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1 EARLY DIAGENESIS OF LACUSTRINE CARBONATES IN
2 VOLCANIC SETTINGS: CHARACTERIZATION AND
3 MODELING
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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}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 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 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 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 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 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^{1,2}, carbonate cementation³, acidic fluids inputs^{4,5}, dissolution of
59 associated magnesium phyllosilicates⁶⁻⁸, and bacterial and thermal sulphate reduction⁹ 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 conditions¹⁰. 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^{11,12}. Relying on thermodynamics and kinetics constants
69 available for an increasing number of reactions¹³⁻¹⁶, 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^{10,17-20}. 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 history²¹⁻²³.

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^{6-8,22,24-28}. 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^{8,22,24,27,29,30}. 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^{28,29}.

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^{31,32}. The Dziani Dzaha sediment, previously characterized in detail by Milesi *et al.*³³, 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 CH₄ dissolved in the lake water,
94 and ¹⁴C 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 processes³⁴. Our study focuses on those processes, which are the foundation toward modeling further
99 diagenetic stages in larger-scale basins.

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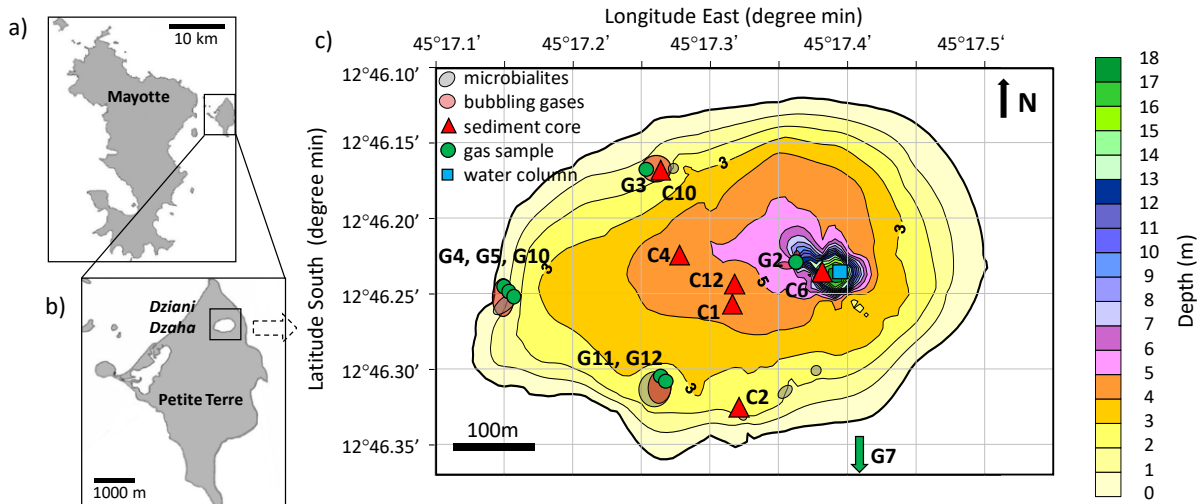
101 **2. Geologic setting and limnology of the Dziani Dzaha**

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 CO₂-rich fluids^{35,36}. 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 Ka³⁷.

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 aragonite³⁸. The lake water has a salinity ranging from 34 and 71 g·kg⁻¹ depending
113 on the season and depth (*i.e.*, between once and twice seawater's salinity), alkalinity of ~0.2 mol·L⁻¹
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 definition³⁹. The lake biomass is
116 dominated by cyanobacteria, with a primary productivity of ~8 g of C·m⁻²·day⁻¹³⁹, close to the
117 maximum rate of photosynthesis for tropical and subtropical lakes⁴⁰. The most likely theory of the lake
118 origin is sea water filling the volcanic crater formed by the phreatomagmatic eruption³⁹. 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 limnigrapher 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_{lake}/Cl_{seawater} 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 hydromagnesite³³. 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.*³³). (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 μm were placed every 2.5 cm along the
153 1 m long sediment core and connected to 12 mL-evacuated Exetainer[®] vials or to plastic syringes in
154 order to avoid silicon contamination from the Exetainer[®] glass. Within a few hours after collection, the
155 27 pore water samples were acidified with high purity 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[®] 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[®] vials filled with water (no headspace) and poisoned with mercuric chloride
160 (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 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[®] 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, H₂S and CH₄ were not measured because of the difficulty of avoiding the degassing
176 and oxidation of H₂S and CH₄ during the sediment core collection and during the sampling and storage
177 of the pore waters.

178 The carbon and hydrogen isotope composition of CH₄ and CO₂ of bubbling gases and of pore
179 waters were analyzed at the IFPEN laboratory by sampling directly the headspaces of Exetainer® vials.
180 CH₄ and CO₂ 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 δ¹³C and ±5‰ for δD.

184 The concentration of CO₂ and CH₄ 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 H₂, He, CO₂, O₂, N₂, and all hydrocarbons from methane to iso- and normal-butane.
190 Precisions for individual components are ±2%. The concentrations of dissolved methane and CO₂
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 C10³³. This approach is reasonable given the steady sediment composition between cores collected
199 close to one another³³. 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⁻³, 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 H₃PO₄ until complete CO₂ 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 CO₂ at 900°C
209 during 4 hours in contact with Cu-oxides and a wire of Ag. The ¹⁴C activities are reported relative to
210 the oxalic acid standard HOxII and normalized to a δ¹³C value of -25‰. Radiocarbon ages and Delta
211 notations are calculated according to the studies by Mook and van der Plicht⁴¹ and Stuiver and
212 Polach^{42,43}, respectively.

213 Terrestrial plant macro-remains were analyzed by means of Aix-MICADAS AMS facility of
214 Aix-en-Provence⁴⁴. The samples were treated with a modified ABA chemical pretreatment to avoid
215 possible contaminations from the lake DIC, carbonates and organic carbon⁴⁵. Standards (OxA2 NIST
216 SRM4990C) and blanks (VIRI K) were analyzed together with samples. The ¹⁴C data are reported in
217 terms of conventional ¹⁴C age in years BP and in F¹⁴C age^{42,46,47}.

218 3.6 Reactive transport modeling

219 The CrunchFlow multicomponent reactive transport code⁴⁸ was used with the Thermoddem
220 database^{13,14} 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^{17,49}. 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 profiles¹¹. For instance, reaction-generated grain-scale permeability is
231 sealed rapidly by compaction, which prevents or at least reduces fluid fluxes⁴⁹.

232 The solid burial rate, ω , can be determined from the conservation of solid sediment mass
233 (where ϕ is the porosity and z is the depth (m)) as follow^{11,17}:

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

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 ϕ 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 ϕ_z the porosity at a given depth z and ϕ_{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 ($\text{Na}_{0.7}\text{K}_{0.3}\text{Si}_3\text{O}_8$)³³.
 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 law⁵⁰⁻⁵³ 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, θ and η 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 CH₂O. 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 waters³⁹.

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

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

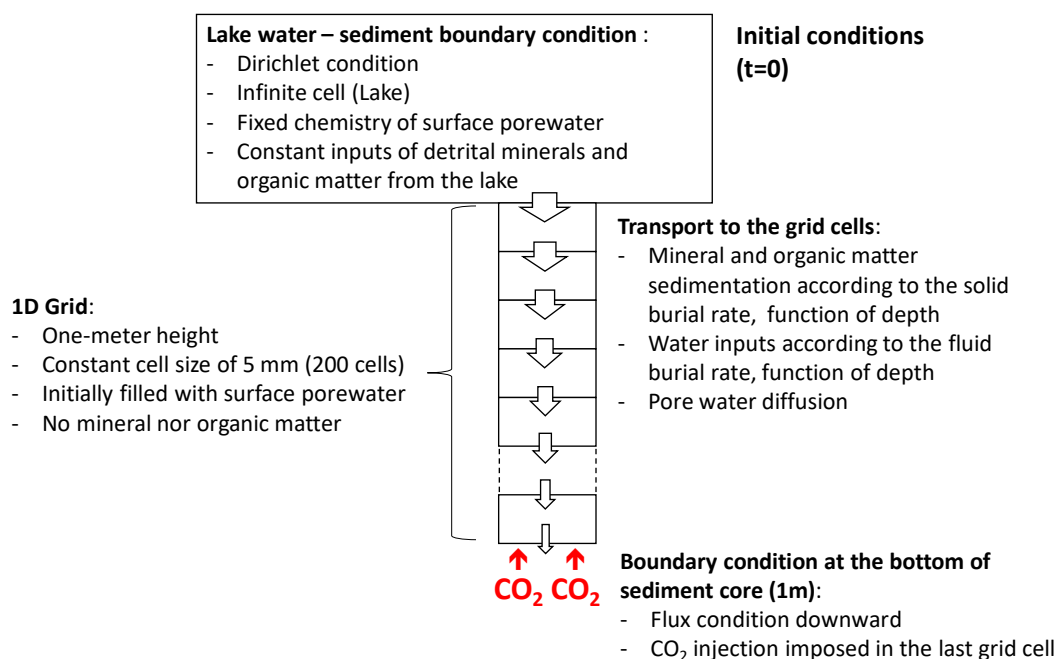
277 §§The first and second term are the empirical parameters Θ and η describing the affinity dependence.

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 sediments³³. 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 CO₂
 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 2·10⁻⁹ m²·s⁻¹, respectively. Each simulation was run
 302 for 4000 years, which corresponds to the estimation of the youngest age of the lake formation³⁷ 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

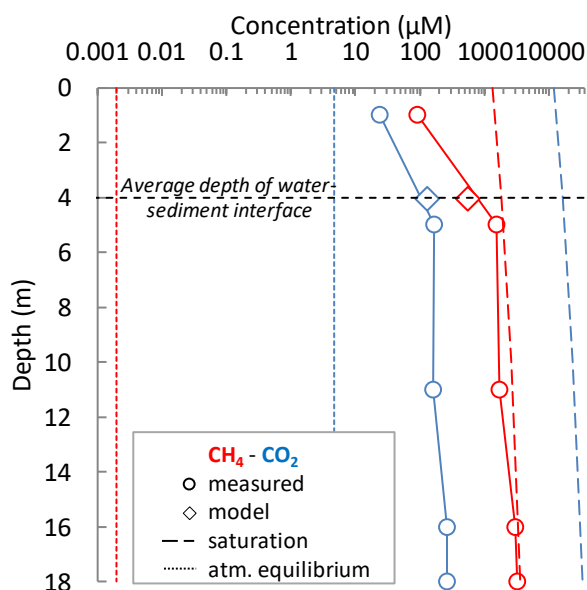
Table 2. Boundary conditions of the reactive transport model at the sediment-water interface

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

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

311 4.1 Dissolved and bubbling gases

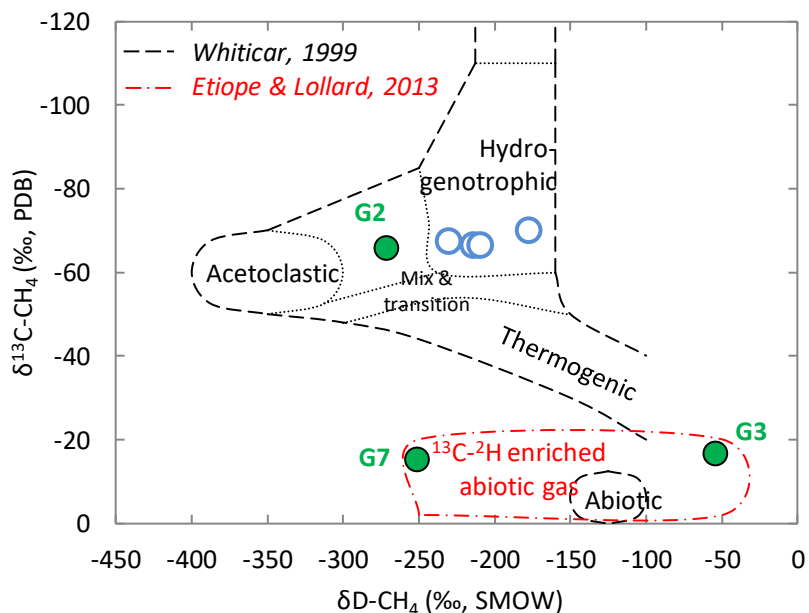
312 The concentration of dissolved methane in the water column evolves along its saturation
313 concentration, increasing with depth to reach 3180 μM at 18 m depth (Fig. 3, Table S3 in supporting
314 information). The CO₂ concentration increases from 24 μM at surface to 263 μM at 18 m depth and
315 remains ca. two orders of magnitude lower than its saturation concentration. Both concentrations of
316 methane and CO₂ 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 CO₂ has $\delta^{13}\text{C}$ values between +2‰ and +7‰. The gases bubbling at the
320 lake surface are mostly made of CO₂, with minor amounts of N₂, O₂ and CH₄ (Table 3). The samples
321 G3, G4, G7 and G10 contain mostly CO₂ (>95 vol.%) with low amounts of methane (~0.3%). The
322 $\delta^{13}\text{C}$ values of CO₂ and CH₄ 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 CO₂ but the $\delta^{13}\text{C}$
324 values of CH₄ 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 CO₂ 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 CO₂ in the water column straight up the 18 m
 331 depression (DZ14-4 WC). Methane and CO₂ data are in red and blue, respectively. The open circles
 332 are the measured concentrations. The modeled CO₂ and CH₄ 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 Whiticar⁷² 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 Lollar⁷³ for abiogenic methane.

343

344

Table 3. Chemical and isotope compositions of bubbling gases

Sample	CO ₂ (vol.%)	CH ₄ (vol.%)	O ₂ (vol.%)	N ₂ (vol.%)	$\delta^{13}\text{C}_{\text{CO}_2}$ (‰)	$\delta^{13}\text{C}_{\text{CH}_4}$ (‰)	$\delta\text{D}_{\text{CH}_4}$ (‰)
	±2% rel.	±2% rel.	±2% rel.	±2% rel.	±1‰	±1‰	±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 lakes⁷⁴. 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}C (5730 ± 40 years), those
 353 measurements indicate that DIC and POC contain between 55% and 60% of "dead" carbon (*i.e.*, non-
 354 atmospheric CO₂), evidencing the input of volcanic CO₂ 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‰) 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 (F^{14}C calibrated at 2σ with the program
 362 CALIBomb, Zone SH1-2⁷⁵).

363

Table 4. Radiocarbon data for water column and sediment

Sampling location ^a	Sampling date	Sample type	Sampling depth (cm)	age BP (year)	1 σ (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

^aWC 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)	¹⁴ C age BP	Err 1 σ	F ¹⁴ C	Err 1 σ	Burial rate (mm·yr ⁻¹)
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

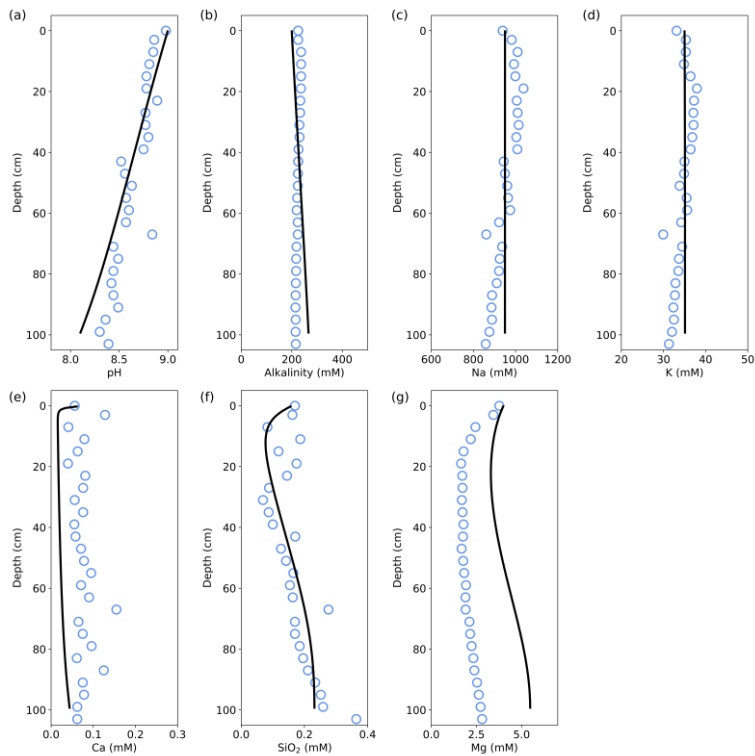
369 4.3 Porosity and sedimentation rate

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 ϕ 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

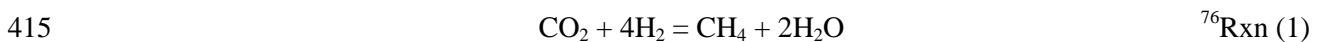


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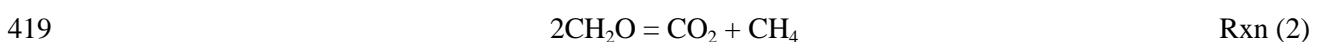
402 **5. Figure 6. Comparison of measured and modeled pH values, alkalinity**
 403 **and major cations concentrations in the pore waters. The blue dots and**
 404 **the full black lines represent the measured and modeled values,**
 405 **respectively. Model results are after 4000 years of calculation. 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 CO₂ 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 pathway⁷². The intense bacterial
 412 methanogenesis in the sediment and in the lake water³⁹ results in saturated concentrations of methane
 413 in the lake water column and in CH₄-dominated bubbling gases (Sample G2). The formation of CH₄
 414 during hydrogenotrophic methanogenesis can be written as:



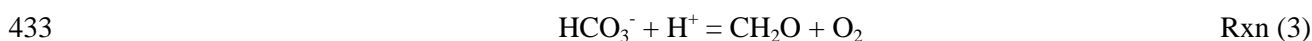
416 The microbial fermentation of the organic matter is the most likely source of CO₂ and H₂ and could
 417 also account for the decrease of pore water pH values with depth. The coupled mechanisms of
 418 methanogenesis and fermentation can be represented by the simplified reaction:



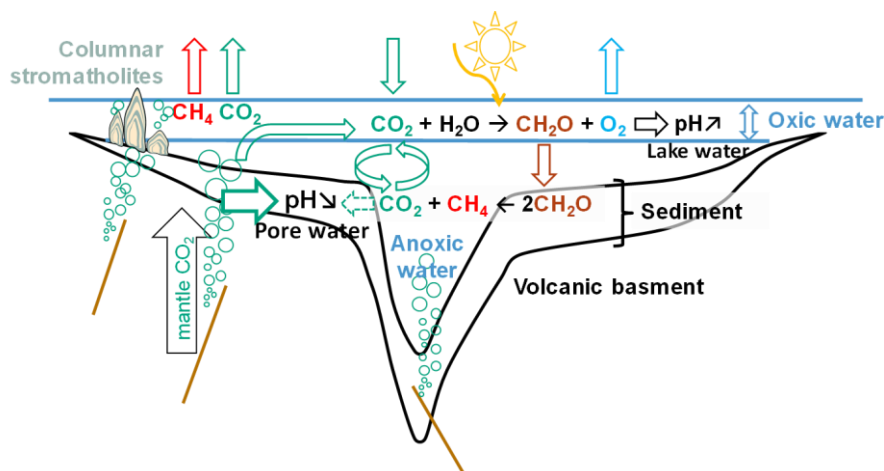
420 with CH₂O being a simplified stoichiometry for the organic matter.

421 Magmatic CO₂ inputs is also likely influencing the pH of pore waters. The CO₂-dominated
422 gases bubbling into the lake evidence an active magmatic degassing. The δ¹³C and δ²H values of CH₄
423 in samples G3, G4, G10 and G7 are consistent with an abiotic origin⁷³. The lower δ¹³C-CH₄ 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 CO₂-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 CO₂ 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 cyanobacteria³⁹. 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 CO₂ originating from the
438 atmosphere, from the magmatic gases CO₂ inputs and from organic matter degradation. The
439 photosynthetic activity results in a production of O₂ 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 CH₄ and CO₂ which, associated to
442 the magmatic CO₂ inputs, induce a decrease of the pore water pH values. Both CO₂ and biogenic CH₄
443 escape to the atmosphere. The size of the arrows pointing toward the pH decrease of pore waters

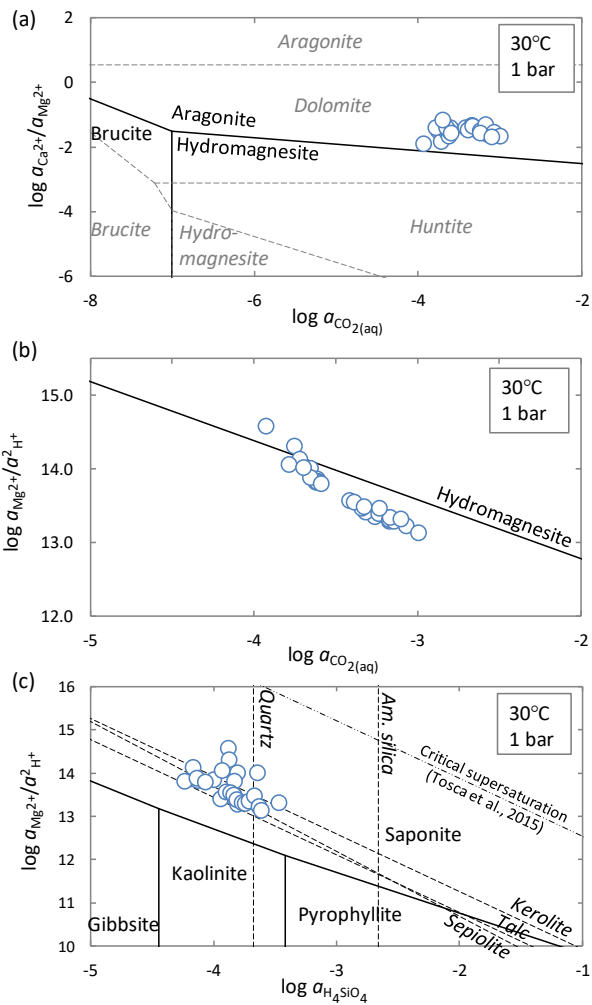
444 illustrates the dominant contribution of the magmatic CO₂ and the lower impact of the organic matter
445 microbial degradation.

446 5.2 Mineral stability

447 The metastable equilibria between aragonite, hydromagnesite and brucite were calculated as a function
448 of Mg²⁺, Ca²⁺ and CO₂ 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^{67,77,78}. 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 Ca²⁺/Mg²⁺ ratio is relatively stable with depth, the
453 decrease of pH induces an increase of the CO₂ activity, which promotes the stability of aragonite at the
454 expense of hydromagnesite. Dolomite has been locally observed at depth in the sediment³³ and could
455 form by Mg incorporation and Ca replacement in calcium carbonates^{78,79}. 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⁺, Mg²⁺ and SiO₂ 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 pressure⁸⁰. 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 nucleation⁸¹. The Al-free
464 Mg-silicates, although stable in the pore waters, are not observed in the sediments. Tosca⁸¹ 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

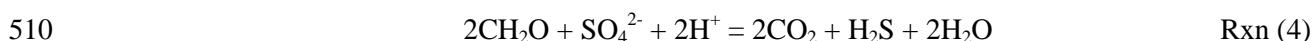


469

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^{13,14} and pore waters were speciated with the Phreeqc
 473 software⁸². (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 Stoessel⁸³. The dashed-dotted line is the critical
 480 supersaturation required for homogenous nucleation of Mg-silicates as suggested by Tosca⁸¹. 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 cores³³. 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 CO₂. 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^{-10.3} mol·m⁻²·s⁻¹ is adopted (Table 1), close to published values⁵⁴. 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 CO₂ is considered, the modeled pH value
496 at 1 m depth is 0.7 pH units higher than the measured value and the total CO₂ pressure is of 6.3·10⁻³
497 bar. In our model, CO₂ is thus injected at the bottom of the sediment column to account for the
498 influence of magmatic CO₂. The best fit of pH is obtained with a CO₂ injection of 4 mmol·s⁻¹·m⁻³ of
499 sediment, which results in a total CO₂ pressure of 7.5·10⁻² bar at 1 m depth, one order of magnitude
500 higher than without CO₂ injection (Fig. 6). The corresponding CO₂ concentration is of 2 mM, which
501 does not exceed the CO₂ solubility of the lake (16 mM) and is consistent with the absence of bubbling
502 CO₂ where the sediment core C4 was collected. At 1 m depth, our model predicts magmatic CO₂
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 water³⁹ 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 CO₂ 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 methanogens³⁹; 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 CO₂ inflows.

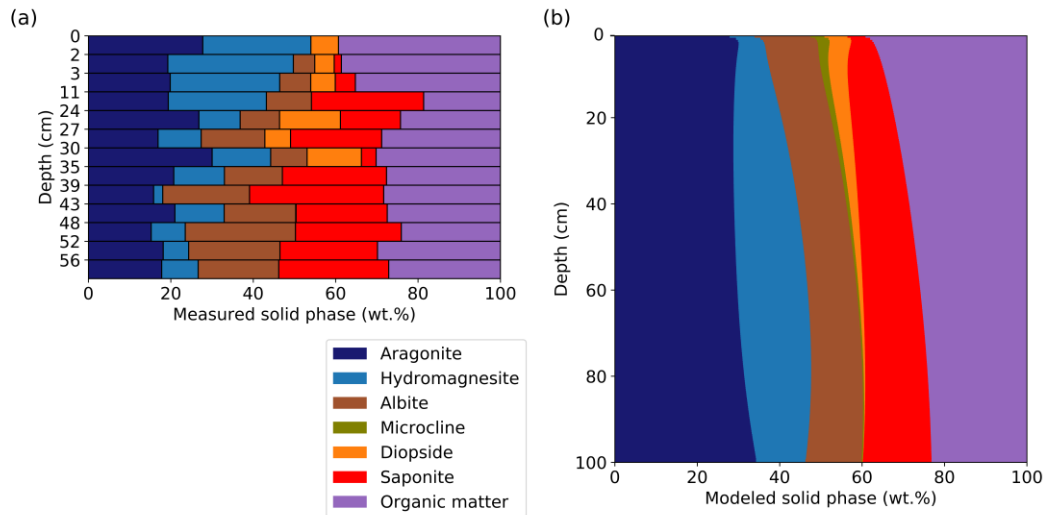
516 The modeled alkalinity and major cation profiles are consistent with the measured data (Fig.
517 6). Magnesium shows a distinctive concentration profile compared to the other dissolved species, with
518 a decrease in concentration in the surface sediment followed by a moderate increase at depth. 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 CO₂ 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 CO₂ 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 phyllosilicates⁸¹, 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^{84,85}.
533 Equilibrium of the pore waters with amorphous Mg-Si phases⁶⁴, 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 CO₂
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 minerals³³; 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} μM to 10^{-6} μM ,
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 CO_2 inflows
569 and organic matter microbial degradation on the diagenetic evolution of the sediment. Without
570 magmatic CO_2 inflows, the decrease of pH and the destabilization of hydromagnesite at depth cannot
571 be explained. The magmatic 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 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^{10,17,86}. 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 C4³³. (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^{6-8,87}. Mg-silicates
 589 (stevensite, kerolite and talc) have been identified in the Cretaceous pre-salt carbonate rocks of the
 590 South Atlantic continental margins²⁷. Their formation was suggested to occur in lakes dominated by
 591 volcanic terrains^{8,88}, 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 Tosca³⁰ 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 mmol·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 lake³⁰.

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 mineralogy²⁸. 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 calcite⁸⁹⁻⁹¹. Delay between carbonates and Mg-silicates formation during
617 early diagenesis tends to increase the Mg/Ca ratio favoring the formation of aragonite³⁰. 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)^{28,29,92}
630 raise questions about the carbon source. During continental rifting, magmatic CO₂ 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 CO₂ inflows to fuel the carbonate production into
633 small-scale basins. By analogy, CO₂ 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 CO₂ 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 sequence⁹³. 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 CO₂ inflows and organic matter microbial degradation
654 on the diagenetic evolution of the sediment. While our ¹⁴C radiometric data show that the magmatic
655 CO₂ 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 CO₂ 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

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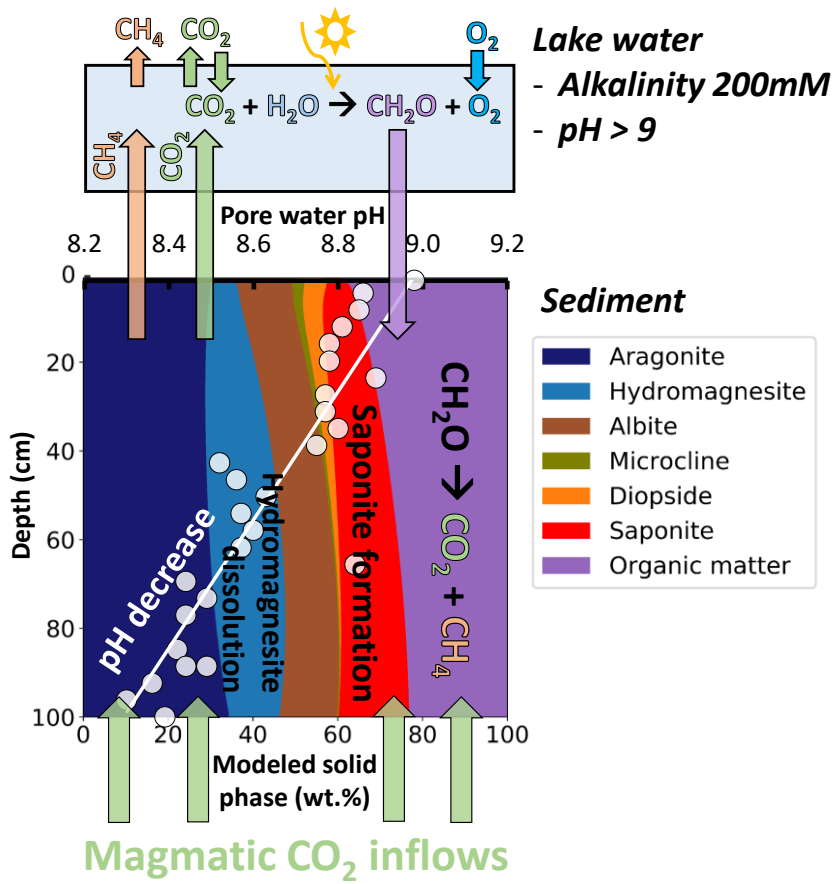
- 686 (1) Back, W.; Hanshaw, B. B.; Plummer, L. N.; Rahn, P. H.; Rightmire, C. T.; Rubin, M. Process and Rate
687 of Dedolomitization: Mass Transfer and ¹⁴C Dating in a Regional Carbonate Aquifer. *GSA Bulletin*
688 **1983**, *94* (12), 1415–1429. [https://doi.org/10.1130/0016-7606\(1983\)94<1415:PARODM>2.0.CO;2](https://doi.org/10.1130/0016-7606(1983)94<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. H₂S-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>.
- 710 (11) Berner, R. A. *Early Diagenesis: A Theoretical Approach*; Princeton University Press, 1980.
- 711 (12) Li, L.; Maher, K.; Navarre-Sitchler, A.; Druhan, J.; Meile, C.; Lawrence, C.; Moore, J.; Perdril, J.;
712 Sullivan, P.; Thompson, A.; et al. Expanding the Role of Reactive Transport Models in Critical Zone
713 Processes. *Earth-Science Reviews* **2017**, *165*, 280–301. <https://doi.org/10.1016/j.earscirev.2016.09.001>.
- 714 (13) Blanc, Ph.; Lassin, A.; Piantone, P.; Azaroual, M.; Jacquemet, N.; Fabbri, A.; Gaucher, E. C.
715 Thermodem: A Geochemical Database Focused on Low Temperature Water/Rock Interactions and
716 Waste Materials. *Applied Geochemistry* **2012**, *27* (10), 2107–2116.
717 <https://doi.org/10.1016/j.apgeochem.2012.06.002>.
- 718 (14) Blanc, P.; Vieillard, P.; Gailhanou, H.; Gaboreau, S.; Gaucher, E.; Fialips, C. I.; Made, B.; Giffaut, E. A
719 Generalized Model for Predicting the Thermodynamic Properties of Clay Minerals. *American Journal of*
720 *Science* **2015**, *315* (8), 734–780. <https://doi.org/10.2475/08.2015.02>.
- 721 (15) Marty, N. C. M.; Claret, F.; Lassin, A.; Tremosa, J.; Blanc, P.; Madé, B.; Giffaut, E.; Cochepin, B.;
722 Tournassat, C. A Database of Dissolution and Precipitation Rates for Clay-Rocks Minerals. *Applied*
723 *Geochemistry* **2015**, *55*, 108–118. <https://doi.org/10.1016/j.apgeochem.2014.10.012>.
- 724 (16) Marty, N. C. M.; Lach, A.; Lerouge, C.; Grangeon, S.; Claret, F.; Fauchet, C.; Madé, B.; Lundy, M.;
725 Lagroix, F.; Tournassat, C.; et al. Weathering of an Argillaceous Rock in the Presence of Atmospheric
726 Conditions: A Flow-through Experiment and Modelling Study. *Applied Geochemistry* **2018**, *96*, 252–
727 263. <https://doi.org/10.1016/j.apgeochem.2018.07.005>.
- 728 (17) Maher, K.; Steefel, C. I.; DePaolo, D. J.; Viani, B. E. The Mineral Dissolution Rate Conundrum: Insights
729 from Reactive Transport Modeling of U Isotopes and Pore Fluid Chemistry in Marine Sediments.
730 *Geochimica et Cosmochimica Acta* **2006**, *70* (2), 337–363. <https://doi.org/10.1016/j.gca.2005.09.001>.
- 731 (18) Arndt, S.; Jørgensen, B. B.; LaRowe, D. E.; Middelburg, J. J.; Pancost, R. D.; Regnier, P. Quantifying
732 the Degradation of Organic Matter in Marine Sediments: A Review and Synthesis. *Earth-Science*
733 *Reviews* **2013**, *123*, 53–86. <https://doi.org/10.1016/j.earscirev.2013.02.008>.
- 734 (19) Paraska, D. W.; Hipsey, M. R.; Salmon, S. U. Sediment Diagenesis Models: Review of Approaches,
735 Challenges and Opportunities. *Environmental Modelling & Software* **2014**, *61*, 297–325.
736 <https://doi.org/10.1016/j.envsoft.2014.05.011>.
- 737 (20) Huber, C.; Druhan, J. L.; Fantle, M. S. Perspectives on Geochemical Proxies: The Impact of Model and
738 Parameter Selection on the Quantification of Carbonate Recrystallization Rates. *Geochimica et*
739 *Cosmochimica Acta* **2017**, *217*, 171–192. <https://doi.org/10.1016/j.gca.2017.08.023>.
- 740 (21) Hayes, J. M.; Waldbauer, J. R. The Carbon Cycle and Associated Redox Processes through Time. *Phil.*
741 *Trans. R. Soc. B* **2006**, *361* (1470), 931–950. <https://doi.org/10.1098/rstb.2006.1840>.
- 742

- 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 ¹⁴C 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 ¹⁴C Data. *Radiocarbon* **1977**, *19* (3), 355–363.
807 <https://doi.org/10.1017/S0033822200003672>.
- 808 (43) Stuiver, M. Workshop On ¹⁴C 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 ¹⁴C 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 ¹⁴C 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 ¹⁴C
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, CO₂,
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 SiO₂: 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 Al₂O₃-H₂O-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 Na₂CO₃–MgCO₃–CaCO₃–H₂O. *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) Etiope, 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.
- 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



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