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## Direct and indirect impact of the bacterial strain *Pseudomonas aeruginosa* on the dissolution of synthetic Fe(III)- and Fe(II)-bearing basaltic glasses

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Anne Perez, Stéphanie Rossano, Nicolas Trcera, Aurélie Verney-Carron, Céline Rommevaux, et al.. Direct and indirect impact of the bacterial strain *Pseudomonas aeruginosa* on the dissolution of synthetic Fe(III)- and Fe(II)-bearing basaltic glasses. *Chemical Geology*, 2019, 523, pp.9-18. 10.1016/j.chemgeo.2019.05.033 . hal-02359923

**HAL Id: hal-02359923**

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Submitted on 3 Feb 2020

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1                   **Direct and indirect impact of the bacterial strain *Pseudomonas***  
2                   ***aeruginosa* on the dissolution of synthetic Fe(III)- and Fe(II)-bearing**  
3                   **basaltic glasses**  
4

5  
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## Abstract

This study is dedicated to the determination of the respective direct and indirect bacterial contributions during the dissolution process of synthetic basaltic glass. In this regard, three different types of glasses – with or without Fe, in the reduced Fe(II) or oxidized Fe(III) states – were prepared on the basis of a simplified basaltic glass composition. In order to assess the direct/indirect bacterial contributions, the experimental set-up included the use of dialysis bags, which prevent the direct contact between the model siderophore-producing strain *Pseudomonas aeruginosa* and the synthetic glasses. The glasses were immersed at 25°C and pH 6.5 in a growth medium inoculated with the strain and submitted to alteration times from 8 hours to 6 days. Throughout the dissolution experiments, the following parameters were monitored: determination of bacterial growth, quantification of siderophore (*i.e.* pyoverdine) production, microscopic observation of the glass surface and determination of dissolution kinetics. The results were compared to identical experiments performed without dialysis bags and show different behaviors depending on the accessibility of the cells to the glass. For all compositions, isolating the glass from the bacterial suspension triggered the biosynthesis of siderophores. This production appeared to be either continuous in the Fe-free system or stopped as soon as the bacteria entered their stationary phase of growth in the Fe-bearing systems. By contrast, allowing a direct contact between the glass surface and the bacterial suspension triggered a high and continuous production of siderophore in the Fe-free system and only a small production in the presence of the Fe(II)-bearing glass. The dissolution rates were approximately increased by a factor of 3 for Fe-free and Fe(III)-bearing glass and by a factor of 2 for Fe(II)-bearing glass compared to sterile experiments. Pyoverdine concentrations similar to those obtained with dialysis bags were obtained in presence of the Fe(II)-bearing glass and were below detection limit in presence of the Fe(III)-bearing glass. The dissolution rates were correlated to siderophore concentrations as they increased this time with respect to sterile experiments in the order Fe(III)-bearing glass < Fe(II)-bearing glass < Fe-free glass. Finally, in all experimental cases, the bacteria appeared to increase the dissolution kinetics of the three model glasses involved. However, the Fe(III) accessibility to the bacterial cells was shown to be the key parameter regulating the bacterial activity and their efficiency in accelerating the dissolution.

## Key-words:

Basaltic glass; *Pseudomonas aeruginosa*; siderophore; bioalteration; dissolution kinetics

66

## Introduction

67

68 Silicate glasses are abundant at the Earth's surface and notably near the oceanic ridge axes where  
69 large amounts of lava are emitted every year, generating a profusion of both amorphous and  
70 crystalline basaltic rocks. The alteration processes of basaltic glasses in permanent contact with  
71 seawater are known for partially controlling the composition of this latter but also the composition of  
72 the oceanic crust and impacting on the geochemistry of the Earth mantle. The alteration of basaltic  
73 glasses could also have a significant impact on the Earth's climate by contributing to the sequestration  
74 of atmospheric CO<sub>2</sub> through carbonation processes resulting from the dissolution of the glass and the  
75 release of earth alkali elements (Berner et al., 1983). Understanding the alteration mechanisms of the  
76 oceanic crust at low temperatures is thus essential to implement the Earth surface mass-balance  
77 studies and then improve the geochemical models predicting the evolution of our planet (Hart, 1970;  
78 Staudigel and Hart, 1983; Spivack and Staudigel, 1994; Gislason and Oelkers, 2003).

79

80 During the last two decades, the high diversity and the abundance of the microorganisms living at the  
81 subsurface of oceanic basalts were evidenced (Thorseth et al., 2001; Santelli et al., 2009; Mason et  
82 al., 2009; Orcutt et al., 2011; Henri et al., 2015; Sudek et al., 2017). As basaltic glasses represent one  
83 of the most profuse source of Fe and also contain additional elements (Mg, Ca, K...) required for  
84 microbial nutrition (Staudigel and Hart, 1983), they are suspected to sustain the development of  
85 microbial communities (Sudek et al., 2009). The literature attests to four main potential bacterial sinks  
86 for the elements constituting silicate materials submitted to bioalteration: 1/ adsorbed or 2/  
87 incorporated inside the bacterial cells, 3/ trapped within the biofilms or 4/ complexed with bacterial  
88 exometabolites such as siderophores (e.g. Uroz et al., 2009). However, the role of basaltic glasses as  
89 a substantial source of nutrients, the impact of such microbial activity on their dissolution rates and its  
90 potential control on the biogeochemical cycling of elements at the rock/water interface is still a matter  
91 of debate (Templeton et al., 2005; Cockell et al., 2010; Henri et al., 2016).

92

93 Numerous laboratory studies were dedicated to the understanding of the basaltic glass dissolution  
94 processes in a various range of abiotic experimental conditions (e.g. Guy and Schott, 1989; Daux et  
95 al., 1997; Techer et al., 2000, 2001; Oelkers, 2001; Oelkers and Gislason, 2001; Stroncik and  
96 Schmincke, 2001; Gordon and Brady, 2002; Crovisier et al., 2003; Gislason and Oelkers, 2003; Wolff-  
97 Boenisch et al., 2004a; Flaathen et al., 2010; Verney-Carron et al., 2011; Parruzot et al., 2015; Perez  
98 et al., 2015). The dissolution of basaltic glass is traditionally defined by two simultaneous mechanisms,  
99 whose predominance notably depends on the pH of the aqueous fluid: (1) an ion exchange between  
100 network-modifying elements of the glass (Na, K, Ca, Mg) and hydrogenated species from the solution  
101 (interdiffusion) and (2) the hydrolysis of the bonds linking oxygen atoms to network-forming elements  
102 of the glass (Si, Al, Fe(III)). Dissolution can also be presented as the breaking of all metal-oxygen  
103 bonds (from the weakest to the strongest) until the structure is completely destroyed (Oelkers, 2001;  
104 Oelkers and Gislason, 2001). As the rate-limiting step of the basaltic glass dissolution process is the  
105 detachment of tetrahedral Si near the glass surface, the change of the other network-forming elements

106 (Al, Fe) speciation is assumed to influence the dissolution rate. For these reasons, the impact of the  
107 introduction in the liquid medium of biomolecules known for their high affinity with such cations should  
108 be investigated.

109  
110 Several field studies conducted in deep-sea water and dedicated to the characterization of microbial  
111 communities show that if the many cultured organisms are metabolically and functionally diverse, they  
112 display at least two of the tested functions: heterotrophy, Fe(II) and Mn(II) oxidation and siderophore  
113 production (e.g. Sudek et al., 2009). Siderophores are molecules produced when bacteria are  
114 submitted to a nutrient stress, and especially to a high need in Fe. The biosynthesis of siderophores  
115 involves several steps catalysed by specific enzymes in different locations from cytoplasm to  
116 periplasm, from where they are secreted to the extracellular medium (Schalk and Guillon, 2013).  
117 Siderophores have generally a very high affinity for two of the three network-forming elements Al and  
118 Fe(III). In two previous studies (Perez et al., 2015, 2016), experiments performed on synthetic Fe(II),  
119 Fe(III)-bearing basaltic glasses (MORB2, MORB3) and Fe-free glass (HAPLO) in the presence of  
120 siderophores and then in the presence of the model siderophore-producing strain *Pseudomonas* (*P.*)  
121 *aeruginosa* exhibited enhanced dissolution rates compared to those performed in sterile controls. The  
122 results highlighted the promoting role of organic ligands as complexing agents, and particularly of  
123 pyoverdines, which are the siderophores produced by *P. aeruginosa*. These conclusions were in  
124 agreement with numerous abiotic studies dealing with dissolution kinetics of minerals/oxides/silicate  
125 glasses in the presence of organic molecules (Welch and Ullman, 1992; Watteau and Berthelin, 1994;  
126 Stillings et al., 1995; Drever and Stillings, 1997; Kraemer et al., 1999; Liermann et al., 2000; Coccozza  
127 et al., 2002; Cheah et al., 2003; Wolff-Boenisch, 2007; Wang et al., 2005; Olsen and Rimstidt, 2008;  
128 Martinez-Luevanos et al., 2011; Torres et al., 2014; Akafia et al., 2014; Lazo et al., 2017). This  
129 promoting effect is in favour of the occurrence of a bacteria-mediated process, which notably contrasts  
130 with several recent studies attesting to a small or negligible impact of the presence of bacteria on  
131 dissolution kinetics of minerals (Hopf et al., 2009; Hutchens, 2009; Sverdrup, 2009; Bray et al., 2015)  
132 and of basaltic glass (Wolff-Boenisch, 2011; Stockmann et al., 2012). It is therefore important to note  
133 that this promoting effect was observed in specific conditions (growth phase and nutrient free systems)  
134 in which the acquisition of nutrient was crucial for the bacterial cells. Even though the impact of  
135 siderophores on the dissolution kinetics of basaltic model glasses was evidenced, the bacterial-  
136 promoted dissolution mechanisms of the glasses remain hard to define as bacteria can also directly  
137 interact with glass surfaces or produce other metabolites that could influence the dissolution rates  
138 (Ullman et al., 1996; Hutchens, 2009; Shirokova et al., 2012; Ahmed and Holmström, 2015; Cornu et  
139 al., 2017; Wang et al., 2018).

140 The present work aims to decipher direct and indirect dissolution mechanisms of basaltic glass by  
141 bacteria. For this purpose, bioalteration experiments were performed on HAPLO, MORB2 and MORB3  
142 synthetic glasses. In order to assess the direct/indirect bacterial contributions, the experimental set-up  
143 included the use of dialysis bags, which prevented the direct contact between the model siderophore-  
144 producing strain *P. aeruginosa* and the basaltic glasses tested. Throughout the dissolution  
145 experiments the following parameters were monitored: determination of bacterial growth, quantification

146 of siderophore (*i.e.* pyoverdine) production, microscopic observation of the glass surface and  
147 determination of dissolution kinetics.

148  
149

## 150 **Material and Methods**

151

### 152 1. Samples

153

154 The theoretical compositions of the three model glasses used in this study are given in Table 1. The  
155 MORB2 and MORB3 glasses were prepared according to a simplified typical *Mid Oceanic Ridge*  
156 *Basalt* composition and contain mainly Fe(II) and Fe(III), respectively. The HAPLO glass is an Fe-free  
157 equivalent composition in which Fe is mainly substituted by Mg.

158

159 Table 1: Nominal compositions of the synthetic Fe(II)-bearing glass (MORB2), Fe(III)-bearing glass (MORB3) and Fe-free glass  
160 (HAPLO) of interest.

	<b>MORB2 &amp; 3</b>	<b>HAPLO</b>
	(wt %)	(wt %)
SiO <sub>2</sub>	48.6	51.6
Al <sub>2</sub> O <sub>3</sub>	15.7	16.7
FeO	12.5	0.0
CaO	11.1	11.8
MgO	7.7	15.2
Na <sub>2</sub> O	2.7	2.9
TiO <sub>2</sub>	1.4	1.5
K <sub>2</sub> O	0.2	0.3

161

162 MORB2, MORB3 and HAPLO glasses were prepared according to the procedure described in the  
163 work of [Perez et al. \(2016\)](#). More details concerning the characterization of these glasses (DRX, XAS,  
164 BET measurements) are also given in this previous study.

165

### 166 2. Bioalteration experiments

167

168 Freshly grown cultures of *P. aeruginosa* ATCC® 9027 (Sigma Aldrich) bacteria having identical age  
169 and initial nutritional status were used in all bioalteration experiments.

170

171 Two growth media were used in this study. The bacteria were first grown in 2 mL of Lysogeny Broth  
172 (LB) medium, a nutritionally rich medium containing: 10 g L<sup>-1</sup> tryptone, 5 g L<sup>-1</sup> yeast extract, 5 g L<sup>-1</sup>  
173 NaCl.

174

175 The prepared glasses were then immersed in a buffered (pH 6.5) MM9 medium whose composition  
176 was adapted from Schwyn and Neilands (1987) and Liermann et al. (2000). Near neutral conditions of  
177 pH were chosen to allow for comparison with similar experiments conducted in abiotic conditions  
178 (Perez et al., 2015). The medium composition was as follows: 6.06 g L<sup>-1</sup> Na<sub>2</sub>HPO<sub>4</sub>, 0.3 g L<sup>-1</sup> KH<sub>2</sub>PO<sub>4</sub>,  
179 0.5 g L<sup>-1</sup> NaCl, 1.0 g L<sup>-1</sup> NH<sub>4</sub>Cl and 50 mM Bis Tris. The pH was adjusted by adding HCl 1 M. The  
180 solutions were sterilised and cooled to 25 °C. They were then supplemented with 0.2% (v/v) 1 M  
181 MgSO<sub>4</sub> (final concentration 2 mM), 1% (v/v) filter-sterilised (cellulose filter, Ø0.2 µm) 20% (w/v)  
182 glucose (final concentration 1 M) and 0.01% (v/v) 1 M CaCl<sub>2</sub> (final concentration 0.1 mM); these  
183 solutions were prepared and sterilized separately. No Fe was detected in the prepared growth medium  
184 and no precipitate formation was observed. Dissolution experiments were performed in sterile  
185 borosilicate erlenmeyers closed with cotton plugs to allow free passage of air over the edge of the  
186 vessels and to maintain an aerobic aqueous environment. A volume of 250 mL of MM9 6.5 medium  
187 was mixed with 0.625 g of glass powder and inoculated together with 125 µL of the LB culture of *P.*  
188 *aeruginosa* after 30 h of incubation at 25 °C and 160 rpm. By contrast with the experiments presented  
189 in Perez et al. (2016), the glasses were isolated from the bacterial suspension by sterile dialysis bags  
190 (©CelluStep T4). Porous dialysis membranes allow small solutes to pass while large species are  
191 retained and can thus effectively be used as a separation process based on size rejection. The  
192 Molecular Weight Cut Off of the membranes used in our experiments is 12000-14000 Da, which  
193 means that: (1) 90% of the species whose molecular weight ranges between 12000 and 14000 Da do  
194 not pass the membrane and do not access to the glass surfaces and (2) 100% of the species whose  
195 molecular weight exceeds 14000 g/mol do not pass the membrane. In the context of this study, the  
196 used membranes allow most exometabolites, in particular siderophores, to interact with the glass  
197 surface whereas the bacteria cells are isolated from the solid samples.

198 At each dissolution time, 2.3 mL of the liquid medium were filtered (cellulose acetate filter, Ø0.2 µm)  
199 and kept for Inductively Coupled Plasma and Optical Emission Spectroscopy (ICP-OES) analysis  
200 whereas 1.7 mL were placed in a spectrophotometer cell for Optical Density (OD) measurements and  
201 200 µL were plated right away on LB agar medium for the microbial counting procedure. Sampling  
202 times were chosen as a function of the bacteria growth: frequent from the beginning until the end of  
203 the exponential phase and then more distant (0.6, 1, 1.6, 2, 3 and 5.7 days). Experiments were  
204 extended until 15 days of experiments and 1.7 mL were sampled at days 8, 10, 13 and 15 and  
205 introduced in a spectrophotometer cell for additional measurements.

206 For each glass, sterile experiments (without introducing *P. aeruginosa*) were conducted following the  
207 same protocol and are mentioned as “abiotic control” in the Results and Discussion section. Moreover,  
208 *P. aeruginosa* was cultivated in identical conditions but without adding the glass into the system.  
209 These experiments were mentioned as “control” in the following sections.

210 All experiments were performed in duplicates.

211

212 3. Analysis

213 The amounts of dissolved Al, Fe and Si were analyzed using a Perkin Elmer Optima 8300 ICP-OES.  
214 Measurements were performed using emission wavelength at 288.16 nm (Si), 308.22 nm (Al),  
215 239.56 nm (Fe). Ca, Mg, Na, K were exempted from analysis being initially present in significant  
216 amounts in the growth medium.

217 For each element and at each dissolution time, the normalized mass loss  $NL_i$  from the glass into the  
218 solution was calculated using Eq. (1).

219 
$$NL_i = \frac{[i]}{\left(\frac{S}{V}\right) \times x_i} \quad (1)$$

220  
221 where  $[i]$  is the concentration ( $\text{mg L}^{-1}$ ) of the element  $i$  in solution,  $S$  the initial surface of the glass  
222 powder in contact with the fluid,  $V$  the volume of solution and  $x_i$  the mass percentage of the element  $i$   
223 in the glass.

224 Considering a linear regression, the initial slope of the curve was calculated in order to evaluate the  
225 *apparent* initial rate of dissolution  $r_i$  as given in Eq. (2):

226 
$$r_i = \frac{dNL_i}{dt} \quad (2)$$

227  
228 At each sampling time, total biomass growth was estimated by measuring the Optical Density (OD) of  
229 the incubated medium at 600 nm and by the Colony Forming Unit (CFU) count procedure. After  
230 2.7 days (respectively 2.9 days for MORB3 glass) and 5.7 days, dilutions of the bacterial medium were  
231 plated on LB agar and incubated 24 h at 25 °C for the counting step while the sampled solution was  
232 also filtered (cellulose acetate filters,  $\text{Ø}0.2 \mu\text{m}$ ) and placed into a spectrophotometric cell. Optical  
233 spectra were recorded between 300 and 600 nm. Identical spectrophotometric cells were used for all  
234 measurements, with a standard optical path length.

235  
236 The samples resulting from the dissolution experiments without dialysis bags (see [Perez et al. \(2016\)](#)  
237 for the presentation and discussion of the liquid analysis results of these experiments) were dried  
238 following a critical point drying (CPD) protocol in order to avoid the damaging effects of surface tension  
239 on bacterial cell and biofilm potentially present at the glass surface. 250  $\mu\text{L}$  of glass in suspension in  
240 the bacterial medium were mixed with 4 mL of 0,05 M 4-(2-hydroxyethyl)-1-piperazineethanesulfonic  
241 acid (HEPES) solution (pH 8) and then slowly injected in a swinnex® containing a polycarbonate filter  
242 ( $\text{Ø} 0,22 \mu\text{m}$ ). The glass grains and bacterial cells were retained on the filter and successively washed  
243 with 5 mL of 50%, 70%, 96% and 100% ethanol (vol.). The filter was carefully kept in an absolute  
244 ethanol bath then introduced in a CPD chamber (*Leica EM CPD300*) and submitted to 20 cycles ( $\text{CO}_2$   
245 injection, increase of temperature and pressure and depressurisation) of 4 min each. After being dried,



246 the samples were immediately carbon coated and observed with Scanning Electron Microscopy (*Zeiss*  
247 *Ultra55* microscope) with a filament tension of 2 kV.

248

249

## 250 Results and Discussion

251

### 252 1. Bacterial growth and siderophore production

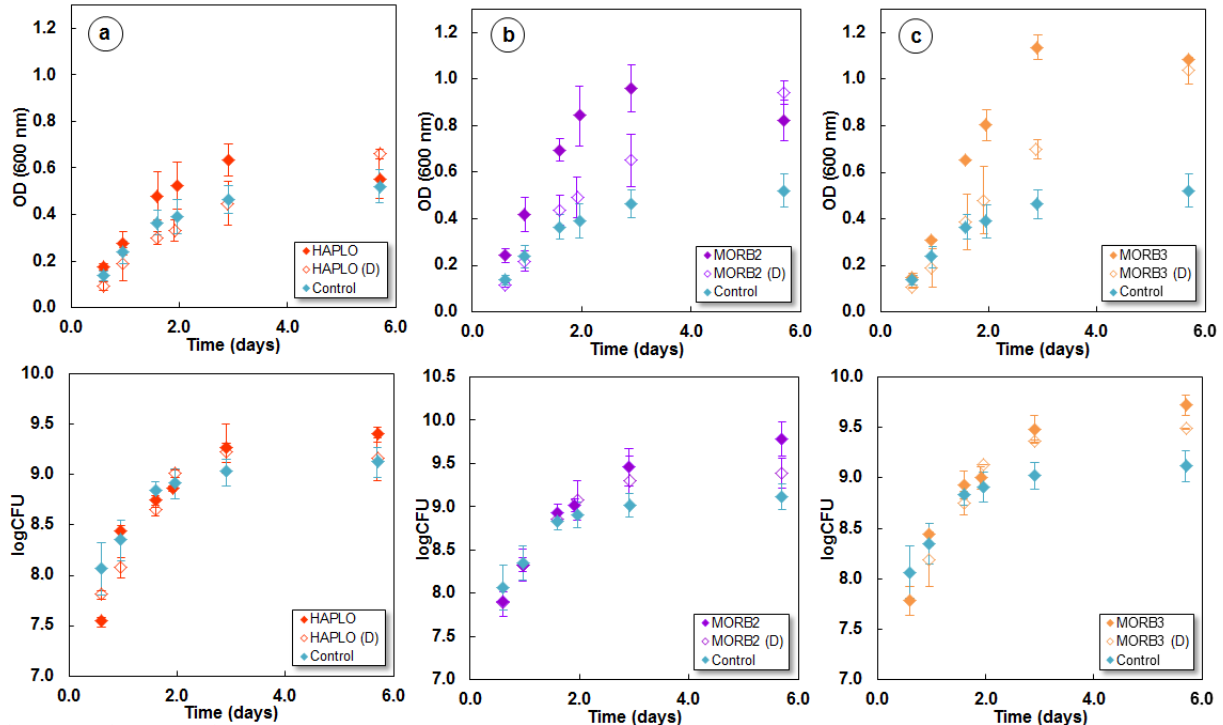
253

#### 254 1.1. Growth

255

256 Optical densities (ODs) at 600 nm of the sampled solutions are plotted versus time in Figure 1 for the  
257 three glasses. For each glass composition, the ODs measured in the presence of dialysis bags (D) are  
258 compared to the ODs measured in dialysis-free experiments ([Perez et al., 2016](#)). The absorbance of a  
259 bacterial medium at 600 nm is correlated to the number of suspended cells within the liquid medium as  
260 it characterizes the turbidity of the solution. OD values are in good agreement with the CFU counting.  
261 Correlation factors between OD and CFU values have been calculated for each experimental condition  
262 and are equal to 0.97 (Control), 0.92 (MORB3), 0.94 (MORB3 D), 0.99 (MORB2), 0.99 (MORB2 D),  
263 0.95 (HAPLO), 0.94 (HAPLO D).

264



265

266 Figure 1: (a) Bacterial growth curves (measured optical densities at 600 nm or Colony Forming Units versus time) of *P.*  
267 *aeruginosa* culture in the presence of the MORB3 (a), MORB2 (b) and HAPLO (d) glasses, confined (empty symbols) or not (full  
268 symbols) in dialysis (D) bags. Blue data points represent the control experiment. Growth experiments in MM9 6.5 were  
269 performed in duplicates and error bars correspond to  $\pm$  standard deviation (SD) between the 2 measured values.

270

271 The experiments in the presence of the HAPLO glass exhibit growth curves very close to those  
 272 obtained in the control experiments (Figure 1a). The bacterial growth is more pronounced when  
 273 bacteria are incubated with Fe-bearing glasses, independently of the presence or absence of dialysis  
 274 membranes (Figures 1b & 1c). This suggests that Fe-bearing glasses, isolated or not from the  
 275 bacterial suspension, might represent substantial nutrient sources for *P. aeruginosa* in exponential  
 276 phase of growth. This result is notably in strong agreement with our previous study (Perez et al. 2016)  
 277 and with a study by Sudek et al. (2017). In this work, the authors evidenced the elevated growth of  
 278 *Pseudomonas stutzeri* VS 10 incubated in the presence of basaltic samples in comparison with basalt-  
 279 free experiments.

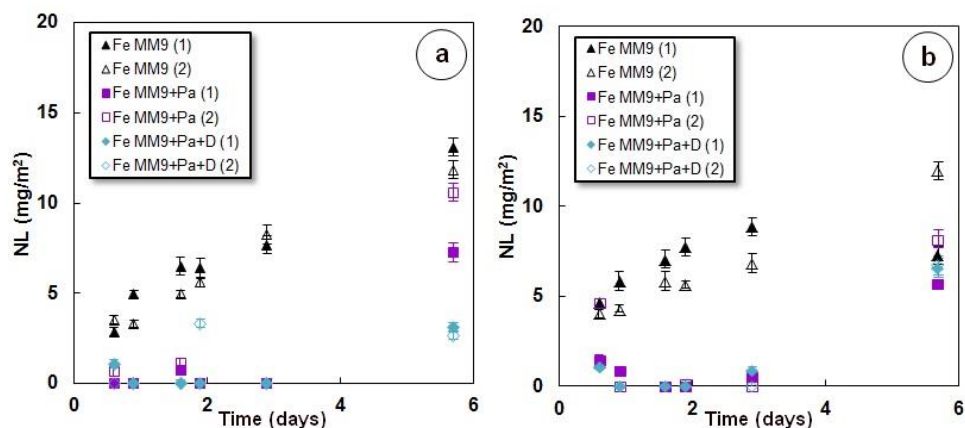
280

281 Moreover, the bacteria concentrations at 5.7 days are similar from one experimental condition (with  
 282 dialysis) to another (without dialysis). Bacteria concentrations are nevertheless systematically lower in  
 283 dialysis experiments from 0 to 3 days of incubation, suggesting that isolating the bacterial suspension  
 284 from the glasses induces a slower cell division process. These results indicate that a direct contact  
 285 between basaltic glasses and the bacterial suspension favors the bacterial cell division process,  
 286 possibly as a consequence of an improved nutrient supply. On this point too, our results corroborate  
 287 the recent findings of Sudek et al. (2017), who observed that a physical contact or at least the  
 288 proximity of the cells to basaltic samples was correlated to a more pronounced bacterial growth.

289

290 The NLs of Fe measured for each duplicate in the cultures incubated in the presence of MORB2 and  
 291 MORB3 glass (isolated or not from the bacterial suspension by dialysis membranes) are plotted  
 292 versus time in Figure 2.

293



294

295 Figure 2: Normalized Loss (NL) profiles of Fe during dissolution experiments of MORB2 (a) and MORB3 (b) glass at 25°C and  
 296 in the medium MM9 at pH 6.5 in a bacterial culture of *P. aeruginosa* (Pa) isolated (in blue) or not (in purple) from the glass by  
 297 dialysis bags (D). Open symbols relate to duplicate (1) while full symbol relate to duplicate (2). Black data points represent the  
 298 NLs measured in sterile controls. Error bars are equal to ± 2SD.

299

300 At the difference with dissolution experiments of those same glasses in UPW (Perez et al., 2015), Fe  
 301 concentration levels in solution are most of the time above the ICP-OES detection limit. Basic  
 302 speciation calculations (CHESS code) show that, regarding the abundant presence of phosphate salts

303 in the MM9 medium, Fe is mainly present as soluble  $\text{FeHPO}_4^+$  (aq), as suggested by Pokrovsky et al.  
304 (2009a,b).

305

306 In abiotic conditions (Fe MM9), Fe is continuously released in the medium all along the experiment  
307 from both glasses. By contrast, in the presence of the strain (Fe MM9+Pa, Fe MM9+Pa+D), Fe is  
308 almost non-detected from 0.6 to 5.7 days independently on the use or not of dialysis membranes. 0.6  
309 to 5.7 days also corresponds to a fast cell division step (Figure 1). The few Fe released in solution is  
310 probably entirely assimilated by the bacteria and used for the bacterial cell division process. At 5.7  
311 days of dissolution experiment, while the bacteria cells are in a stationary phase of growth, Fe is  
312 detected in the liquid medium. The presence of Fe at this point shows that Fe is naturally continuously  
313 released into the solution, efficiently used by the cells to sustain their growth until they enter a  
314 stationary phase and finally remains in solution as it is not needed anymore.

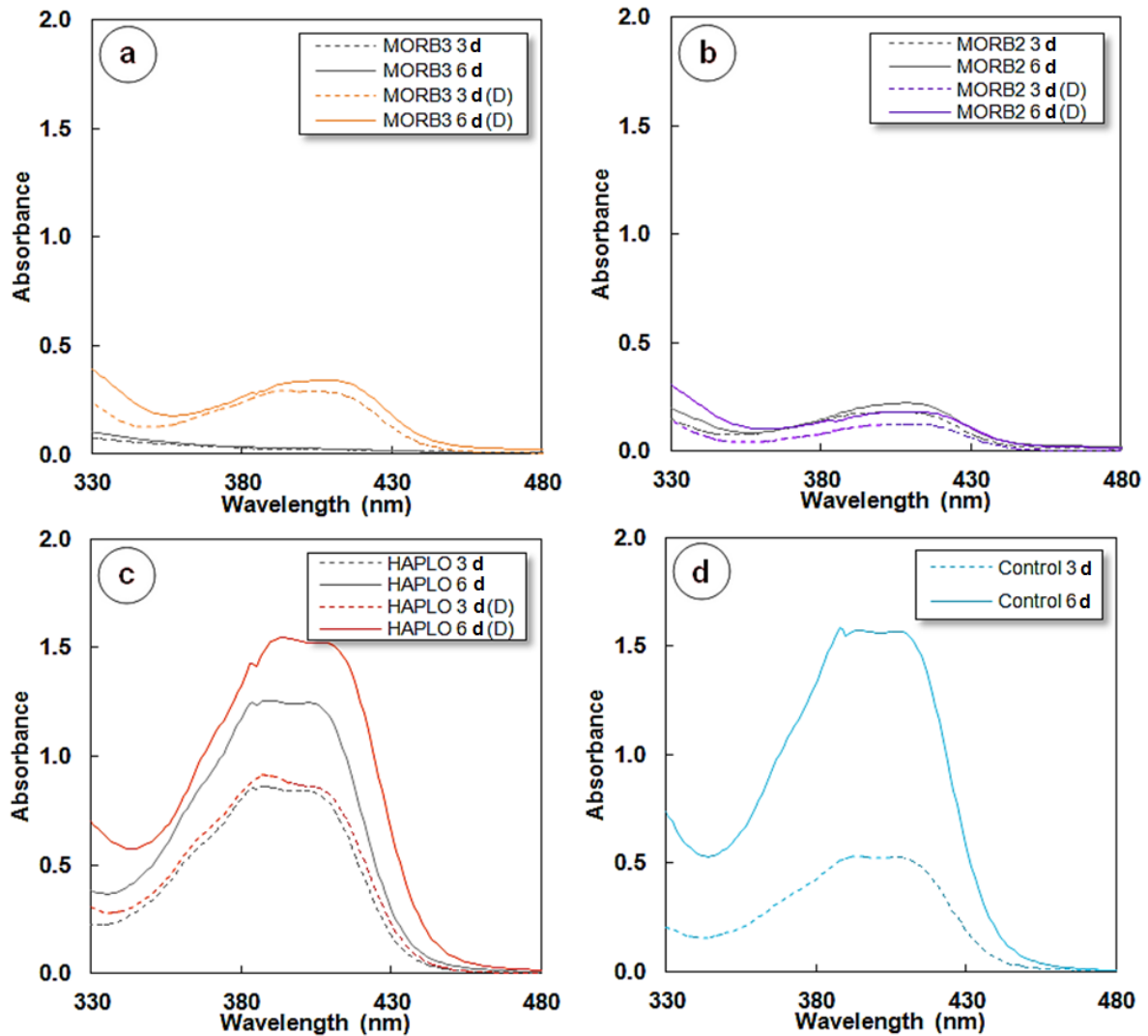
315

316 Coupling bacterial growth and Fe concentrations finally highlights the high-affinity transport  
317 mechanisms that *P. aeruginosa* presents in order to acquire Fe. The following section will be  
318 dedicated to the identification of the strategies used by the strain to acquire this nutrient.

### 319 1.2. Siderophore production

320

321 Pyoverdines can be detected between 380 and 420 nm with a UV-Vis spectrophotometer through the  
322 observation of a two-shoulder characteristic absorption peak (Meyer and Abdallah, 1978). The  
323 absorbance spectra of the bacterial cultures, recorded in the UV absorption region characteristic of  
324 pyoverdine, are plotted in Figure 3 and compared with the spectra obtained in no dialysis-using  
325 experiments.



326  
 327 Figure 3: UV Absorption spectra of the MM9 6.5 bacterial medium in the absence (Control) (d) or the presence of the MORB3  
 328 (a), MORB2 (b), and HAPLO (c) glasses contained (colored lines) or not (greys lines) in dialysis bags, recorded at 3 days (3d)  
 329 and 6 days (6d) of the experiments.  
 330

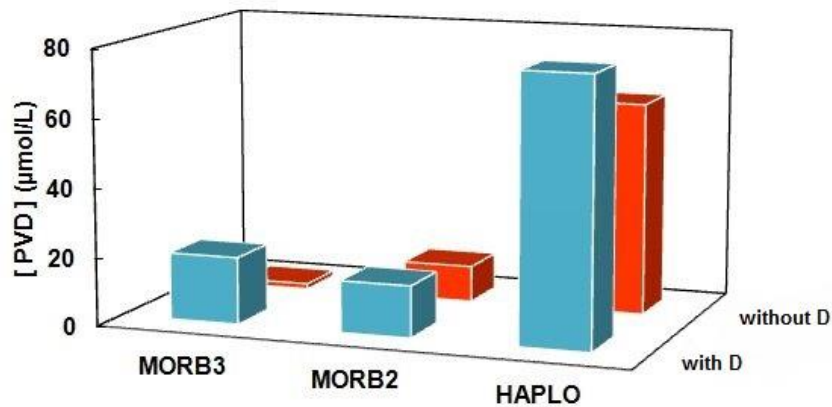
331 According to the shape of the recorded spectra, pyoverdine molecules are detected in all experiments  
 332 except when bacteria are incubated in contact with the MORB3 glass (no membranes) (Figure 3a).  
 333

334 On the basis of the measured absorbance value at 405 nm ( $A_{405}$ ), an estimated free pyoverdine  
 335 concentration can be calculated according to the Beer Lambert law:  
 336

337 
$$[PVD] = \frac{A_{405}}{19000} \times 10^6 \quad (3)$$
  
 338

339 The pyoverdine is characterized by different molar extinction coefficients depending on its form in  
 340 solution. The coefficient of free pyoverdine (19000 L/mol/cm) is lower than that of  $Fe^{3+}$ -pyoverdine  
 341 complexes (26000 L/mol/cm) and greater than that of  $Al^{3+}$ -pyoverdine complexes (18000 L/mol/cm).  
 342 Considering that in our systems, it was not possible to experimentally distinguish between the free  
 343 pyoverdine,  $Fe^{3+}$ -pyoverdine and  $Al^{3+}$ -pyoverdine fractions, approximate values of total pyoverdine

344 concentrations in solution were calculated by using the molar extinction coefficient of free pyoverdine  
345 given in Equation (3). These concentrations are plotted in function of the experimental conditions on  
346 Figure 4.  
347



348  
349 Figure 4: Apparent concentrations in pyoverdine in HAPLO, MORB2 and MORB3 systems after 6 days of experiments  
350 with/without dialysis (D) membranes.  
351

352 In the case of the HAPLO glass (Figure 3c, Figure 4), high amounts of pyoverdine are detected in the  
353 incubated medium, independently of the presence or absence of dialysis bags, with pyoverdine  
354 concentrations after 6 days greater than or equal to 80 µM and 70 µM, respectively. These results are  
355 very close to those obtained in the control experiments (Figure 3d), as both control and HAPLO  
356 systems are Fe-free systems.

357  
358 In the case of the MORB2 glass, the absorbance spectra presented in Figure 3b show similar  
359 intensities (corresponding to pyoverdine concentration of ~10 µM, Figure 4) either at 3 and 6 days  
360 suggesting that isolating this glass from the bacterial suspension does induce any significant changes  
361 regarding the siderophore production. The spectra recorded at days 3 and 6 mainly differ by a change  
362 in the shape of the absorption peak of pyoverdine species (Figure 3b). In order to highlight this  
363 evolution, more absorbance spectra of the cultures recorded until 15 days of incubation for MORB2  
364 experiments are represented in Figure 5.

365

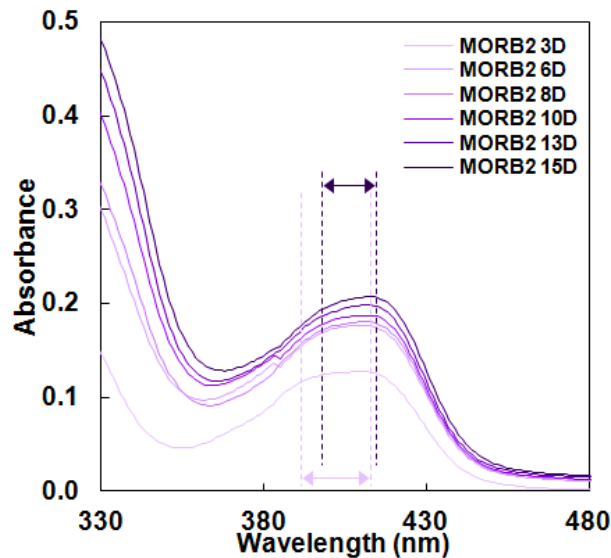


Figure 5: Absorption spectra of the MM9 6.5 bacterial medium in the presence of the MORB2 glass contained in dialysis bags, recorded at 3, 6, 8, 10, 13 and 15 days (D) of the experiments. The arrows materialize the shift of the pyoverdine absorption region toward higher wavelengths with time.

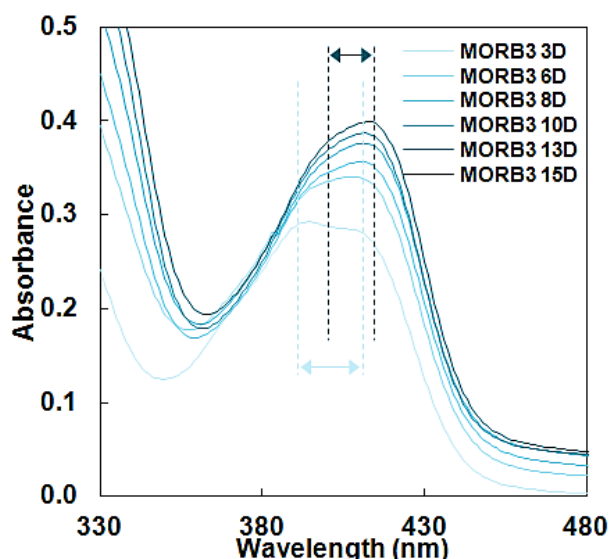
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The spectra show a constantly-evolving signal with time (shifted toward higher wavelengths and changing into a one-shoulder peak). At near neutral pH condition, this particular shape characterizes the presence of  $\text{Fe}^{3+}$ -pyoverdine complexes (Albrecht-Gary et al., 1994). Such an evolution could attest the continuous formation of  $\text{Fe}^{3+}$ -pyoverdine complexes in solution. The increase in Fe concentration after 5.7 days of MORB2 experiment (Figure 2) was suggesting that no more Fe was incorporated inside the cells once Fe homeostasis conditions were reached. This result shows now that the Fe fraction continuously released from the glass over the course of the experiments (from day 6 to 15) must be, once oxidized into  $\text{Fe}^{3+}$  in contact with the oxygenated medium, progressively chelated by the free-pyoverdine molecules remaining in solution.

380

Finally, Figures 3a and 4 show that the presence of dialysis membranes in the MORB3 experiments impacts on siderophore production. If pyoverdine is not detected in the no-dialysis systems, isolating the glass from the bacterial suspension results in a significant production of siderophore in the medium over the course of the experiments. Pyoverdine concentration after 6 days of experiments in the incubated medium is estimated to be lower than or equal to  $20 \mu\text{M}$ . Figure 6 illustrates the change in the shape and the position of the absorption peak of pyoverdine thorough 15 days of experiments.

387



388 Figure 6: Absorption spectra of the MM9 6.5 bacterial medium in the presence of the MORB2 (a) and MORB3 (b) glasses  
 389 contained in dialysis bags, recorded at 3, 6, 8, 10, 13 and 15 days (D) of the experiments. The arrows materialize the shift of the  
 390 pyoverdine absorption region toward higher wavelengths with time.  
 391

392  
 393 As observed for the MORB2 glass, the two-shoulder peak characteristic of free-pyoverdine  
 394 continuously evolve into the single absorption peak of  $\text{Fe}^{3+}$ -pyoverdine complexes, leading to the  
 395 same conclusion than those made for the reduced glass.

396  
 397 A previous study performed in identical experimental conditions showed that without any separation  
 398 between the glass and the bacterial suspension, the Fe fraction abiotically released in solution was  
 399 lower than the Fe fraction measured within the bacterial cells (Perez et al., 2016). This result suggests  
 400 that, in the presence of the strain, the Fe fraction naturally released from the glass into the liquid  
 401 medium is not sufficient to sustain bacterial needs and that, in consequence, more Fe is mobilized  
 402 from the glass through a non-identified biological process. In the same previous study, the absence of  
 403 siderophore in the system indicated that pyoverdine molecules were not responsible for enhancing the  
 404 Fe release. In this work, the results highlight that separating the glass from the bacterial suspension  
 405 induces a high pyoverdine production by the cells. This production of pyoverdine in presence of  
 406 dialysis membranes is a good indicator of a high bacterial need in Fe, not observed when the bacteria  
 407 can access to the glass. This demonstrates that the biological process that enhance the Fe release  
 408 consists in direct glass surface/bacteria interactions.

### 409 1.3. Evidence of direct bacteria/glass interactions

410  
 411  
 412 The SEM images of the surface of a MORB3 glass sample incubated in the presence of *P. aeruginosa*  
 413 without dialysis bags (direct contact) are presented in Figure 7.

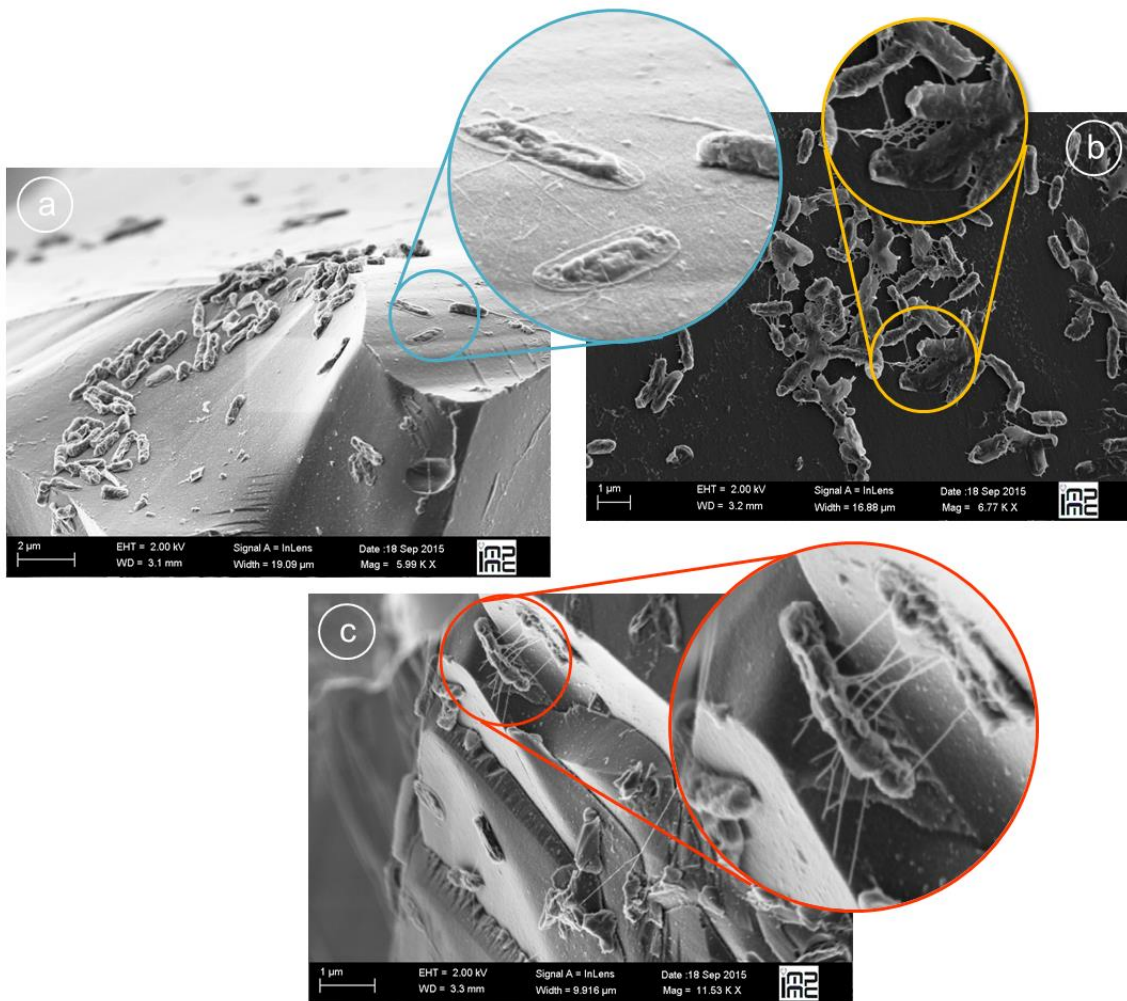


Figure 7: SEM images of the MORB3 glass surface after 15 days of experiments (without dialysis bags).

414  
415  
416

If bacteria do not seem to massively colonize the surface, they are however homogeneously present on the glass grains. The images show that the cells are strongly attached to the glass, as dead cell residues remain at the surface after the CPD protocol (Figure 7a). They also show that biofilm communities start to develop: bacteria produce filamentous structures that allow them to progressively connect to each other (Figure 5b) and to the surface of the glass (Figure 7c). Very similar biofilm patterns were presented in the work on *Pseudomonas stutzeri* of Sudek et al. (2017) between 4 and 7 days of incubation with basaltic glass samples.

424

#### *Impact on dissolution kinetics*

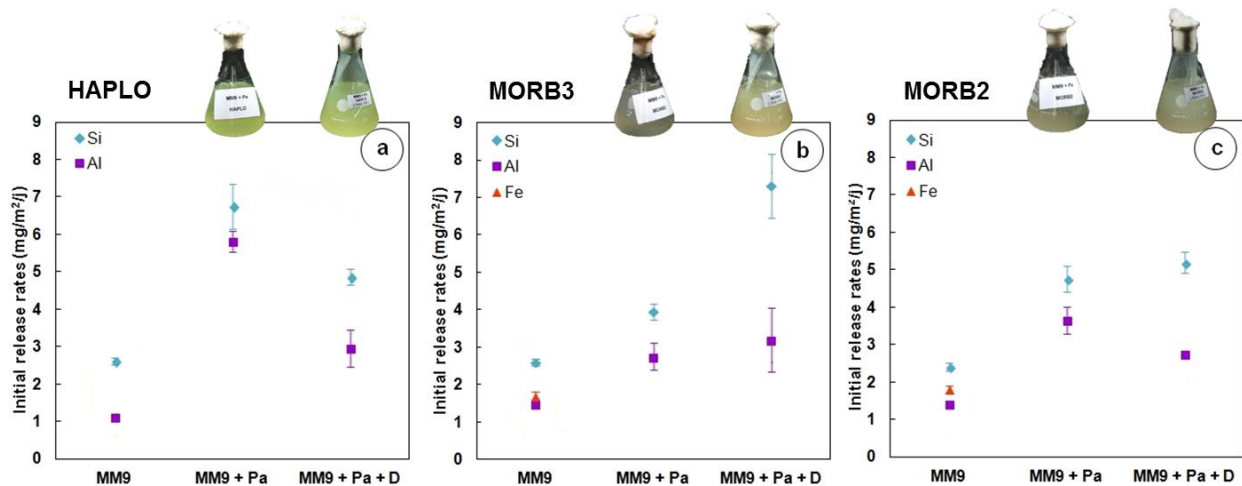
426

Apparent dissolution rates calculated in abiotic control experiments and in *P. aeruginosa* (with glass confinement or not) based on Si, Al and Fe concentrations measured in the liquid medium are plotted in Figure 8. As free pyoverdine molecules are fluorescent and the formation of complexes between pyoverdine and Fe<sup>3+</sup> cations is known to induce fluorescence quenching (Albrecht-Gary et al., 1994), the color of the medium after 6 days of experiments is visually represented on the graphics in order to

431



432 help the reader to remember the pyoverdine production in each biotic system and its possible  
 433 interactions with Fe.  
 434



435 Figure 8: Initial release rates of the HAPLO (a), MORB3 (b) and MORB2 (c) glass confined in dialysis bags and immersed in *P.*  
 436 *aeruginosa* culture (MM9 + Pa + D) in comparison with initial rates determined in sterile MM9 and in *P. aeruginosa* cultures  
 437 (MM9 + Pa) (Perez et al., 2016). The rates were calculated using the average of NL values for both sets of duplicates  
 438 experiments. Error bars are equal to  $\pm 2SD$ .  
 439  
 440

441 Considering that a fraction of dissolved Al or Fe from the glasses is likely to be trapped within the  
 442 bacterial cells or adsorbed at their surface (and in consequence not taken in account by ICP-OES  
 443 measurements), the dissolution rates of the three glasses will be mainly discussed on the basis on Si  
 444 data.

445 First of all, the presence of bacterial life in the aqueous medium (MM9) has a positive impact on the  
 446 global dissolution of the three glasses: the Si release rates are enhanced by a factor of 1.5 to 3  
 447 depending on the experimental conditions, whether the glasses are contained in dialysis bag or not.

448 The dissolution rates calculated from Si concentration of the three glasses are enhanced by  
 449 comparison with abiotic systems in the order: MORB3 < MORB2  $\approx$  MORB2-dialysis < HAPLO-dialysis  
 450 < HAPLO < MORB3-dialysis.

451 All these results show that:

452 1/ the presence of pyoverdine molecules has the most significant catalyzing effect on the dissolution.  
 453 This effect is notably evidenced by the comparison between dialysis and no dialysis-using MORB3  
 454 experiments. Without dialysis membranes, the lowest bacterial impact on the dissolution kinetics  
 455 among all the tested glasses ( $4.0 \pm 0.2 \text{ mg.m}^{-2}.\text{d}^{-1}$  for Si, Figure 8b) is correlated with the non-detection  
 456 of pyoverdine in the system (Figure 4). These experiments show that the moderate enhancement  
 457 relative to the experiment without bacteria is caused by a direct bacteria/glass interaction. By contrast,  
 458 the dialysis-membrane-using experiments, in which low but significant amounts of pyoverdine (around  
 459  $20 \mu\text{M}$ ) are detected in solution, are characterized by the highest Si release rates ( $7.3 \pm 0.8 \text{ mg.m}^{-2}.\text{d}^{-1}$   
 460 for Si, Figure 8b).

461 2/ the relative effect of pyoverdine correlates well with the complex stability constants of the  
462 siderophore with the cations in presence ( $K^{\text{Fe}^{2+}} < K^{\text{Al}^{3+}} < K^{\text{Fe}^{3+}}$ ) (Albrecht-Garyet al., 1994; Chen et al.,  
463 1994; Hernlem et al., 1996; Szabo et Karkas, 2011). In particular, the siderophore has the most  
464 significant effect on the dissolution rates when the cations that are the most likely to form complexes  
465 with it are involved as network-forming elements in the glass structure ( $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ). This confirms that  
466 complexation reactions between pyoverdine and structural Al and/or Fe promote the dissolution either  
467 by a surface-controlled mechanism (Cocozza et al., 2003) or by increasing the solubility of these  
468 metallic elements in solution (Oelkers and Schott, 1998). Such siderophore-promoted dissolution has  
469 already been well investigated in studies dedicated to the interactions between desferrioxamine-B and  
470 Fe(III)-bearing minerals/glass (Reichard et al., 2005; Wolff-Boenisch and Traina, 2007; Cervini-Silva,  
471 2008; Haack et al., 2008; Dehner et al., 2010; Perez et al., 2015). However, there is only a limited  
472 number of existing studies exploring the promotion of mineral/glass dissolution by other siderophores  
473 and notably pyoverdine (Ferret et al., 2014; Parello et al., 2016; Perez et al., 2016). The results of this  
474 work contribute to show the efficiency of pyoverdine in promoting the dissolution of an Fe(III) or Al(III)-  
475 bearing glass. For the MORB2 glass, the very similar results in terms of siderophore production  
476 (Figure 4) and dissolution rates (Figure 8) from dialysis-membrane to no dialysis-membrane-using  
477 experiments confirm that the bacteria-promoting process mainly takes place in solution. This  
478 corroborates what was assessed in a previous study by Perez et al. (2016): during the MORB2 glass  
479 dissolution, the release of Fe first as  $\text{Fe}^{2+}$  cations in solution induces the production of pyoverdine  
480 molecules. The  $\text{Fe}^{2+}$  cations being quickly oxidized into  $\text{Fe}^{3+}$  cations in contact with the oxygenated  
481 liquid medium are preferentially chelated by the pyoverdine molecules. Although the change of Fe  
482 speciation in solution favors the release of  $\text{Fe}^{2+}$ , its structural role (network-modifier cation) can explain  
483 the lower impact of this preferential release on the global dissolution kinetics of the glass.

484 3/ the correlation between the effect of pyoverdine on the dissolution kinetics and the complex stability  
485 constants does not seem to depend on the concentrations of pyoverdine in the systems. As an  
486 example, pyoverdine has the highest impact on dissolution rates of the MORB3 glass with a maximum  
487 concentration in the medium equal to 20  $\mu\text{M}$  (Figure 4). By contrast, it has a lower impact on the  
488 dissolution kinetics of the HAPLO glass although it is continuously produced by the cells and its  
489 concentration approximates 70-80  $\mu\text{M}$  after 6 days of dissolution (Figure 4). Moreover, isolating the  
490 HAPLO glass from the bacterial suspension induces a more intense production of pyoverdine (80  $\mu\text{M}$   
491 versus 70  $\mu\text{M}$ ) but these experiments are characterized by lower global dissolution rates of the glass  
492 ( $4.9 \pm 0.2 \text{ mg.m}^{-2}.\text{d}^{-1}$  versus  $6.8 \pm 0.6 \text{ mg.m}^{-2}.\text{d}^{-1}$  for Si, Figure 8a). These results echo to several  
493 studies evidencing a potential “threshold effect” on dissolution rates concerning the abundance of  
494 chelating molecules in solution (Cheah et al., 2003; Wolff-Boenisch and Traina, 2006). A slight  
495 decrease in the dissolution rate of basalts was even observed by Neaman et al. (2005) by increasing  
496 the concentration of organic ligands in solution.

497

498

499

## 500           **Conclusion**

501   This work attests of the impact of bacterial life on the dissolution kinetics of three synthetic basaltic  
502   model glasses. Isolating the samples from the bacterial suspension was essential to target more  
503   precisely the bacterial impact on the dissolution mechanisms/kinetics of basaltic glass and quantifying  
504   the different types of bacterial contributions. A direct access to the surface of an Fe(III)-bearing glass  
505   is shown to inhibit the production of siderophore by the bacteria and consequently to minimize the  
506   bacteria-promoted effect, as the dissolution rates are increased by 1.5 times compared to sterile  
507   experiments. By contrast, isolating the glass from the bacterial suspension with dialysis bags triggers  
508   the biosynthesis of siderophore, stopped as soon as the bacteria reach a stationary phase of growth.  
509   This limited quantity of pyoverdine molecules in solution (around 20  $\mu\text{M}$ ) is sufficient to significantly  
510   improve the dissolution rate of the MORB3 glass, which is increased by 3 times compared to sterile  
511   experiments. By contrast, the dissolution kinetics of an Fe(II)-bearing glass incubated with *P.*  
512   *aeruginosa* are not impacted by the limited access of bacteria to the glass in dialysis experiments:  
513   small amounts of siderophore are produced in both cases and the dissolution rate is increased by 2  
514   times compared to sterile experiments. Finally, the Fe-starved bacteria incubated in the presence of  
515   the HAPLO glass are shown to continuously produce pyoverdine. As most siderophores, pyoverdine  
516   has also a high affinity with  $\text{Al}^{3+}$  and the dissolution seems to be promoted by the preferential release  
517   of Al from the glass induced by the formation of  $\text{Al}^{3+}$ -pyoverdine complexes.

518   This work is a new contribution regarding the high affinity of microorganisms for basaltic glasses as an  
519   Fe-source. In this case Fe is the most likely used by the ferri-reductive model strain *P. aeruginosa* in  
520   its  $\text{Fe}^{3+}$  form as an electron sink. Its quick uptake by *P. aeruginosa* is shown to significantly carry  
521   benefit to the growth of the bacteria. Moreover, this study brings new evidences of the positive impact  
522   on the dissolution kinetics of these glasses, of the strategies developed by the bacteria to acquire Fe,  
523   depending on the form under which it is primarily available to them: 1/ as structural Fe(II) or Fe(III)  
524   within the glass network, directly accessible (or not) to them depending on the presence of dialysis-  
525   membranes or 2/ in solution first as  $\text{Fe}^{2+}$  ions or forming soluble complexes with phosphates initially  
526   present within the liquid medium. For each Fe source, one bacterial response was identified and each  
527   response was shown to impact differently on the dissolution kinetics. Among these bacterial  
528   responses, siderophore production was shown to particularly regulate the dissolution rates. In a  
529   basaltic environment where Fe solubility is low and where siderophore-producing strains are  
530   commonly detected, the biosynthesis of these complexing agents operates as a mechanism  
531   developed to ensure nutritional Fe-availability.

532

## 533           **Acknowledgements**

534   This work was supported by grants from Region Ile de France and by CNRS-INSU (INTERVIE).

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