates and subsequent precipitation in the presence of cyanobacteria are highlighted. As evidenced by our study, several points have to be improved in order to achieve carbonate nucleation and precipitation. *Synechococcus* cyanobacteria have to be grown in proper conditions with enough space and time to get to cell population saturation (at least 2 weeks). Active cells lead to an alkaline (high pH) environment by the photosynthesis process, and indirectly to the formation of carbonate  $CO_3^{2-}$ . The "flow through reactor" open system

permits a constant CO<sub>2</sub> supply and other nutrients required for photosynthesis and cell growth. 308 309 On another hand, basaltic glass has to be dissolved in optimal conditions so as to reach high aqueous  $[Ca^{2+}]$  and  $[Mg^{2+}]$  concentrations. Providing all these conditions, calcite or magnesite 310 precipitation could be expected in the flow through reactors. Using the rate model in Eq.11 an 311 approximation of the total carbonate precipitation amount could be calculated for potential 312 implementation of these systems at the larger scale. Scanning electron microscopy and energy-313 314 dispersive X-ray spectroscopy analyses could then help to the analysis and identification of carbonates to confirm the presence of calcite or aragonite polymorphs or that of magnesite. By 315 finding optimal conditions for cyanobacteria induced bio-mineralization, this method could be 316 317 used to stock significant quantities of CO<sub>2</sub> at a large scale.

Overall, our results highlight that our current understanding of the long-term carbon cycle suggests that Earth's climate is stabilized by a negative feedback involving CO<sub>2</sub> consumption and especially during chemical weathering of silicate minerals (Penman *et al.*, 2020).

321

### 322 Acknowledgments

323 The authors would like to thank the Institut Polytechnique UniLaSalle, for funding part of this study and T.F. and O.G. bachelor thesis. In addition the authors would like to thank Ms. Sigrid 324 Hirth-Walther of the Institute of Geosciences at the University of Freiburg for F-AAS 325 326 measurements, Dr. Petru Jitaru of Institut Polytechnique UniLaSalle for ICP-MS analysis. Furthermore, the authors would like to extend their gratitude to Dr. Christian Grimm and Dr. 327 Eric H. Oelkers of the GET-CNRS in Toulouse, France, for providing the basaltic glass samples 328 329 used in this study. Eventually, we thank Dr. Daniel E. Ibarra for insightful review of the manuscript. 330

### 332 **References**

- Dessert, C., Dupré, B., Gaillardet, J., François, L. M. and Allègre, C. J. (2003) Basalt weathering laws
  and the impact of basalt weathering on the global carbon cycle. *Chem. Geol.* 202, 257-273.
- Ferrini, T. and Grandjouan, O. (2015) CO<sub>2</sub> storage by cyanobacteria induced biomineralization in
   presence of basaltic glass. Bachelor.
- Fridlyand, L. E. and Scheibe, R. (1999) Regulation of the Calvin cycle for CO2 fixation as an example
   for general control mechanisms in metabolic cycles. *Biosystems*. 51, 79-93.
- Gerlach, T. (2011) Volcanic versus anthropogenic carbon dioxide. *Eos, Transactions American Geophysical Union.* 92, 201-202.
- Grimm, C., Martinez, R. E., Pokrovsky, O. S., Benning, L. G. and Oelkers, E. H. (2019) Enhancement
   of cyanobacterial growth by riverine particulate material. *Chem. Geol.* 525, 143-167.
- 343 Harris, D. C. (2010) *Quantitative Chemical Analysis, Eight Edition*. MacMillan Publishing
- Jansson, C. and Northen, T. (2010) Calcifying cyanobacteria—the potential of biomineralization for
   carbon capture and storage. *Current Opinion in Biotechnology*. 21, 365-371.
- Langdon, C., Takahashi, T., Sweeney, C., Chipman, D., Goddard, J., Marubini, F., Aceves, H., Barnett,
  H. and Atkinson, M. J. (2000) Effect of calcium carbonate saturation state on the calcification
  rate of an experimental coral reef. *Global Biogeochem. Cy.* 14, 639-654.
- Martinez, R. E., Gardés, E., Pokrovsky, O. S., Schott, J. and Oelkers, E. H. (2010) Do photosynthetic
   bacteria have a protective mechanism against carbonate precipitation at their surfaces?
   *Geochim. Cosmochim. Acta.* 74, 1329-1337.
- Martinez, R. E., Pokrovsky, O. S., Schott, J. and Oelkers, E. H. (2008) Surface charge and zeta-potential
   of metabolically active and dead cyanobacteria. *J. Colloid Interface Sci.* 323, 317-325.
- Martinez, R. E., Weber, S. and Bucher, K. (2014) Quantifying the kinetics of olivine dissolution in partially closed and closed batch reactor systems. *Chem. Geol.* **367**, 1-12.
- Martinez, R. E., Weber, S. and Grimm, C. (2016) Effects of freshwater Synechococcus sp. cyanobacteria
   pH buffering on CaCO3 precipitation: Implications for CO2 sequestration. *Appl. Geochem.* 75, 76-89.
- Obst, M., Wehrli, B. and Dittrich, M. (2009) CaCO3 nucleation by cyanobacteria: laboratory evidence
   for a passive, surface-induced mechanism. *Geobiology*. 7, 324-347.
- Penman, D. E., Caves Rugenstein, J. K., Ibarra, D. E. and Winnick, M. J. (2020) Silicate weathering as
  a feedback and forcing in Earth's climate and carbon cycle. *Earth-Science Reviews*. 209, 103298.
- Price, G. D., Badger, M. R., Woodger, F. J. and Long, B. M. (2008) Advances in understanding the
   cyanobacterial CO2-concentrating-mechanism (CCM): functional components, Ci transporters,
   diversity, genetic regulation and prospects for engineering into plants. *Journal of Experimental Botany*. 59, 1441-1461.
- Riding, R. (2006) Cyanobacterial calcification, carbon dioxide concentrating mechanisms, and
   Proterozoic–Cambrian changes in atmospheric composition. *Geobiology*. 4, 299-316.
- Schlesinger, W. H. and Bernhardt, E. S. (2013) Chapter 5 The Biosphere: The Carbon Cycle of
   Terrestrial Ecosystems. *Biogeochemistry (Third Edition)* (Schlesinger, W. H. and Bernhardt, E.
   S. eds.), 135-172, Academic Press.
- Schott, J., Pokrovsky, O. S., Spalla, O., Devreux, F., Gloter, A. and Mielczarski, J. A. (2012) Formation,
   growth and transformation of leached layers during silicate minerals dissolution: The example
   of wollastonite. *Geochim. Acta.* 98, 259-281.
- Schubert, W.-D., Klukas, O., Krauß, N., Saenger, W., Fromme, P. and Witt, H. T. (1997) Photosystem
   I of Synechococcus elongatus at 4 Å resolution: comprehensive structure analysis. *Journal of Molecular Biology*. 272, 741-769.
- Spreitzer, R. J. and Salvucci, M. E. (2002) RUBISCO: Structure, Regulatory Interactions, and
   Possibilities for a Better Enzyme. *Annual Review of Plant Biology*. 53, 449-475.
- 381 Stumm, W. and Morgan, J. J. (1996) *Aquatic Chemistry*. Wiley Intersciences
- Weber, S. and Martinez, R. E. (2017) Effects of Synechococcus sp. cyanobacteria inert biomass on
   olivine dissolution: Implications for the application of enhanced weathering methods. *Appl. Geochem.* 84, 162-172.

Element	Unit	Concentration
SiO <sub>2</sub>	%	47.49
$Al_2O_3$	%	14.06
$Fe_2O_3$	%	13.51
MgO	%	9.38
CaO	%	11.62
Na <sub>2</sub> O	%	1.85
$K_2O$	%	0.28
TiO <sub>2</sub>	%	1.53
$P_2O_5$	%	0.17
MnO	%	0.2
$Cr_2O_3$	%	0.086

**Table 2** Composition of flow through reactors initial solution for AFT experiment.

5L of active cyanobacteria stock					
Reagent	Quantity				
aliquot BG-11	10 mL				
Synechococcus sp.					
at the stationary phase	20 mL				
NaNO <sub>3</sub>	0.04 mol/L				
MgSO <sub>4</sub>	0.003 mol/L				
"Inorganic" stock					
Basaltic glass	20 g				
NaNO <sub>3</sub>	0.04 mol/L				
MgSO <sub>4</sub>	0.003 mol/L				

# **Table 3** Composition of flow through reactors initial solution for CFT experiment.

5 L dead cyanobacteria "autoclaved" stock						
Reagent	Quantity					
Active cyanobacteria "autoclaved"						
(20 min at 121°C)	60 mL					
NaNO <sub>3</sub>	0.04 mol/L					
MgSO <sub>4</sub>	0.003 mol/L					
Calcium chloride stock						
CaCl	0.09 mol/L					
NaNO3	0.04 mol/L					
MgSO4	0.003 mol/L					

## **Figure captions**

**Figure 1** Schematic interpretation of optimal conditions leading to cyanobacteria induced biomineralization in presence of basaltic glass.

Figure 2 Active cyanobacteria Flow Through open reactor (AFT) experimental set up.

Figure 3 Calcium Flow Through reactor (CFT) experimental set up.

**Figure 4** Evolution of pH and total alkalinity through time experiment (0.04 mol/L NaNO<sub>3</sub>;

AFT experiment 2). Experiment was duplicated between 0 and 120 h.

**Figure 5** Evolution of saturation index through time experiment (0.04 mol/L NaNO<sub>3</sub>; AFT experiment 2).

**Figure 6** Evolution of pH and total alkalinity through time experiment (0.04 mol/L NaNO<sub>3</sub>; CFT experiment).

**Figure 7** Evolution of Saturation index through time experiment (0.04 mol/L NaNO<sub>3</sub>; CFT experiment).



Figure 1



# Figure 2



Figure 3



Figure 4



Figure 5



Figure 6



Figure 7