



**HAL**  
open science

## Early Diagenesis of Lacustrine Carbonates in Volcanic Settings: The Role of Magmatic CO<sub>2</sub> (Lake Dziani Dzaha, Mayotte, Indian Ocean)

Vincent Milesi, Mathieu Debure, Nicolas C.M. Marty, Manuela Capano, Didier Jézéquel, Carl Steefel, Virgile Rouchon, Patrick Albéric, Edouard Bard, Gérard Sarazin, et al.

### ► To cite this version:

Vincent Milesi, Mathieu Debure, Nicolas C.M. Marty, Manuela Capano, Didier Jézéquel, et al.. Early Diagenesis of Lacustrine Carbonates in Volcanic Settings: The Role of Magmatic CO<sub>2</sub> (Lake Dziani Dzaha, Mayotte, Indian Ocean). ACS Earth and Space Chemistry, 2020, 4 (3), pp.363-378. 10.1021/acsearthspacechem.9b00279 . insu-02499121

**HAL Id: insu-02499121**

**<https://insu.hal.science/insu-02499121v1>**

Submitted on 4 May 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 EARLY DIAGENESIS OF LACUSTRINE CARBONATES IN  
2 VOLCANIC SETTINGS: CHARACTERIZATION AND  
3 MODELING  
4  
5  
6

7 VINCENT P. MILESI<sup>1</sup>, MATHIEU DEBURE<sup>2</sup>, NICOLAS C.M. MARTY<sup>2</sup>, MANUELA  
8 CAPANO<sup>3</sup>, DIDIER JÉZÉQUEL<sup>1</sup>, CARL STEEFEL<sup>4</sup>, VIRGILE ROUCHON<sup>5</sup>, PATRICK  
9 ALBÉRIC<sup>6</sup>, EDOUARD BARD<sup>3</sup>, GÉRARD SARAZIN<sup>1</sup>, FRANÇOIS GUYOT<sup>7</sup>, AURÉLIEN  
10 VIRGONE<sup>8</sup>, ÉRIC C. GAUCHER<sup>8</sup> AND MAGALI ADER<sup>1</sup>

11  
12  
13  
14  
15  
16  
17  
18  
19 <sup>1</sup>Université de Paris, Institut de physique du globe de Paris, CNRS, F-75005 Paris, France,  
20 vincentmilesi@hotmail.fr

21 <sup>2</sup>BRGM, French Geological Survey, Orléans, France

22 <sup>3</sup>Collège de France, CEREGE, Aix en Provence, France

23 <sup>4</sup>Lawrence Berkeley National Laboratory, USA

24 <sup>5</sup>IFP Energies Nouvelles, Direction Géosciences, Rueil-Malmaison, France

25 <sup>6</sup>Institut des Sciences de la Terre d'Orléans, Orléans, France

26 <sup>7</sup>IMPMC, Sorbonne Université, MNHN, Paris, France

27 <sup>8</sup>Total, EP CSTJF, Pau, France  
28

30 The interplay of diagenetic processes in time and space makes quantitative assessments for  
31 paleoenvironmental reconstructions and reservoirs property predictions difficult. We studied the first  
32 meter of carbonate sediments of the Dziani volcanic crater lake (Mayotte Island), seen as an analog of  
33 lacustrine carbonates formed in rift settings and developed a new reactive-transport model with the  
34 Crunchflow code, which allows the quantification of diagenetic reactions by considering burial rate  
35 and sediment compaction. The model is constrained by the already-known solid phase composition of  
36 the lake sediment and by a series of new data:  $^{14}\text{C}$  dating of plant macro-remains to characterize the  
37 sediment age model, chemical composition of sediment pore waters and chemical and isotopic  
38 composition of gases dissolved and bubbling through the lake. These new data reveal a massive  
39 magmatic  $\text{CO}_2$  contribution to the dissolved inorganic carbon of the lake, which fuels the primary  
40 productivity and the carbonate formation. The intense primary productivity raises the lake water pH  
41 above 9, inducing supersaturations of the surface sediment pore waters relative to aragonite,  
42 hydromagnesite and saponite. The model allows quantifying the contributions of microbial  
43 degradation of organic matter and magmatic  $\text{CO}_2$  inflows (2 mol.% and 22 mol.% at 1 m depth,  
44 respectively) to the dissolved inorganic carbon of sediment pore waters. These magmatic  $\text{CO}_2$  inflows  
45 induce a pH decrease at depth, leading to the destabilization of hydromagnesite while saponite and  
46 aragonite remains stable. These results bring new insights on the origin and diagenetic evolution of  
47 lacustrine carbonates in rift settings. They demonstrate the possible role of magmatic  $\text{CO}_2$  in setting  
48 the chemical conditions required for the co-precipitation of carbonate and Mg-silicates, in fueling the  
49 carbonate production, and in controlling the diagenetic evolution of the sediment mineralogy.

50 Keywords: magnesium phyllosilicates, rift settings, reactive transport modeling, kinetics, magmatic  
51  $\text{CO}_2$ , saponite, isotopy, Dziani Dzaha, volcanic crater lake

## 52 **1. Introduction**

53 Diagenetic processes are an important feature of the functioning of the Earth system, from the  
54 reconstruction of paleoenvironments and biogeochemical cycles to the prediction of sedimentary rocks  
55 porosity and permeability. The diagenesis of reactive minerals, such as carbonates, is an especially  
56 complex system as both chemical and physical processes occur concurrently. In addition to  
57 compaction during burial, diagenetic evolution of carbonate-bearing rocks can be affected by  
58 dolomitization and dedolomitization<sup>1,2</sup>, carbonate cementation<sup>3</sup>, acidic fluids inputs<sup>4,5</sup>, dissolution of  
59 associated magnesium phyllosilicates<sup>6-8</sup>, and bacterial and thermal sulphate reduction<sup>9</sup> among others.  
60 Thus, the outcomes of diagenesis are the results of a combination of processes occurring  
61 simultaneously or successively and in various extents depending on the initial sediment composition,  
62 the nature of the pore fluids, and the pressure and temperature conditions<sup>10</sup>. One of the main

63 challenges to further improve our understanding of the depositional and post depositional conditions  
64 leading to sedimentary rocks is to quantify how diagenetic processes interact together in time and  
65 space.

66 Numerical models allow exploring the highly nonlinear coupling that characterizes natural  
67 systems. It allows quantitative evaluation of the coupling between physical, chemical, and biological  
68 processes that control Earth surface systems<sup>11,12</sup>. Relying on thermodynamics and kinetics constants  
69 available for an increasing number of reactions<sup>13–16</sup>, reactive transport codes can be used to perform  
70 forward modeling of compositional changes of fluid and solid phases of sedimentary columns as burial  
71 and fluid circulation occur<sup>10,17–20</sup>. Because of the chemical reactivity of carbonates, this approach is  
72 especially valuable for paleoenvironmental interpretations of carbonate sediments which are among  
73 the most abundant and widely used archives of Earth chemical and climatic history<sup>21–23</sup>.

74 Cretaceous pre-salt carbonates of the South Atlantic continental margins and Proterozoic  
75 carbonates of the Ediacaran Doushantuo formation have been the focused of many studies of  
76 paleoenvironmental reconstruction in recent years<sup>6–8,22,24–28</sup>. Pre-salt carbonate rocks contain some of  
77 the most significant petroleum reservoirs discovered in decades while the Ediacaran formation (635 to  
78 551 Ma) hosts the earliest animal fossils in the geological record. In both formations, carbonates are  
79 associated with Mg-phyllsilicates; however, the sources of magnesium, silica and high pH values  
80 required for the Mg-phyllsilicates formation remain unclear, preventing accurate paleoenvironmental  
81 reconstruction<sup>8,22,24,27,29,30</sup>. Questions remain on the initial mineralogy of the Ca-carbonates and on the  
82 source of carbon capable of producing carbonates in lacustrine environments with the volume and the  
83 spatial extent of the pre-salt carbonates<sup>28,29</sup>.

84 The geochemical and sedimentological study of contemporaneous analogs of those  
85 paleoenvironments, coupled with quantitative diagenetic models, is a method to assess these questions.  
86 In this contribution, we studied the first meter of carbonate sediments of the Dziani Dzaha volcanic  
87 crater lake (Mayotte Island), seen as a good analog of lacustrine environments in the early stages of  
88 continental rifting during which low mantle uplift results in low partial melting, producing alkaline  
89 magma<sup>31,32</sup>. The Dziani Dzaha sediment, previously characterized in detail by Milesi *et al.*<sup>33</sup>, shows  
90 significant compositional changes with depth, with a decrease of hydromagnesite and organic matter  
91 and a simultaneous increase of a Mg- and Al-rich smectite characterized as a saponite-like mineral  
92 (referred hereafter as saponite). The pore water chemistry, the chemical and carbon isotopic  
93 composition of gases bubbling through the lake, the concentration of CH<sub>4</sub> dissolved in the lake water,  
94 and <sup>14</sup>C dating of plant macro-remains in the sediment cores were acquired to develop a fully-  
95 constrained reactive transport model of the diagenetic processes at play. The model accounts for the  
96 fluid and solid burial as well as the sediment compaction with time. The early diagenesis is a stage of  
97 considerable compositional changes due to the interplay of biological, chemical and physical

98 processes<sup>34</sup>. Our study focuses on those processes, which are the foundation toward modeling further  
99 diagenetic stages in larger-scale basins.

100

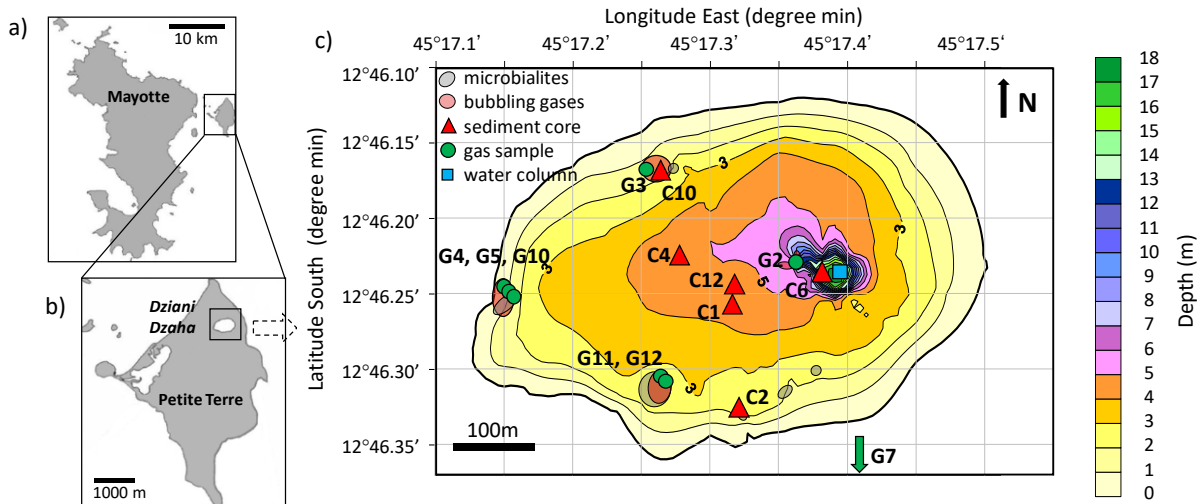
## 101 **2. Geologic setting and limnology of the Dziani Dzaha**

102 The Dziani Dzaha is a tropical crater lake located on the island complex of Mayotte, which is the most  
103 southern island complex of the Comoros Archipelago (western Indian Ocean). The island of Petite  
104 Terre results from the most recent magmatic events in the Mayotte history, starting 80,000 years ago.  
105 It is made primarily of pyroclastic rocks of phonolitic/alkaline composition produced by partial  
106 melting of the lithospheric mantle metasomatized by CO<sub>2</sub>-rich fluids<sup>35,36</sup>. The Dziani Dzaha is hosted  
107 in a volcanic crater formed by a phreatomagmatic eruption, which may correspond to one of the most  
108 recent volcanic events of the island of Petite Terre dated from 9 Ka to 4 Ka<sup>37</sup>.

109 The lake is meromictic. It is approximately at sea level, with an average depth of 3.5 m, and a  
110 singular depression down to 18 m where the water does not intermix (monimolimnion layer) (Fig. 1).  
111 Four sites of volcanic gas bubbling are identified within the lake associated with microbialites mainly  
112 made of calcite and aragonite<sup>38</sup>. The lake water has a salinity ranging from 34 and 71 g·kg<sup>-1</sup> depending  
113 on the season and depth (*i.e.*, between once and twice seawater's salinity), alkalinity of ~0.2 mol·L<sup>-1</sup>  
114 and pH values ranging from 9.1 to 9.4. The surface temperature varies between 28 and 36°C.  
115 Together, these characteristics correspond to the thalassohaline lake definition<sup>39</sup>. The lake biomass is  
116 dominated by cyanobacteria, with a primary productivity of ~8 g of C·m<sup>-2</sup>·day<sup>-1</sup><sup>39</sup>, close to the  
117 maximum rate of photosynthesis for tropical and subtropical lakes<sup>40</sup>. The most likely theory of the lake  
118 origin is sea water filling the volcanic crater formed by the phreatomagmatic eruption<sup>39</sup>. The  
119 limnigraphic measurements performed since 2014 show a balanced hydrologic budget. The lake water  
120 level is constant, with maxima reached from December to February and minima from Mai to  
121 September. Contribution of seawater inflows pulsed by tidal waves to the hydrologic budget can be  
122 ruled out as, even mitigated, they would have been recorded by the limnigraph considering its  
123 sensitivity (±10 mm) and the magnitude of the tidal waves (3 m). The absence of external water  
124 inflows is confirmed by the concentration of the conservative elements, Cl and Br which are not  
125 involve in any biogeochemical processes. The Cl/Br ratio of the lake water is within 10% equal to that  
126 of seawater (Table S1). Therefore, the Cl<sub>lake</sub>/Cl<sub>seawater</sub> ratio of ca. 1.7 can be attributed to the lack of  
127 meteoric inputs compared with evaporation over the life time of the lake (Table S1). Given this  
128 preliminary interpretation of the lake origin and functioning (further investigations in progress), the  
129 massive photosynthetic activity in the lake is the most likely process at the origin of the high pHs.

130 The uppermost sediment of the Dziani Dzaha is dominated by organic matter and the  
131 authigenic carbonates, aragonite and hydromagnesite<sup>33</sup>. With increasing depth, the content of

132 hydromagnesite decreases while the one of saponite increases. Over the same interval, the organic  
 133 matter which represents up to 40wt.% of the uppermost sediment in the deep parts of the lake  
 134 decreases to 25-30wt.% at 1 m depth. Detrital inputs made of alkaline feldspar, clinopyroxene and  
 135 volcanic pumice are present along the first meter of sediment. This mineral composition is observed in  
 136 all sediment cores collected between 2 to 5 meters of water depth.



137

138 Figure 1. (a and b) Situation map of the study site (modified from the study of Milesi *et al.*<sup>33</sup>). (c)  
 139 Bathymetric map of the Dziani Dzaha showing bubbling sites (light red circles), microbialites (light  
 140 grey circles), sites of sediment core sampling (CX, red triangles), sampled water column (blue square)  
 141 and bubbling gases (GX, green circles).

### 142 **3. Material and Method**

#### 143 3.1 Nomenclature

144 All samples are named as follows. For DZ14-10 C4, “DZ” is for Dziani, “14-10” is for the year (2014)  
145 and month (October) of the survey and C4 refers to the sediment core 4. In this nomenclature, “C”  
146 stands for sediment core, “G” for gas sample and “WC” for water column. The samples are listed in  
147 Table S2 in supporting information. As the sediment cores and the gas samples were named according  
148 to their sampling order, they are named in Figure 1 and in the article only as CX and GX, with X the  
149 number of the sample.

#### 150 3.2 Sampling

151 The pore waters of sediment core C12 were sampled with Rhizon samplers during the survey of  
152 August 2016. The porous tubes with a mean pore size of 0.15  $\mu\text{m}$  were placed every 2.5 cm along the  
153 1 m long sediment core and connected to 12 mL-evacuated Exetainer<sup>®</sup> vials or to plastic syringes in  
154 order to avoid silicon contamination from the Exetainer<sup>®</sup> glass. Within a few hours after collection, the  
155 27 pore water samples were acidified with high purity  $\text{HNO}_3$  for ulterior analysis of major cations  
156 concentrations.

157 The water column was sampled above the 18 m depression of the lake with a Niskin<sup>®</sup> bottle  
158 during the surveys of September 2010, 2011, April 2012, 2014 and August 2016. The lake waters were  
159 stored in 12 mL Exetainer<sup>®</sup> vials filled with water (no headspace) and poisoned with mercuric chloride  
160 ( $\text{HgCl}_2$ ) to prevent microbial activity.

161 Radiocarbon measurements were performed on dissolved inorganic carbon (DIC), particulate  
162 organic carbon (POC), sediment inorganic carbon (SIC), sediment organic carbon (SOC) and on  
163 terrestrial plants macro-remains. Dissolved inorganic carbon (DIC) was sampled as Ba-precipitates. At  
164 field, a solution of concentrated Ba-hydroxide is introduced into headspace-free sampling bottles (1L),  
165 causing the precipitation of DIC as Ba-carbonates which are later filtered (glass fiber filter grade GF/C  
166  $\approx 1.2\mu\text{m}$ ) and dried under an atmosphere free of  $\text{CO}_2$ . Particulate organic carbon (POC) was sampled  
167 by filtration of water on GF/F glass fiber filters ( $\approx 0.7\mu\text{m}$ ).

168 For the sampling of gases bubbling at the lake surface (survey of August 2016), 12 mL  
169 Exetainer<sup>®</sup> vials were filled with the lake water and then flushed with the bubbling gases until water is  
170 completely removed. Contamination from atmosphere is carefully avoided by constantly keeping the  
171 vials under the water level during sampling.

172           3.3 Chemical and isotopic composition of pore waters and gas samples

173   The pH values of pore waters were measured within a few hours after sampling. Major cations were  
174   analyzed at the IPGP laboratory with inductively-coupled plasma atomic emission spectroscopy (ICP-  
175   AES). Sulfate, H<sub>2</sub>S and CH<sub>4</sub> were not measured because of the difficulty of avoiding the degassing  
176   and oxidation of H<sub>2</sub>S and CH<sub>4</sub> during the sediment core collection and during the sampling and storage  
177   of the pore waters.

178           The carbon and hydrogen isotope composition of CH<sub>4</sub> and CO<sub>2</sub> of bubbling gases and of pore  
179   waters were analyzed at the IFPEN laboratory by sampling directly the headspaces of Exetainer® vials.  
180   CH<sub>4</sub> and CO<sub>2</sub> were separated by on-line gas chromatography and their carbon and hydrogen isotope-  
181   ratios were measured by mass spectrometry. Isotopic compositions are reported relative to the Pee Dee  
182   belemnite (PDB) standard for carbon and relative to the Standard Mean Ocean Water for hydrogen  
183   (SMOW). Precisions for isotopic compositions are of ±1‰ for δ<sup>13</sup>C and ±5‰ for δD.

184           The concentration of CO<sub>2</sub> and CH<sub>4</sub> dissolved in the water column was measured at the IFPEN  
185   laboratory after splitting the water samples in two parts in order to create headspaces in the Exetainer®  
186   vials (a syringe is introduced through the septa to transfer the liquid from one vial to another). After  
187   48h of equilibration, the gas phase was sampled with a gas tight syringe and injected in a gas  
188   chromatograph connected to a thermal conductivity detector and a flame ionization detector, allowing  
189   quantification of H<sub>2</sub>, He, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and all hydrocarbons from methane to iso- and normal-butane.  
190   Precisions for individual components are ±2%. The concentrations of dissolved methane and CO<sub>2</sub>  
191   were calculated considering gas/solution equilibrium.

192           3.4 Porosity profile and density calculations

193   The water content was estimated in the sediment core C12 by weighting 29 fresh samples before and  
194   after drying (80°C). The measurements were corrected for the precipitation of halite (NaCl) during  
195   drying, using the pore water salinity and the water content to calculate the amount of precipitated  
196   halite. As no data was available for the sediment composition of the core C12, the density of the dried  
197   sediment was calculated using the organic matter and mineral contents of the sediment core C4 and  
198   C10<sup>33</sup>. This approach is reasonable given the steady sediment composition between cores collected  
199   close to one another<sup>33</sup>. The densities for aragonite, hydromagnesite, alkaline feldspar, clinopyroxene,  
200   saponite, organic matter, halite, pyrite and magnetite are taken to be 2.9, 2.2, 2.6, 3.2, 2.5, 0.8, 2.2, 5.0  
201   and 5.2 kg·m<sup>-3</sup>, respectively.

202           3.5 Radiocarbon measurements

203   Water column and bulk sediment samples were analyzed by accelerator mass spectrometry (AMS) at  
204   the LMC14 Artemis AMS facility (CEA Saclay - Gif/Yvette, France). Dissolved and sediment



205 inorganic carbon (DIC as Ba-carbonates and SIC, respectively) were extracted at 60°C by adding  
206 anhydrous H<sub>3</sub>PO<sub>4</sub> until complete CO<sub>2</sub> outgassing occurred. For particulate and sediment organic  
207 carbon (POC and SOC, respectively), the samples were acidified (0.5M HCl, 80°C, 1 hour) to remove  
208 the carbonates and rinsed with deionized water. POC and SOC were then converted to CO<sub>2</sub> at 900°C  
209 during 4 hours in contact with Cu-oxides and a wire of Ag. The <sup>14</sup>C activities are reported relative to  
210 the oxalic acid standard HOxII and normalized to a δ<sup>13</sup>C value of -25‰. Radiocarbon ages and Delta  
211 notations are calculated according to the studies by Mook and van der Plicht<sup>41</sup> and Stuiver and  
212 Polach<sup>42,43</sup>, respectively.

213 Terrestrial plant macro-remains were analyzed by means of Aix-MICADAS AMS facility of  
214 Aix-en-Provence<sup>44</sup>. The samples were treated with a modified ABA chemical pretreatment to avoid  
215 possible contaminations from the lake DIC, carbonates and organic carbon<sup>45</sup>. Standards (OxA2 NIST  
216 SRM4990C) and blanks (VIRI K) were analyzed together with samples. The <sup>14</sup>C data are reported in  
217 terms of conventional <sup>14</sup>C age in years BP and in F<sup>14</sup>C age<sup>42,46,47</sup>.

### 218 3.6 Reactive transport modeling

219 The CrunchFlow multicomponent reactive transport code<sup>48</sup> was used with the Thermoddem  
220 database<sup>13,14</sup> to model the early diagenesis of the sediment. The model accounts for kinetic and  
221 thermodynamic chemical processes (water/rock interaction), diffusive transport, together with fluid  
222 and sediment burial and compaction with time.

#### 223 3.6.1 Solid and fluid burial

224 Sediment compaction depends on the time-scale, the stress, the pressure, the temperature and the  
225 rheology of the sediments<sup>17,49</sup>. The downward advection of the pore water (*i.e.*, fluid burial rate) is  
226 identical to the burial rate of solids relative to the water-sediment interface only if the compaction is  
227 negligible and if there is no external driving force for the fluid (such as upwelling from hydrothermal  
228 vents or lateral fluid flow). Compaction over long time scales in fine-grained sediments results in non-  
229 constant pore water and solid burial rates that can produce appreciable changes in the water content,  
230 and therefore, in the chemical profiles<sup>11</sup>. For instance, reaction-generated grain-scale permeability is  
231 sealed rapidly by compaction, which prevents or at least reduces fluid fluxes<sup>49</sup>.

232 The solid burial rate,  $\omega$ , can be determined from the conservation of solid sediment mass  
233 (where  $\phi$  is the porosity and  $z$  is the depth (m)) as follow<sup>11,17</sup>:

$$234 \quad \frac{\partial[(1-\phi)\omega]}{\partial z} = 0 \quad \text{Eqs (1)}$$

235 The fluid flow due to compaction,  $v$ , can be determined from the conservation of fluid mass given the  
236 assumption of steady-state compaction:

237 
$$\frac{\partial(\phi v)}{\partial z} = 0 \quad \text{Eqs (2)}$$

238 The porosity profile  $\phi$  as a function of the depth  $z$  was fitted in this study assuming that the  
 239 dissolution/precipitation mechanisms influence the porosity. Considering the asymptotic burial rate of  
 240 fluid and solid as boundary condition, the equations (1) and (2) become respectively:

241 
$$\omega = \frac{W(1-\phi_{bottom})}{1-\phi_z}, \quad \text{Eqs (3)}$$

242 
$$v = \frac{W\phi_{bottom}}{\phi_z}, \quad \text{Eqs (4)}$$

243 with  $\phi_z$  the porosity at a given depth  $z$  and  $\phi_{bottom}$  and  $W$  the porosity and the asymptotic burial rate,  
 244 respectively. Then, solid and fluid burial rates were calculated by solving numerically the equations  
 245 (3) and (4) using the expression of the porosity profile. The fluid and solid burial rates are considered  
 246 asymptotic at 5 m depth, which, according to most recent coring, is the approximated depth of the  
 247 volcanic basement. The value of the asymptotic burial rate at 5 m depth ( $W$ ) was adjusted for the  
 248 calculated solid burial rate to fit at best the sedimentation rate determined using the plant macro-  
 249 remains ages.

### 250 *3.6.2 Minerals, organic matter and associated reactions*

251 The sediment composition is dominated by organic matter and authigenic minerals (aragonite,  
 252 hydromagnesite and Mg-rich saponite) with lower amounts of detrital silicates, mostly clinopyroxenes  
 253 and alkaline feldspars with a chemical composition close to the one of anorthoclase ( $\text{Na}_{0.7}\text{K}_{0.3}\text{Si}_3\text{O}_8$ )<sup>33</sup>.  
 254 Accordingly, albite, diopside, aragonite, hydromagnesite, dolomite, gibbsite, quartz, microcline and  
 255 Mg-rich saponite are considered in the model. Those minerals may either precipitate or dissolve  
 256 depending on the saturation state of the pore waters. The reaction kinetics  $R$  ( $\text{mol}\cdot\text{s}^{-1}$ ) are described  
 257 according to the TST rate law<sup>50-53</sup> as:

258 
$$R = A * k * e^{\frac{-E_a}{RT}} \prod a_i^n (1 - \frac{Q}{K})^\theta \eta \quad \text{Eqs (5)}$$

259 where  $A$  is the mineral surface area ( $\text{m}^2\cdot\text{g}^{-1}$ ),  $k$  is the intrinsic rate constant ( $\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ ),  $E_a$  is the  
 260 activation energy ( $\text{kcal}\cdot\text{mol}^{-1}$ ),  $R$  is the gas constant ( $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ),  $T$  is the temperature in Kelvin,  $\prod a_i^n$   
 261 is a product of the activities  $a$  of various ions  $i$  in solution raised to the power  $n$ , which represents the  
 262 inhibition or catalysis of the reaction by these ions. Especially, it allows considering a dependence of  
 263 the reaction on pH.  $Q$  is the ion activity product for the mineral-water reaction,  $K$  is the corresponding  
 264 equilibrium constant,  $\theta$  and  $\eta$  are empirical parameters describing the affinity dependence of the  
 265 reaction. The thermodynamic and kinetic parameters for minerals are based on literature values (Table  
 266 1). The rate constant of Mg-saponite is adjusted to fit the observation as no data exists in the literature.

267 The organic matter is treated as a solid phase with a simplified stoichiometry of CH<sub>2</sub>O. The  
 268 mineralization of the organic matter is represented by a reaction that describes a simplified process of  
 269 microbial methanogenesis coupled to microbial fermentation (Table 1). This approach relies on the  
 270 observation of high densities of methanogens and heterotrophs in the lake waters<sup>39</sup>.

271 Table 1. Thermodynamic and kinetic parameters of the modeled reactions

Solid phases	Reaction stoichiometry	log K* (25°C)	log k** (mol·m <sup>-2</sup> ·s <sup>-1</sup> )	Surface area (m <sup>2</sup> ·g <sup>-1</sup> )	Activation energy (kcal·mol <sup>-1</sup> )	Ion activity dependence <sup>§</sup> (i, n)	Affinity dependence <sup>§§</sup> (Θ, η)
Organic matter	2CH <sub>2</sub> O → CO <sub>2</sub> + CH <sub>4</sub>	10	-10.5 <sup>54</sup>	1.5 <sup>55</sup>	0		1, 1
Albite	NaAlSi <sub>3</sub> O <sub>8</sub> + 4H <sup>+</sup> + 4H <sub>2</sub> O Al <sup>3+</sup> + Na <sup>+</sup> + 3H <sub>4</sub> SiO <sub>4(aq)</sub>	2.9962 <sup>56</sup>	-9.85 <sup>15</sup>	0.6 <sup>57</sup>	13.4 <sup>15</sup>	OH <sup>-</sup> 0.32 <sup>15</sup> / none	0.48, 100 <sup>15</sup> / 1, 1
Microcline	KAlSi <sub>3</sub> O <sub>8</sub> + 4H <sub>+</sub> + 4H <sub>2</sub> O = Al <sup>3+</sup> + K <sup>+</sup> + 3H <sub>4</sub> SiO <sub>4(aq)</sub>	0.0036 <sup>56</sup>	-9.85 <sup>based on 15</sup>	0.6 <sup>57</sup>	13.4 <sup>based on 15</sup>		1, 1
Diopside	CaMgSi <sub>2</sub> O <sub>6</sub> + 4H <sub>+</sub> + 2H <sub>2</sub> O = Ca <sup>2+</sup> + Mg <sup>2+</sup> + 2H <sub>4</sub> SiO <sub>4(aq)</sub>	21.7345 <sup>58</sup>	-9.54 <sup>59</sup>	3 <sup>57</sup>	9.7 <sup>59</sup>	H <sup>+</sup> 0.18 <sup>59</sup>	1, 1
Quartz	SiO <sub>2</sub> + 2H <sub>2</sub> O = H <sub>4</sub> SiO <sub>4(aq)</sub>	-3.7372 <sup>60</sup>	-9.72 <sup>5</sup> / -11.49 <sup>15</sup>	0.2 <sup>15</sup>	19.12 <sup>15</sup> / 11.95 <sup>15</sup>	OH <sup>-</sup> 0.34 <sup>15</sup> / none	1, 1 / 4.58, 0.54 <sup>15</sup>
Gibbsite	Al(OH) <sub>3</sub> + 3H <sup>+</sup> = Al <sup>3+</sup> + 3H <sub>2</sub> O	7.7341 <sup>61</sup>	-5.51 <sup>15</sup>	1 <sup>15</sup>	11.5 <sup>15</sup>	OH <sup>-</sup> 1.0 <sup>15</sup>	1, 1
Aragonite	CaCO <sub>3</sub> + H <sup>+</sup> = Ca <sup>2+</sup> + HCO <sub>3</sub> <sup>-</sup>	2.0143 <sup>62</sup>	-5.57 <sup>63</sup> / -7.65 <sup>64</sup>	0.1 <sup>65</sup>	0 / 17.02 <sup>64</sup>		1, 0.86 <sup>63</sup> / 1, 1.7 <sup>64</sup>
Hydromagnesite	Mg <sub>5</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>4</sub> ·4H <sub>2</sub> O + 6H <sup>+</sup> = 4HCO <sub>3</sub> <sup>-</sup> + 5Mg <sup>2+</sup> + 6H <sub>2</sub> O	31.3922 <sup>66</sup>	-10.39 <sup>67</sup>	1.0 <sup>67</sup>	10.87 <sup>67</sup>		0.2, 1 <sup>67</sup>
Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub> + 2H <sup>+</sup> = 2HCO <sub>3</sub> <sup>-</sup> + Ca <sup>2+</sup> + Mg <sup>2+</sup>	3.5328 <sup>66</sup>	-7.96 <sup>15</sup> / -14.02 <sup>15</sup>	0.1 <sup>15</sup>	7.41 <sup>15</sup> / 24.61 <sup>15</sup>		0.16, 2.1 <sup>15</sup> / 1, 1
Saponite	Mg <sub>0.17</sub> Mg <sub>3</sub> Al <sub>0.34</sub> Si <sub>3.66</sub> O <sub>10</sub> (OH) <sub>2</sub> + 7.36H <sup>+</sup> = 2.64H <sub>2</sub> O + 0.34Al <sup>3+</sup> + 3.17Mg <sup>2+</sup> + 3.66H <sub>4</sub> SiO <sub>4(aq)</sub>	28.7937 <sup>14</sup>	-18 <sup>1</sup>	150 <sup>68-71</sup>	14.58 <sup>based on 15</sup>		1, 1

272 Values on the left and right side of the slash symbol are for dissolution and precipitation reactions, respectively. In case of  
 273 single value, the value is used for both dissolution and precipitation reactions.

274 \*K is the equilibrium constant of the reaction. Thermodynamic data are from the Thermoddem database (Blanc et al., 2012).

275 \*\*k is the intrinsic rate constant.

276 §The first term i is the ion in solution, the second term n is the power to which the activity of ion i is raised.

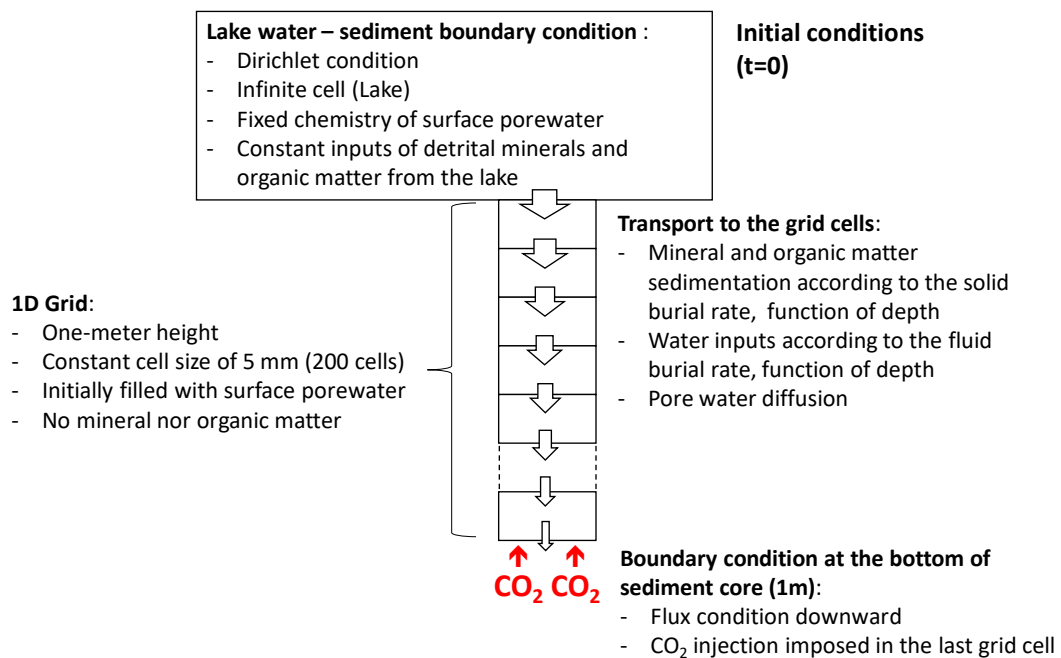
277 §§The first and second term are the empirical parameters Θ and η describing the affinity dependence.

278 †fitted with the observation

### 279 3.6.3 Model conditions and parameters

280 The model domain consists of a one-dimensional column of sediment with a Dirichlet-type boundary  
 281 condition at the sediment-water interface (infinite reservoir with constant concentrations for dissolved  
 282 species and constant volume fractions for solids), and a pure advective, no diffusive flux boundary  
 283 condition at the bottom (1 m depth) (Fig. 2). A fixed grid of 1 m height is used, made of 200 cells with  
 284 a constant grid spacing of 5 mm. Initially, the entire column is free of organic matter or minerals and  
 285 filled with the surface porewater charge balanced with chloride (Table 2). The aluminum  
 286 concentration is set at equilibrium with gibbsite. Iron was not considered which appears reasonable  
 287 considering its low concentrations in pore waters (mostly <50μM) and the absence of significant  
 288 amounts of iron bearing mineral in the sediments<sup>33</sup>. The Dirichlet-type boundary condition at the  
 289 sediment-water interface allows modeling constant inputs of water, minerals and organic matter from  
 290 the lake to the sediment column. The supplied water has a constant composition equal to the one of  
 291 surface pore waters. The volume fraction of supplied minerals and organic matter at the Dirichlet-type  
 292 boundary condition is adjusted to fit the observations (Table 2). In addition to albite and diopside, an  
 293 input of hydromagnesite is considered as it is expected to precipitate in the lake-water column or at the

294 sediment surface due to its supersaturation in the lake water. Fluids and solids are supplied to the  
 295 sediment column considering the calculated burial rate and water diffusion. There are no additional  
 296 transport processes such as advection, therefore no permeability value is required in the model. The  
 297 initial porosity of 100% (column free of solid phases) is updated at each calculation step as minerals  
 298 and organic matter are brought from the sediment-water interface and precipitate or dissolve during  
 299 the calculation. At the flux boundary condition (bottom of the sediment column), an injection of CO<sub>2</sub>  
 300 is considered. The gas flow rate is adjusted to fit the pH profile. The temperature, pressure, and pore  
 301 diffusion coefficient are fixed at 30°C, 1 bar, and 2·10<sup>-9</sup> m<sup>2</sup>·s<sup>-1</sup>, respectively. Each simulation was run  
 302 for 4000 years, which corresponds to the estimation of the youngest age of the lake formation<sup>37</sup> and is  
 303 equal to 4 times the approximate age of the sediment at 1 m depth . This results in the sediment from  
 304 the sediment-water interface moving completely through the column, thus achieving quasi-steady state  
 305 results.



306

307 Figure 2. Schematic diagram of the reactive transport model.

308

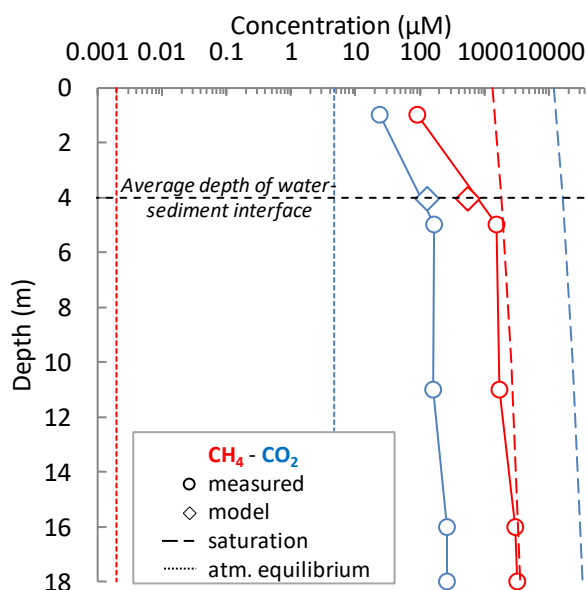
Table 2. Boundary conditions of the reactive transport model at the sediment-water interface

Water		Organic matter and minerals	
-	Concentration (mol·kg <sup>-1</sup> )	-	Volume fraction (m <sup>3</sup> ·m <sup>-3</sup> )
Temperature (°C)	30	Organic matter	0.0038
pH	9	Albite	0.003
HCO <sub>3</sub> <sup>-</sup>	2·10 <sup>-1</sup>	Diopside	0.001
Cl <sup>-</sup>	charge balanced	Hydromagnesite	0.0015
Na <sup>+</sup>	0.95		
K <sup>+</sup>	3.5·10 <sup>-2</sup>		
Mg <sup>2+</sup>	4·10 <sup>-3</sup>		
Ca <sup>2+</sup>	1·10 <sup>-4</sup>		
Al <sup>3+</sup>	Gibbsite*		
SiO <sub>2(aq)</sub>	1.7·10 <sup>-4</sup>		
O <sub>2(aq)</sub>	1·10 <sup>-10</sup>		

#### 310 4. \*Al concentration set at equilibrium with gibbsite Results

##### 311 4.1 Dissolved and bubbling gases

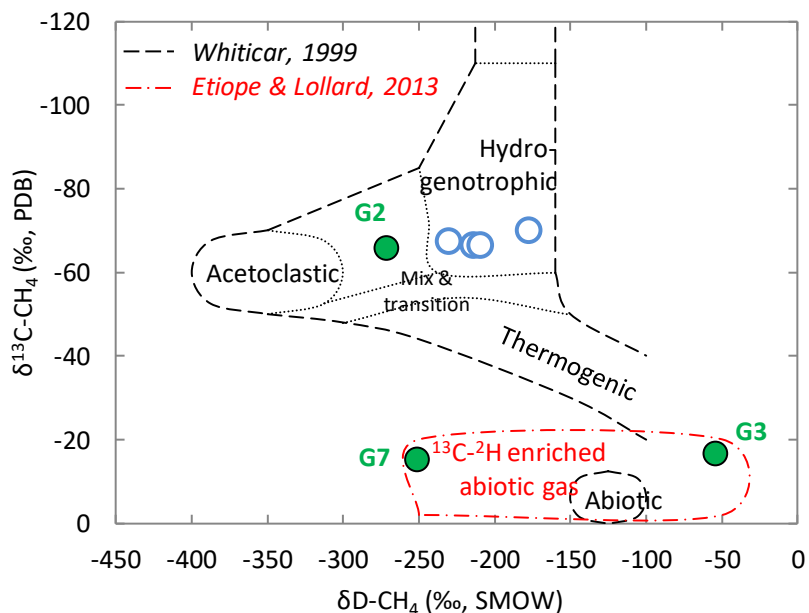
312 The concentration of dissolved methane in the water column evolves along its saturation  
313 concentration, increasing with depth to reach 3180  $\mu\text{M}$  at 18 m depth (Fig. 3, Table S3 in supporting  
314 information). The CO<sub>2</sub> concentration increases from 24  $\mu\text{M}$  at surface to 263  $\mu\text{M}$  at 18 m depth and  
315 remains ca. two orders of magnitude lower than its saturation concentration. Both concentrations of  
316 methane and CO<sub>2</sub> are orders of magnitude higher than their respective concentrations at equilibrium  
317 with atmosphere. In the pore waters, the  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  values of dissolved methane range between -  
318 72‰ and -62‰ and between -177‰ and -230‰, respectively (Fig. 4, Table S4 in supporting  
319 information), while dissolved CO<sub>2</sub> has  $\delta^{13}\text{C}$  values between +2‰ and +7‰. The gases bubbling at the  
320 lake surface are mostly made of CO<sub>2</sub>, with minor amounts of N<sub>2</sub>, O<sub>2</sub> and CH<sub>4</sub> (Table 3). The samples  
321 G3, G4, G7 and G10 contain mostly CO<sub>2</sub> (>95 vol.%) with low amounts of methane (~0.3%). The  
322  $\delta^{13}\text{C}$  values of CO<sub>2</sub> and CH<sub>4</sub> gases range between 0 and -3‰, and between -17 and -11‰, respectively.  
323 The samples G5, G11 and G12 have similar chemical composition and  $\delta^{13}\text{C}$  values of CO<sub>2</sub> but the  $\delta^{13}\text{C}$   
324 values of CH<sub>4</sub> are lower, ranging from -21 to -29‰. Sample G2 has a different chemical and isotopic  
325 composition. Methane represents 80 vol.% of the gas and its carbon isotope composition is of -66‰,  
326 close to the one of dissolved methane of pore waters. The CO<sub>2</sub> represents only 1.4 vol.% of the gases  
327 and its  $\delta^{13}\text{C}$  value of -20‰ is lower than in other samples.



329

330 Figure 3. Concentration of dissolved methane and CO<sub>2</sub> in the water column straight up the 18 m  
 331 depression (DZ14-4 WC). Methane and CO<sub>2</sub> data are in red and blue, respectively. The open circles  
 332 are the measured concentrations. The modeled CO<sub>2</sub> and CH<sub>4</sub> concentrations in the first 10 cm of  
 333 sediment are shown with open diamonds, at the average depth of the lake water – sediment interface.  
 334 The dashed and dotted lines are the saturation concentrations and the concentrations at equilibrium  
 335 with atmosphere, respectively. Calculation is done at 30°C.

336



337

338 Figure 4. Carbon isotope composition ( $\delta^{13}\text{C}$ ) as a function of hydrogen isotope composition ( $\delta^2\text{H}$ ) for  
 339 dissolved methane of pore waters (blue dots) and for methane of bubbling gases (green dots). The  
 340 dotted black lines correspond to the range of  $\delta^{13}\text{C}$ - $\delta^2\text{H}$  values defined by Whiticar<sup>72</sup> for thermogenic

341 and bacterial methane (acetoclastic and hydrogenotrophic pathways). The red dotted line is the range  
 342 of  $\delta^{13}\text{C}$ - $\delta^2\text{H}$  values defined by Etiope and Lollar<sup>73</sup> for abiogenic methane.

343

344

Table 3. Chemical and isotope compositions of bubbling gases

Sample	CO <sub>2</sub> (vol.%) ±2% rel.	CH <sub>4</sub> (vol.%) ±2% rel.	O <sub>2</sub> (vol.%) ±2% rel.	N <sub>2</sub> (vol.%) ±2% rel.	$\delta^{13}\text{C}_{\text{CO}_2}$ (‰) ±1‰	$\delta^{13}\text{C}_{\text{CH}_4}$ (‰) ±1‰	$\delta\text{D}_{\text{CH}_4}$ (‰) ±5‰
DZ16-08 G2	1.4	80.4	6.5	10.1	-20.1	-65.9	-272
DZ16-08 G3	95.5	0.6	2.6	2.7	-0.6	-16.8	-54
DZ16-08 G4	98.1	0.4	1.0	1.1	-0.3	-16.6	-
DZ16-08 G5	98.5	0.4	0.7	0.8	-2.0	-22.2	-
DZ16-08 G7*	99.2	0.3	0.2	0.6	-3.2	-15.4	-251
DZ16-08 G10	99.6	0.3	0.1	0.6	-2.4	-11.1	-
DZ16-08 G11	99.8	0.6	0.2	0.7	-2.2	-28.1	-
DZ16-08 G12	96.3	0.7	1.7	2.6	-1.4	-21.3	-

345 \*Sample G7 is from the "Plage de l'aéroport" (airport beach), south of the volcanic crater.  
 346 ±2% rel. indicates that the value is known with a precision of 2% relative to the measured value.

347

#### 348 4.2 Radiocarbon measurements

349 Radiocarbon measurements of DIC and POC of the water column were performed to assess the lake  
 350 reservoir effect, which can be large in volcanic crater lakes<sup>74</sup>. DIC and POC have mean values of  $\Delta^{14}\text{C}$   
 351 of  $-566\pm 3\text{‰}$  and  $-554\pm 2\text{‰}$ , respectively (Table 4), which correspond to conventional radiocarbon ages  
 352 of  $6650\pm 1\%$  years and  $6420\pm 1\%$  years. Given the half-life time of  $^{14}\text{C}$  ( $5730\pm 40$  years), those  
 353 measurements indicate that DIC and POC contain between 55% and 60% of "dead" carbon (*i.e.*, non-  
 354 atmospheric CO<sub>2</sub>), evidencing the input of volcanic CO<sub>2</sub> into the lake and its contribution to  
 355 autochthonous carbonate and organic matter production. Expectedly, the  $\Delta^{14}\text{C}$  value of SIC and SOC  
 356 in the surface sediment is close to that of DIC in the water column (except for one sample in the  
 357 sediment core C2 ( $-87\text{‰}$ ) composed primarily of terrestrial plant remains). Accordingly, plant macro-  
 358 remains coming from the volcanic catchment rather than SIC and SOC were used to date the sediment.  
 359 The radiocarbon data of macro-remains indicate ages of ca. 550 and 650 years at 45 cm and 79 cm,  
 360 respectively (Table 5). The macro-remain recovered in the surface sediment (1 cm depth) has pre-  
 361 Bomb values corresponding to 1955-1957 years AD ( $\text{F}^{14}\text{C}$  calibrated at  $2\sigma$  with the program  
 362 CALIBomb, Zone SH1-2<sup>75</sup>).

363

Table 4. Radiocarbon data for water column and sediment

Sampling location <sup>a</sup>	Sampling date	Sample type	Sampling depth (cm)	age BP (year)	1 $\sigma$ (year)	$\Delta^{14}\text{C}$ (‰)
DZ11-9 WC	Sept. 2011	DIC	10	6700	35	-569
DZ12-4 WC	April 2012	DIC	10	6590	30	-563
DZ10-9 WC	Sept. 2010	POC	50	6460	35	-556
DZ10-9 WC	Sept. 2010	POC	300	6375	35	-551
DZ12-4 C1	April 2012	SIC	2.5-5.0*	6460	30	-556
DZ12-4 C1	April 2012	SIC	11-16*	5515	30	-500
DZ12-4 C1	April 2012	SOC	5.0-7.5*	5720	30	-513
DZ12-4 C1	April 2012	SOC	11-16*	4875	30	-459
DZ12-4 C1	April 2012	SOC	11-16*	4415**	30	-427
DZ12-4 C1	April 2012	SOC	22-30*	5730**	30	-514
DZ12-4 C1	April 2012	SOC	37-40*	6045**	35	-532
DZ12-4 C2	April 2012	SIC	0-2.5*	6545	30	-561
DZ12-4 C2	April 2012	SIC	10.5-14.0*	6205	30	-542
DZ12-4 C2	April 2012	SOC	2.5-4.5*	5450	30	-496
DZ12-4 C2	April 2012	SOC	10.5-14.0*	675	30	-87
DZ12-4 C2	April 2012	SOC	27-30*	5600	35	-506

<sup>a</sup>WC is for water column, C1 and C2 for the sediment core 1 and 2

\*depth of the sediment layer; \*\* additional acid pre-treatment with 1M HCl solution at room temperature

365

366

Table 5. Radiocarbon dating of terrestrial plant macro-remains of the sediment core C12

Depth (cm)	<sup>14</sup> C age BP	Err 1 $\sigma$	F <sup>14</sup> C	Err 1 $\sigma$	Burial rate (mm·yr <sup>-1</sup> )
1	-	-	1.0161	0.0084	
	-	-	1.0135	0.0084	
45	582	71	0.9301	0.0078	0.77
	508	69	0.9387	0.0077	0.89
79	666	68	0.9204	0.0078	1.19
	653	63	0.9219	0.0072	1.21

367 Two measurements per sample.

368

### 369 4.3 Porosity and sedimentation rate

370 The porosity decreases from 98% in the surface sediment to 80-85% at depth (Fig. 5, Table S5 in  
 371 supporting information). The best fit of the porosity profile ( $r^2=0.6$ ) can be expressed as a log  
 372 distribution because of the large porosity changes in the upper centimeters:

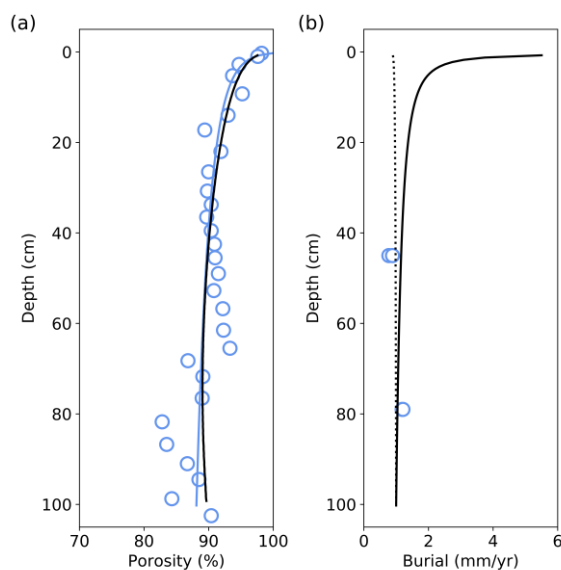
$$373 \quad \phi(z) = -0.0199 \cdot \ln(z) + 0.881 \quad \text{Eqs (6)}$$

374 where  $\phi$  is the porosity and  $z$  is the depth in meter. The correlation coefficient is explained by the  
 375 spread of the porosity values at depth. Equation 6 is consistent with the mean porosity values all along  
 376 the sedimentary column.

377 Radiocarbon measurements of plant macro-remains in the sediment enabled to determine ages as  
 378 function of depth (Table 5). This approach is reasonable as no textural evidence has been observed on  
 379 the first meter of sediment that could indicate erosion episodes or changes in the depositional



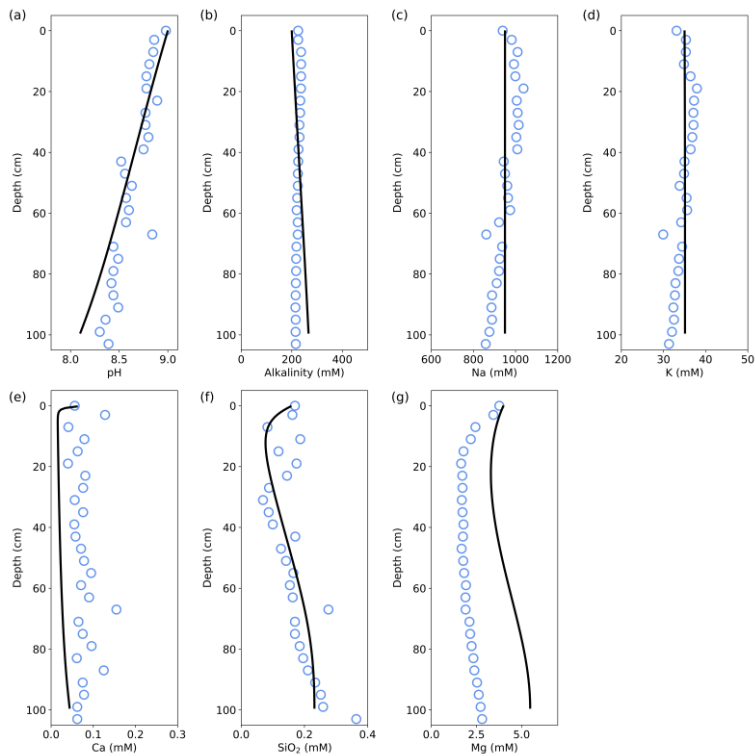
380 environment<sup>33</sup>. The age-depth model allowed estimating an asymptotic burial rate at 5 m depth of 0.75  
381 mm·yr<sup>-1</sup>. Then, the asymptotic burial rate and the porosity profile were used solved the equations (3)  
382 and (4). The solid burial rate decreases from 5 mm·yr<sup>-1</sup> in the uppermost sediment to 1 mm·yr<sup>-1</sup> at 1 m  
383 depth (Fig. 5).



384  
385 Figure 5. Measured and modeled porosity profiles (a) and calculated profiles for fluid and solid burial  
386 rates (b) as a function of depth. (a) Measured porosity (blue circles), and modeled porosity profile  
387 (black thick line). The blue line is a fit of the porosity data used for the burial rate calculation (Eqs 6;  
388  $r^2=0.6$ ). (b) Fluid and solid burial rates (mm·yr<sup>-1</sup>) used in the model. The depth-age constrains used for  
389 the burial rate calculation are shown with open blue circles and are obtained from the radiocarbon  
390 dating of plant macro-remains.

#### 391 392 4.4 Chemical composition of pore waters

393 The pH values of pore waters decrease from 9 near the water-sediment interface to 8.3 at 1 m depth  
394 (Fig. 6, Table S6 in supporting information). The alkalinity and the concentrations of sodium and  
395 potassium are of 235 mM, 1000 mM and 37 mM, respectively, in the surface sediment and decrease  
396 slightly at depth. The calcium concentration remains constant at ca. 75  $\mu$ M, while the silicon  
397 concentration increases from 150  $\mu$ M at the sediment surface to 250  $\mu$ M at 1 m depth. The magnesium  
398 concentration decreases down to 2 mM near the water-sediment interface and then increases slowly  
399 below 20 cm depth.

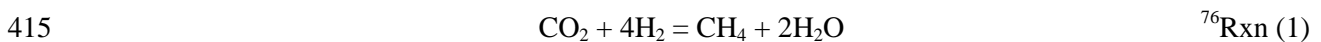


401

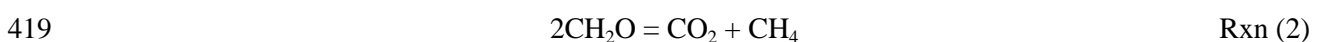
402 **5. Figure 6. Comparison of measured and modeled pH values, alkalinity**  
 403 **and major cations concentrations in the pore waters. The blue dots and**  
 404 **the full black lines represent the measured and modeled values,**  
 405 **respectively. Model results are after 4000 years of calculation. Modeling**  
 406 **and discussion**

407 5.1 Carbon cycle and controls on pH

408 The Dziani Dzaha is characterized by an unusual carbon cycle, for which the main characteristics are  
 409 caught in Figure 7. Both CO<sub>2</sub> and methane are outgassing from the lake water to the atmosphere. The  
 410 carbon and hydrogen isotope signatures of dissolved methane of sediment pore waters are typical of  
 411 bacterial methanogenesis through the hydrogenotrophic pathway<sup>72</sup>. The intense bacterial  
 412 methanogenesis in the sediment and in the lake water<sup>39</sup> results in saturated concentrations of methane  
 413 in the lake water column and in CH<sub>4</sub>-dominated bubbling gases (Sample G2). The formation of CH<sub>4</sub>  
 414 during hydrogenotrophic methanogenesis can be written as:



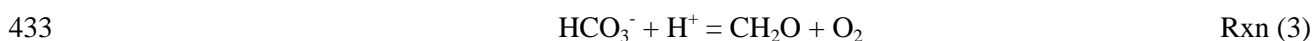
416 The microbial fermentation of the organic matter is the most likely source of CO<sub>2</sub> and H<sub>2</sub> and could  
 417 also account for the decrease of pore water pH values with depth. The coupled mechanisms of  
 418 methanogenesis and fermentation can be represented by the simplified reaction:



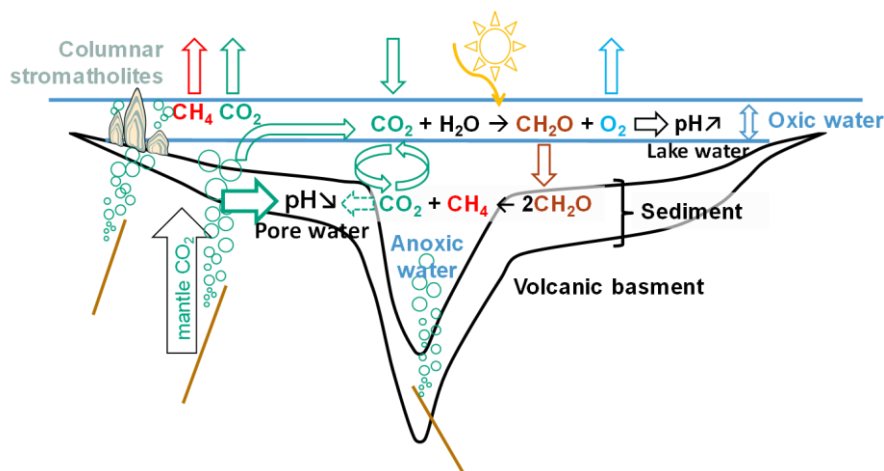
420 with CH<sub>2</sub>O being a simplified stoichiometry for the organic matter.

421 Magmatic CO<sub>2</sub> inputs is also likely influencing the pH of pore waters. The CO<sub>2</sub>-dominated  
422 gases bubbling into the lake evidence an active magmatic degassing. The δ<sup>13</sup>C and δ<sup>2</sup>H values of CH<sub>4</sub>  
423 in samples G3, G4, G10 and G7 are consistent with an abiotic origin<sup>73</sup>. The lower δ<sup>13</sup>C-CH<sub>4</sub> values of  
424 G5, G11, G12 and G2 reflect mixing between abiotic and microbial methane during the ascent of the  
425 bubbling gases through the water column, with an overwhelming dominance of microbial methane for  
426 G2, possibly due to the higher height of the water column where G2 was sampled. The chemical and  
427 isotopic compositions of CO<sub>2</sub>-dominated bubbling gases are consistent with a magmatic origin.

428 The radiocarbon measurements of inorganic and organic carbon of the water column indicate  
429 that the magmatic CO<sub>2</sub> contributes to the carbonate and organic matter production by more than 50  
430 mol.%. This additional source of carbon fuels the massive primary productivity of the lake dominated  
431 by cyanobacteria<sup>39</sup>. In turn, the photosynthetic activity of the cyanobacteria is the most likely  
432 processes at the origin of the overall high pH values, according to the reaction:



434



435

436 Figure 7. Schematic diagram of the carbon cycle and its controls on both lake water and pore  
437 waters pH values. Photosynthetic organisms in shallow waters use CO<sub>2</sub> originating from the  
438 atmosphere, from the magmatic gases CO<sub>2</sub> inputs and from organic matter degradation. The  
439 photosynthetic activity results in a production of O<sub>2</sub> which is lost to the atmosphere, in an increase of  
440 the lake water pH, and in organic matter accumulating in the sediment. In the water column and the  
441 sediment, the microbial degradation of the organic matter produces CH<sub>4</sub> and CO<sub>2</sub> which, associated to  
442 the magmatic CO<sub>2</sub> inputs, induce a decrease of the pore water pH values. Both CO<sub>2</sub> and biogenic CH<sub>4</sub>  
443 escape to the atmosphere. The size of the arrows pointing toward the pH decrease of pore waters

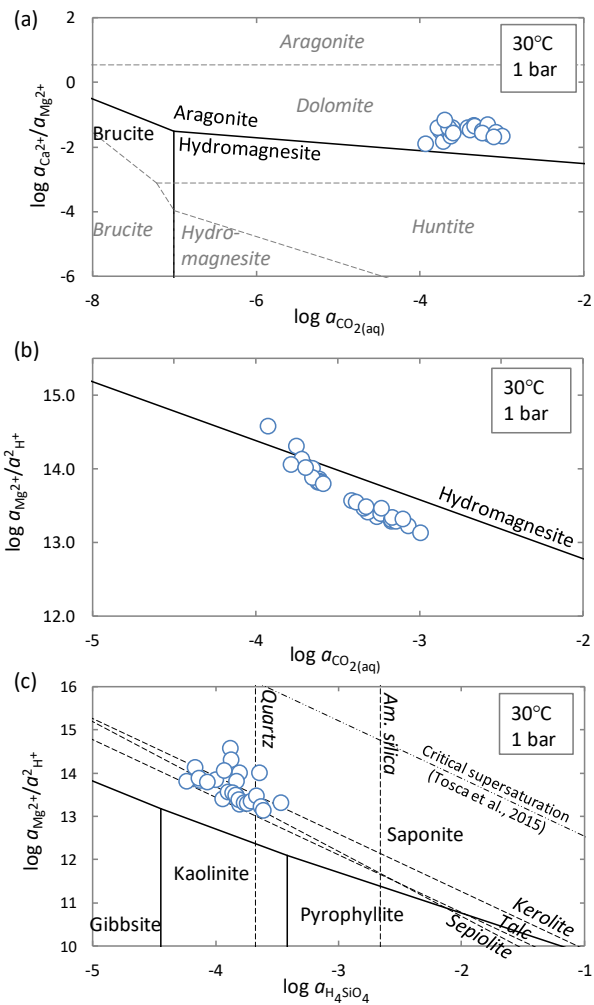
444 illustrates the dominant contribution of the magmatic CO<sub>2</sub> and the lower impact of the organic matter  
445 microbial degradation.

## 446 5.2 Mineral stability

447 The metastable equilibria between aragonite, hydromagnesite and brucite were calculated as a function  
448 of Mg<sup>2+</sup>, Ca<sup>2+</sup> and CO<sub>2</sub> activities (Fig. 8a). Although thermodynamics suggests that magnesite and  
449 dolomite are the most stable Mg-bearing carbonates at surface temperature and pressure, kinetics  
450 exerts a strong primary control on their formation<sup>67,77,78</sup>. The pore waters are close to metastable  
451 equilibrium between aragonite and hydromagnesite, which is consistent with the presence of the two  
452 carbonates in the surface sediment. While the Ca<sup>2+</sup>/Mg<sup>2+</sup> ratio is relatively stable with depth, the  
453 decrease of pH induces an increase of the CO<sub>2</sub> activity, which promotes the stability of aragonite at the  
454 expense of hydromagnesite. Dolomite has been locally observed at depth in the sediment<sup>33</sup> and could  
455 form by Mg incorporation and Ca replacement in calcium carbonates<sup>78,79</sup>. The progressive  
456 hydromagnesite undersaturation with depth stems from the pH decrease in pore waters (Fig. 8b).

457 The stability domains of Mg-aluminosilicates and those of talc, kerolite and sepiolite are  
458 calculated as function of H<sup>+</sup>, Mg<sup>2+</sup> and SiO<sub>2</sub> activities considering that aluminum behaves  
459 conservatively between the Al-bearing minerals (Fig. 8c). Chlorites are not considered as their  
460 formations are kinetically limited at ambient temperature and pressure<sup>80</sup>. The pore waters are  
461 supersaturated relative to saponite and remain supersaturated at depth despite the pH decrease. The  
462 Mg-aluminosilicate likely forms through heterogeneous nucleation involving mineral precursors such  
463 as alkaline feldspars, which lower the supersaturation required for mineral nucleation<sup>81</sup>. The Al-free  
464 Mg-silicates, although stable in the pore waters, are not observed in the sediments. Tosca<sup>81</sup> proposed a  
465 critical supersaturation above which those Mg-silicates would precipitate through homogeneous  
466 nucleation. The precipitation of hydromagnesite and saponite, by removing magnesium and silica from  
467 the pore waters, likely hinder the formation of Al-free Mg-silicates.

468

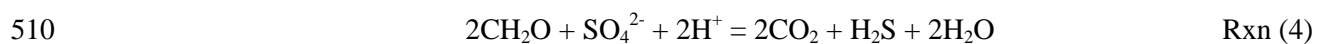


469

470 Figure 8. Pore water compositions (blue circles) and mineral stability domains in the systems (a) Mg-  
 471 Ca-C-O-H, (b) Mg-C-O-H and (c) Mg-Al-Si-O-H at 30°C and 0.1 MPa. Mineral stability domains  
 472 were calculated with the Thermoddem database<sup>13,14</sup> and pore waters were speciated with the Phreeqc  
 473 software<sup>82</sup>. (a) Magnesite and calcite are not considered in the calculation as they are not present in the  
 474 sediment. The grey dotted lines are metastable equilibria between dolomite, huntite, aragonite,  
 475 hydromagnesite and brucite. The full lines are metastable equilibria between aragonite,  
 476 hydromagnesite and brucite. (b) The full line corresponds to fluid composition at equilibrium with  
 477 hydromagnesite. (c) The full lines are metastable equilibria between Mg-aluminosilicates without  
 478 considering chlorites. The dotted lines are fluid compositions at equilibrium with talc, sepiolite and  
 479 kerolite. Thermodynamic data for kerolite are from Stoessel<sup>83</sup>. The dashed-dotted line is the critical  
 480 supersaturation required for homogenous nucleation of Mg-silicates as suggested by Tosca<sup>81</sup>. Silica  
 481 activities at equilibrium with quartz and amorphous silica are shown for reference (vertical dotted  
 482 lines).

483 5.3 Reactive transport modeling

484 The model is based on the sediment composition of the core C4, which was collected  
485 approximately at the average lake water depth (Fig. 1) and has a composition well representative of the  
486 dominant sediment composition observed in most sediment cores<sup>33</sup>. The mineral and pore water  
487 compositions are constant from 1500 years to 4000 years (end of the simulation), showing that a  
488 steady state has been reached. The microbial degradation of organic matter according to Reaction (2)  
489 results in a decrease of its content with depth and a decrease of pH through the release of CO<sub>2</sub>. The  
490 rate constant of the organic matter degradation is adjusted to best fit the profile of organic matter  
491 content. A value of 10<sup>-10.3</sup> mol·m<sup>-2</sup>·s<sup>-1</sup> is adopted (Table 1), close to published values<sup>54</sup>. The modeled  
492 concentration of methane in the uppermost part of the sediment column is consistent with the  
493 dissolved methane measured in the lake water column at the corresponding depth (i.e., 3-4 m of water  
494 height) (Fig. 3), which supports the use of methanogenesis and fermentation to approximate the  
495 overall organic matter degradation. If no external source of CO<sub>2</sub> is considered, the modeled pH value  
496 at 1 m depth is 0.7 pH units higher than the measured value and the total CO<sub>2</sub> pressure is of 6.3·10<sup>-3</sup>  
497 bar. In our model, CO<sub>2</sub> is thus injected at the bottom of the sediment column to account for the  
498 influence of magmatic CO<sub>2</sub>. The best fit of pH is obtained with a CO<sub>2</sub> injection of 4 mmol·s<sup>-1</sup>·m<sup>-3</sup> of  
499 sediment, which results in a total CO<sub>2</sub> pressure of 7.5·10<sup>-2</sup> bar at 1 m depth, one order of magnitude  
500 higher than without CO<sub>2</sub> injection (Fig. 6). The corresponding CO<sub>2</sub> concentration is of 2 mM, which  
501 does not exceed the CO<sub>2</sub> solubility of the lake (16 mM) and is consistent with the absence of bubbling  
502 CO<sub>2</sub> where the sediment core C4 was collected. At 1 m depth, our model predicts magmatic CO<sub>2</sub>  
503 inflows and organic matter degradation accounting for 22 and 2 mol.% of the pore water DIC,  
504 respectively. The remaining DIC is inherited from the lake water by diffusion and fluid burial. The  
505 sulfur cycle, not considered in the model, is not expected to modify significantly these results. The  
506 sulfate concentrations of ca. 2 mM in the lake water<sup>39</sup> indicate a low contribution of sulfate to the  
507 alkalinity compared to bicarbonate ions. Sulfate reduction coupled to organic matter oxidation would  
508 produce twice as many times CO<sub>2</sub> per mole of reaction as the organic matter degradation considered in  
509 the model (Reaction 2) according to:



511 The low sulfate concentration does not seem compatible with high densities of sulfate-  
512 reducing bacteria outcompeting methanogens<sup>39</sup>; however, even in the unlikely case where all organic  
513 matter degradation results from sulfate reduction, the process would only account, in first  
514 approximation, for ca. 4 mol.% of the total pore water DIC which remains a minor contribution  
515 compared to the magmatic CO<sub>2</sub> inflows.

516 The modeled alkalinity and major cation profiles are consistent with the measured data (Fig.  
517 6). Magnesium shows a distinctive concentration profile compared to the other dissolved species, with  
518 a decrease in concentration in the surface sediment followed by a moderate increase at depth. Despite  
519 a shift toward higher values, the modeled profile is consistent with the measurements. Hydromagnesite  
520 exerts a strong control on the dissolved Mg. Its precipitation in the shallow sediment lowers the Mg  
521 concentrations, which increase at further depth where hydromagnesite is destabilized. A decrease of  
522 the CO<sub>2</sub> inflows at the bottom of the sediment column allows a better fit of the Mg profile; however,  
523 the pH values become higher than the measured ones and the hydromagnesite is less destabilized at  
524 depth. When CO<sub>2</sub> inflows are suppressed, the pH does not decrease enough to destabilize the  
525 hydromagnesite. A decrease of the hydromagnesite solubility decreases the Mg concentration but  
526 increases the Mg-carbonate content at depth. The discrepancy between the measured and modeled Mg  
527 profile could be explained by the precipitation of amorphous Mg-Si phases as precursors of Mg-  
528 phyllosilicates<sup>81</sup>, which are not considered in our model. The silica concentration is controlled by the  
529 formation of saponite and microcline. If saponite or microcline are suppressed from the model, the  
530 silica concentration increases to value up to one order of magnitude higher than the measured ones,  
531 showing the role of these phases in the silica balance of the lake. The formation of microcline is  
532 consistent with evidences of low-temperature K-feldspars authigenesis in natural environments<sup>84,85</sup>.  
533 Equilibrium of the pore waters with amorphous Mg-Si phases<sup>64</sup>, not considered in the model, could  
534 also contribute to the buffering of the silica concentration. A reasonable consistency is obtained  
535 between the modeled and measured calcium concentrations. The underestimation of the Ca  
536 concentrations can result from an aragonite solubility higher in the Dziani Dzaha than reported in the  
537 Thermoddem database. An increase by 0.5 of the logarithmic value of the aragonite equilibrium  
538 constant shifts the modeled calcium concentrations toward values consistent with the measured ones.

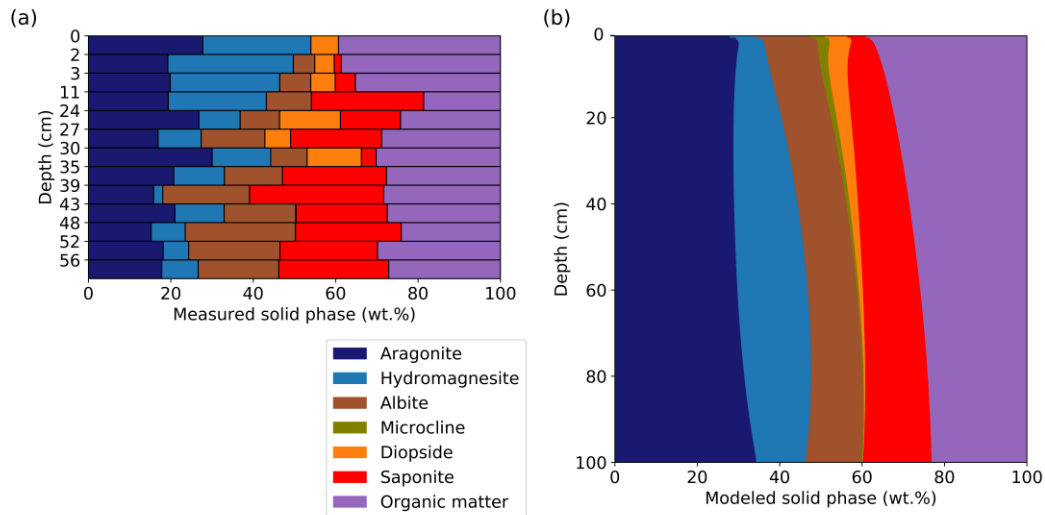
539 The modeled sediment composition is also consistent with the observations (Fig. 9). The solid  
540 phase of surface sediment is dominated by organic matter and aragonite, with lower amounts of  
541 detrital silicates and saponite. The hydromagnesite content represents 17 wt.% of the solid phase at 60  
542 cm and decreases at further depth. The organic matter content decreases from 42 wt.% of the solid  
543 phase in the uppermost sediment to 23 wt.% at depth due to microbial degradation. The decrease of  
544 pH down to 8.2 at 1 m depth induces the destabilization of hydromagnesite, which matches the  
545 observations although the model overestimates the hydromagnesite content. An increase of the CO<sub>2</sub>  
546 inflows decreases the hydromagnesite content at depth, which is more consistent with the  
547 observations; however, the pH values and the Mg concentrations become under and overestimated,  
548 respectively. Aragonite and saponite remain stable despite the pH decrease and saponite accumulates  
549 at depth to reach 17 wt.% of the solid phase. The destabilization of hydromagnesite in parallel to the  
550 formation of saponite could evidence a reaction relationship between the two minerals<sup>33</sup>; however,  
551 suppressing the hydromagnesite of the model leads to similar yield of saponite, showing that the

552 magnesium required for the saponite formation is primarily supplied by the lake water. An increase of  
553 the precipitation rate of saponite does not lead to a significant increase of the saponite content;  
554 however, it results in a drastic decrease of the aluminium concentration from  $10^{-4}$   $\mu\text{M}$  to  $10^{-6}$   $\mu\text{M}$ ,  
555 which highlights aluminium as the limiting reactant in the saponite formation. As consequence, the  
556 pore waters become undersaturated relative to the K-feldspar due to the aluminium decrease.  
557 Microcline does not form anymore, and the silica concentrations increase above measured values. The  
558 diopside content decreases with depth as the mineral dissolves; however, a specific surface area one  
559 order of magnitude higher than the literature values is used to achieve this result (Table 1).  
560 Alternatively, higher inputs of detrital materials to the lake in recent times could explain the observed  
561 increase of the diopside content in the uppermost sediment. Quartz and dolomite do not form due to  
562 kinetic limitations and the pore waters are undersaturated relative to gibbsite.

563           The role of the sediment compaction was tested running the model considering a same burial  
564 rate for fluid and solid phases. The results are very similar, which shows that the sediment compaction  
565 has low influence on the temporal and spatial time scale of the Dziani Dzaha early diagenetic  
566 processes. Additional sensitivity tests were performed to validated the robustness of the model  
567 (supporting information).

568           In summary, the model allowed to discriminate and quantify the role of magmatic  $\text{CO}_2$  inflows  
569 and organic matter microbial degradation on the diagenetic evolution of the sediment. Without  
570 magmatic  $\text{CO}_2$  inflows, the decrease of pH and the destabilization of hydromagnesite at depth cannot  
571 be explained. The magmatic  $\text{CO}_2$  inputs oversees 90% of the pH decrease of the pore waters. The  
572 organic matter degradation accounts for the remaining 10% while the only mineral reactivity has no  
573 significant impact on pH. The model allowed quantifying the flux of magmatic  $\text{CO}_2$  ( $4 \text{ mmol}\cdot\text{s}^{-1}\cdot\text{m}^{-3}$ )  
574 and the fraction of the lake DIC inherited from the magmatic gases (22 mol.%). The model also  
575 highlights the lake water as the primary source of Mg, aluminum as the limiting reactant in the  
576 saponite formation and the K-feldspar controlling the Si concentrations. Isotopes composition, not  
577 treated in the model, could bring additional constrain on rate and processes<sup>10,17,86</sup>. Future modeling  
578 efforts will have to integrate isotopic data to fully decipher the early diagenesis of the Dziani Dzaha  
579 sediment.





580

581 Figure 9. Observed and modeled sediment composition (wt.%) as a function of depth. (a) Measured  
 582 composition in the sediment core C4<sup>33</sup>. (b) Modeled sediment composition. Dark blue, light blue,  
 583 brown, green, orange, red and purple are for aragonite, hydromagnesite, albite, microcline, diopside,  
 584 saponite and organic matter, respectively. Model results are after 4000 years of calculation.

585

#### 586 5.4 Insights on the formation of lacustrine carbonates in volcanic-dominated settings

587 These data provide new insights on the origin of carbonates and Mg-silicates produced in  
 588 lacustrine environments in volcanic-dominated settings such as continental rifts<sup>6-8,87</sup>. Mg-silicates  
 589 (stevensite, kerolite and talc) have been identified in the Cretaceous pre-salt carbonate rocks of the  
 590 South Atlantic continental margins<sup>27</sup>. Their formation was suggested to occur in lakes dominated by  
 591 volcanic terrains<sup>8,88</sup>, but it is unclear whether it is a sufficient source of silica and magnesium to fuel  
 592 the Mg-silicates precipitation. Experimental work by Tutolo and Tosca<sup>30</sup> showed that, at elevated pH  
 593 and Si concentration, the precipitation of Mg-silicates and spheroidal calcium carbonates typical of the  
 594 pre-salt formation requires moderate Ca and Mg concentrations,  $< 1-2 \text{ mmol}\cdot\text{kg}^{-1}$ . This implies high  
 595 fluxes of Ca and Mg to the site of deposition to explain the volume of the carbonate rocks. Our study  
 596 shows that the weathering of alkaline volcanic rocks in a small-scale basin can be enough to supply  
 597 the Ca, Mg and Si needed for carbonates and Mg-silicates to form. The formation of Mg-silicates and  
 598 K-feldspars would buffer the silica concentration. Alkaline volcanic terrains can also supply enough  
 599 aluminium for saponite to form. Aluminium being shown as the limiting reactant in the saponite  
 600 formation, the occurrence of Mg-aluminosilicates sets paleoenvironmental constraints on the nature of  
 601 the volcanic terrains required for their formation.

602 The origin of the high pH values required for the formation of Mg-silicates remains unclear.  
 603 Specific geochemical conditions are required to produce high pH waters in evaporating lake<sup>30</sup>.

604 Depending on the ratio between Ca concentration and alkalinity, the formation of carbonates can  
605 prevent the pH to reach values high enough for Mg-silicates to form. An intense primary productivity,  
606 as identified in the Dziani Dzaha, can make the difference by pushing the pH to those high values.  
607 This intense primary productivity is probably due to the combination of nutrient input by the  
608 weathering of alkaline volcanic rocks and the lake functioning, ammonium and phosphate generated  
609 by the organic matter degradation in the anoxic part of the water column being recycled for primary  
610 productivity rather than denitrified (for ammonium) or buried in the sediment together with iron  
611 oxides.

612 The initial mineralogy of the carbonate rocks of the South Atlantic margins is still unknown.  
613 High contents of Sr measured in spherulitic calcite of the pre-salt deposits of the Angolan margin  
614 could support an aragonitic component of initial mineralogy<sup>28</sup>. Precipitation of aragonite rather than  
615 calcite is dependent on the Mg/Ca ratio, for which values above 10 tend to promote the formation of  
616 aragonite at the expense of calcite<sup>89-91</sup>. Delay between carbonates and Mg-silicates formation during  
617 early diagenesis tends to increase the Mg/Ca ratio favoring the formation of aragonite<sup>30</sup>. The Mg/Ca  
618 ratio of ca. 20 of the Dziani Dzaha lake and pore waters is consistent with the occurrence of aragonite.  
619 Our field and model results highlight the differing time scales of carbonates and Mg-silicates  
620 formation during the early diagenesis, with saponite accumulating mostly at depth whereas aragonite is  
621 present in the surface sediment. The Dziani Dzaha is a good example of geochemical environments  
622 co-precipitating carbonates and Mg-silicates and promoting the formation of aragonite at the expense of  
623 calcite. Moreover, the Mg concentration of the Dziani Dzaha pore waters is shown to be controlled by  
624 the precipitation and destabilization of hydromagnesite, which can thus influence both the formation  
625 of Mg-silicates and the nature of the Ca-carbonates. The formation of hydromagnesite in the surface  
626 sediment can hinder the formation of Mg-silicates whereas its destabilization at depth can fuel the Mg-  
627 silicates formation and increase the Mg/Ca ratio, stabilizing the aragonite.

628 The volume and spatial extent of the continental carbonate rocks deposited in the South  
629 Atlantic continental rift at a time of isolation from the ocean (Early Cretaceous, 142-113Ma)<sup>28,29,92</sup>  
630 raise questions about the carbon source. During continental rifting, magmatic CO<sub>2</sub> inflows could have  
631 occurred as the continental crust became thinner and the influence of asthenospheric mantle increased.  
632 Our study demonstrates the ability of magmatic CO<sub>2</sub> inflows to fuel the carbonate production into  
633 small-scale basins. By analogy, CO<sub>2</sub> inflows may have set the appropriate geochemical conditions for  
634 the pre-salt Mg-silicate-rich carbonates to form by fueling the carbonate factory and the primary  
635 productivity, which in turn resulted in high pHs promoting the Mg-silicates formation.

636 The occurrence of pore-filling Mg-silicates in carbonate reservoir rocks is expected to lower  
637 the reservoir quality by decreasing porosity and permeability. However, the diagenetic processes  
638 which may affect the stability of these chemically labile minerals are not well understood. Although

639 the pore waters remain supersaturated relative to saponite all along the first meter of the Dziani Dzaha  
640 sediment, the decrease of pH induces a progressive decrease of the saponite supersaturation. In a  
641 context of continental rifting under magmatic CO<sub>2</sub> influence, a further decrease of pH at depth could  
642 eventually destabilize the Mg-silicates and increase the porosity. Investigating the fate of saponite at  
643 further depth in the Dziani Dzaha sediment would provide new insights on the stability of these labile  
644 minerals during diagenesis.

645 This study did not account for the iron and sulfur cycle. Considering the iron cycle is an  
646 unavoidable step towards the understanding of geological units such as pre-salt sedimentary sequences  
647 in which iron bearing phases such as titanomagnetite and siderite were identified in the paragenetic  
648 sequence<sup>93</sup>. Further characterization efforts will have to focus on the iron and sulfur sources and sinks  
649 to fully investigate diagenetic evolution of the Dziani Dzaha sedimentary sequences.

## 650 **6. Concluding remarks**

651 A detailed characterization of the Dziani Dzaha sediments was performed and used to develop a  
652 reactive-transport model accounting for burial rate and sediment compaction. The model allowed to  
653 discriminate and quantify the role of magmatic CO<sub>2</sub> inflows and organic matter microbial degradation  
654 on the diagenetic evolution of the sediment. While our <sup>14</sup>C radiometric data show that the magmatic  
655 CO<sub>2</sub> fuels both the primary productivity and the carbonate formation, the model indicates that it is also  
656 responsible of the decrease of the pore water pHs from 9 to 8.2 in the first-meter of sediment. As  
657 consequence, the hydromagnesite is destabilized at depth leaving behind an aragonite - saponite  
658 mineral assemblage. Saponite formation is shown to be limited by aluminium availability, which  
659 brings constrain on the paleoenvironments of formation of Mg-aluminosilicates. These results bring  
660 new insight on the formation and diagenesis of carbonate sediments associated with Mg-silicates in  
661 volcanic-dominated settings such as continental rifting. They demonstrate the possible role of  
662 magmatic CO<sub>2</sub> in setting the geochemical conditions required for the co-precipitation of carbonate and  
663 Mg-silicates, by supplying carbon to the carbonate factory, by fueling the primary production which in  
664 turn raises the pHs and enhances the carbonate and Mg-silicates formation, and by controlling the  
665 pore water pHs during diagenesis. The ability of our model to reproduce the porosity, the pore water  
666 chemistry and the mineral assemblage of the Dziani Dzaha sediments makes it very promising to  
667 predict the full evolution of chemical and physical properties of larger-scale carbonate formation from  
668 their deposition to their current settings.

669

670

672 This work was supported by IPGP, TOTAL (project FR00008189), Agence Nationale de la Recherche  
673 (France) (grant number ANR-13-BS06-0001) and one INSU-INTERRVIE grant (grant number  
674 AO2013-785992). Radiocarbon analysis benefited from funding by INSU-CNRS (ARTEMIS 2014)  
675 and the Deep Carbon Observatory and analytical support by J.P. Dumoulin and C. Moreau, LMC14.  
676 The funding for Carl Steefel was provided by the Director, Office of Science, Basic Energy Sciences,  
677 Chemical Sciences, Geosciences, and Biosciences Division, of the U.S. Department of Energy under  
678 Contract No. DE-AC02-05CH11231 to Lawrence Berkeley National Laboratory. The authors also  
679 wish to thank their colleagues (C. Leboulanger, C. Bernard, P. Got, E. Fouilland, M. Bouvy, E. Le  
680 Floch, V. Grossi and D. Sala) for their support and assistance during sampling campaigns on Dziani  
681 Dzaha. H el ene Vermesse and Sonia Noirez are acknowledged for their assistance during molecular  
682 and isotopic analyses of gases at IFPEN. Finally, the authors thank the Air Austral Airline Company  
683 and Alexandra and Laurent at the “Les Couleurs” Guest House in Mayotte for their valuable assistance  
684 and support.

- 686 (1) Back, W.; Hanshaw, B. B.; Plummer, L. N.; Rahn, P. H.; Rightmire, C. T.; Rubin, M. Process and Rate  
687 of Dedolomitization: Mass Transfer and <sup>14</sup>C Dating in a Regional Carbonate Aquifer. *GSA Bulletin*  
688 **1983**, *94* (12), 1415–1429. [https://doi.org/10.1130/0016-7606\(1983\)94<1415:PARODM>2.0.CO;2](https://doi.org/10.1130/0016-7606(1983)94<1415:PARODM>2.0.CO;2).
- 689 (2) Machel, H. G. Concepts and Models of Dolomitization: A Critical Reappraisal. *Geological Society,*  
690 *London, Special Publications* **2004**, *235* (1), 7–63. <https://doi.org/10.1144/GSL.SP.2004.235.01.02>.
- 691 (3) Morad, S. *Carbonate Cementation in Sandstones: Distribution Patterns and Geochemical Evolution*;  
692 John Wiley & Sons, 2009; Vol. 72.
- 693 (4) Hill, C. A. Sulfuric Acid Speleogenesis of Carlsbad Cavern and Its Relationship to Hydrocarbons,  
694 Delaware Basin, New Mexico and Texas (1). *AAPG bulletin* **1990**, *74* (11), 1685–1694.
- 695 (5) Hill, C. A. H<sub>2</sub>S-Related Porosity and Sulfuric Acid Oil-Field Karst. **1995**.
- 696 (6) Bertani, R. T.; Carozzi, A. V. Lagoa Feia Formation (Lower Cretaceous) Campos Basin, Offshore Brazil:  
697 Rift Valley Type Lacustrine Carbonate Reservoirs - I. *J Petroleum Geol* **1985**, *8* (1), 37–58.  
698 <https://doi.org/10.1111/j.1747-5457.1985.tb00190.x>.
- 699 (7) Bertani, R. T.; Carozzi, A. V. Lagoa Feia Formation (Lower Cretaceous) Campos Basin, Offshore Brazil:  
700 Rift Valley Type Lacustrine Carbonate Reservoirs - II. *Journal of Petroleum Geology* **1985**, *8* (2), 199–  
701 220. <https://doi.org/10.1111/j.1747-5457.1985.tb01011.x>.
- 702 (8) Wright, V. P. Lacustrine Carbonates in Rift Settings: The Interaction of Volcanic and Microbial  
703 Processes on Carbonate Deposition. *Geological Society, London, Special Publications* **2012**, *370* (1), 39–  
704 47. <https://doi.org/10.1144/SP370.2>.
- 705 (9) Machel, H. G. Bacterial and Thermochemical Sulfate Reduction in Diagenetic Settings — Old and New  
706 Insights. *Sedimentary Geology* **2001**, *140* (1–2), 143–175. [https://doi.org/10.1016/S0037-0738\(00\)00176-7](https://doi.org/10.1016/S0037-0738(00)00176-7).
- 707 (10) Ahm, A.-S. C.; Bjerrum, C. J.; Blättler, C. L.; Swart, P. K.; Higgins, J. A. Quantifying Early Marine  
708 Diagenesis in Shallow-Water Carbonate Sediments. *Geochimica et Cosmochimica Acta* **2018**, *236*, 140–  
709 159. <https://doi.org/10.1016/j.gca.2018.02.042>.
- 711 (11) Berner, R. A. *Early Diagenesis: A Theoretical Approach*; Princeton University Press, 1980.
- 712 (12) Li, L.; Maher, K.; Navarre-Sitchler, A.; Druhan, J.; Meile, C.; Lawrence, C.; Moore, J.; Perdril, J.;  
713 Sullivan, P.; Thompson, A.; et al. Expanding the Role of Reactive Transport Models in Critical Zone  
714 Processes. *Earth-Science Reviews* **2017**, *165*, 280–301. <https://doi.org/10.1016/j.earscirev.2016.09.001>.
- 715 (13) Blanc, Ph.; Lassin, A.; Piantone, P.; Azaroual, M.; Jacquemet, N.; Fabbri, A.; Gaucher, E. C.  
716 Thermodem: A Geochemical Database Focused on Low Temperature Water/Rock Interactions and  
717 Waste Materials. *Applied Geochemistry* **2012**, *27* (10), 2107–2116.  
718 <https://doi.org/10.1016/j.apgeochem.2012.06.002>.
- 719 (14) Blanc, P.; Vieillard, P.; Gailhanou, H.; Gaboreau, S.; Gaucher, E.; Fialips, C. I.; Made, B.; Giffaut, E. A  
720 Generalized Model for Predicting the Thermodynamic Properties of Clay Minerals. *American Journal of*  
721 *Science* **2015**, *315* (8), 734–780. <https://doi.org/10.2475/08.2015.02>.
- 722 (15) Marty, N. C. M.; Claret, F.; Lassin, A.; Tremosa, J.; Blanc, P.; Madé, B.; Giffaut, E.; Cochepin, B.;  
723 Tournassat, C. A Database of Dissolution and Precipitation Rates for Clay-Rocks Minerals. *Applied*  
724 *Geochemistry* **2015**, *55*, 108–118. <https://doi.org/10.1016/j.apgeochem.2014.10.012>.
- 725 (16) Marty, N. C. M.; Lach, A.; Lerouge, C.; Grangeon, S.; Claret, F.; Fauchet, C.; Madé, B.; Lundy, M.;  
726 Lagroix, F.; Tournassat, C.; et al. Weathering of an Argillaceous Rock in the Presence of Atmospheric  
727 Conditions: A Flow-through Experiment and Modelling Study. *Applied Geochemistry* **2018**, *96*, 252–  
728 263. <https://doi.org/10.1016/j.apgeochem.2018.07.005>.
- 729 (17) Maher, K.; Steefel, C. I.; DePaolo, D. J.; Viani, B. E. The Mineral Dissolution Rate Conundrum: Insights  
730 from Reactive Transport Modeling of U Isotopes and Pore Fluid Chemistry in Marine Sediments.  
731 *Geochimica et Cosmochimica Acta* **2006**, *70* (2), 337–363. <https://doi.org/10.1016/j.gca.2005.09.001>.
- 732 (18) Arndt, S.; Jørgensen, B. B.; LaRowe, D. E.; Middelburg, J. J.; Pancost, R. D.; Regnier, P. Quantifying  
733 the Degradation of Organic Matter in Marine Sediments: A Review and Synthesis. *Earth-Science*  
734 *Reviews* **2013**, *123*, 53–86. <https://doi.org/10.1016/j.earscirev.2013.02.008>.
- 735 (19) Paraska, D. W.; Hipsey, M. R.; Salmon, S. U. Sediment Diagenesis Models: Review of Approaches,  
736 Challenges and Opportunities. *Environmental Modelling & Software* **2014**, *61*, 297–325.  
737 <https://doi.org/10.1016/j.envsoft.2014.05.011>.
- 738 (20) Huber, C.; Druhan, J. L.; Fantle, M. S. Perspectives on Geochemical Proxies: The Impact of Model and  
739 Parameter Selection on the Quantification of Carbonate Recrystallization Rates. *Geochimica et*  
740 *Cosmochimica Acta* **2017**, *217*, 171–192. <https://doi.org/10.1016/j.gca.2017.08.023>.
- 741 (21) Hayes, J. M.; Waldbauer, J. R. The Carbon Cycle and Associated Redox Processes through Time. *Phil.*  
742 *Trans. R. Soc. B* **2006**, *361* (1470), 931–950. <https://doi.org/10.1098/rstb.2006.1840>.

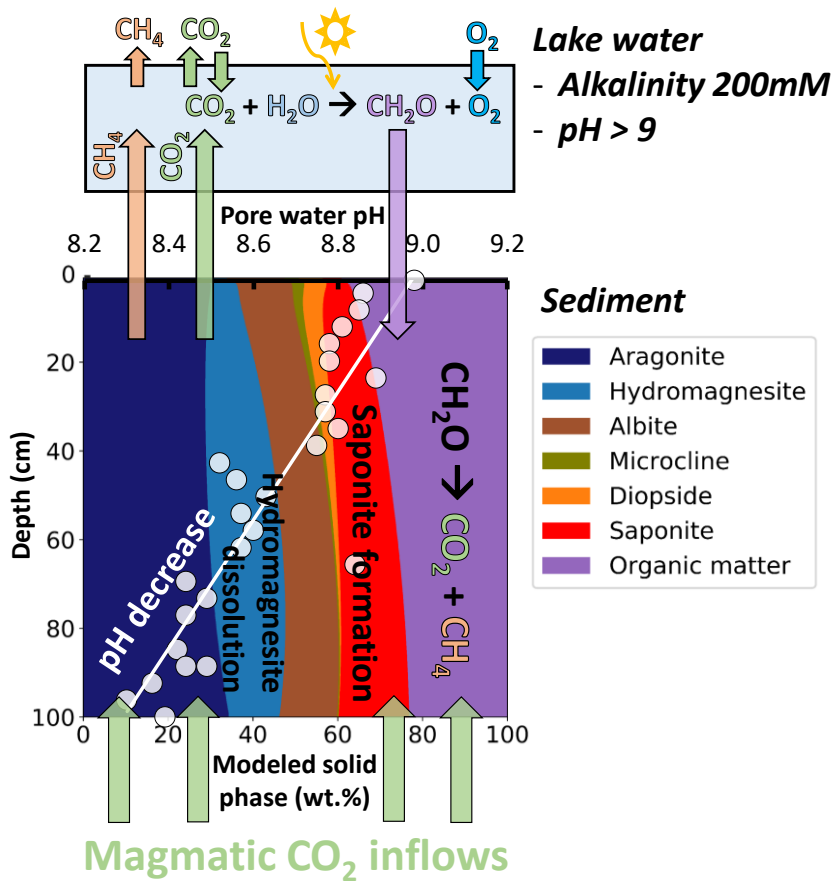
- 743 (22) Bristow, T. F.; Kennedy, M. J.; Derkowski, A.; Droser, M. L.; Jiang, G.; Creaser, R. A. Mineralogical  
744 Constraints on the Paleoenvironments of the Ediacaran Doushantuo Formation. *Proceedings of the*  
745 *National Academy of Sciences* **2009**, *106* (32), 13190–13195. <https://doi.org/10.1073/pnas.0901080106>.
- 746 (23) Higgins, J. A.; Blättler, C. L.; Lundstrom, E. A.; Santiago-Ramos, D. P.; Akhtar, A. A.; Crüger Ahm, A.-  
747 S.; Bialik, O.; Holmden, C.; Bradbury, H.; Murray, S. T.; et al. Mineralogy, Early Marine Diagenesis,  
748 and the Chemistry of Shallow-Water Carbonate Sediments. *Geochimica et Cosmochimica Acta* **2018**,  
749 *220*, 512–534. <https://doi.org/10.1016/j.gca.2017.09.046>.
- 750 (24) Huang, J.; Chu, X.; Lyons, T. W.; Planavsky, N. J.; Wen, H. A New Look at Saponite Formation and Its  
751 Implications for Early Animal Records in the Ediacaran of South China. *Geobiology* **2013**, *11* (1), 3–14.  
752 <https://doi.org/10.1111/gbi.12018>.
- 753 (25) Chitale, V. D.; Alabi, G.; Gramin, P.; Lepley, S.; Piccoli, L. Reservoir Characterization Challenges Due  
754 to the Multiscale Spatial Heterogeneity in the Presalt Carbonate Sag Formation, North Campos Basin,  
755 Brazil. *Petrophysics* **2015**, *56* (06), 552–576.
- 756 (26) Thompson, D. L.; Stilwell, J. D.; Hall, M. Lacustrine Carbonate Reservoirs from Early Cretaceous Rift  
757 Lakes of Western Gondwana: Pre-Salt Coquinas of Brazil and West Africa. *Gondwana Research* **2015**,  
758 *28* (1), 26–51. <https://doi.org/10.1016/j.gr.2014.12.005>.
- 759 (27) Tosca, N. J.; Wright, V. P. Diagenetic Pathways Linked to Labile Mg-Clays in Lacustrine Carbonate  
760 Reservoirs: A Model for the Origin of Secondary Porosity in the Cretaceous Pre-Salt Barra Velha  
761 Formation, Offshore Brazil. *Geological Society, London, Special Publications* **2018**, *435* (1), 33–46.  
762 <https://doi.org/10.1144/SP435.1>.
- 763 (28) Saller, A.; Rushton, S.; Buambua, L.; Inman, K.; McNeil, R.; Dickson, J. A. D. (Tony). Presalt  
764 Stratigraphy and Depositional Systems in the Kwanza Basin, Offshore Angola. *Bulletin* **2016**, *100* (07),  
765 1135–1164. <https://doi.org/10.1306/02111615216>.
- 766 (29) Wright, V. P.; Barnett, A. J. An Abiotic Model for the Development of Textures in Some South Atlantic  
767 Early Cretaceous Lacustrine Carbonates. *Geological Society, London, Special Publications* **2015**, *418*  
768 (1), 209–219. <https://doi.org/10.1144/SP418.3>.
- 769 (30) Tutolo, B. M.; Tosca, N. J. Experimental Examination of the Mg-Silicate-Carbonate System at Ambient  
770 Temperature: Implications for Alkaline Chemical Sedimentation and Lacustrine Carbonate Formation.  
771 *Geochimica et Cosmochimica Acta* **2018**, *225*, 80–101. <https://doi.org/10.1016/j.gca.2018.01.019>.
- 772 (31) White, R.; McKenzie, D. Magmatism at Rift Zones: The Generation of Volcanic Continental Margins  
773 and Flood Basalts. *J. Geophys. Res.* **1989**, *94* (B6), 7685. <https://doi.org/10.1029/JB094iB06p07685>.
- 774 (32) Wilson, M. Magmatism and Continental Rifting during the Opening of the South Atlantic Ocean: A  
775 Consequence of Lower Cretaceous Super-Plume Activity? *Geological Society, London, Special*  
776 *Publications* **1992**, *68* (1), 241–255. <https://doi.org/10.1144/GSL.SP.1992.068.01.15>.
- 777 (33) Milesi, V. P.; Jézéquel, D.; Debure, M.; Cadeau, P.; Guyot, F.; Sarazin, G.; Claret, F.; Vennin, E.;  
778 Chaduteau, C.; Virgone, A.; et al. Formation of Magnesium-Smectite during Lacustrine Carbonates Early  
779 Diagenesis: Study Case of the Volcanic Crater Lake Dziani Dzaha (Mayotte - Indian Ocean).  
780 *Sedimentology* **2019**, *66* (3), 983–1001. <https://doi.org/10.1111/sed.12531>.
- 781 (34) Irwin, H.; Curtis, C.; Coleman, M. Isotopic Evidence for Source of Diagenetic Carbonates Formed  
782 during Burial of Organic-Rich Sediments. *Nature* **1977**, *269* (5625), 209–213.  
783 <https://doi.org/10.1038/269209a0>.
- 784 (35) Coltorti, M.; Bonadiman, C.; Hinton, R. W.; Siena, F.; Upton, B. G. J. Carbonatite Metasomatism of the  
785 Oceanic Upper Mantle: Evidence from Clinopyroxenes and Glasses in Ultramafic Xenoliths of Grande  
786 Comore, Indian Ocean. *Journal of Petrology* **1999**, *40* (1), 133–165.  
787 <https://doi.org/10.1093/ptro/40.1.133>.
- 788 (36) Pelleter, A.-A.; Caroff, M.; Cordier, C.; Bachelery, P.; Nehlig, P.; Debeuf, D.; Arnaud, N. Melilite-  
789 Bearing Lavas in Mayotte (France): An Insight into the Mantle Source below the Comores. *Lithos* **2014**,  
790 *208–209*, 281–297. <https://doi.org/10.1016/j.lithos.2014.09.012>.
- 791 (37) Zinke, J.; Reijmer, J. J. G.; Thomassin, B. A. Systems Tracts Sedimentology in the Lagoon of Mayotte  
792 Associated with the Holocene Transgression. *Sedimentary Geology* **2003**, *160* (1–3), 57–79.  
793 [https://doi.org/10.1016/S0037-0738\(02\)00336-6](https://doi.org/10.1016/S0037-0738(02)00336-6).
- 794 (38) Gérard, E.; De Goeyse, S.; Hugoni, M.; Agogué, H.; Richard, L.; Milesi, V.; Guyot, F.; Lecourt, L.;  
795 Borensztajn, S.; Joseph, M.-B.; et al. Key Role of Alphaproteobacteria and Cyanobacteria in the  
796 Formation of Stromatolites of Lake Dziani Dzaha (Mayotte, Western Indian Ocean). *Front. Microbiol.*  
797 **2018**, *9*, 796. <https://doi.org/10.3389/fmicb.2018.00796>.
- 798 (39) Leboulanger, C.; Agogué, H.; Bernard, C.; Bouvy, M.; Carré, C.; Cellamare, M.; Duval, C.; Fouilland,  
799 E.; Got, P.; Intertaglia, L.; et al. Microbial Diversity and Cyanobacterial Production in Dziani Dzaha  
800 Crater Lake, a Unique Tropical Thalassohaline Environment. *PLoS ONE* **2017**, *12* (1), e0168879.  
801 <https://doi.org/10.1371/journal.pone.0168879>.

- 802 (40) Lewis Jr, W. M. Global Primary Production of Lakes: 19th Baldi Memorial Lecture. *Inland Waters* **2011**,  
803 *1* (1), 1–28.
- 804 (41) Mook, W. G.; van der Plicht, J. Reporting <sup>14</sup>C Activities and Concentrations. *Radiocarbon* **1999**, *41* (3),  
805 227–239. <https://doi.org/10.1017/S0033822200057106>.
- 806 (42) Stuiver, M.; Polach, H. A. Discussion Reporting of <sup>14</sup>C Data. *Radiocarbon* **1977**, *19* (3), 355–363.  
807 <https://doi.org/10.1017/S0033822200003672>.
- 808 (43) Stuiver, M. Workshop On <sup>14</sup>C Data Reporting. *Radiocarbon* **1980**, *22* (3), 964–966.  
809 <https://doi.org/10.1017/S0033822200010389>.
- 810 (44) Bard, E.; Tuna, T.; Fagault, Y.; Bonvalot, L.; Wacker, L.; Fahrni, S.; Synal, H.-A. AixMICADAS, the  
811 Accelerator Mass Spectrometer Dedicated to <sup>14</sup>C Recently Installed in Aix-En-Provence, France.  
812 *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and*  
813 *Atoms* **2015**, *361*, 80–86. <https://doi.org/10.1016/j.nimb.2015.01.075>.
- 814 (45) Capano, M.; Miramont, C.; Guibal, F.; Kromer, B.; Tuna, T.; Fagault, Y.; Bard, E. Wood <sup>14</sup>C Dating  
815 with AixMICADAS: Methods and Application to Tree-Ring Sequences from the Younger Dryas Event  
816 in the Southern French Alps. *Radiocarbon* **2018**, *60* (1), 51–74. <https://doi.org/10.1017/RDC.2017.83>.
- 817 (46) Reimer, P. J.; Brown, T. A.; Reimer, R. W. Discussion: Reporting and Calibration of Post-Bomb <sup>14</sup>C  
818 Data. *Radiocarbon* **2004**, *46* (3), 1299–1304. <https://doi.org/10.1017/S0033822200033154>.
- 819 (47) Vanderplight, J.; Hogg, A. A Note on Reporting Radiocarbon. *Quaternary Geochronology* **2006**, *1* (4),  
820 237–240. <https://doi.org/10.1016/j.quageo.2006.07.001>.
- 821 (48) Steefel, C. I.; Appelo, C. A. J.; Arora, B.; Jacques, D.; Kalbacher, T.; Kolditz, O.; Lagneau, V.; Lichtner,  
822 P. C.; Mayer, K. U.; Meeussen, J. C. L.; et al. Reactive Transport Codes for Subsurface Environmental  
823 Simulation. *Comput Geosci* **2015**, *19* (3), 445–478. <https://doi.org/10.1007/s10596-014-9443-x>.
- 824 (49) Connolly, J. A. D. The Mechanics of Metamorphic Fluid Expulsion. *Elements* **2010**, *6* (3), 165–172.  
825 <https://doi.org/10.2113/gselements.6.3.165>.
- 826 (50) Lasaga, A. C. Rate Laws of Chemical Reactions. *Rev. Mineral.:(United States)* **1981**, *8*.
- 827 (51) Lasaga, A. C. Chemical Kinetics of Water-Rock Interactions. *J. Geophys. Res.* **1984**, *89* (B6), 4009–  
828 4025. <https://doi.org/10.1029/JB089iB06p04009>.
- 829 (52) Aagaard, P.; Helgeson, H. C. Thermodynamic and Kinetic Constraints on Reaction Rates among  
830 Minerals and Aqueous Solutions; I, Theoretical Considerations. *American Journal of Science* **1982**, *282*  
831 (3), 237–285. <https://doi.org/10.2475/ajs.282.3.237>.
- 832 (53) Burch, T. E.; Nagy, K. L.; Lasaga, A. C. Free Energy Dependence of Albite Dissolution Kinetics at 80°C  
833 and PH 8.8. *Chemical Geology* **1993**, *105* (1–3), 137–162. [https://doi.org/10.1016/0009-2541\(93\)90123-Z](https://doi.org/10.1016/0009-2541(93)90123-Z).
- 834 (54) Regnier, P.; Steefel, C. I. A High Resolution Estimate of the Inorganic Nitrogen Flux from the Scheldt  
835 Estuary to the Coastal North Sea during a Nitrogen-Limited Algal Bloom, Spring 1995. *Geochimica et*  
836 *Cosmochimica Acta* **1999**, *63* (9), 1359–1374. [https://doi.org/10.1016/S0016-7037\(99\)00034-4](https://doi.org/10.1016/S0016-7037(99)00034-4).
- 837 (55) Pennell, K. D.; Abriola, L. M.; Boyd, S. A. Surface Area of Soil Organic Matter Reexamined. *Soil*  
838 *Science Society of America Journal* **1995**, *59* (4), 1012.  
839 <https://doi.org/10.2136/sssaj1995.03615995005900040008x>.
- 840 (56) Robie, R. A.; Hemingway, B. S. *Thermodynamic Properties of Minerals and Related Substances at*  
841 *298.15 K and 1 Bar (105 Pascals) Pressure and at Higher Temperatures*; US Government Printing  
842 Office, 1995; Vol. 2131.
- 843 (57) Brantley, S. L.; Mellott, N. P. Surface Area and Porosity of Primary Silicate Minerals. *American*  
844 *Mineralogist* **2000**, *85* (11–12), 1767–1783. <https://doi.org/10.2138/am-2000-11-1220>.
- 845 (58) Helgeson, H. C. Summary and Critique of the Thermodynamic Properties of Rock-Forming Minerals.  
846 *American Journal of Science* **1978**, *278*, 1–229.
- 847 (59) Knauss, K. G.; Nguyen, S. N.; Weed, H. C. Diopside Dissolution Kinetics as a Function of PH, CO<sub>2</sub>,  
848 Temperature, and Time. *Geochimica et Cosmochimica Acta* **1993**, *57* (2), 285–294.  
849 [https://doi.org/10.1016/0016-7037\(93\)90431-U](https://doi.org/10.1016/0016-7037(93)90431-U).
- 850 (60) Richet, P.; Bottinga, Y.; Denielou, L.; Petitet, J. P.; Tequi, C. Thermodynamic Properties of Quartz,  
851 Cristobalite and Amorphous SiO<sub>2</sub>: Drop Calorimetry Measurements between 1000 and 1800 K and a  
852 Review from 0 to 2000 K. *Geochimica et Cosmochimica Acta* **1982**, *46* (12), 2639–2658.  
853 [https://doi.org/10.1016/0016-7037\(82\)90383-0](https://doi.org/10.1016/0016-7037(82)90383-0).
- 854 (61) Pokrovskii, V. A.; Helgeson, H. C. Thermodynamic Properties of Aqueous Species and the Solubilities  
855 of Minerals at High Pressures and Temperatures: The System Al<sub>2</sub>O<sub>3</sub>-H<sub>2</sub>O-KOH. *Chemical Geology*  
856 **1997**, *137* (3–4), 221–242. [https://doi.org/10.1016/S0009-2541\(96\)00167-2](https://doi.org/10.1016/S0009-2541(96)00167-2).
- 857 (62) Medvedev, V. A.; Cox, J. D.; Wagman, D. D. *CODATA Key Values for Thermodynamics*; Hemisphere  
858 Publishing Corporation New York, 1989.

- 860 (63) Cubillas, P.; Köhler, S.; Prieto, M.; Chaïrat, C.; Oelkers, E. H. Experimental Determination of the  
861 Dissolution Rates of Calcite, Aragonite, and Bivalves. *Chemical Geology* **2005**, *216* (1–2), 59–77.  
862 <https://doi.org/10.1016/j.chemgeo.2004.11.009>.
- 863 (64) Romanek, C. S.; Grossman, E. L.; Morse, J. W. Carbon Isotopic Fractionation in Synthetic Aragonite  
864 and Calcite: Effects of Temperature and Precipitation Rate. *Geochimica et Cosmochimica Acta* **1992**, *56*  
865 (1), 419–430. [https://doi.org/10.1016/0016-7037\(92\)90142-6](https://doi.org/10.1016/0016-7037(92)90142-6).
- 866 (65) Busenberg, E.; Plummer, L. N.; Mumpston, F. A. A Comparative Study of the Dissolution and Crystal  
867 Growth Kinetics of Calcite and Aragonite. *Studies Diagenesis USGS Bull* **1986**, *1578*, 139–168.
- 868 (66) Königsberger, E.; Königsberger, L.-C.; Gamsjäger, H. Low-Temperature Thermodynamic Model for the  
869 System Na<sub>2</sub>CO<sub>3</sub>–MgCO<sub>3</sub>–CaCO<sub>3</sub>–H<sub>2</sub>O. *Geochimica et Cosmochimica Acta* **1999**, *63* (19–20), 3105–  
870 3119. [https://doi.org/10.1016/S0016-7037\(99\)00238-0](https://doi.org/10.1016/S0016-7037(99)00238-0).
- 871 (67) Gautier, Q.; Bénézeth, P.; Mavromatis, V.; Schott, J. Hydromagnesite Solubility Product and Growth  
872 Kinetics in Aqueous Solution from 25 to 75°C. *Geochimica et Cosmochimica Acta* **2014**, *138*, 1–20.  
873 <https://doi.org/10.1016/j.gca.2014.03.044>.
- 874 (68) Vicente, M. A.; Suárez, M.; López-González, J. de D.; Bañares-Muñoz, M. A. Characterization, Surface  
875 Area, and Porosity Analyses of the Solids Obtained by Acid Leaching of a Saponite. *Langmuir* **1996**, *12*  
876 (2), 566–572. <https://doi.org/10.1021/la950501b>.
- 877 (69) Kooli, F.; Jones, W. Characterization and Catalytic Properties of a Saponite Clay Modified by Acid  
878 Activation. *Clay miner.* **1997**, *32* (4), 633–643. <https://doi.org/10.1180/claymin.1997.032.4.13>.
- 879 (70) Suárez Barrios, M.; de Santiago Buey, C.; García Romero, E.; Martín Pozas, J. M. Textural and  
880 Structural Modifications of Saponite from Cerro Del Aguila by Acid Treatment. *Clay miner.* **2001**, *36*  
881 (4), 483–488. <https://doi.org/10.1180/0009855013640003>.
- 882 (71) Steudel, A.; Friedrich, F.; Schuhmann, R.; Ruf, F.; Sohling, U.; Emmerich, K. Characterization of a  
883 Fine-Grained Interstratification of Turbostratic Talc and Saponite. *Minerals* **2017**, *7* (1), 5.  
884 <https://doi.org/10.3390/min7010005>.
- 885 (72) Whitticar, M. J. Carbon and Hydrogen Isotope Systematics of Bacterial Formation and Oxidation of  
886 Methane. *Chemical Geology* **1999**, *161* (1–3), 291–314. [https://doi.org/10.1016/S0009-2541\(99\)00092-3](https://doi.org/10.1016/S0009-2541(99)00092-3).
- 887 (73) Etiopie, G.; Sherwood Lollar, B. Abiotic Methane on Earth. *Rev. Geophys.* **2013**, *51* (2), 276–299.  
888 <https://doi.org/10.1002/rog.20011>.
- 889 (74) Albéric, P.; Jézéquel, D.; Bergonzini, L.; Chapron, E.; Viollier, E.; Massault, M.; Michard, G. Carbon  
890 Cycling and Organic Radiocarbon Reservoir Effect in a Meromictic Crater Lake (Lac Pavin, Puy-de-  
891 Dôme, France). *Radiocarbon* **2013**, *55* (2), 1029–1042. <https://doi.org/10.1017/S0033822200058161>.
- 892 (75) Hua, Q.; Barbetti, M.; Rakowski, A. Z. Atmospheric Radiocarbon for the Period 1950–2010.  
893 *Radiocarbon* **2013**, *55* (4), 2059–2072. [https://doi.org/10.2458/azu\\_js\\_rc.v55i2.16177](https://doi.org/10.2458/azu_js_rc.v55i2.16177).
- 894 (76) Canfield, D. E.; Kristensen, E.; Thamdrup, B. *Aquatic Geomicrobiology*; Gulf Professional Publishing,  
895 2005.
- 896 (77) Sayles, F. L.; Fyfe, W. S. The Crystallization of Magnesite from Aqueous Solution. *Geochimica et*  
897 *Cosmochimica Acta* **1973**, *37* (1), 87–99. [https://doi.org/10.1016/0016-7037\(73\)90246-9](https://doi.org/10.1016/0016-7037(73)90246-9).
- 898 (78) Arvidson, R. S. The Dolomite Problem; Control of Precipitation Kinetics by Temperature and Saturation  
899 State. *American Journal of Science* **1999**, *299* (4), 257–288. <https://doi.org/10.2475/ajs.299.4.257>.
- 900 (79) Baker, P. A.; Kastner, M. Constraints on the Formation of Sedimentary Dolomite. *Science* **1981**, *213*  
901 (4504), 214–216. <https://doi.org/10.1126/science.213.4504.214>.
- 902 (80) Meunier, A. *Clays*; Springer Science & Business Media, 2005.
- 903 (81) Tosca, N. Geochemical Pathways to Mg-Silicate Formation. *Magnesian Clays: Characterization, Origin*  
904 *and Applications*; Pozo, M., Galán, E., Eds **2015**, 283–329.
- 905 (82) Parkhurst, D. L.; Appelo, C. A. J. *Description of Input and Examples for PHREEQC Version 3: A*  
906 *Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse*  
907 *Geochemical Calculations*; US Geological Survey, 2013.
- 908 (83) Stoessell, R. K. 25°C and 1 Atm Dissolution Experiments of Sepiolite and Kerolite. *Geochimica et*  
909 *Cosmochimica Acta* **1988**, *52* (2), 365–374. [https://doi.org/10.1016/0016-7037\(88\)90092-0](https://doi.org/10.1016/0016-7037(88)90092-0).
- 910 (84) Ali, A. D.; Tuner, P. Authigenic K-Feldspar in the Bromsgrove Sandstone Formation (Triassic) of  
911 Central England. *Journal of Sedimentary Research* **1982**, *52* (1), 187–197.  
912 <https://doi.org/10.1306/212F7F09-2B24-11D7-8648000102C1865D>.
- 913 (85) Per Arne Bjorkum, Norvald Gjelsvik. An Isochemical Model for Formation of Authigenic Kaolinite, K-  
914 Feldspar and Illite in Sediments. *SEPM JSR* **1988**, Vol. 58. <https://doi.org/10.1306/212F8DD2-2B24-11D7-8648000102C1865D>.
- 915 (86) Druhan, J. L.; Steefel, C. I.; Molins, S.; Williams, K. H.; Conrad, M. E.; DePaolo, D. J. Timing the Onset  
916 of Sulfate Reduction over Multiple Subsurface Acetate Amendments by Measurement and Modeling of  
917 Sulfur Isotope Fractionation. *Environ. Sci. Technol.* **2012**, *46* (16), 8895–8902.  
918 <https://doi.org/10.1021/es302016p>.



- 920 (87) Rehim, H.; Pimentel, A. M.; Carvalho, M. D.; Monteiro, M. Talco e Estevensita Na Formação Lagoa  
921 Feia Da Bacia de Campos-Possíveis Implicações No Ambiente Depositional. In *Anais XXXIV Congresso*  
922 *Brasileiro de Geologia*; 1986; Vol. 1, pp 416–422.
- 923 (88) Cerling, T. E. Chemistry of Closed Basin Lake Waters: A Comparison between African Rift Valley and  
924 Some Central North American Rivers and Lakes. *The Global Geological Record of Lake Basins* **1994**, *1*,  
925 29–30.
- 926 (89) Balthasar, U.; Cusack, M. Aragonite-Calcite Seas—Quantifying the Gray Area. *Geology* **2015**, *43* (2),  
927 99–102. <https://doi.org/10.1130/G36293.1>.
- 928 (90) Rossi, C.; Lozano, R. P. Hydrochemical Controls on Aragonite versus Calcite Precipitation in Cave  
929 Dripwaters. *Geochimica et Cosmochimica Acta* **2016**, *192*, 70–96.  
930 <https://doi.org/10.1016/j.gca.2016.07.021>.
- 931 (91) Zeyen, N.; Daval, D.; Lopez-Garcia, P.; Moreira, D.; Gaillardet, J.; Benzerara, K. Geochemical  
932 Conditions Allowing the Formation of Modern Lacustrine Microbialites. *Procedia Earth and Planetary*  
933 *Science* **2017**, *17*, 380–383. <https://doi.org/10.1016/j.proeps.2016.12.096>.
- 934 (92) Torsvik, T. H.; Rousse, S.; Labails, C.; Smethurst, M. A. A New Scheme for the Opening of the South  
935 Atlantic Ocean and the Dissection of an Aptian Salt Basin. *Geophysical Journal International* **2009**, *177*  
936 (3), 1315–1333. <https://doi.org/10.1111/j.1365-246X.2009.04137.x>.
- 937 (93) Teboul, P.-A.; Kluska, J.-M.; Marty, N. C. M.; Debure, M.; Durlet, C.; Virgone, A.; Gaucher, E. C.  
938 Volcanic Rock Alterations of the Kwanza Basin, Offshore Angola - Insights from an Integrated  
939 Petrological, Geochemical and Numerical Approach. *Marine and Petroleum Geology* **2017**, *80*, 394–411.  
940 <https://doi.org/10.1016/j.marpetgeo.2016.12.020>.
- 941



942

943 FOR TOC GRAPHIC USE ONLY

944