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Formation of magnesium-smectite during lacustrine carbonates early diagenesis: Study case of the volcanic crater lake Dziani Dzaha (Mayotte – Indian Ocean)

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Vincent Milesi, Didier Jézéquel, Mathieu Debure, Pierre Cadeau, Francois Guyot, et al.. Formation of magnesium-smectite during lacustrine carbonates early diagenesis: Study case of the volcanic crater lake Dziani Dzaha (Mayotte – Indian Ocean). *Sedimentology*, 0025, 66 (3), pp.983-1001. 10.1111/sed.12531 . hal-04755674

HAL Id: hal-04755674

<https://hal.science/hal-04755674v1>

Submitted on 28 Oct 2024

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Abstract

26 The volcanic crater lake of Dziani Dzaha in Mayotte is studied to constrain the geochemical settings
27 and the diagenetic processes at the origin of Mg-phyllsilicates associated with carbonate rocks. The
28 Dziani Dzaha is characterized by an intense primary productivity, volcanic gases bubbling in three
29 locations and a volcanic catchment of phonolitic/alkaline composition. The lake water has an
30 alkalinity of $\sim 0.2 \text{ mol}\cdot\text{L}^{-1}$ and pH values of ~ 9.3 . Cores of the lake sediments reaching up to one meter
31 in length were collected and studied by means of CHN elemental analyzer, X-ray fluorescence
32 spectrometry and X-ray powder diffraction. In surface sediments, the content of total organic carbon
33 reaches up to 35wt.%. The mineral content consists of aragonite and hydromagnesite with minor
34 amounts of alkaline feldspar and clinopyroxene from the volcanic catchment. Below 30cm deep, XRD
35 analyses of the $<2 \mu\text{m}$ clay fraction indicate the presence of a saponite-like mineral, a Mg-rich
36 smectite. The saponite-like mineral accumulates at depth to reach up to $\sim 25\text{wt.}\%$, concurrent with a
37 decrease of the contents of hydromagnesite and organic matter. Thermodynamic considerations and
38 mineral assemblages suggest that the evolution of the sediment composition resulted from early
39 diagenetic reactions. The formation of the saponite-like mineral instead of Al-free Mg-silicates
40 resulted from high aluminum availability, which is favored in restricted lacustrine environments
41 hosted in alkaline volcanic terrains commonly emplaced during early stages of continental rifting.
42 Supersaturation of the lake water relative to saponite is especially due to high pH values, themselves
43 derived from high primary productivity. This suggests that a genetic link may exist between saponite
44 and the development of organic-rich carbonate rocks, which may be fueled by the input of CO_2 -rich
45 volcanic gases. This provides novel insights into the composition and formation of saponite-rich
46 deposits under specific geodynamic context such as the Cretaceous South Atlantic carbonate
47 reservoirs.

48 Keywords: lacustrine carbonates, early diagenesis, saponite, volcanic lake, authigenesis, organic
49 matter decomposition, magnesian clays

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1. Introduction

Mg-rich clay minerals, referred hereafter as Mg-silicates, are increasingly reported associated with ancient and modern carbonates rocks (*e.g.*, Hover *et al.*, 1999; Bristow *et al.*, 2009; Wright, 2012; Zeyen *et al.*, 2015, 2017; Pace *et al.*, 2016; Gérard *et al.*, 2018). In particular, Mg-silicates have been reported in lacustrine carbonate reservoirs of the South-Atlantic (*e.g.*, Bertani and Carozzi, 1985a, 1985b; Rehim *et al.*, 1986; Wright, 2012) and their dissolution during diagenesis was proposed to explain the high porosity of these carbonate rocks (Wright and Barnett, 2015; Tosca and Wright, 2015). These phases seem to form either through direct precipitation from water or during very early diagenesis (*e.g.*, Tosca, 2015) and record specific chemical conditions, especially high pH values. Thus, they have a strong potential to help in palaeoenvironmental reconstruction of continental carbonates deposits and their evolution through the diagenesis (Chamley, 1989; Weaver, 1989; Bristow *et al.*, 2009).

The variety of geologic environments allowing Mg-rich clays to form is unclear. In Phanerozoic rocks, the presence of Mg-silicates has been attributed to different depositional environments including weathering profiles developed on Mg-rich rocks such as basic or ultrabasic igneous rocks (Huang *et al.*, 2013), hydrothermal settings where fluids interact with Mg-rich igneous material (Setti *et al.*, 2004), alkaline lakes and evaporative basins (Van Denburgh, 1975; Yuretich and Cerling, 1983; Darragi and Tardy, 1987; Banfield *et al.*, 1991; Hay *et al.*, 1991; Hover *et al.*, 1999; Martini *et al.*, 2002; Bristow *et al.*, 2009; Zeyen *et al.*, 2015, 2017; Pace *et al.*, 2016; Gérard *et al.*, 2018). Spring inflows into lakes hosted in basic volcanic terrains could also contribute to create the right set of conditions, *i.e.*, high carbonate alkalinity, high Si, Mg and Ca concentrations, for the development of lacustrine carbonates associated with Mg-silicates (Wright, 2012). The Doushantuo carbonate formation, which hosts fossil records of the early Ediacaran period (635 – 551 Ma), illustrates the controversy about the formation of Mg-rich clays. In this carbonate formation, the presence of saponite, a Mg- and Al-rich smectite, was interpreted as either an early diagenetic phase formed *in situ* in an alkaline and non-marine environment (Bristow *et al.*, 2009), or as a detrital phase resulting from local to regional weathering of adjacent continental areas dominated by mafic to ultramafic volcanic rocks (Huang *et al.*, 2013). In this respect, the aluminum content of Mg-silicates may be of key interest for such reconstructions as it has been proposed to provide insights into the nature and the amounts of detrital silicate inputs in lacustrine environments (*e.g.*, Millot, 1970).

Present-day sedimentary features can inform on the palaeoenvironments where Mg-rich clays formed. Sediments developed in lakes characterized by waters with high pH (>9), and either relatively high silica concentrations (Van Denburgh, 1975; Yuretich and Cerling, 1983; Darragi and Tardy, 1987; Banfield *et al.*, 1991; Hay *et al.*, 1991; Zeyen *et al.*, 2015, 2017; Gérard *et al.*, 2018) or high magnesium concentrations (Hover *et al.*, 1999; Martini *et al.*, 2002), were found to host Mg-silicates.

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3 86 To date, however, the specific geochemical conditions controlling their formation remain unclear. In
4 87 particular, the role of volcanic catchment and spring inflow is uncertain, limiting palaeoenvironmental
5 88 and early diagenesis interpretations. To tackle this issue, the tropical volcanic crater lake Dziani Dzaha
6 89 in Mayotte (Indian Ocean) was chosen as a possible palaeoenvironmental analogue for the formation
7 90 model of Mg-rich silicates associated with continental carbonates. The lake waters are known to be
8 91 alkaline and the catchment is composed of volcanic rocks of phonolitic/alkaline composition. Mg-
9 92 silicate minerals were recently identified in the stromatholites of the lake (Gérard *et al.*, 2018),
10 93 suggesting that they may also be present in the soft carbonated sediments. The mineralogy of the first
11 94 meter of the sediment column was studied to identify possible occurrences of Mg-silicates and provide
12 95 insights on the processes leading to the formation of carbonates associated with Mg-silicates during
13 96 early diagenesis.

19 20 97 **2. Geologic setting and limnology of the Dziani Dzaha**

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23 98 The Dziani Dzaha (meaning volcanic crater lake in Mahorian) is a tropical volcanic crater lake
24 99 located in the island complex of Mayotte in the Northern Mozambique Channel. Mayotte is the most
25 100 southern and oldest island complex of the Comoros Archipelago. The initial volcanism period is
26 101 estimated to ~ 15-10 Ma (Nougier *et al.*, 1986); however, the Mayotte complex island has displayed a
27 102 late volcanic activity for the last 2.5Ma (Pelleter *et al.*, 2014). The alkaline volcanism at the origin of
28 103 the Comoros Archipelago was suggested as deriving from the partial melt of lithospheric mantle
29 104 metasomatized by CO₂-rich fluids beneath an ocean-continent transitional crust (Nougier *et al.*, 1986;
30 105 Mougénot *et al.*, 1989; Bertil and Reynoult, 1998; Coltorti *et al.*, 1999; Pelleter *et al.*, 2014). Mayotte
31 106 is made of two main volcanic islands: Grande Terre and Petite Terre (Fig. 1a and b). The island of
32 107 Petite Terre was emplaced during the late stage of the volcanic activity in Mayotte. It is mostly made
33 108 of pyroclastic rocks of phonolite/alkaline composition resulting from the crystal fractionation of
34 109 magmas deriving from the partial melt of an oceanic lithosphere enriched in CO₂ (Pelleter *et al.*,
35 110 2014). The Dziani Dzaha is located in a volcanic crater formed by a phreatomagmatic eruption. The
36 111 pyroclastic rocks rest over a coral reef dated from 9 ka, which surrounds the biggest island of Mayotte
37 112 (*i.e.*, Grande Terre). The most recent volcanic event being dated at 4 ka (Zinke *et al.*, 2003), the age of
38 113 the Dziani Dzaha may range from 9 ka to 4 ka.

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47 114 The lake shows a roughly elliptical shape with a length of 640 meters and a width of 470
48 115 meters. The lake watershed is very restricted. The volcanic crater is ~1.2 km long from top to top, 50m
49 116 high in average and the flanks consist of indurated layers of volcanic ashes and pumices. The lake
50 117 bottom is approximately at sea level. It has an average depth of 3 meters and a maximal depth of 5
51 118 meters, except for a singular depression which downs to 18 meters (Fig. 1 and 2). This morphological
52 119 feature is likely related to the phreatomagmatic eruption at the origin of the Dziani Dzaha. Magmatic
53 120 degassing is still active in the island of Petite Terre, as evidenced by the four bubbling areas of

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3 121 volcanic CO₂ identified at the lake surface. Microbialites, *i.e.*, organo-sedimentary structures formed
4 122 in close association with microorganisms, thrive in the shallow waters of the lake and are mainly
5 123 composed of aragonite and calcite (Gérard *et al.*, 2018). The distribution of the microbialites is patchy
6 124 and mostly limited to the lake shore (Fig. 1) such that below a few tens of centimeters of water depth,
7 125 most of the sediments are composed of gelatinous and non-indurated material.

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11 126 The physical, chemical and biological features of the lake are very singular (Leboulanger *et*
12 127 *al.*, 2017). The salinity of the lake water reaches up to 52 psu, *i.e.*, 1.5 times higher than seawater. The
13 128 alkalinity is $\sim 0.2 \text{ mol}\cdot\text{L}^{-1}$, with pH values ranging from 9.1 to 9.4. The mean daily surface temperature
14 129 varies between 28 and 36°C. The lake ecosystem is massively dominated by prokaryotes with a dense
15 130 and perennial bloom of filamentous cyanobacteria accounting for more than 90% of the primary
16 131 producer biomass. The biologic activity is massive all year round, with a primary productivity of $\sim 8 \text{ g}$
17 132 of $\text{C}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$, close to the maximum for tropical and subtropical lakes proposed by Lewis (2011).

133 3. Materials and methods

134 3.1. Nomenclature

135 The samples are named as follows. For DZ14-10 C4, “DZ” is for Dziani, “14-10” is for the year
136 (2014) and the month (October) of the survey and C4 refers to the sediment core number 4 (see
137 location in Figure 1). As the sediment cores were numbered according to their sampling order, they are
138 named in Figure 1 and in the text only as CX, with X the number of the core from 1 to 13. Sediment
139 cores C3, C5, C7, C8 and C12 were not dedicated to the study of the sediment composition and are not
140 used in this study, except for the water content of sediment core C12. The samples are listed in Table
141 A1 in supporting information.

142 3.2. Sampling, sample treatment and water content of sediment

143 Sediment cores were collected at different sites within the lake during the surveys performed in April
144 2012, April 2014, October 2014 and August 2016 (Table A1, Fig. 1). Data from 9 sediment cores are
145 presented in this study: C1, C2, C4, C6, C9, C10, C11, C12 and C13. A Uwitec core sampler (90 mm
146 in diameter PVC tubes) was used to collect sediment from the water-sediment interface to a maximum
147 of one meter deep. The sediment cores were subsampled, as much as possible, on a color basis in the
148 form of 3 to 5 cm thick slices, which were preserved under anoxic conditions in a cold room. The
149 samples were freeze-dried, before being rinsed with deionized water, centrifuged 3 to 4 times, and
150 crushed down to $<80 \mu\text{m}$. In the sediment core C12, the water content was estimated for 29 samples
151 by weighting fresh samples before and after drying at 60°C. The precipitation of halite (NaCl) was
152 corrected assuming salinity similar to that of the water column, *i.e.* of $52\text{g}\cdot\text{kg}^{-1}$ (Leboulanger *et al.*,
153 2017). Given the number and size of sediment cores and their samplings during 4 different surveys

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3 154 spread on a 4 year period, the analytical procedures presented below could not be performed on all
4 155 samples.

6 156 3.3. Total carbon content and carbon isotope composition

9 157 The total carbon (TC) content and carbon isotope composition were analyzed on 101 samples of 7
10 158 sediment cores. The TC content was quantified with CHN elemental analyzer (Shimadzu TOC V
11 159 CSH) on bulk samples with a precision of $\pm 5\text{wt.}\%$. The isotopic composition of total carbon was
12 160 analyzed with Flash-EA1112 elemental analyzer coupled to a Thermo Finnigan Delta^{plus} XP mass-
13 161 spectrometer via a ConFlo IV interface. Four organic laboratory standards were analyzed for
14 162 concentration and isotopic calibration: VH1, CAP, MX33 and LC. Carbon isotopic compositions are
15 163 reported relative to the Peedee belemnite (PDB) standard with a precision of $\pm 0.5\text{‰}$. In some samples,
16 164 carbonates or organic matter were removed to measure the isotopic composition of the carbon
17 165 endmembers. Decarbonation was performed on 33 samples with HCl 6N and the carbon isotope
18 166 composition of organic matter was measured by EA-IRMS. For 7 samples, organic matter was
19 167 removed using low-temperature oxygen-plasma ashing in a POLARON PT7160 RF system and the
20 168 carbon isotope composition of carbonates was measured with a Gas bench coupled to a Thermo
21 169 Finnigan Delta^{plus} XP mass-spectrometer. Three laboratory carbonate standards were used for both
22 170 carbonate quantification and for isotopic calibration: Across, Merck and Rennes II (details in Assayag
23 171 *et al.*, 2006; Lebeau *et al.*, 2014). Isotopic compositions are reported relative to the Peedee belemnite
24 172 (PDB) standard for carbon with a precision of $\pm 0.1\text{‰}$. All carbonate and organic laboratory standards
25 173 for C-isotope composition were calibrated independently against NBS19 and IAEA CO 1 international
26 174 standards.

36 175 3.4. XRPD and XRF analyses

39 176 X-ray powder diffraction (XRPD) analyses were performed on 128 samples of 7 sediment cores and
40 177 12 samples of the volcanic catchment with an Empyrean (Panalytical) diffractometer equipped with a
41 178 multichannel PIXcel 3D detector and a Cu K α X-ray source ($\lambda = 1.541874 \text{ \AA}$). Each pattern was
42 179 recorded in the θ - θ Bragg-Brentano geometry, in the 5° - 90° 2θ range (0.0131° for 70 s). Analysis of
43 180 X-ray patterns and mineralogical identification was performed using the High Score Plus software, the
44 181 Crystallography Open Database (COD) and the Inorganic Crystal Structures Database (ICSD). The
45 182 Reference Intensity Ratio (RIR) method was used for semi-quantifications of mineral phases;
46 183 however, reference intensity ratios for clay minerals were frequently missing from the databases.

51
52 184 Elemental analyses were further conducted by Energy Dispersive X-ray fluorescence
53 185 (EDXRF) on 99 samples of 6 sediment cores and 4 samples of the volcanic catchment with an epsilon
54 186 3XL (Panalytical) spectrometer equipped with a silver X-ray tube. A 10-minute measurement repeated
55 187 6 times for each sample yielded accurate quantitative analysis.

188 3.5. SEM and TEM analyses

189 Scanning and transmission electron microscopy were performed on crushed (<80 μ m) samples after
190 freeze-drying and rinsing. Crushed samples were used for the microscope analyses because the
191 preservation of textural relationships among different components was rendered difficult by the
192 gelatinous texture of the sediment (see Section 4.1 below). Scanning Electron Microscopy (SEM) was
193 performed on 19 samples with a Zeiss Ultra 55 FEG microscope operated at 10 kV and a working
194 distance of 7.5 mm using mostly a backscattered electron detector for imaging. Transmission Electron
195 Microscopy (TEM) was performed with a Jeol FEG 2100F operated at 200 kV on one clay-rich
196 sample selected on the basis of the XRPD analyses. Both SEM and TEM were equipped with an
197 energy dispersive X-ray system from Bruker and Jeol, respectively.

198 3.6. Clay fraction

199 Clay fraction analysis was performed on two clay-rich samples selected on the basis of the XRPD
200 analyses of bulk samples. Carbonates were removed using the acetic acid-acetate buffer method
201 (Ostrom, 1961). Organic matter was removed at 50°C by adding small aliquots of H₂O₂ to the
202 suspension until gaseous emission had ceased. The <2 μ m fraction was separated using gravity
203 sedimentation of particles in water (Stoke's law), and then saturated with a 1 M NaCl solution for 24 h
204 at room temperature. Oriented preparations of the Na-saturated <2 μ m fraction were carried out on
205 glass slides and dried at room temperature to obtain an air-dried (AD) preparation. Ethylene glycol
206 (EG) solvation was achieved by exposing the oriented slides to ethylene glycol vapor for 12 h.
207 Glycerol (GL) solvation was carried out by saturation of samples with a 2 M MgCl₂ solution for 24 h
208 at room temperature and then exposure to glycerol vapor 3 days at 80°C. The air-dried oriented slide
209 was also heated at 500°C for 90 minutes and then solvated in EG for 16h as described in details by
210 Christidis and Koutsopoulou (2013). X-ray diffraction patterns were acquired on the oriented
211 preparations over the 2–50 angular region, with 0.03° 2 θ angular steps, using a Bruker D8
212 diffractometer equipped with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Counting time was adapted to the low
213 amount of sample available and is 1.65 s per step; the two Soller slits were 2.5°. Analysis of XRD
214 patterns and mineralogical identification was performed using the Bruker Diffracplus EVA software
215 and the ICDD database.

216 Electron microprobe analyses (EMPA) were conducted after coating of the < 2 μ m clay
217 fraction with carbon. Spot analyses were performed using a CAMEBAX SX Five electron microprobe
218 with an accelerating voltage of 15 kV, a beam current of 12 nA, and a 1 μ m beam diameter. More
219 details on the analytical methods are in Lerouge *et al.* (2017).

220 Cation Exchange Capacity (CEC) was measured using the hexamine cobalt(III) chloride
221 method developed by Hadi *et al.* (2013) and adapted from Orsini and Remy (1976). The CEC is

222 deduced from two cross analyses: the amount of hexamine cobalt(III) that disappears from the solution
 223 (adsorbed on the clay), which is directly measured by spectrophotometry at 475 nm, and analysis by
 224 ionic chromatography (HPLC, Dionex) of the major cations present in the supernatant (Na^+ , K^+ , Ca^{2+} ,
 225 Mg^{2+}) that also indicates the relative populations of desorbed exchangeable cations.

226 3.7. Quantification of sediment composition

227 On the basis of XRPD and XRF analyses, bulk carbon contents and carbon isotope compositions,
 228 calculation was performed to quantify the contents of the different mineral phases and of the organic
 229 matter. The organic matter content was calculated in two steps. First, the content of total organic
 230 carbon (TOC) is calculated using an isotope mass balance calculation. The total carbon content is a
 231 mixture between organic and inorganic carbon, for which the isotopic compositions were measured in
 232 this study. The contribution of organic carbon x in the total carbon content can hence be calculated
 233 with the equation:

$$234 \quad \delta^{13}\text{C}_{\text{TC}} = x * \delta^{13}\text{C}_{\text{TOC}} + (1-x) * \delta^{13}\text{C}_{\text{TIC}} \quad (1)$$

235 with $\delta^{13}\text{C}$ of TC, TOC and TIC being the isotopic composition of total carbon, total organic carbon
 236 and total inorganic carbon, respectively. Then the TOC content is given by:

$$237 \quad \text{TOC} = x * \text{TC} \quad (2)$$

238 Second, the content of organic matter was calculated considering a TOC to organic matter weight ratio
 239 of 1.9 (Broadbent, 1953). The mineral content is deduced by simple mass balance. For the sediment
 240 core C13, as the carbon content and the carbon isotope composition were not measured, the content of
 241 organic matter is considered to be the same as in C6, which is a reasonable assumption since the two
 242 cores were collected in the depression of the lake.

243 The content of each mineral phase was calculated using the XRF analyses, which requires
 244 fixing the chemical formula of each phase. Empirical formulas were used for most minerals (Table 1).
 245 For saponite, the structural formula has been determined in this study (Section 4.5). On the basis of
 246 SEM-EDS analyses of alkaline feldspars and volcanic pumices in lake sediment samples, the empirical
 247 formula of anorthoclase is considered for these phases. Then, the content of each mineral is calculated
 248 based on a given element.

249 3.8. Thermodynamic calculation

250 Mineral stability domains in the system Mg-Ca-C-O-H and Mg-Al-Si-O-H were calculated at 30°C
 251 and 1 bar with the Thermoddem database (Blanc *et al.*, 2012) and compared with lake water
 252 compositions (Leboulanger *et al.*, 2017). The speciation of dissolved species is calculated with the
 253 Phreeqc software (Parkhurst and Appelo, 2013).

254 4. Results

255 4.1. Description of lake sediment textures

256 Three main sediment textures have been observed within the lake (Fig. 2a). In the sediment cores
257 collected at water depth ranging from 1 to 5 meters, which represents most of the lake area, the
258 sediment texture is highly gelatinous and characterized by horizontal laminae (Fig. 2b). The
259 uppermost sediment is markedly laminated with colors ranging from light to dark brown. The laminae
260 are mostly <1 mm thick but seem to be organized, on a color basis, in laminae packages of few
261 centimeters thick, which were used when possible to describe the slices cut from the sediment cores.
262 In most case, grain size is indistinguishable to the eye, except in rare mudstone layers which contain
263 grains of millimeter size. Below ~ 50 cm deep, the laminae tend to disappear and the sediment aspect
264 changes to a more massive and darker texture. The water/rock weight ratio decreases from ~33 in
265 surface sediments to ~4 at 20 cm deep and ~2 at one meter deep (Fig. 2d). Thus, water is by far the
266 dominant phase of the sediment and most of the sediment compaction occurs in the first 20 cm below
267 the sediment surface. This sedimentary facies is very homogeneous and no lateral variation has been
268 observed in the area of 1 to 5 meter of water depth.

269 The sediment cores C12 and C13 collected in the depression of the lake show a similar
270 sediment texture (highly gelatinous, laminated and with very fine grain size); however, deformation of
271 the laminae is observed below ~30 cm deep (Fig. 2c). In the sediment cores close to the shoreline in
272 shallow (<1 m) water depth (C9, C11), the sediment is grayish and grain size can increase up to the
273 millimeter size. In C9, the sediment texture is close to that of a mudstone and remains relatively
274 gelatinous and laminated. In C11, the sediment texture is close to a packstone and laminae are not
275 visible. The thickness of the sediment column is unknown; however, attempts to collect longer
276 sediment cores (C3, C4 and C5) in the area of 4 to 5 meters of water depth suggests that it is thicker
277 than 2.3 m in this area.

278 4.2. Total carbon content and isotopic composition of the lake sediments

279 The content of total carbon decreases from ~ 35-40wt.% in the uppermost sediment to ~ 10-15wt.% at
280 depth, except for the sediment cores collected in the depression of the lake (C6) and close to the
281 shoreline (C9 and C11) (Table A2 in supporting information). In the depression of the lake (C6), the
282 TC content ranges between 25 and 20wt.% and is relatively constant with depth. The TC content in C9
283 and C11 is lower with values of ~10wt.%. The sediment core C2 shows a local decrease of TC content
284 down to 3wt.% at 7-14 cm deep.

285 The isotopic composition of total carbon is relatively constant with depth; however, the $\delta^{13}\text{C}$
286 values vary between ~ -15‰ and ~ +5‰ depending on the sediment core (Table A2). The highest

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3 287 values are found in C11, whereas C1 and C2 show the lowest values. The variations of $\delta^{13}\text{C}$ values of
4 288 total carbon between the sediment cores reflect variable proportions of organic and inorganic carbon.
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6 289 The isotopic compositions of the two carbon endmembers measured on samples of C6 and C9 are
7 290 relatively constant with depth, with average $\delta^{13}\text{C}$ values of $\sim -14\text{‰}$ for organic carbon and $\sim +16\text{‰}$ for
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9 291 inorganic carbon (Table A2).

10 292 4.3. Chemical and mineralogical characterization of the sediment cores

11 293 4.3.1. Bulk analysis of the sediment cores (XRF)

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13 294 The mineral content consists mostly of silicon, magnesium, calcium and aluminum (Table A3 in
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15 295 supporting information). Except for the sediment cores collected at the shoreline (C11) and in the lake
16 296 depression (C6, C13), all sediment cores (*i.e.*, C4, C9 and C10) show a decrease of the magnesium
17 297 content with depth and a concurrent increase of the aluminum and silicon contents, while the calcium
18 298 content remains relatively stable. In the sediment core C11, the evolution of the chemical composition
19 299 with depth is approximately the same, but the aluminum and silicon contents are higher than in C4, C9
20 300 and C10. In the sediment cores C6 and C13, the calcium, magnesium, aluminum and silicon contents
21 301 are relatively stable with depth.
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28 302 4.3.2. XRPD analyses of sediment cores

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30 303 Aragonite, hydromagnesite and diopside or clinoenstatite, referred hereafter as clinopyroxene, are
31 304 detected in the uppermost sediment (see Table A4 in supporting information). This mineral
32 305 assemblage is relatively constant up to ~ 20 cm deep and occurs in all sediment cores collected under a
33 306 water depth of $>1\text{m}$ (*i.e.*, C2, C4, C6, C10, C13). Semi-quantifications with the RIR method indicate
34 307 contents of aragonite, hydromagnesite and clinopyroxene of 40wt.%, 40wt.% and 20wt.%,
35 308 respectively. Minor phases such as magnetite, dolomite and quartz are sometimes identified with
36 309 abundances of $\sim 5\text{-}10\text{wt.}\%$. Halite is also occasionally detected but results from precipitation during
37 310 freeze-drying. Some sediment cores present a peculiar assemblage: high amounts of alkaline feldspars
38 311 in C11 close to the shoreline, calcite and alkaline feldspars between 7 and 14 cm deep in C2,
39 312 magnesite in the uppermost sediment of C9 and pyrite and dolomite at depth.
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46 313 In addition to the aragonite-hydromagnesite-clinopyroxene assemblage, clay minerals occur at
47 314 depth, characterized by a diffraction peak close to 14.5 angstroms (\AA), consistent with the basal
48 315 spacing (001) of smectites, chlorite or vermiculite (Fig. 3) (the precise characterization of clay
49 316 minerals is presented later in the paper). Overall, clays were detected in all sediment cores below $\sim 10\text{-}$
50 317 15cm , except for the sediment cores collected at the shoreline (core C11 of only 30cm long) and in the
51 318 depression of the lake (cores C6 and C13), in which clays may be absent or below XRD detection
52 319 limit. Concurrent to the occurrence of clays, the content of hydromagnesite decreases with depth until
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3 320 complete disappearance in the sediment cores sampled between 2 and 5 m of water depth (C2, C4, C9
4 321 and C10). In the other cores (C11, C6 and C13), the content of hydromagnesite remains relatively
5 322 constant with depth.
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8 323 4.3.3. Scanning and transmission electron microscopy 9

10 324 Observations with scanning electron microscope and chemical mapping show Mg-rich minerals
11 325 forming platelets, typical of hydromagnesite, together with Ca-rich minerals corresponding to
12 326 aragonite (Fig. 4a and b). Associated with the carbonates, a mineral phase rich in silicon, magnesium
13 327 and aluminum is recognized (Fig. 4a, b and c). Observations with transmission electron microscope of
14 328 minerals of similar chemical composition highlight the sheet structure of the phase (Fig. 4d and e).
15 329 Significant amount of volcanic glass containing silicon, aluminum and lower amount of sodium and
16 330 potassium, is also observed (Fig. 4f and g). The chemical composition is close to that of anorthoclase
17 331 ($\text{Na}_{0.7}\text{K}_{0.3}\text{AlSi}_3\text{O}_8$) (Fig. 4h). This is consistent with the XRF and XRPD analysis of volcanic pumices
18 332 and ash layers of the volcanic catchment (see Section A1, Figure A1, Table A5 and A6 in supporting
19 333 information).
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26 334 4.3.4. Characterization of the clay fraction 27

28 335 The $<2 \mu\text{m}$ clay fraction was extracted from two samples: one from 27-30 cm deep in the sediment
29 336 core C4 which corresponds to a layer rich in clays (Table A4); the other one from 67-72 cm deep in
30 337 sediment core C6. The XRD patterns acquired on oriented slides are similar for the two samples. One
31 338 may notice that although the clays were Na-saturated, the 001 reflection was at $\sim 14.5 \text{ \AA}$ instead of
32 339 12.5 \AA as expected for relative humidity condition normally occurring in the laboratory (Brindley and
33 340 Brown, 1980, p. 204) (Fig. 5a and b). As this will be later on illustrated, CEC measurement carried out
34 341 on this Na-saturated fraction indicates that the exchanger still contains a significant amount of
35 342 magnesium, which therefore explains this value. The swelling of the (001) from 14.5 \AA in the air-dried
36 343 state towards 17 \AA in the ethylene glycol state (Fig. 5b) indicates the presence of smectite or
37 344 vermiculite (Brindley and Brown, 1980). Powder XRD indicates that the (060) peak position is 1.53 \AA
38 345 (Fig. 5a), which is characteristic of trioctahedral phyllosilicates (Moore and Reynolds, 1997). Based
39 346 on EPMA analysis (*e.g.*, no Li and Zn that ruled out hectorite and saunonite, presence of Al that ruled
40 347 out stevensite) and the fact that the phyllosilicate is trioctahedral, the remaining possibilities are
41 348 saponite and vermiculite (Brindley and Brown, 1980, ch. 2, p. 172; Debure *et al.* 2016). Distinguishing
42 349 between smectite or vermiculite is not an easy task. However, glycerol solvation on Mg-saturated
43 350 samples, led to swelling with a basal reflection at 16.5 \AA (Fig. 5c). This is consistent with the presence
44 351 of saponite as vermiculite is not supposed to swell under these conditions (Walker, 1958; Brindley,
45 352 1966; Suquet *et al.*, 1975, Tosca *et al.*, 2011). The cation exchange capacity of $\sim 87.1 \text{ meq/100g}$ is also
46 353 consistent with saponite, whereas values of approximately 120 meq/100g are reported for vermiculite
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3 354 (Brindley and Brown, 1980, ch. 3, p. 204). In addition, the fact that the sample heated at 500°C still
4 355 showed a 001 reflection expanding to 17.4 Å after ethylene glycol solvation (Fig. 5b) further supports
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6 356 the saponite hypothesis (Christidis and Koutsopoulou, 2013).
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8 357 Cation population obtained from CEC measurement is consistent with EPMA (Table 2). The
9 358 two methods led to similar Na⁺ content, which is the main interlayer cation. Ca²⁺ and K⁺ values are a
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11 359 bit higher by EPMA because part of K⁺ present in the inner sphere complexes might be difficult to
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13 360 extract with the hexamine cobalt method (Hadi *et al.*, 2013). Mg content obtained by EPMA was ten
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15 361 times higher than the value obtain by CEC. The structural Mg content was deduced from the
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17 362 difference between EPMA and CEC measurements.

18 363 The mean structural formula was determined assuming that Al was preferentially tetrahedral,
19 364 the rest being octahedral, and that Na, Ca and K were preferentially in the interlayers (Lerouge *et al.*,
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21 365 2017). The calculation revealed that Fe was not in tetrahedral sites but in the octahedral ones. In order
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23 366 to equilibrate the charge, Fe was only in its ferric form (Fe³⁺). Based on all those considerations, the
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25 367 mean structural formulae is $K_{0.01}Mg_{0.12}Ca_{0.02}Na_{0.28}(Mg_{2.22}Fe_{0.18}Al_{0.28}\square_{0.32})(Si_{3.61}Al_{0.39})O_{10}(OH)_2$ where \square
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27 368 is a vacant site. Due to its trioctahedral character, this formula is not in agreement with the clay
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29 369 mineralogy nomenclature defined by Guggenheim (2006) for saponite; however, it is consistent with
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31 370 literature data that reported vacancies (from 0.15 to 0.56 depending of the studies) in the octahedral
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33 371 position of ferric saponite (Post, 1984; Kodama *et al.*, 1988; Vincente *et al.*, 1996; Hicks *et al.*, 2014).
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35 372 In addition, the calculated charge per formula unit (0.57) is below 0.6 which is considered in the
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37 373 nomenclature as the boundary between saponite and vermiculite. The differences observed in the
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39 374 structural formula could be related to the occurrence of minor amounts of other clay minerals or minor
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41 375 non-clay impurities (amorphous and/or crystalline phases) in the samples that have not been identified.
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43 376 The terminology “saponite-like mineral” will be used in this paper to be consistent with the
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45 377 nomenclature and the characterization.

41 378 4.4. Quantification of the sediment content

43 379 Results of the calculation of the evolution of mineral composition and organic matter content with
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45 380 depth are shown in Figure 6 (Table A7 in supporting information). Apart for the sediment core C11,
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47 381 organic matter represents ~50wt.% of the uppermost sediment. In the sediment cores C4 and C10,
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49 382 hydromagnesite decreases with depth while the saponite-like mineral accumulates to reach up to
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51 383 25wt.% at ~70 cm deep in C10. Concurrently, the content of organic matter decreases. The content of
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53 384 aragonite is relatively constant around 20wt.% whereas the proportion of primary silicates, dominated
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55 385 by alkaline feldspar, increases with depth to reach up to ~25wt.%. The sediment core C11 shows much
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57 386 higher amounts of alkaline feldspars than the others sediment cores, up to 50wt.%. Compared to C4
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59 387 and C10, the sediment cores sampled in the depression of the lake (*i.e.*, C6 and C13) have lower
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3 388 amounts of saponite-like mineral at depth and relatively stable contents of hydromagnesite and organic
4 389 matter.

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6 390 If correct, the calculation of mineral contents should fulfill an internal consistency. For
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8 391 instance, the sum of silicon content in alkaline feldspar and in the saponite-like mineral, which is
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10 392 calculated independently using the measured content of potassium and aluminum, respectively, should
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12 393 not exceed the total measured content of silicon. For the sediment cores C4, C10, C6 and C13, the
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14 394 calculated silicon content exceed by 10mol.% the measured silicon content for only ~10% of samples.
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16 395 These low errors validate the calculation for these sediment cores. In contrast, calculation for C9 is not
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18 396 shown due to a lack of internal consistency. The core C9 was collected close to the shoreline, where
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20 397 detrital influence is high. In this case, considering only alkaline feldspar and pyroxene as detrital
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22 398 inputs might be an oversimplification.

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24 399 Sensitivity tests have been performed on several parameters including the TOC to organic
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26 400 matter weight ratio (± 0.1 unit), the empirical formula of clinopyroxene (enstatite or diopside), and the
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28 401 chemical composition of the saponite-like mineral (± 0.1 mol/mol of mineral on the Al, Si and Mg
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30 402 content). Most of these parameters modify by less than 10% the percentage content of each phase,
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32 403 except for aragonite (up to 20%).

33 404 4.5. Thermodynamic model

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35 405 The chemical compositions of lake waters (Table A8 in supporting information) (Leboulanger *et al.*,
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37 406 2017; Gerard *et al.*, 2018) are compared to the stability domains of carbonates and brucite in the
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39 407 system Mg-Ca-C-O-H (Fig. 7a). The pore waters are close to metastable equilibrium between
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41 408 aragonite and hydromagnesite, and supersaturated relative to dolomite.

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43 409 The stability domains of Mg-silicates are represented in the system Mg-Al-Si-O-H,
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45 410 considering that aluminum behaves conservatively between the Al-bearing phases (Fig. 7b). Chlorites
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47 411 are not considered in the calculation as their formations are kinetically limited at ambient temperature
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49 412 and pressure (Meunier, 2005). High pH values together with high activities of Mg^{2+} and dissolved
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51 413 silica favor the stability of saponite compared to other aluminosilicates. The chemical composition of
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53 414 lake water is close to equilibrium with quartz and supersaturated relative to saponite, kerolite, talc and
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55 415 sepiolite.

56 416 **5. Discussion**

57 417 5.1. Sediment composition and distribution

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59 418 Three main sedimentary facies were observed within the lake, which respond to a shore to basin
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419 central lake transect. Close to the shoreline, the grayish facies dominated by millimeter size grains is

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3 420 relatively poor in organic matter and rich in primary silicates, alkaline feldspars and pyroxene, which
4 421 highlights high detrital input from the volcanic catchment. In the 1 to 5 meter deep lake area, the
5 422 gelatinous facies is dominated by organic matter and records low lateral variation. The detrital
6 423 components decrease with distance to the lake shore. The laminated uppermost sediment is mostly
7 424 formed of aragonite and hydromagnesite whereas, at depth, the sediment texture becomes massive and
8 425 dark, and the hydromagnesite is replaced by the saponite-like mineral. The layers containing coarser
9 426 grains and enriched in calcite and alkaline feldspar with less organic carbon (sediment core C2)
10 427 reflects a local higher energy detrital input to the lake margin. In the central lake depression, the soft-
11 428 sediment deformations are interpreted as slump events (Alsop and Marco, 2011). In this area, the
12 429 apparently undeformed uppermost sediment is also rich in organic matter, aragonite and
13 430 hydromagnesite but hydromagnesite persists at depth and the saponite-like mineral occurs in much
14 431 lower amounts. No clay mineral has been detected in the uppermost part of sediment cores suggesting
15 432 low amounts of detrital clays inherited from the weathering of the surrounding volcanic rocks.

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23 433 Overall, the sediment deposited below 1 meter of water depth is singular by its extremely high
24 434 content in organic matter (>50wt.%), a consequence of the intense primary productivity in the lake,
25 435 and by the anomalously positive carbon isotope signature of both carbonates and organic matter,
26 436 which probably resulted from a combination of volcanic CO₂ input and methanogenesis. The sediment
27 437 collected between 1 and 5 meters of water depth is the most representative of the sedimentary deposits
28 438 observed within the lake. It is used hereafter as a case study to develop a better understanding of the
29 439 co-occurrences of carbonates and Mg-silicates.

30 31 32 33 34 440 5.2. Thermodynamic and kinetic controls on carbonates and saponite-like mineral formation

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36 441 The lake water composition is close to equilibrium with aragonite and hydromagnesite and the
37 442 presence of these two carbonates in the uppermost sediment indicates that they precipitate relatively
38 443 rapidly from the lake water, either in the water column or at the sediment-water interface. The
39 444 occurrence of aragonite is consistent with the Mg/Ca molar ratio >10 of the lake waters, which has
40 445 been shown to favor the formation of aragonite rather than calcite (Simkiss, 1964; Taft, 1967; Debure
41 446 *et al.*, 2013a and b; Zeyen *et al.*, 2017) Although thermodynamics suggests that magnesite and
42 447 dolomite are the most stable Mg-bearing carbonates at surface temperature and pressure, kinetics
43 448 exerts a strong primary control on their formation (*e.g.*, Sayles, 1973; Arvidson and MacKenzie, 1999;
44 449 Gautier *et al.*, 2014), which may explain why they are only observed punctually.

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50 450 Despite supersaturation of the lake water relative to saponite, kerolite, talc and sepiolite, none
51 451 of these phases were detected in the mineral assemblage of the uppermost sediments, suggesting that
52 452 they do not precipitate from the lake waters. Precipitation of Al-free Mg-silicates from lake waters is
53 453 nonetheless possible, as exemplified by the magnesium depletion in Lake Turkana attributed to the
54 454 precipitation of stevensite (Yuretich and Cerling, 1983; Cerling, 1996). Tosca (2015) proposed a

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3 455 critical supersaturation allowing Al-free Mg-silicates to overcome kinetic barriers and to precipitate
4 456 directly from the water column. In the Dziani Dzaha, the removal of magnesium by hydromagnesite
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6 457 precipitation likely hinders the achievement of this critical supersaturation, preventing the
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8 458 homogeneous nucleation of Al-free Mg-silicates in the water column. Regarding the Mg-
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10 459 aluminosilicates, they are expected to form mostly through heterogeneous nucleation (*e.g.*, Tosca,
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12 460 2015; Tosca and Wright, 2015), because of the low solubility of aluminium in most cases and
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14 461 especially in alkaline lakes ($2.2 \cdot 10^{-6} \text{ mol L}^{-1}$ at pH 9). In this process, detrital Al-bearing silicates act
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16 462 as mineral precursors, lowering the supersaturation required for the formation of aluminosilicates. In
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18 463 the Dziani Dzaha, alkaline feldspars and volcanic glasses are the likely Al-bearing precursors,
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20 464 allowing the formation of the saponite-like mineral in the sediment.

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22 465 Achievement of high pH values in the water column is one of the chief factors that enable
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24 466 supersaturation relative to saponite, aragonite and hydromagnesite. Consistently, Mg-silicates
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26 467 associated with carbonate sediments have been widely reported in alkaline lakes and evaporative
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28 468 basins of pH values > 9 (Van Denburgh, 1975; Yuretich and Cerling, 1983; Darragi and Tardy, 1987;
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30 469 Banfield *et al.*, 1991; Hay *et al.*, 1991; Hover *et al.*, 1999; Martini *et al.*, 2002; Bristow *et al.*, 2009).
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32 470 As for other alkaline and hypereutrophic lakes (López-Archilla *et al.*, 2004), the intense primary
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34 471 productivity in the Dziani Dzaha is the most likely mechanism responsible for these pH values,
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36 472 according to the simplified reaction:



474 The development of this massive primary productivity could be linked to the input of volcanic CO_2
475 within the lake, which probably supplies primary productivity with carbon.

476 In addition to pH, magnesium and silica concentrations are critical for the formation of
477 saponite. The magnesium concentration of $\sim 4 \text{ mM}$ is comparable to the ones of other alkaline lakes
478 producing Mg-silicates (Van Denburgh, 1975; Yuretich and Cerling, 1983; Darragi and Tardy, 1987;
479 Banfield *et al.*, 1991). However, due to the competition for magnesium between Mg-silicates and Mg-
480 carbonates, silica might have a greater influence than magnesium on the formation of saponite (Zeyen
481 *et al.*, 2017). The silica concentrations ($\sim 0.3 \text{ mM}$) are around two orders of magnitude higher than the
482 usual concentration of surface oceans ($< 2 \text{ }\mu\text{M}$; Treguer *et al.*, 1995), where the efficiency of diatoms
483 in precipitating silica drastically lowers the concentration (*e.g.*, Siever, 1992; Racki and Cordey,
484 2000). Because no spring inflows have been identified, these high silica concentrations are attributed
485 to the weathering of volcanic terrains in a diatoms-poor lacustrine environment.

486 5.3. Early diagenetic formation of the saponite-like mineral

487 The evolution of the sediment composition with depth is the likely result of early diagenetic
488 reactions. The appearance of the saponite-like mineral only at depth, in spite of its supersaturation in
489 the lake water, can be explained by the intrinsic kinetics limit of saponite precipitation (*e.g.*, Tosca,
490 2015) and by the kinetics of dissolution of the Al-bearing detrital phase. The mineralization of organic
491 matter is evidenced by the decrease of the TOC content with depth in all the cores. In the right
492 proportions, the CO₂ produced by the mineralization of organic matter could account for a decrease of
493 pH destabilizing hydromagnesite while allowing both aragonite and the saponite-like mineral to
494 remain supersaturated. In addition, a genetic relationship may exist between hydromagnesite and the
495 saponite-like mineral. Calculation of mineral stability domains (Fig. 7b) shows that the precipitation of
496 saponite from supersaturated water tends to decrease the pH values, favoring the destabilization of
497 hydromagnesite, which, in return, could supply with Mg the formation of saponite (Fig. 8). In addition
498 to organic matter mineralization, CO₂-rich volcanic gases seeping from the volcanic basement could
499 contribute to the pH decrease of pore waters.

500 Changes of palaeoenvironmental conditions throughout the lake history are less consistent
501 than early diagenetic reactions to explain the evolution of the sediment composition. If the decreasing
502 amount of hydromagnesite with depth was due to lower Mg concentrations in the palaeo-lake waters
503 and/or lower pH values than currently observed, saponite supersaturation would also be lower, which
504 is not compatible with the increasing amount of saponite-like mineral at depth. The diagenetic
505 scenario is thus the most likely, even though it remains to be validated. This would require the
506 assessment of the saturation state of pore waters and the quantitative evaluation, with reactive
507 transport modeling, of the diagenetic reactions occurring in the sediment, including saponite
508 precipitation, hydromagnesite destabilization and organic matter mineralization.

509 5.4. Implications for the formation and distribution of Mg-silicates of the South Atlantic rift basins

510 Mg-silicates (stevensite, kerolite and talc) have been identified in lacustrine Cretaceous carbonate
511 reservoir rocks of the South Atlantic (Bertani and Carozzi, 1985a, 1985b; Rehim *et al.*, 1986; Wright,
512 2012; Tosca and Wright, 2015). Their formation was suggested to occur in lakes where volcanic
513 terrains predominated (Cerling, 1994; Wright, 2012). However, the source of Si and Mg to account for
514 the amount of Mg-silicate found in those rocks remains under discussion. Wright (2012) suggested
515 that spring inflows, in addition to the weathering of volcanic terrains, might have been required to
516 enable the formation of both carbonates and Mg-silicates.

517 The study case of the Dziani Dzaha suggests that high silica and magnesium concentrations
518 can be reached in lakes throughout the weathering of volcanic alkaline terrains, without necessarily
519 involving external inputs such as spring or hydrothermal inflows. The development of an intense

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3 520 primary productivity, sustained both by the magmatic CO₂ and by the nutrients supplied by the
4 521 volcanic terrains (such as iron, potassium and phosphorous), is most likely responsible for the high pH
5 522 values. Thus, a genetic link may exist between volcanic alkaline terrains, organic-rich sediment and
6 523 Mg-silicates. In the Doushantuo Formation (635-551 Ma), saponite is associated with TOC contents
7 524 reaching up to 4wt.% (Bristow *et al.*, 2009). Using a carbon to organic matter ratio of 1.9 (Broadbent,
8 525 1953) and considering 66 wt.% loss of initial organic carbon by thermal maturation (Tissot and Welte,
9 526 1984), the initial content of organic matter in the Doushantuo sediments may have been of ~23wt.%,
10 527 which is comparable to the Dziani Dzaha sediments. The deposition of lacustrine carbonates
11 528 containing more than 20wt.% of organic matter could have required a significant source of carbon in
12 529 addition to the atmospheric CO₂. In the Dziani Dzaha, the volcanic CO₂ may have played a major role
13 530 by fueling both the primary productivity and the carbonate factory. Similarly, the Cretaceous lakes at
14 531 the origin of the South Atlantic carbonate reservoir rocks could have been influenced by CO₂-rich
15 532 magmatic inflows during the continental rifting, as the continental crust becomes thinner and the
16 533 influence of mantle fluids increases.

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19 534 The absence of Al-free Mg-silicates in the Dziani Dzaha sediment, whereas they prevail in the
20 535 carbonate reservoirs of the South Atlantic, supports two mutually compatible hypotheses as to the
21 536 factors controlling the presence or absence of Al in Mg-silicates. At the local scale, this supports the
22 537 “clay-zoning” scenario of Millot *et al.* (1970), who suggested that the presence of detrital Al-bearing
23 538 silicates at the basin margin allows Al-rich clay minerals to form, whereas, toward the basin center,
24 539 lower amounts of detrital materials indirectly promote the homogeneous nucleation of Al-free Mg-
25 540 silicates (Weaver and Beck, 1977; Jones and Weir, 1983; Jones, 1986; Calvo *et al.*, 1999; Deocampo
26 541 *et al.*, 2009; Galán and Pozo, 2011). Accordingly, the occurrence of a saponite-like mineral in the
27 542 Dziani Dzaha is consistent with the presence of detrital component in the sediments and the prevalence
28 543 of Al-free Mg-silicates in the South Atlantic carbonate reservoirs would rather indicate large lake
29 544 systems with open water lake deposits free from detrital inputs.

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41 545 At the regional scale, the formation of saponite or Al-free Mg-silicates may also reflect the
42 546 nature of the volcanic terrains hosting the lacustrine environments. At the early stage of continental
43 547 rifting, low mantle uplift results in low partial melting, producing alkaline magma (*e.g.*, White and
44 548 McKenzie, 1989; Wilson, 1992). Below the thick continental lithosphere, the slow cooling of magmas
45 549 generates highly differentiated basalts enriched in alkaline elements, aluminum and silicon, *i.e.*, a
46 550 phonolite/alkaline composition comparable to the one of magmas at the origin of the Mayotte Islands.
47 551 In contrast, during later stages of continental rifts, higher partial melting and lower magmatic
48 552 differentiation produce tholeiitic basalts with lower aluminum content. The relatively low availability
49 553 of aluminum in the Cretaceous lakes at the origin of the South Atlantic carbonate reservoirs may
50 554 indicate lacustrine environments formed during the late stage of continental rifting. This is consistent
51 555 with the suggestion of Tosca and Wright (2015) that the water chemistry of these lakes may have been

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3 556 influenced by the serpentinization of exhumed mantle at the transition between continental and
4 557 oceanic crusts.
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6 558 **6. Concluding remarks**

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9 559 The Dziani Dzaha sediment exhibits a particular evolution of composition in the first meter of
10 560 sediment, which can be explained by early diagenetic reactions within the lake sediments. These are
11 561 mainly gelatinous and exhibit homogeneous facies distribution with local increases in detrital inputs
12 562 close to the shore. Mineralization of organic matter within the sediment, possibly associated with
13 563 inputs of volcanic CO₂, can explain the destabilization of hydromagnesite and the decrease of organic
14 564 matter content with depth, while aragonite remains stable. Kinetic limitation prevents the formation of
15 565 the saponite-like mineral in the uppermost sediment, such that it only accumulates below 15 cm depth.
16 566 Reactive transport modeling is now needed to allow a quantitative evaluation of the role of all
17 567 diagenetic processes occurring in these sediments: saponite precipitation, hydromagnesite
18 568 destabilization, organic matter mineralization and/or CO₂-rich gas inputs.
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24 569 The formation of the saponite-like mineral in the Dziani Dzaha results from the high silica
25 570 activities and the high pH values of the lake waters. This water chemistry is attributed to the delivery
26 571 in a restricted lake system of chemical elements, among which nutrients, produced by the weathering
27 572 of volcanic terrains, which favors the development of an intense primary productivity. The bubbling of
28 573 magmatic gases in the Dzaini Dzaha suggests that magmatic CO₂ may fuel the primary productivity
29 574 and the carbonate precipitation. Thus, our study suggests that a genetic link may exist between
30 575 volcanic contexts and carbonate sediments rich in organic matter and Mg-silicates, which may be key
31 576 in understanding their formation throughout the fossil record. As an example, the migration through
32 577 the crust of mantle-derived fluids during continental rifting could have influenced the formation of the
33 578 Cretaceous South Atlantic carbonate reservoir rocks. In these rocks, the formation of Al-free Mg-
34 579 silicates rather than saponite may be indicative of low aluminum availability, favored in large
35 580 lacustrine environments hosted in poorly differentiated volcanic terrains commonly emplaced during
36 581 late stages of continental rifting.
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3 583**ACKNOWLEDGMENT**

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5 584 This work was supported by IPGP, TOTAL (project FR00008189), Agence Nationale de la Recherche
6 585 (France) (ANR DZIANI, grant number ANR-13-BS06-0001), Total Corporate Foundation (project
7 586 755 DZAHA) and one INSU-INTERRVIE grant (grant number AO2013-785992). The Deep Carbon
8 587 Observatory community is thanked here for several informative discussions on the importance of
9 588 studying environments related to magmatic CO₂ emissions. The authors also wish to thank their
10 589 colleagues (C. Leboulanger, C. Bernard, P. Got, E. Fouilland, M. Bouvy, E. Le Floch, V. Grossi and
11 590 D. Sala) for their support and assistance during sampling campaigns on Dziani Dzaha. Last but not
12 591 least, they thank the Air Austral Airline Company and Alexandra and Laurent at the “Les Couleurs”
13 592 Guest House in Mayotte for their valuable assistance and support.
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593 REFERENCES

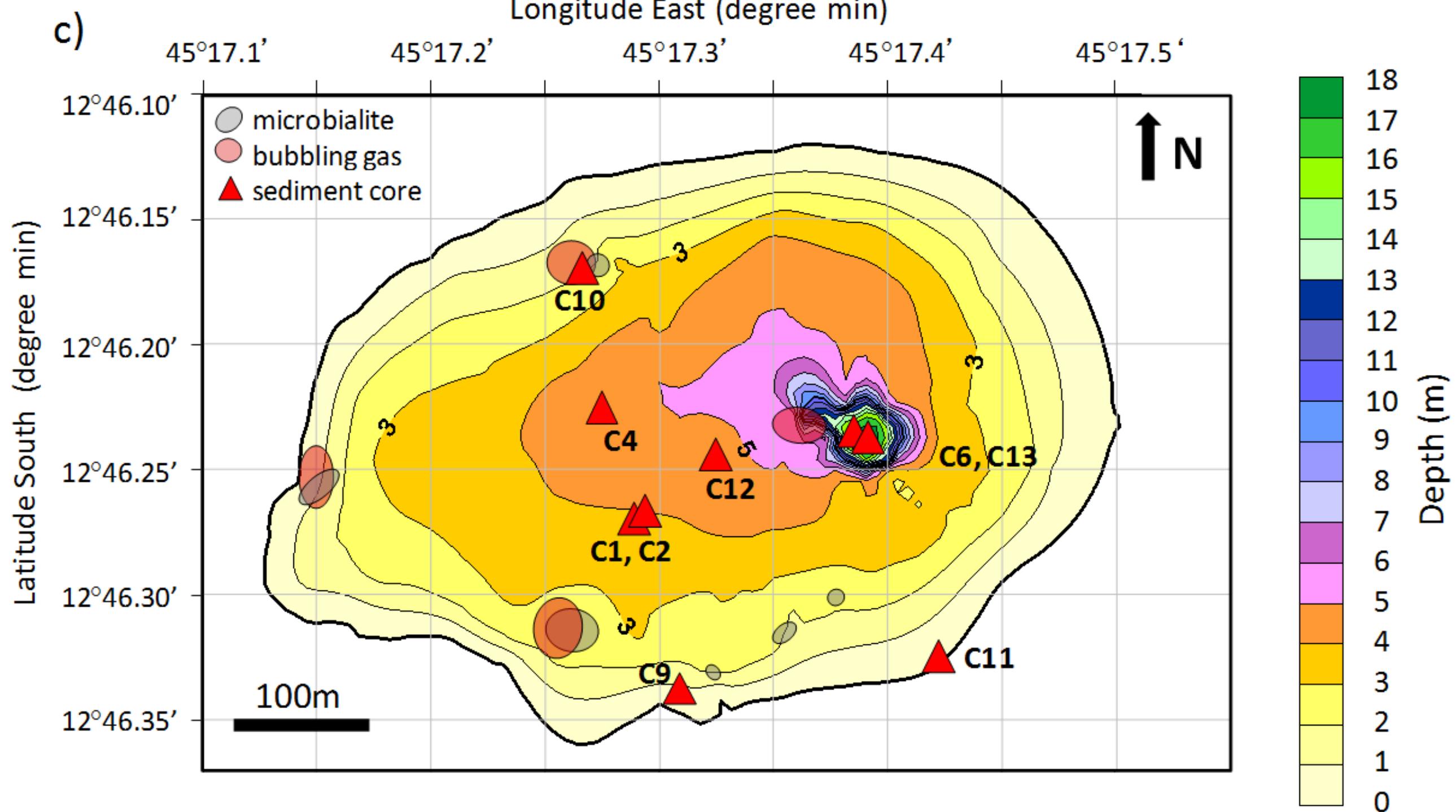
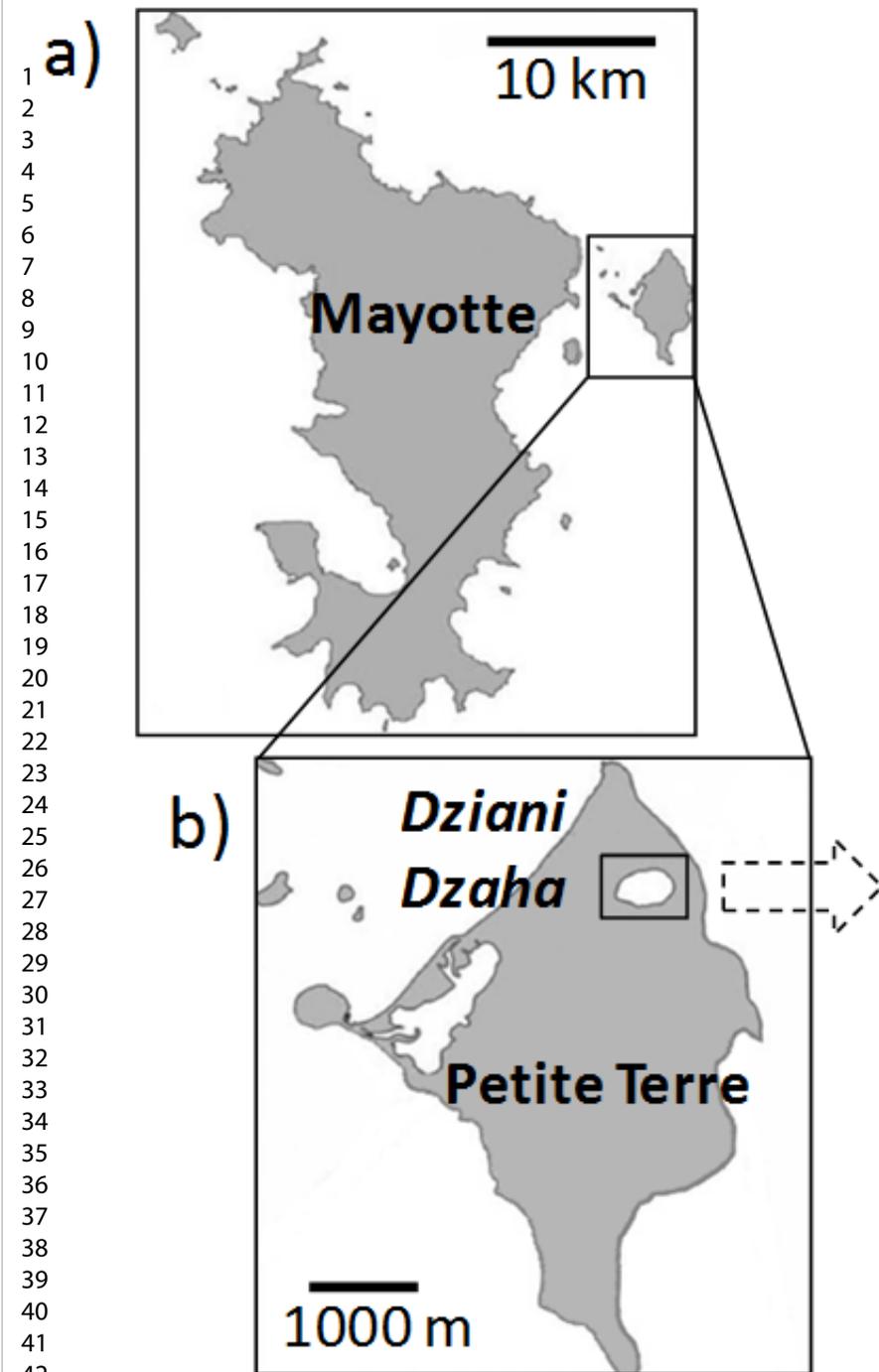
- 594 Alsop G.I. and Marco S. (2011) Soft-sediment deformation within seismogenic slumps of the Dead Sea
595 Basin. *Journal of Structural Geology*, **33**(4), 433-457.
- 596 Arvidson R.S. and Mackenzie F.T. (1999) The dolomite problem; control of precipitation kinetics by
597 temperature and saturation state. *American Journal of Science*, **299**(4), 257-288.
- 598 Assayag N., Rivé K., Ader M., Jézéquel D. and Agrinier P. (2006) Improved method for isotopic and
599 quantitative analysis of dissolved inorganic carbon in natural water samples. *Rapid Communications in Mass
600 Spectrometry*, **20**(15), 2243-2251.
- 601 Banfield J.F., Jones B.F. and Veblen D.R. (1991) An AEM-TEM study of weathering and
602 diagenesis, Abert Lake, Oregon, II. Diagenetic modification of the sedimentary assemblage. *Geochimica and
603 Cosmochimica Acta*, **55**, 2795-2810.
- 604 Bertil D. and Regnault J.M. (1998) Seismotectonic of Madagascar. *Tectonophysics*, **294**, 57-74.
- 605 Bertani R.T. and Carozzi A.V. (1985) Lagoa feia formation (Lower Cretaceous), Campos basin,
606 offshore Brazil: rift valley stage lacustrine carbonate reservoirs-I. *Journal of Petroleum Geology*, **8**(1), 37-58.
- 607 Bertani R.T. and Carozzi A.V. (1985) Lagoa feia formation (Lower Cretaceous), Campos basin,
608 offshore Brazil: rift valley type lacustrine carbonate reservoirs-II. *Journal of Petroleum Geology*, **8**(2), 199-220.
- 609 Blanc P., Lassin A., Piantone P., Azaroual M., Jacquemet N., Fabbri A. and Gaucher E. C. (2012)
610 Thermoddem: A geochemical database focused on low temperature water/rock interactions and waste materials.
611 *Applied Geochemistry*, **27**(10), 2107-2116.
- 612 Brindley G.W. (1966) Ethylene Glycol and Glycerol Complexes of Smectites and Vermiculites. *Clay
613 Minerals* **6**, 237-259.
- 614 Brindley G.W. and Brown G. (1980) Crystal structures of clay minerals and their X-Ray identification.
615 *Mineralogical Society Monograph* **5**, London.
- 616 Bristow T.F., Kennedy M.J., Derkowski A., Droser M.L., Jiang G.Q. and Creaser R.A. (2009)
617 Mineralogical constraints on the palaeoenvironments of the Ediacaran Doushantuo Formation. *Proceedings of
618 the National Academy of Sciences of the USA*, **106**, 13190-13195.
- 619 Broadbent F.E. (1953) The soil organic fraction. *Advances in agronomy*, **5**, 153-183.
- 620 Calvo J.P., Blanc-Valleron M.M., Rodriguez-Arandia J.P., Rouchy J.M. and Sanz M.E. (1999)
621 Authigenic clay minerals in continental evaporitic environments. In: Thiry M. and Simon-Coinçon R. (eds)
622 Palaeoweathering, Palaeosurfaces and Related Continental Deposits. International Association of
623 Sedimentologists, Special Publications, **27**, 129-151.
- 624 Cerling T.E. (1996) Pore water chemistry of an alkaline lake: Lake Turkana, Kenya. In: Johnson, T. C.
625 & Odada, E. O. (eds) Limnology, Climatology and Paleoclimatology of the East African Lakes. Gordon and
626 Breach, Amsterdam, 225-240.
- 627 Chamley H. (1989) *Clay Sedimentology* (Springer, Berlin).
- 628 Christidis G.E. and Koutsopoulou E. (2013) A simple approach to the identification of trioctahedral
629 smectites by X-ray diffraction. *Clay Minerals*, **48**(5), 687-696.

- 1
2
3 630 Coltorti M., Bonadiman C., Hinton R.W., Siena F. and Upton B.G.J. (1999) Carbonatite metasomatism
4 631 of the oceanic upper mantle: evidence from clinopyroxenes and glasses in ultramafic xenoliths of Grande
5 632 Comore, Indian Ocean. *Journal of Petrology*, **40**, 133-165.
- 6
7 633 Darragi F. and Tardy Y. (1987) Authigenic trioctahedral smectites controlling pH, alkalinity, silica and
8 634 magnesium concentrations in alkaline lakes. *Chemical Geology*, **63**, 59–72.
- 9
10 635 Debure M., De Windt L., Frugier P., Gin S. and Vieillard P. (2016) Mineralogy and thermodynamic
11 636 properties of magnesium phyllosilicates formed during the alteration of a simplified nuclear glass. *Journal of*
12 637 *Nuclear Materials*, **475**, 255-265.
- 13
14 638 Debure M., De Windt L., Frugier P. and Gin S. (2013a) HLW glass dissolution in the presence of
15 639 magnesium carbonate: Diffusion cell experiment and coupled modeling of diffusion and geochemical
16 640 interactions. *Journal of Nuclear Materials*, **443**(1), 507-521.
- 17
18 641 Debure M., Frugier P., De Windt L. and Gin S. (2013b) Dolomite effect on borosilicate glass alteration.
19 642 *Applied geochemistry*, **33**, 237-251.
- 20
21 643 Deocampo D.M., Cuadros J., Wing-Dudek T., Olives J. and Amouric M. (2009) Saline lake diagenesis
22 644 as revealed by coupled mineralogy and geochemistry of multiple ultrafine clay phases: Pliocene Olduvai Gorge,
23 645 Tanzania. *American Journal of Science*, 309, 834–858.
- 24
25 646 Galán E. and Pozo M. (2011) Palygorskite and sepiolite deposits in continental environments.
26 647 Description, genetic patterns and sedimentary settings. In: Galán E. and Singer A. (eds) Developments in
27 648 Palygorskite–Sepiolite Research. Developments in Clay Science, 3. Elsevier, Amsterdam, 125–173.
- 28
29 649 Gautier Q., Bénézech P., Mavromatis V. and Schott J. (2014) Hydromagnesite solubility product and
30 650 growth kinetics in aqueous solution from 25 to 75°C. *Geochimica et Cosmochimica Acta*, 138, 1-20.
- 31
32 651 Gérard E., De Goeyse S., Hugoni M., Agogue H., Richard L., Milesi V., Guyot F., Lecourt L.,
33 652 Borensztajn S., Leclerc T., Joseph M., Sarazin G., Jezequel D., Leboulanger C. and Ader M. (2018) Key role of
34 653 Alphaproteobacteria and Cyanobacteria in the formation of stromatolites of Lake Dziani Dzaha (Mayotte,
35 654 Western Indian Ocean). *Front. Microbiol.* **9**, 796.
- 36
37 655 Guggenheim S., Adams J. M., Bain D. C., Bergaya F., Brigatti M. F., Drits V. A., Formoso Mr LL,
38 656 Galán E., Kogure T. and Stanjek H. (2006). Summary of recommendations of nomenclature committees relevant
39 657 to clay mineralogy: report of the Association Internationale pour l'Etude des Argiles (AIPEA) Nomenclature
40 658 Committee for 2006. *Clay Minerals*, **41**(4), 863-877.
- 41
42 659 Hadi J., Tournassat C., Ignatiadis I., Greneche J. M. and Charlet L. (2013) Modelling CEC variations
43 660 versus structural iron reduction levels in dioctahedral smectites. Existing approaches, new data and model
44 661 refinements. *Journal of colloid and interface science*, **407**, 397-409.
- 45
46 662 Hay R.L., Guldman S.G., Matthews J.C., Lander R.H., Duffin M.E. and Kyser T.K. (1991) Clay
47 663 mineral diagenesis in core KM-3 of Searles Lake, California. *Clays and Clay Minerals*, **39**(1), 84-96.
- 48
49 664 Hicks L.J., Bridges J.C. and Gurman S.J. (2014) Ferric saponite and serpentine in the nakhlite martian
50 665 meteorites. *Geochim. Cosmochim. Ac.*, **136**, 194-210.
- 51
52 666 Hover V.C., Walter L.M., Peacor D.R. and Martini A.M. (1999) Mg-smectite authigenesis in a marine
53 667 evaporative environment, Salina Ometepec, Baja California. *Clays and Clay Minerals*, **47**, 252–268.
- 54
55 668 Huang J., Chu X., Lyons T. W., Planavsky N. J. and Wen H. (2013) A new look at saponite formation
56 669 and its implications for early animal records in the Ediacaran of South China. *Geobiology*, **11**(1), 3-14.

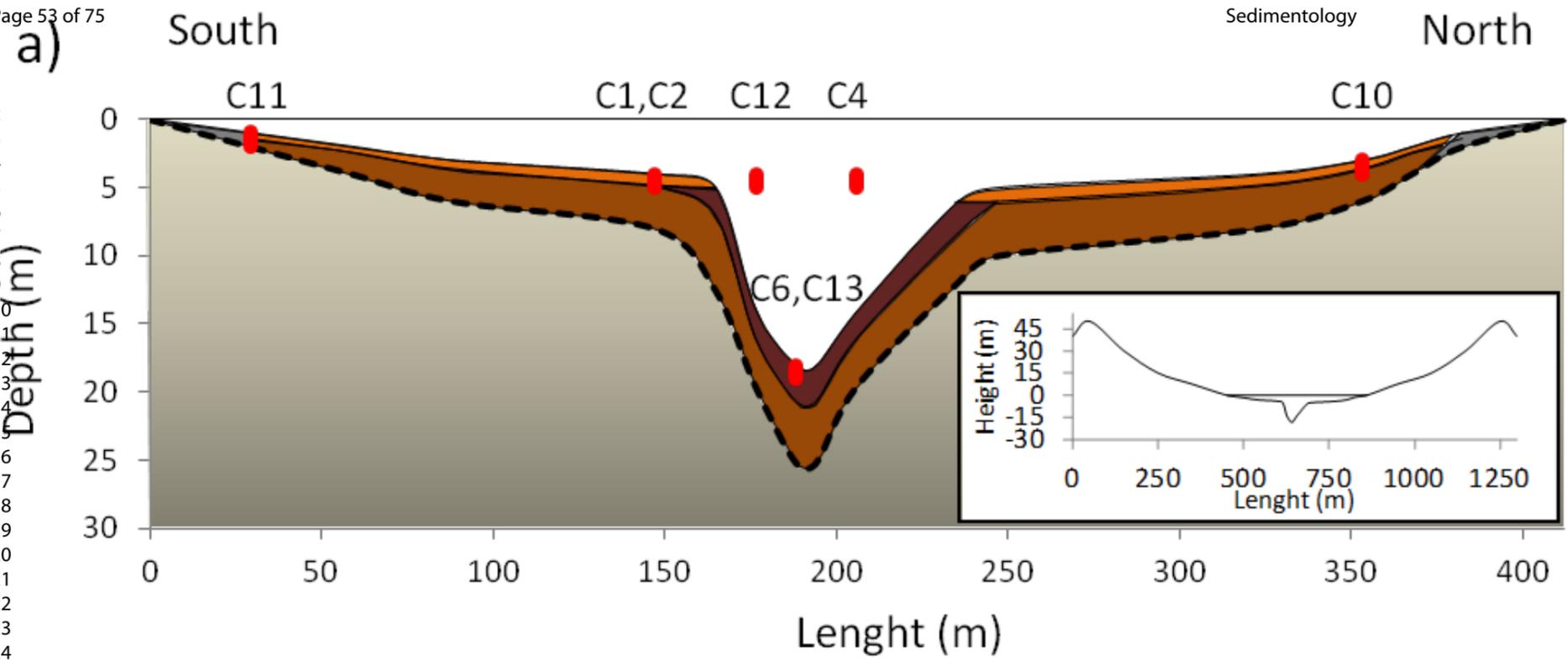
- 1
2
3 670 Jones B.F. (1986) Clay mineral diagenesis in lacustrine sediments. In: Mumpton, F. A. (ed.) Studies in
4 671 Diagenesis. United States Geological Survey, Bulletin, **1578**, 291–300.
- 5
6 672 Jones B.F. and Weir A.H. (1983) Clay minerals of Lake Abert, an alkaline, saline lake. *Clays and Clay*
7 673 *Minerals*, **31**, 161-172.
- 8
9 674 Kodama H., De Kimpe C.R. and Dejou J. (1988) Ferrian saponite in a gabbro saprolite at Mont
10 675 Mégantic, Quebec. *Clays Clay Miner.*, 36(2), 102-110.
- 11
12 676 Lebeau O., Busigny V., Chaduteau C. and Ader M. (2014) Organic matter removal for the analysis of
13 677 carbon and oxygen isotope compositions of siderite. *Chemical Geology*, **372**, 54-61.
- 14
15 678 Leboulanger C., Agogu e H., Bernard C., Bouvy M., Carr e C., Cellamare M., *et al.* (2017) Microbial
16 679 Diversity and Cyanobacterial Production in Dziani Dzaha Crater Lake, a Unique Tropical Thalassohaline
17 680 Environment. *PLoS ONE* **12**(1): e0168879.
- 18
19 681 Lerouge C., Gaboreau S., Grangeon S., Claret F., Warmont F., Jenni A., Cloet V. and M ader U. (2017)
20 682 In situ interactions between Opalinus Clay and Low Alkali Concrete, *Physics and Chemistry of the Earth*, **99**, 3-
21 683 21.
- 22
23 684 Lewis Jr, W.M. (2011) Global primary production of lakes: 19th Baldi Memorial Lecture. *Inland*
24 685 *Waters*, **1**(1), 1-28.
- 25
26 686 L opez-Archilla A.I., Moreira D., L opez-Garc a P. and Guerrero C. (2004) Phytoplankton diversity and
27 687 cyanobacterial dominance in a hypereutrophic shallow lake with biologically produced alkaline pH.
28 688 *Extremophiles*, **8**(2), 109-115.
- 29
30 689 Martini A.M., Walter L.M., Lyons T.W., Hover V.C. and Hansen J. (2002) Significance of
31 690 earlydiagenetic water-rock interactions in a modern marine siliciclastic/evaporite environment: Salina Ometepec,
32 691 Baja California. *Geol. Soc. Am. Bull.* **114**, 1055–1069.
- 33
34 692 Meunier A. (2005) in *Clays*. (Springer, Berlin).
- 35
36 693 Millot G. (1970) in *Geology of clays* (Springer-Verlag).
- 37
38 694 Moug enot D., Hernandez J. and Virlogeux P. (1989) Structure et volcanisme d'un rift sous-marin; le
39 695 fosse des Kerimbab (marge nord-mozambique). Bulletin de la Soci et  G eologique de France, (2), 401-410.
- 40
41 696 Moore D.M. and Reynolds R.C. (1989) X-ray Diffraction and the Identification and Analysis of Clay
42 697 Minerals (Vol. 332). New York: Oxford university press.
- 43
44 698 Nougier J., Cantagrel J.M. and Karche J.P. (1986) The Comores archipelago in the western Indian
45 699 Ocean: volcanology, geochronology and geodynamic setting. *Journal of African Earth Sciences*, **5**, 135-145.
- 46
47 700 Orsini L. and Remy J.C. (1976) Utilisation du chlorure de cobaltihexamine pour la d etermination
48 701 simultan ee de la capacit  d' change et des bases  changeables des sols. *Sci. Sol*, **4**, 269-275.
- 49
50 702 Ostrom M.E. (1961) Separation of clay minerals from carbonate rocks by using acid. *Journal of*
51 703 *Sedimentary Research*, **31**(1).
- 52
53 704 Pace A., Bourillot R., Bouton A., Vennin E., Galaup S., Bundeleva I., Patrier P., Dupraz C., Thomazo
54 705 C., Sansjofre P., Yokoyama Y., Franceschi M., Anguy Y., Pigot L., Virgone A. and Visscher P.T. (2016)
55 706 Microbial and diagenetic steps leading to the mineralisation of Great Salt Lake microbialites. *Scientific reports*,
56 707 **6**.

- 1
2
3 708 Parkhurst D.L. and Appelo C.A.J. (2013) Description of input and examples for PHREEQC version 3: a
4 709 computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical
5 710 calculations (No. 6-A43). US Geological Survey.
- 6
7 711 Pelleter A.A, Caro M., Cordier C., Bachélery P., Nehlig P., Debeuf D. and Arnaud N. (2014) Melilite-
8 712 bearing lavas in Mayotte (France): An insight into the mantle source below the Comores. *Lithos*, **208-209**, 281-
9 713 297.
- 10
11 714 Post J.L. (1984) Saponite from near Ballarat, California. *Clays Clay Miner.*, 32(2), 147.
- 12
13 715 Racki G. and Cordey F. (2000) Radiolarian palaeoecology and radiolarites: is the present the key to the
14 716 past? *Earth-Science Reviews*, **52**(1), 83-120.
- 15
16 717 Rehim H., Mizusaki A.M.P., Carvalho M.D. and Monteiro M. (1986) Talco e estevensita na formação
17 718 lagoa feia da bacia de campos--possíveis implicações no ambiente deposicional. In: SBG, congresso brasileiro de
18 719 geologia, 34, 416-425.
- 19
20 720 Sayles F L. and Fyfe W.S. (1973) The crystallization of magnesite from aqueous solution. *Geochimica*
21 721 *et Cosmochimica Acta*, **37**(1), 87-96.
- 22
23 722 Setti M., Marinoni L. and Lopez-Galindo A. (2004) Mineralogical and geochemical characteristics
24 723 (major, minor, trace elements and REE) of detrital and authigenic clay minerals in a Cenozoic sequence from
25 724 Ross Sea, Antarctica. *Clay Minerals*, **39**, 405-421.
- 26
27 725 Siever R. (1992) The silica cycle in the Precambrian. *Geochimica et Cosmochimica Acta*, **56**(8), 3265-
28 726 3272.
- 29
30 727 Simkiss K. (1964) Variation of the crystallization form of calcium carbonate from artificial sea water.
31 728 *Nature*, **201**, 492-493.
- 32
33 729 Stoessel R. K. (1988) 25°C and 1 atm dissolution experiments of sepiolite and kerolite. *Geochim. et*
34 730 *Cosmochim. Ac.* **52**(2), 365-374.
- 35
36 731 Suquet H., de la Calle C. and Pezerat H. (1975) Swelling and Structural Organization of Saponite. *Clays*
37 732 *and Clay Minerals* **23**, 1-9.
- 38
39 733 Taft W.H. (1967) Physical chemistry of formation of carbonates. Elsevier, Amsterdam.
- 40
41 734 Tissot B.P. and Welte D.H. (1984) Diagenesis, catagenesis and metagenesis of organic matter. In
42 735 *Petroleum Formation and Occurrence* (pp. 69-73). Springer Berlin Heidelberg.
- 43
44 736 Tosca N.J. (2015) Geochemical pathways to Mg-clay formation. In: Pozo M. and Galán E. (eds)
45 737 *Magnesian Clays: Characterization, Origins and Applications*. AIPEA (Association Internationale pour l'Etude
46 738 des Argiles), Special Publications, **2**, 283-329.
- 47
48 739 Tosca N.J., Macdonald F.A., Strauss J.V., Johnston D.T. and Knoll A.H. (2011) Sedimentary talc in
49 740 Neoproterozoic carbonate successions. *Earth and Planetary Science Letters*, **306**(1-2), 11-22.
- 50
51 741 Tosca N.J. and Wright V.P. (2015) Diagenetic pathways linked to labile Mg-clays in lacustrine
52 742 carbonate reservoirs: a model for the origin of secondary porosity in the Cretaceous pre-salt Barra Velha
53 743 Formation, offshore Brazil. Geological Society, London, Special Publications, 435, SP435-1.
- 54
55 744 Treguer P., Nelson D.M., Van Bennekom A.J., DeMaster D.J., Leynaert A. and Quéguiner B. (1995)
56 745 The silica balance in the world ocean: a reestimate. *SCIENCE-NEW YORK THEN WASHINGTON*, 375-375.
- 57
58 746 Van Denburgh A.S. (1975) in: Solute Balance at Abert and Summer Lake, South-central Oregon. (US
59 747 Geological Survey, Washington), Professional paper 502-C.

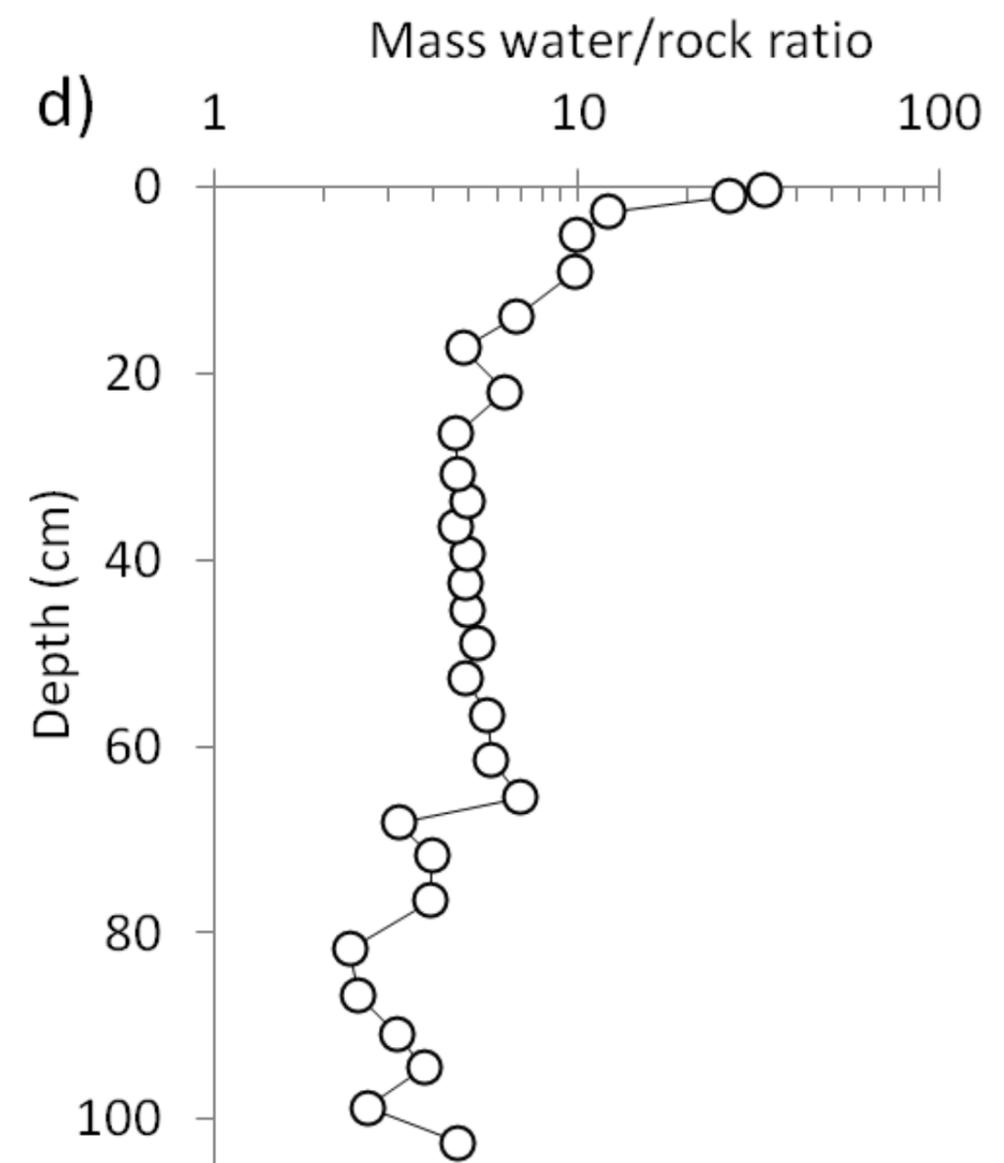
- 1
2
3 748 Vicente M.A., Suárez M., López-González J.D.D. and Banares-Munoz M.A. (1996) Characterization,
4 749 surface area, and porosity analyses of the solids obtained by acid leaching of a saponite. *Langmuir*, **12**(2), 566-
5 750 572.
- 6
7 751 Walker G.F. (1958) Reactions of expanding-lattice clay minerals with glycerol and ethylene glycol.
8 752 *Clay Minerals Bulletin*, **3**, 302-313.
- 9
10 753 Weaver C.E. (1989) *Clays, Muds, and Shales* (Elsevier, Amsterdam).
- 11
12 754 Weaver C.E. and Beck K.C. (1977) Miocene of the S.E. United States: A model for chemical
13 755 sedimentation in a peri-marine environment. *Sedimentary Geology*, **17**, 1-234.
- 14
15 756 White R. and McKenzie D. (1989) Magmatism at rift zones: the generation of volcanic continental
16 757 margins and flood basalts. *Journal of Geophysical Research: Solid Earth*, **94**(B6), 7685-7729.
- 17
18 758 Wilson M. (1992) Magmatism and continental rifting during the opening of the South Atlantic Ocean: a
19 759 consequence of Lower Cretaceous super-plume activity? Geological Society, London, Special Publications,
20 760 **68**(1), 241-255.
- 21
22 761 Wright V.P. (2012) Lacustrine carbonates in rift settings: the interaction of volcanic and microbial
23 762 processes on carbonate deposition. Geological Society, London, Special Publications, **370**(1), 39-47.
- 24
25 763 Wright V.P. and Barnett A. (2015) An abiotic model for the development of textures in some South
26 764 Atlantic early Cretaceous lacustrine carbonates. In: Bosence D.W.J., Gibbons K.A., Le Heron D.P., Morgan
27 765 W.A., Pritchard T. and Vining B.A. (eds) *Microbial Carbonates in Space and Time: Implications for Global
28 766 Exploration and Production*. Geological Society, London, Special Publications, 418, 209–219.
- 29
30 767 Yuretich R.F. and Cerling T.E. (1983) Hydrogeochemistry of Lake Turkana, Kenya: Mass balance and
31 768 mineral reactions in an alkaline lake. *Geochimica and Cosmochimica Acta*, **47**, 1099–1109.
- 32
33 769 Zeyen N., Benzerara K., Li J., Groleau A., Balan E., Estève I., Tavera R., Moreira D. and López-García
34 770 P. (2015) Formation of low-T hydrated silicates in modern microbialites from Mexico and implications for
35 771 microbial fossilization. *Frontiers in Earth Science*, **3**, 64.
- 36
37 772 Zeyen N., Daval D., Lopez-Garcia P., Moreira D., Gaillardet J. and Benzerara K. (2017) Geochemical
38 773 Conditions Allowing the Formation of Modern Lacustrine Microbialites. *Procedia Earth and Planetary Science*,
39 774 **17**, 380-383.
- 40
41 775 Zinke J., Reijmer J.J.G. and Thomassin B.A. (2003) Systems tracts sedimentology in the lagoon of
42 776 Mayotte associated with the Holocene transgression. *Sedimentary Geology*, **160**, 57-784.
- 43
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45
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47
48
49
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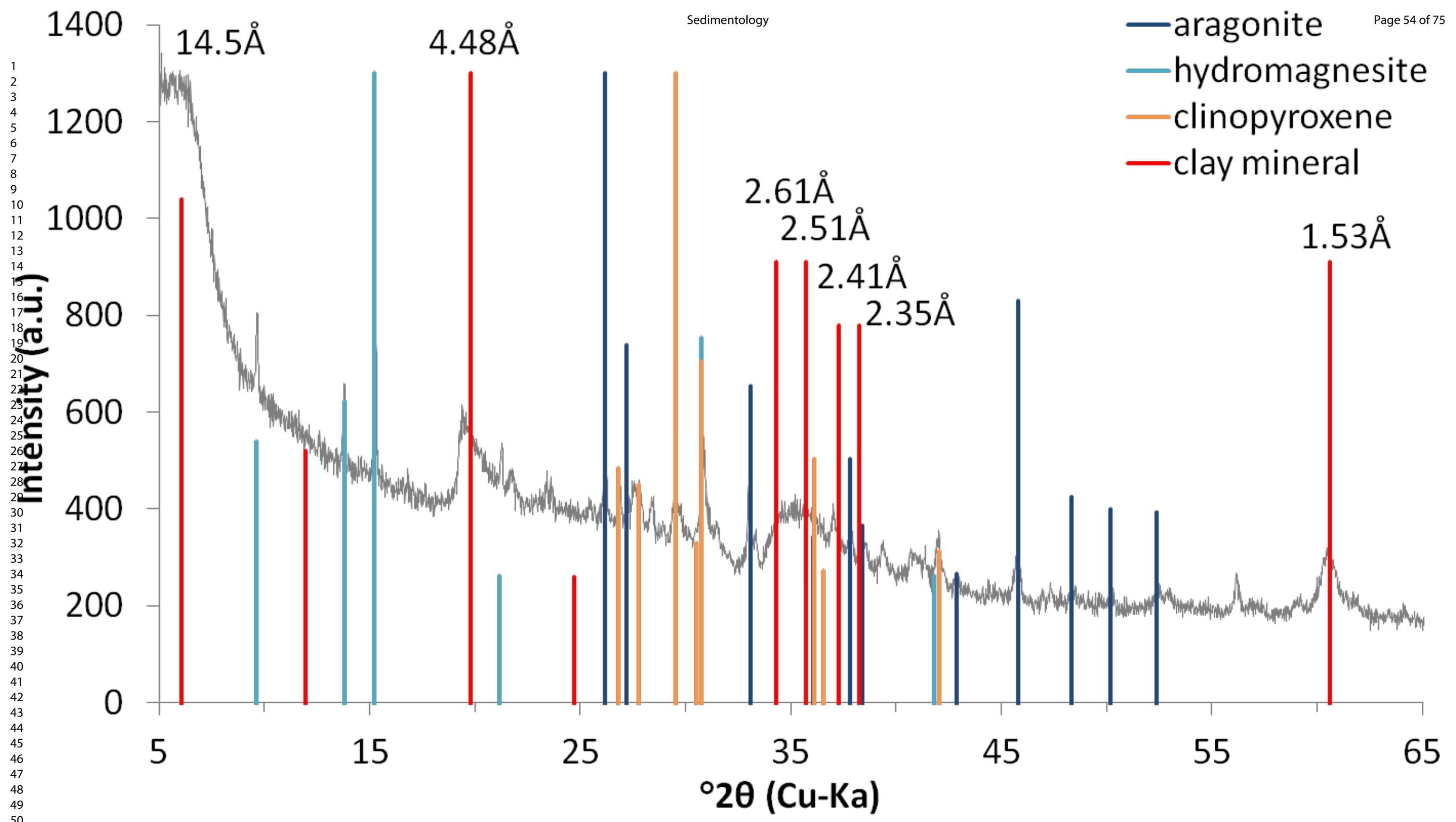


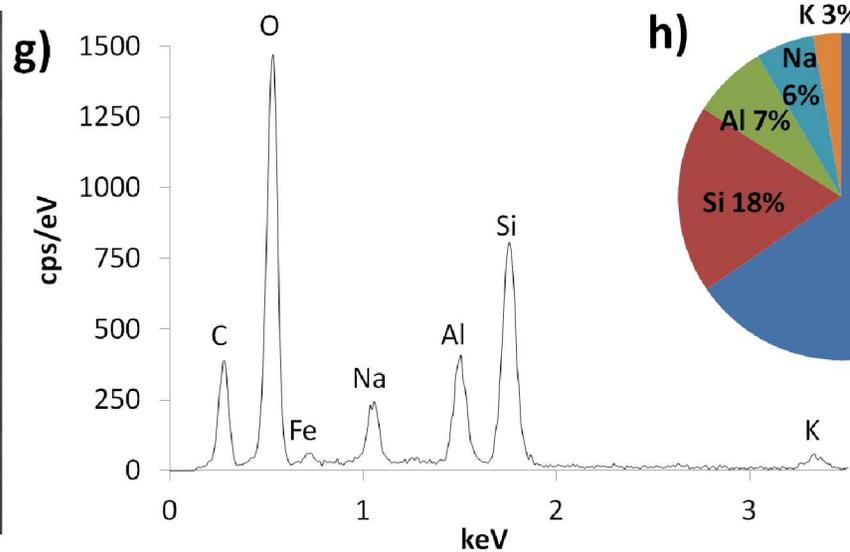
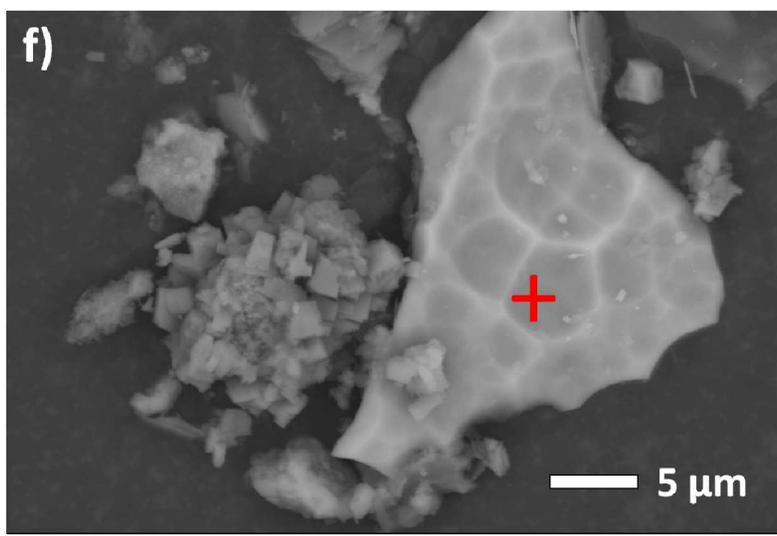
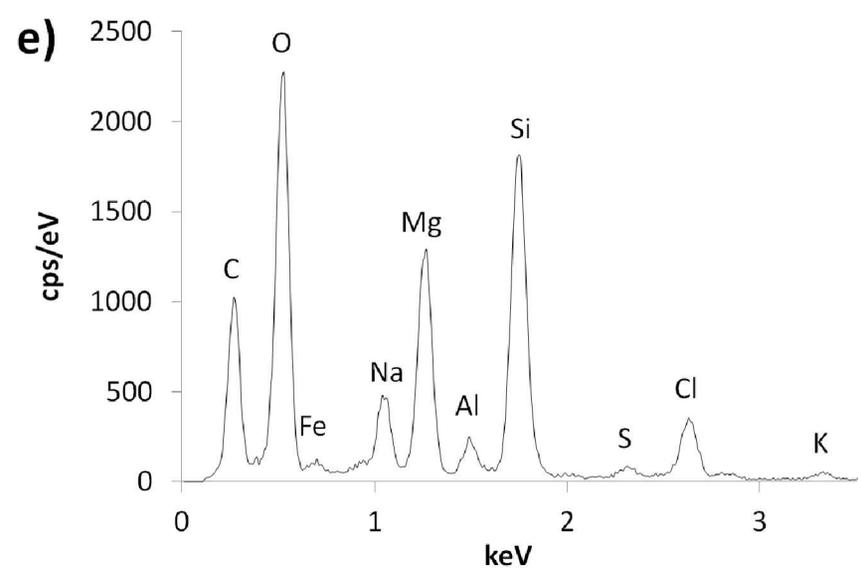
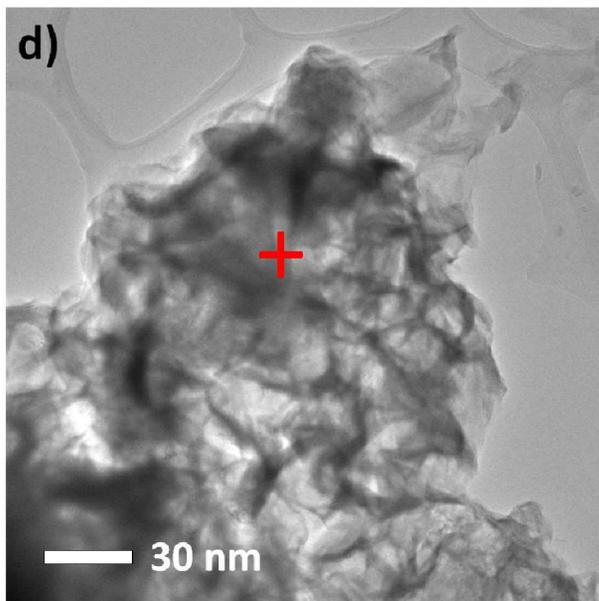
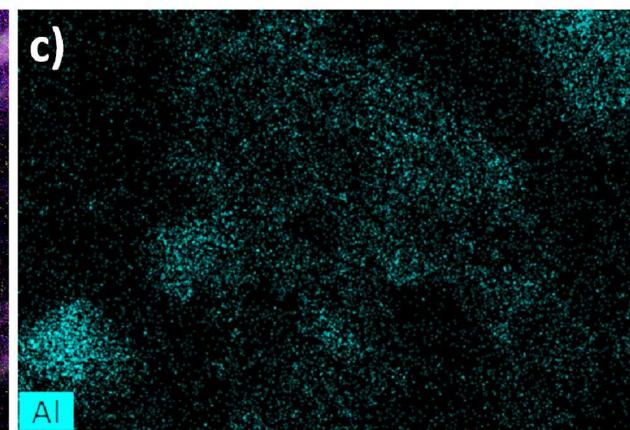
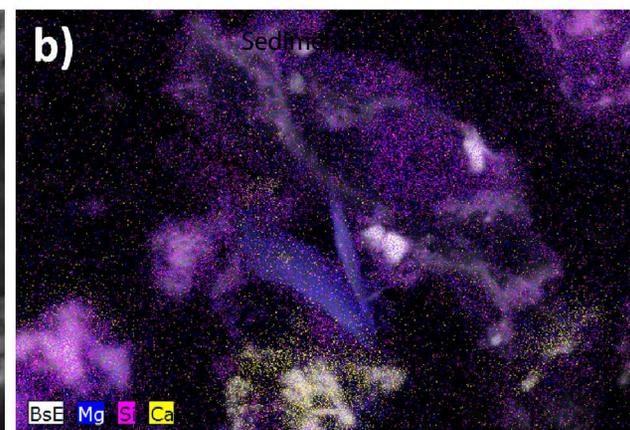
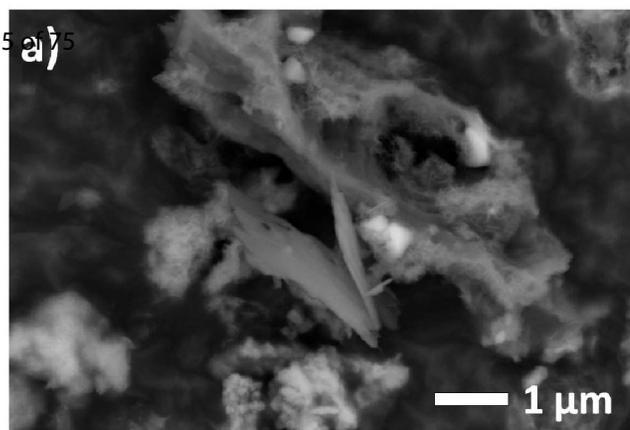
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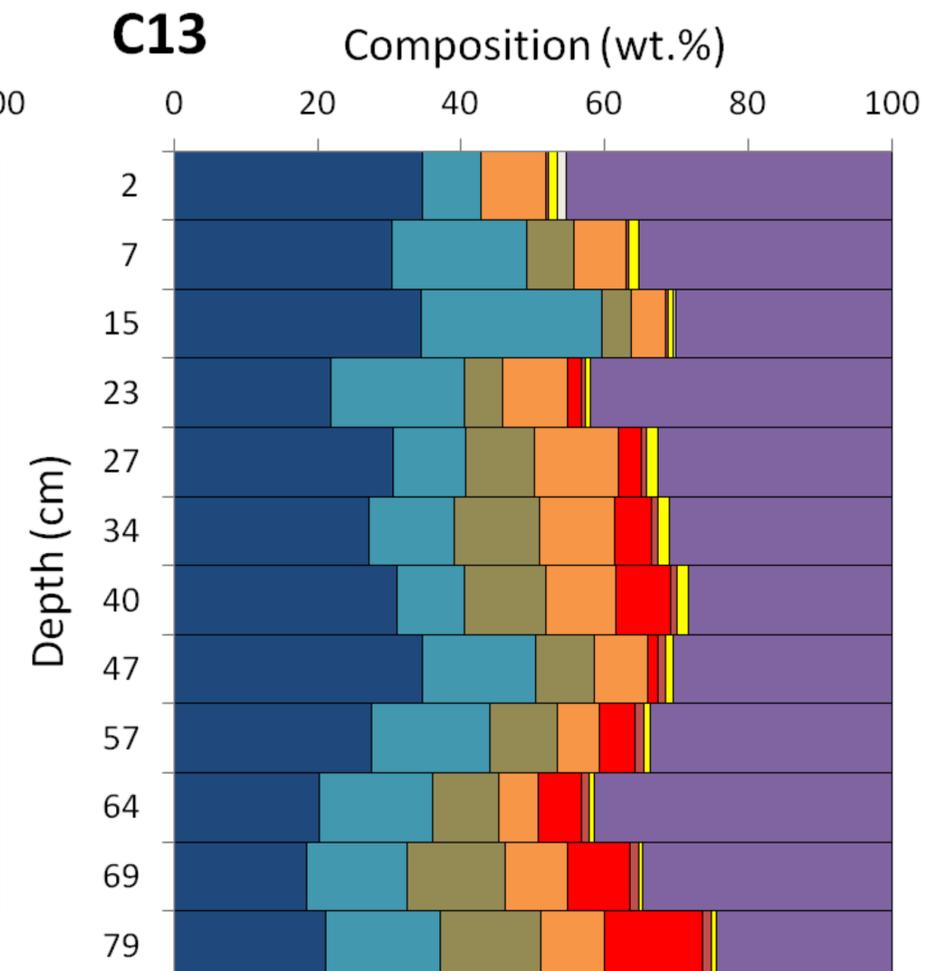
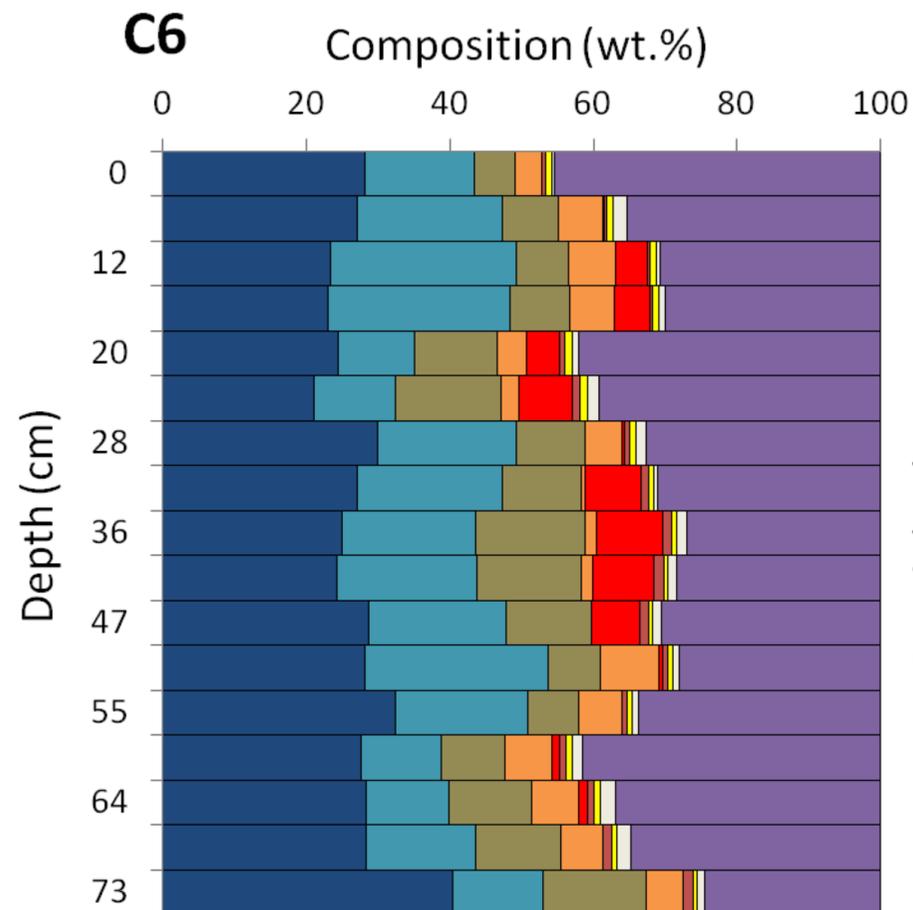
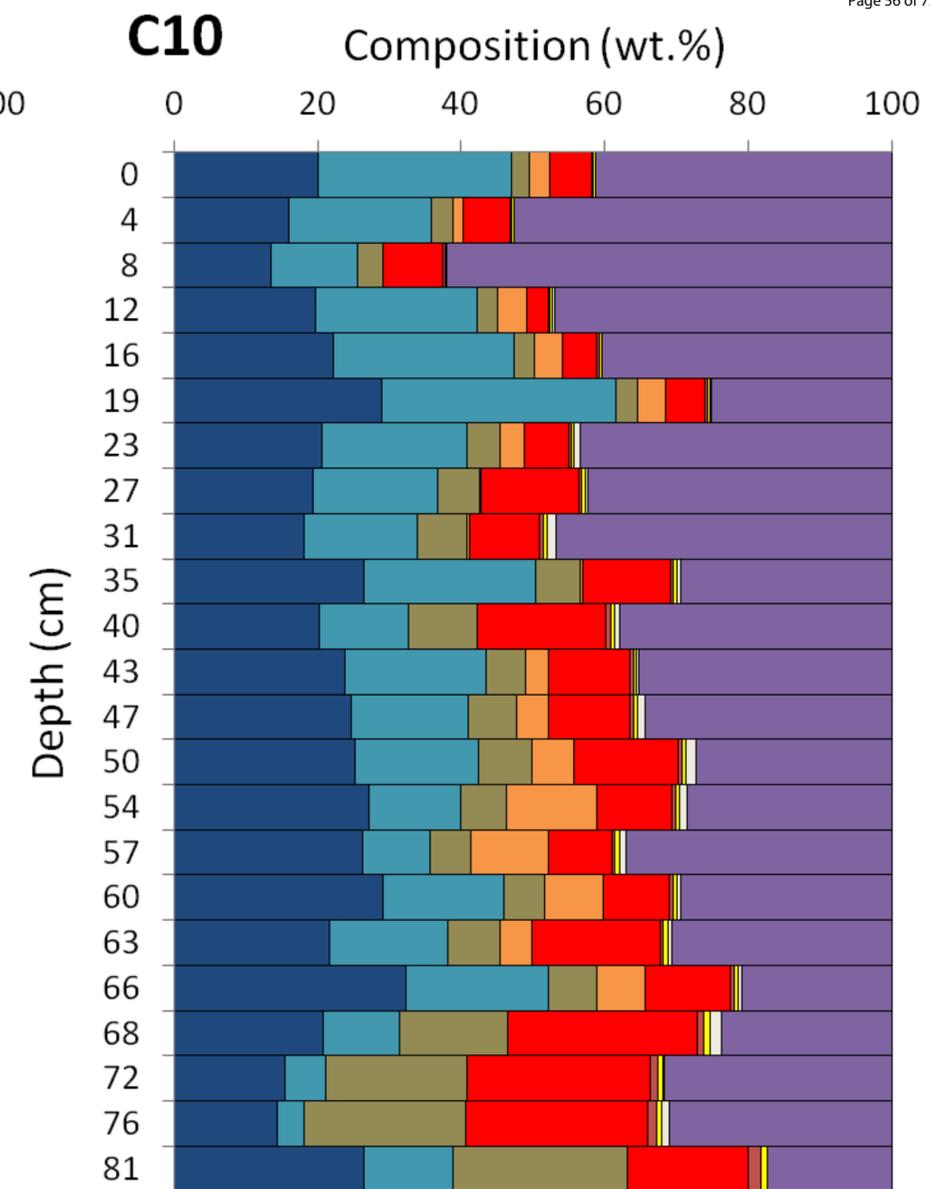
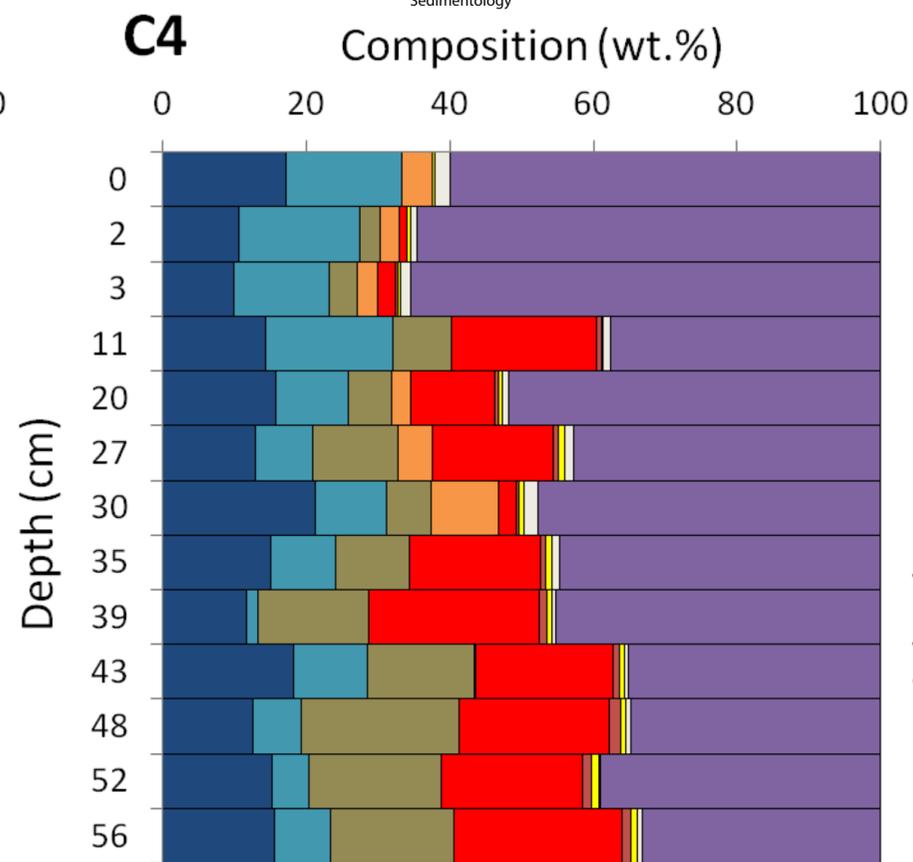
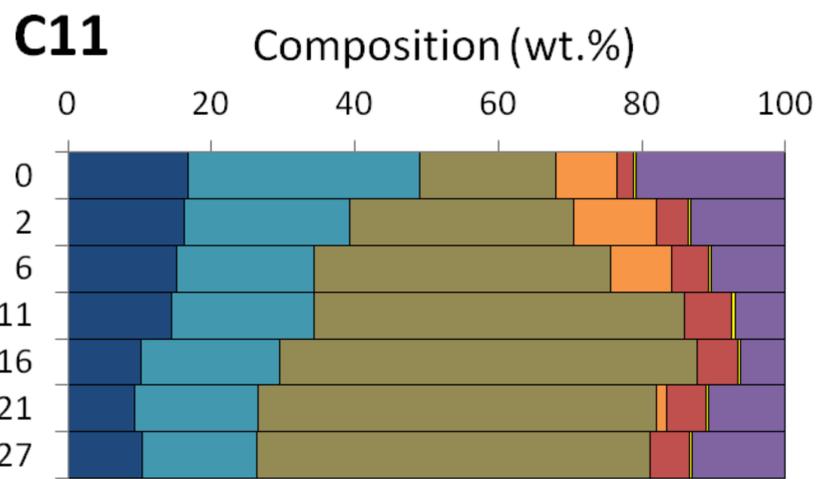
- Greyish shoreline sediment of millimeter grain size
- Light brown, highly laminated, gelatinous sediment of high water/rock weight ratio (>4)
- Slumped gelatinous sediment
- Dark brown, poorly laminated, gelatinous sediment of lower water/rock weight ratio (<4)
- Basement/volcanic rocks
- Erosive limit between sediment and basement
- Sediment cores (location of sediment cores projected onto the N-S cross section)

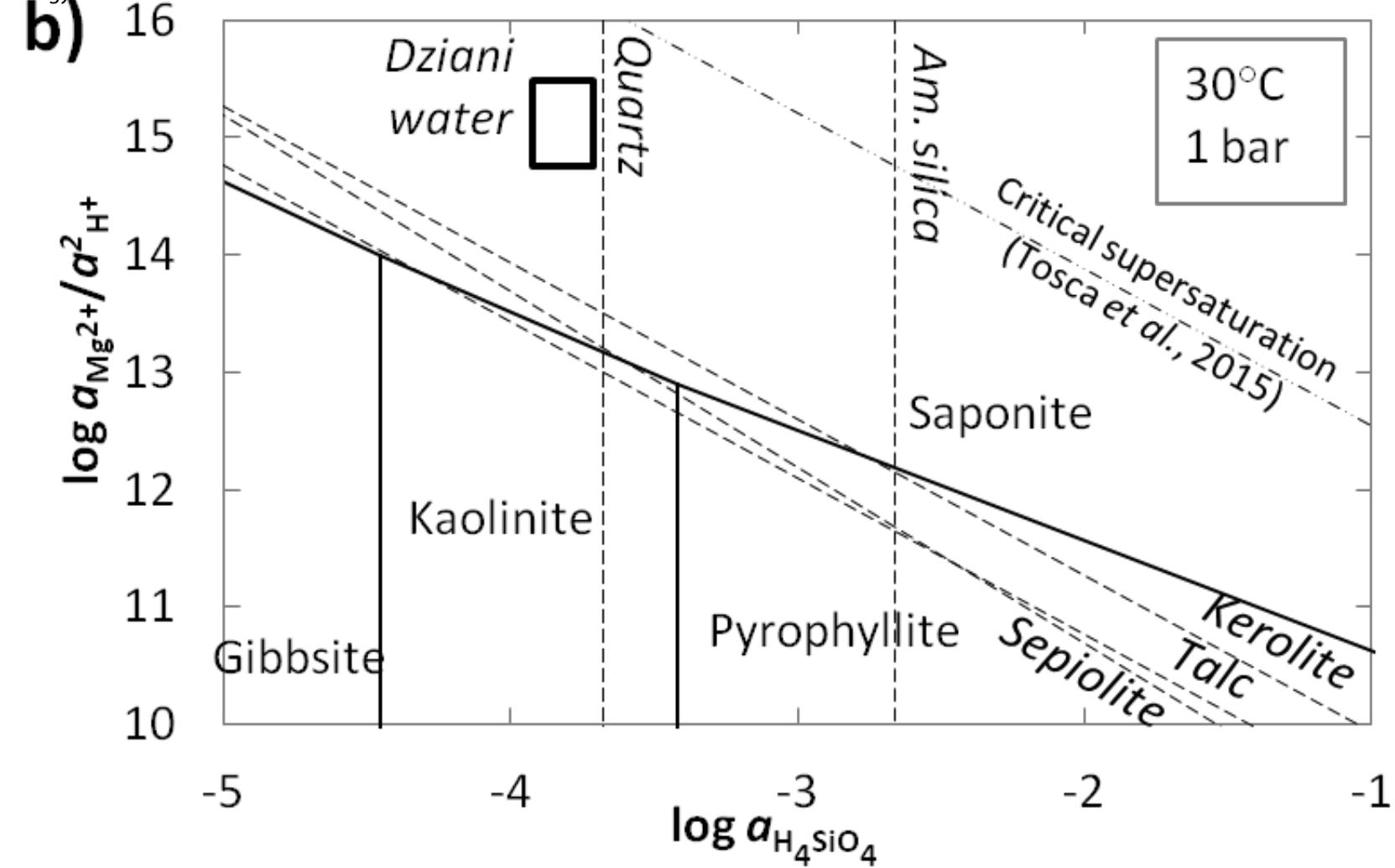
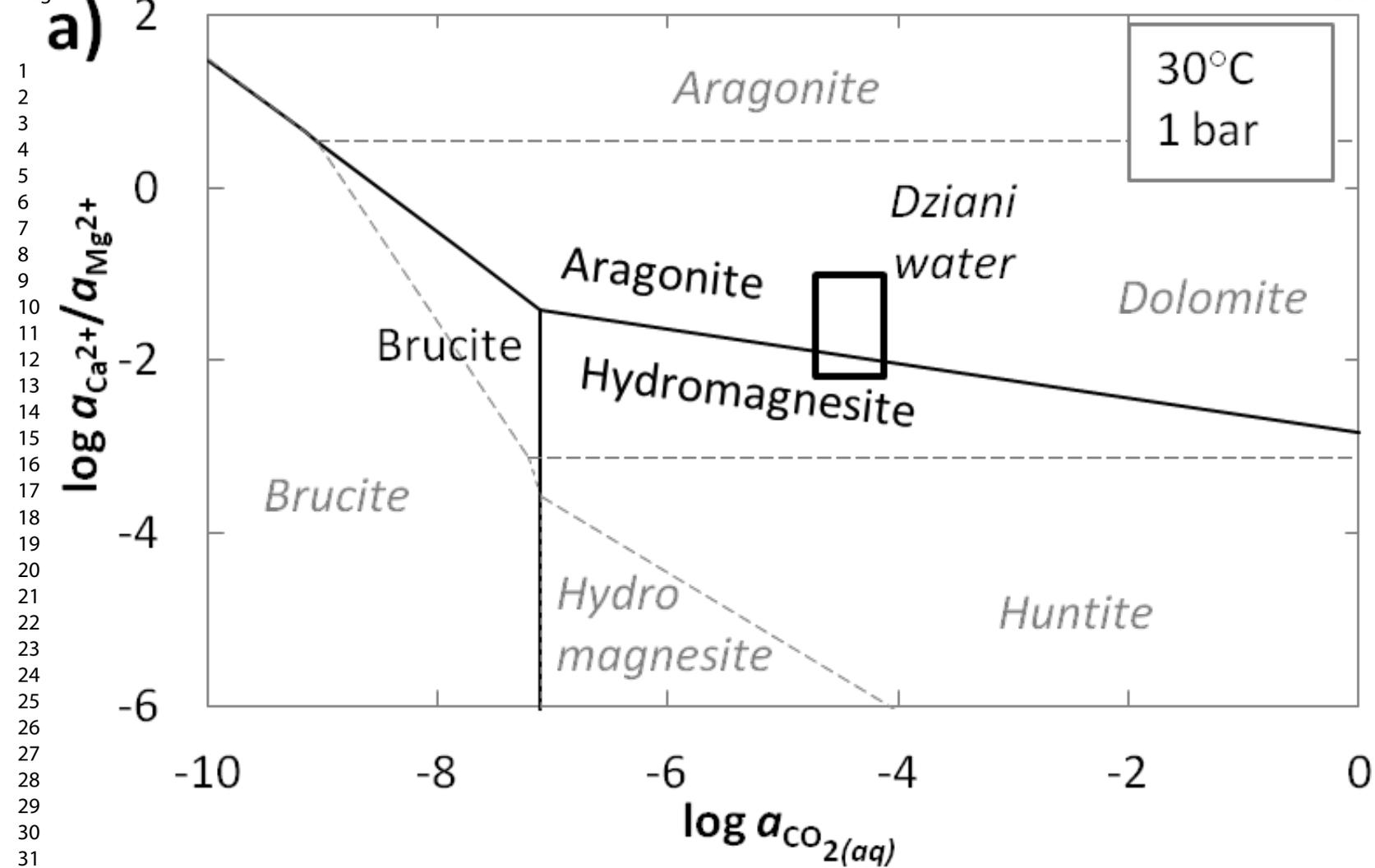






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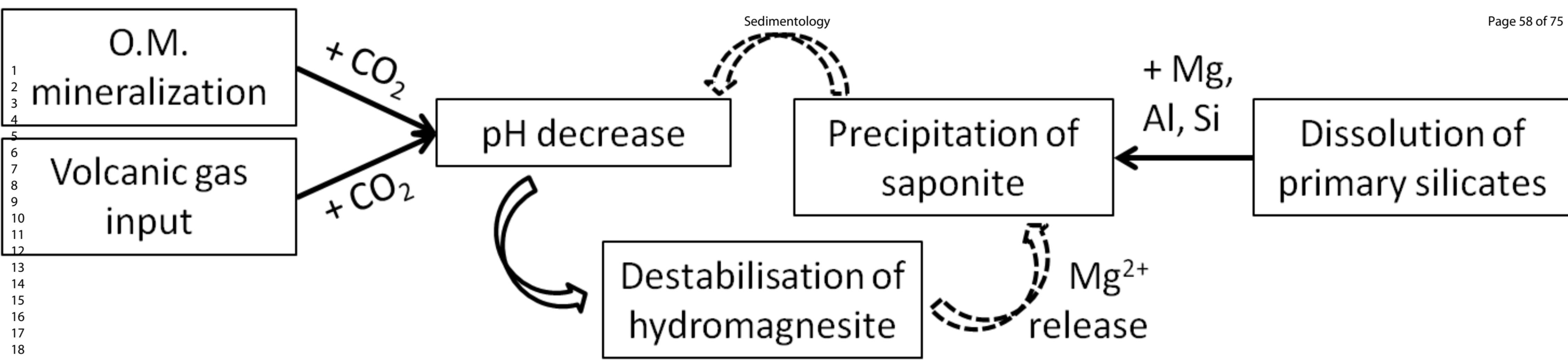


Table 1. Method for quantification of mineral phases

Mineral	Chemical formula	Calculation*
Halite	NaCl	Halite = [Cl]
Alkaline feldspars	$\text{Na}_{0.7}\text{K}_{0.3}\text{AlSi}_3\text{O}_8$	Alk feld = [K]/0.3
Saponite	$\text{K}_{0.01}\text{Mg}_{0.12}\text{Ca}_{0.02}\text{Na}_{0.28}(\text{Mg}_{2.22}\text{Fe}_{0.18}\text{Al}_{0.28})$ $(\text{Si}_{3.61}\text{Al}_{0.39})\text{O}_{10}(\text{OH})_2$	Sap = ([Al] - Alk feld)/0.67
Clinopyroxene	$(\text{Ca}_y\text{Mg}_{1-y})\text{SiO}_3$	Px = [Si] - 3*Alk feld - 3.61*Sap
Hydromagnesite	$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot (\text{H}_2\text{O})_4$	Hydromag = ([Mg] - 2.34*Sap - (1 - y)*Px)/5
Aragonite	CaCO_3	Ara = ([Ca] - y*Px - 0.02*Sap)
Pyrite	FeS_2	Pyr = [S]/2
Magnetite	Fe_3O_4	Mag = ([Fe] - Pyr - 0.18*Sap)/3

*[X] are the concentrations in mol.% of Cl, K, Al, Si, Mg, Ca, S and Fe measured with XRF.

Table 2. Refined composition of saponite in sediment core C4 (in weight %)

Sample	According to EPMA								According to exchanged cations			
	Al	Ca	Fe	K	Mg	Mn	Na	Si	Na	K	Ca	Mg
C4	3.65	0.20	2.01	0.07	11.62	0.07	0.70	20.78	0.65	0.02	0.04	0.15

SUPPORTING INFORMATION

Table A1. Sediment cores and rock samples of the Dziani Dzaha

Sample	GPS coordinates (degree min)	
	Latitude South	Longitude East
<i>Sediment cores</i>		
DZ12-4 C1	S 12°46.269'	E 45°17.288'
DZ12-4 C2	S 12°46.269'	E 45°17.288'
DZ14-4 C4	S 12°46.223'	E 45°17.275'
DZ14-10 C6	S 12°46.235'	E 45°17.392'
DZ14-10 C9	S 12°46.337'	E 45°17.310'
DZ14-10 C10	S 12°46.169'	E 45°17.265'
DZ14-10 C11	S 12°46.325'	E 45°17.425'
DZ16-8 C12	S 12°46.245'	E 45°17.335'
DZ16-8 C13	S 12°46.235'	E 45°17.392'
<i>Volcanic catchment</i>		
DZ14-10 R1	-	-
DZ14-10 R2	-	-
DZ14-10 R3	-	-
DZ14-10 R4	-	-
DZ14-10 R5	-	-
DZ14-10 R6	-	-
DZ16-8 R1	S 12°46.520'	E 45°17.472'
DZ16-8 R2	S 12°46.532'	E 45°17.475'
DZ16-8 R3	S 12°46.582'	E 45°17.365'
DZ16-8 R4	S 12°46.318'	E 45°17.537'
DZ16-8 R5	S 12°46.318'	E 45°17.537'
DZ16-8 R6	S 12°46.318'	E 45°17.537'

Table A2. Total carbon content and carbon isotope composition of the sediment cores

Depth (cm)	TC (wt %)	$\delta^{13}\text{C}$ TC (‰)	$\delta^{13}\text{C}$ TOC (‰)	$\delta^{13}\text{C}$ TIC (‰)	Calculated TOC (wt %)*	Calculated organic matter (wt.%)*
<i>DZ12-4 C1</i>						
5 - 7,5	36.8	-15.6	-	-	38.8	73.7
7,5 - 8,5	40.0	-14.4	-	-	40.4	76.8
8,5 - 11	35.1	-14.2	-	-	35.3	67.1
-	29.9	-13.5	-	-	29.4	55.9
16 - 18	23.1	-14.9	-	-	23.8	45.3
18 - 22	17.4	-14.8	-	-	17.9	34.0
22 - 23	17.0	-15.0	-	-	17.5	33.3
23 - 28	29.4	-15.4	-	-	30.7	58.4
28 - 29	22.3	-16.0	-	-	23.8	45.1
29 - 34	20.5	-14.3	-	-	20.7	39.3
34 - 37	18.6	-13.6	-	-	18.3	34.8
37 - 40	19.5	-13.5	-	-	19.1	36.4
<i>DZ12-4 C2</i>						
2,5 - 4,5	33.9	-14.8	-	-	34.9	66.2
4,5 - 7	14.0	-14.8	-	-	14.4	27.3
7 - 10,5	4.0	-17.8	-	-	4.6	8.7
10,5 - 14	3.1	-18.5	-	-	3.5	6.7
14 - 16,5	16.1	-14.9	-	-	16.6	31.5
16,5 - 20	19.1	-14.1	-	-	19.2	36.4
20 - 23,5	13.9	-14.2	-	-	14.0	26.7
23,5 - 27	13.1	-14.3	-	-	13.3	25.2
27 - 30	12.7	-15.2	-	-	13.2	25.1
<i>DZ14-4 C4</i>						
0 - 1	35.2	-10.9	-	-	31.6	60.0
1 - 2	33.1	-	-	-	-	-
2 - 3	37.2	-11.4	-	-	34.0	64.6
3 - 7	39.0	-10.5	-	-	34.5	65.5
7 - 11	33.6	-	-	-	-	-
11 - 14	23.9	-8.8	-	-	19.8	37.6
14 - 16	31.2	-	-	-	-	-
16 - 20	29.9	-	-	-	-	-
20 - 24	23.5	-18.7	-	-	27.2	51.7
24 - 27	19.7	-	-	-	-	-
27 - 30	23.5	-12.7	-	-	22.5	42.8
30 - 35	28.6	-10.3	-	-	25.1	47.7
35 - 39	25.4	-11.8	-	-	23.5	44.7
39 - 43	24.7	-13.0	-	-	23.8	45.3
43 - 48	19.3	-12.7	-	-	18.5	35.1
48 - 52	18.6	-13.5	-	-	18.3	34.8
52 - 56	21.1	-13.3	-	-	20.6	39.1
56 - 60	17.4	-14.1	-	-	17.4	33.1
<i>DZ14-10 C6</i>						
0 - 3	27.3	-10.3	-15.4	16.0	23.9	45.4
8.5 - 12	23.2	-8.0	-14.0	17.2	18.6	35.2
12 - 16	21.2	-6.9	-15.7	-	16.2	30.8
16 - 20	20.8	-6.8	-13.9	15.8	15.8	30.0
20 - 24	26.1	-9.4	-13.1	-	22.1	42.0
24 - 28	23.8	-10.0	-13.2	15.9	20.6	39.2
28 - 32	23.4	-5.9	-13.5	16.3	17.2	32.6
32 - 36	20.6	-7.8	-13.7	-	16.3	31.0
36 - 40	18.2	-7.4	-13.6	16.9	14.2	27.0
40 - 44	18.8	-7.7	-12.6	-	14.9	28.3
44 - 46.5	-	-	-14.2	-	-	-
46.5 - 51	19.7	-8.5	-14.4	-	16.1	30.5
51 - 55	20.1	-6.0	-12.0	-	14.8	28.0
55 - 59	22.7	-7.4	-14.3	-	17.7	33.6

Sedimentology

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59 - 64	24.9	-10.3	-15.1	-	21.8	41.5
64 - 69	22.5	-9.9	-15.0	-	19.4	36.9
69 - 73	21.9	-9.0	-14.8	-	18.3	34.7
73 - 78	17.6	-5.9	-12.9	-	12.8	24.4
<i>DZ14-10 C9</i>						
10 - 14	8.1	-12.6	-14.9	16.3	7.8	14.7
14 - 20	4.7	-12.0	-14.1	-	4.4	8.4
20 - 24	10.7	-12.3	-13.9	-	10.1	19.2
29 - 32	10.8	-11.6	-13.6	-	9.9	18.9
32 - 36	12.7	-13.5	-13.9	-	12.5	23.8
36 - 39	11.7	-11.9	-14.2	-	10.8	20.6
39 - 42	10.9	-12.7	-13.7	-	10.4	19.7
42 - 46	10.0	-12.1	-13.3	-	9.4	17.8
46 - 50	9.4	-9.9	-12.6	-	8.1	15.4
50 - 54	8.6	-11.1	-12.5	-	7.8	14.8
54 - 58	7.1	-12.8	-14.3	-	6.8	13.0
58 - 62	6.7	-12.0	-14.0	-	6.2	11.8
62 - 68	4.9	-12.8	-16.3	-	4.7	8.9
68 - 73	7.4	-9.5	-15.0	-	6.3	11.9
73 - 78	7.9	-	-10.4	-	-	-
<i>DZ14-10 C10</i>						
0 - 4	35.7	-2.2	-	-	21.7	41.2
4 - 8	38.0	-5.8	-	-	27.7	52.6
8 - 12	41.2	-7.8	-	-	32.7	62.1
12 - 16	36.9	-4.1	-	-	24.7	46.9
16 - 19	34.3	-2.6	-	-	21.2	40.4
19 - 23	29.3	2.4	-	-	13.3	25.2
23 - 27	36.5	-2.8	-	-	22.8	43.4
27 - 31	32.3	-4.7	-	-	22.3	42.3
31 - 35	35.8	-4.7	-	-	24.7	46.9
35 - 39.5	32.1	1.5	-	-	15.5	29.4
39.5 - 43	28.4	-5.1	-	-	19.9	37.9
43 - 47	31.3	-1.7	-	-	18.5	35.2
47 - 50	28.0	-3.4	-	-	18.1	34.4
50 - 54	23.3	-2.5	-	-	14.4	27.3
54 - 57	24.9	-2.0	-	-	15.0	28.5
57 - 60	29.6	-3.8	-	-	19.5	37.1
60 - 63	29.9	0.5	-	-	15.5	29.4
63 - 66	25.4	-3.0	-	-	16.1	30.7
66 - 68	23.1	1.7	-	-	11.0	20.9
68 - 72	18.9	-3.9	-	-	12.5	23.8
72 - 76	24.0	-4.9	-	-	16.7	31.8
76 - 81	20.9	-7.4	-	-	16.3	30.9
81 - 86	15.9	-1.3	-	-	9.1	17.3
<i>DZ14-10 C11</i>						
0 - 2	27.6	4.1	-	-	11.0	20.8
2 - 6	15.0	2.1	-	-	6.9	13.1
6 - 11	10.7	0.9	-	-	5.4	10.3
11 - 16	8.6	3.3	-	-	3.6	6.9
16 - 21	7.5	2.9	-	-	3.3	6.2
21 - 27	9.5	-1.7	-	-	5.6	10.7
27 - 33	10.8	-3.0	-	-	6.8	12.9

TC, TOC and TIC are for total carbon, total organic carbon and total inorganic carbon, respectively.

* See section "Material and Method" for details on the calculation

Table A3. Chemical composition of the mineral content of sediment cores

Depth (cm)	Na (wt.%)	Mg (wt.%)	Al (wt.%)	Si (wt.%)	S (wt.%)	Cl (wt.%)	K (wt.%)	Ca (wt.%)	Fe (wt.%)
<i>DZ14-4 C4</i>									
0-1	11.9	54.3	0.4	0.4	0.1	0.3	0.0	1.2	0.0
2-3	9.0	57.8	0.9	0.8	0.1	0.1	0.0	0.8	0.0
3-7	11.0	50.2	1.1	1.1	0.1	0.2	0.0	0.8	0.0
7-11	6.5	53.9	1.9	1.1	0.0	0.1	0.0	0.9	0.0
11-14	6.9	43.9	3.2	2.0	0.0	0.1	0.0	0.7	0.1
14-16	7.6	42.1	2.8	1.6	0.1	0.1	0.0	1.0	0.1
16-20	7.4	50.5	1.3	1.1	0.1	0.1	0.0	1.1	0.0
20-24	7.9	37.4	2.3	2.2	0.1	0.1	0.0	1.1	0.1
24-27	7.7	36.3	1.9	2.5	0.1	0.1	0.0	1.1	0.1
27-30	8.6	32.8	2.8	3.0	0.1	0.1	0.1	0.7	0.1
30-35	10.5	37.7	1.1	1.7	0.1	0.2	0.0	1.3	0.1
35-39	8.3	32.2	3.0	2.8	0.1	0.1	0.1	1.0	0.1
39-43	7.9	26.1	4.5	3.7	0.1	0.1	0.1	0.9	0.2
43-48	7.3	30.0	3.6	3.2	0.1	0.1	0.1	1.0	0.1
48-52	8.5	26.0	4.1	3.8	0.1	0.1	0.1	0.7	0.1
52-56	7.1	24.9	4.5	4.0	0.1	0.0	0.1	1.0	0.2
56-60	7.9	28.7	3.8	3.4	0.1	0.1	0.1	0.9	0.1
<i>DZ14-10 C6</i>									
0 - 3	7.6	39.8	1.1	1.1	0.1	0.0	0.0	2.0	0.1
3 - 6.5	8.6	36.6	2.4	1.8	0.1	0.1	0.1	1.3	0.1
8.5 - 12	11.0	43.5	1.0	1.1	0.1	0.2	0.0	1.3	0.0
12 - 16	6.2	50.3	1.8	1.3	0.1	0.0	0.0	1.0	0.0
16 - 20	7.2	48.5	1.8	1.3	0.1	0.1	0.0	1.0	0.1
20 - 24	11.4	30.4	1.7	2.1	0.2	0.1	0.1	1.6	0.1
24 - 28	11.5	28.8	2.1	2.4	0.1	0.2	0.1	1.3	0.1
28 - 32	10.1	39.4	1.3	1.2	0.1	0.1	0.1	1.6	0.1
32 - 36	7.0	39.0	2.5	1.7	0.1	0.1	0.1	1.5	0.1
36 - 40	8.9	34.8	2.4	2.1	0.1	0.1	0.1	1.2	0.1
40 - 44	8.9	36.5	2.4	2.0	0.1	0.1	0.1	1.2	0.1
44 - 46.5	8.4	22.8	4.0	3.4	0.1	0.1	0.2	1.5	0.2
46.5 - 51	8.3	35.9	2.2	1.7	0.1	0.1	0.1	1.6	0.1
51 - 55	6.3	49.3	1.4	1.1	0.1	0.1	0.0	1.3	0.1
55 - 59	7.7	41.0	1.1	1.2	0.1	0.1	0.0	1.8	0.1
59 - 64	10.1	32.3	1.3	1.7	0.1	0.2	0.1	1.8	0.1
64 - 69	11.3	30.6	1.4	1.9	0.1	0.2	0.1	1.7	0.1
69 - 73	11.5	34.1	1.3	1.6	0.1	0.2	0.1	1.6	0.1
73 - 76	8.7	26.6	1.8	2.0	0.1	0.1	0.1	2.5	0.1
<i>DZ14-10 C9</i>									
0 - 3	0.0	73.2	7.6	0.5	0.0	0.0	0.0	0.6	0.0
6 - 10	0.0	83.9	11.1	0.4	0.0	0.0	0.0	0.2	0.0
10 - 14	4.2	59.7	6.2	1.2	0.0	0.1	0.1	0.2	0.1
14 - 20	5.9	27.9	8.0	3.9	0.1	0.0	0.2	0.3	0.2
20 - 24	2.6	64.6	5.5	1.1	0.0	0.0	0.0	0.4	0.0
24 - 28	2.5	58.3	3.7	1.4	0.0	0.0	0.0	0.6	0.0
28 - 32	3.8	46.0	4.6	2.2	0.0	0.0	0.0	0.7	0.1
32 - 36	3.7	50.0	2.5	1.8	0.0	0.0	0.0	0.9	0.0
36 - 39	0.0	59.9	6.8	1.3	0.0	0.0	0.0	0.7	0.0
39 - 42	2.9	54.5	3.5	1.5	0.0	0.0	0.0	0.8	0.0
42 - 46	2.4	61.8	4.5	1.1	0.0	0.0	0.0	0.6	0.0
46 - 50	0.0	60.7	17.0	1.3	0.0	0.0	0.0	0.4	0.0
50 - 54	2.4	44.5	10.0	2.5	0.0	0.0	0.0	0.3	0.1
54 - 58	2.7	41.2	9.0	2.9	0.0	0.0	0.1	0.4	0.1
58 - 62	3.1	34.3	8.5	3.6	0.1	0.0	0.1	0.5	0.1
62 - 68	4.4	16.1	9.8	8.0	0.1	0.0	0.2	0.2	0.2
68 - 73	4.0	22.6	8.4	5.9	0.1	0.0	0.1	0.5	0.2
73 - 78.5	3.5	26.7	7.9	4.5	0.1	0.0	0.1	0.9	0.1

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<i>DZ14-10 C10</i>										
0-4	0.0	58.8	7.4	0.9	0.0	0.0	0.0	1.0	0.0	
4-8	2.4	54.6	3.6	1.1	0.0	0.0	0.0	1.1	0.0	
8-12	1.9	47.1	6.0	1.5	0.0	0.0	0.0	1.3	0.1	
12-16	4.4	56.0	1.5	0.9	0.0	0.0	0.0	1.2	0.0	
16-19	0.0	56.4	6.5	1.0	0.0	0.0	0.0	1.2	0.0	
19-23	2.4	57.1	2.3	0.8	0.0	0.0	0.0	1.3	0.0	
23-27	5.9	49.5	1.8	1.2	0.0	0.1	0.0	1.2	0.0	
27-31	4.9	43.7	3.2	1.8	0.1	0.0	0.0	1.2	0.1	
31-35	8.1	41.4	2.2	1.6	0.1	0.2	0.1	1.1	0.1	
35-39.5	4.7	46.4	2.8	1.4	0.0	0.1	0.0	1.3	0.1	
39.5-43	6.1	36.9	3.6	2.2	0.1	0.1	0.1	1.2	0.1	
43-47	4.2	45.4	2.9	1.6	0.0	0.0	0.0	1.3	0.1	
47-50	6.7	41.1	2.1	1.8	0.1	0.1	0.0	1.3	0.1	
50-54	6.6	40.7	2.3	2.0	0.1	0.1	0.0	1.2	0.1	
54-57	6.1	40.0	1.9	2.1	0.1	0.1	0.0	1.3	0.1	
57-60	6.5	37.3	1.8	2.2	0.1	0.1	0.0	1.5	0.1	
60-63	5.1	42.1	2.1	1.8	0.1	0.1	0.0	1.5	0.1	
63-66	5.3	41.4	3.0	2.2	0.1	0.0	0.0	1.0	0.1	
66-68	4.6	42.3	2.4	1.7	0.1	0.0	0.0	1.5	0.1	
68-72	7.9	31.3	3.3	2.9	0.1	0.1	0.1	1.0	0.1	
72-76	6.4	27.1	5.0	3.9	0.1	0.0	0.1	0.9	0.1	
76-81	8.5	24.0	4.2	4.1	0.1	0.1	0.2	0.8	0.1	
81-86	5.8	25.4	4.6	3.9	0.1	0.0	0.1	1.4	0.1	
<i>DZ14-10 C11</i>										
0-2	3.4	47.2	6.5	1.9	0.0	0.0	0.1	0.6	0.1	
2-6	4.2	33.8	7.6	3.2	0.0	0.0	0.1	0.6	0.2	
6-11	5.6	26.0	7.0	4.2	0.0	0.0	0.2	0.6	0.2	
11-16	6.5	19.8	6.4	5.2	0.1	0.0	0.3	0.7	0.3	
16-21	7.1	18.4	6.5	5.8	0.0	0.0	0.3	0.5	0.3	
21-27	6.3	18.1	7.3	6.1	0.0	0.0	0.3	0.4	0.3	
27-30	6.9	16.2	6.9	6.4	0.0	0.0	0.3	0.5	0.3	
<i>DZ16-8 C13</i>										
2-3cm	13.8	34.1	0.5	0.8	0.1	0.2	0.1	2.2	0.1	
7-11	6.2	43.3	1.2	1.2	0.2	0.0	0.0	1.7	0.1	
15-20	5.3	49.7	0.8	0.7	0.1	0.0	0.0	1.8	0.0	
22.5-25	5.3	48.6	1.6	1.4	0.1	0.0	0.0	1.2	0.1	
27-30.5	8.6	33.8	1.5	2.1	0.2	0.0	0.1	1.7	0.1	
34-38	7.4	34.6	2.1	2.3	0.2	0.0	0.1	1.4	0.1	
40-43	6.6	31.5	2.3	2.5	0.2	0.0	0.1	1.7	0.1	
47-51	5.8	37.4	1.8	1.6	0.1	0.0	0.1	2.0	0.1	
57-60	4.4	38.8	2.9	1.9	0.1	0.0	0.1	1.6	0.1	
63.5-66	4.0	41.0	3.5	2.1	0.1	0.0	0.1	1.2	0.1	
68.5-74	5.3	37.8	3.5	2.7	0.1	0.0	0.1	1.0	0.1	
79-85	3.1	38.2	5.0	2.8	0.1	0.0	0.1	1.0	0.1	
90.5-94	1.0	47.7	3.9	1.4	0.1	0.0	0.0	1.5	0.1	
97.5-101	5.2	26.4	2.9	3.2	0.2	0.0	0.1	2.1	0.1	
105-106	4.4	26.9	3.4	3.6	0.1	0.0	0.1	1.9	0.1	

Table A4. Characterization and semi-quantification of mineral phases in the sediment cores with XRPD

Depth (cm)	Aragonite (wt.%)	Hydro-magnesite (wt.%)	Alkaline feldspar (wt.%)	Clino-pyroxene* (wt.%)	Quartz (wt.%)	Calcite (wt.%)	Dolomite (wt.%)	Magnesite (wt.%)	Magnetite (wt.%)	Pyrite (wt.%)	Halite (wt.%)	Clay**
<i>DZ12-4 C2</i>												
0-2.5	30	50	-	15	-	-	-	-	-	-	5	-
-2.5-4.5	31	63	-	-	-	-	-	-	-	-	6	-
4.5-7	49	33	-	18	-	-	-	-	-	-	-	D
7-10.5	-	-	49	-	16	35	-	-	-	-	-	-
10.5-14	-	-	67	-	-	33	-	-	-	-	-	-
14-16.5	43	33	-	20	-	-	-	-	-	-	4	D
16.5-20	71	-	-	-	-	-	-	-	20	-	9	D
20-23.5	76	-	-	-	-	-	-	-	14	-	10	D
23.5-27	100	-	-	-	-	-	-	-	-	-	-	D
27-30	100	-	-	-	-	-	-	-	-	-	-	D
<i>DZ14-4 C4</i>												
0-1	39	43	-	14	-	-	-	-	-	-	4	-
1-2	42	58	-	-	-	-	-	-	-	-	-	-
2-3	37	53	-	10	-	-	-	-	-	-	-	-
3-7	44	43	-	13	-	-	-	-	-	-	-	-
7-11	46	45	-	10	-	-	-	-	-	-	-	D
11-14	50	38	-	12	-	-	-	-	-	-	-	-
14-16	57	33	-	10	-	-	-	-	-	-	-	D
16-20	54	35	-	11	-	-	-	-	-	-	-	-
20-24	70	17	-	13	-	-	-	-	-	-	-	D
24-27	93	-	-	-	-	-	-	-	7	-	-	D
27-30	88	-	-	-	-	-	-	-	12	-	-	D
30-35	72	21	-	-	-	-	-	-	-	-	7	-
35-39	89	-	-	-	-	-	-	-	11	-	-	D
39-43	99	-	-	-	-	-	-	-	-	-	-	-
43-48	96	-	-	-	-	-	-	-	4	-	-	D
48-52	100	-	-	-	-	-	-	-	-	-	-	D
52-56	94	-	-	-	-	-	-	-	5	-	-	-
56-60	93	-	-	-	-	-	-	-	6	-	-	D
<i>DZ14-10 C6</i>												
0-3	65	24	-	11	-	-	-	-	-	-	-	-
3-8.5	-	-	-	-	-	-	-	-	-	-	-	-
8.5-12	66	26	-	8	-	-	-	-	-	-	-	-
12-16	54	32	-	15	-	-	-	-	-	-	-	-
16-20	49.0	40	-	11	-	-	-	-	-	-	-	-
20-24	84	-	-	-	-	-	-	-	6	-	10	-
24-28	84	-	-	-	-	-	-	-	16	-	-	-
28-32	57	26	-	-	5	-	12	-	-	-	-	-
32-36	54	32	-	-	5	-	9	-	-	-	-	-
36-40	70	20	-	-	7	-	3	-	-	-	-	-
40-44	64	23	-	-	5	-	4	-	-	-	4	-
44-46	70	19	-	-	8	-	3	-	-	-	-	-
46-51	59	25	-	-	6	-	10	-	-	-	-	-
51-55	55	29	-	-	3	-	13	-	-	-	-	-
55-59	37	30	-	33	-	-	-	-	-	-	-	-
59-64	72	13	-	-	9	-	6	-	-	-	-	-
64-69	57	22	-	-	16	-	-	-	-	-	5	-
69-73	77	17	-	-	6	-	-	-	-	-	-	-
73-76	55	29	-	-	12	-	-	-	-	-	4	-
<i>DZ14-10 C9</i>												
6-10	6	73	-	16	-	-	-	5	-	-	-	-
10-14	-	55	-	11	-	-	-	34	-	-	-	-

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22,5-25	62	28	-	10	-	-	-	-	-	-	-	-	-
25-27	43	57	-	-	-	-	-	-	-	-	-	-	-
27-30,5	98	-	-	-	2	-	-	-	-	-	-	-	-
30,5-34	81	9	-	-	10	-	-	-	-	-	-	-	-
34-38	89	-	-	-	11	-	-	-	-	-	-	-	-
38-40	69	26	-	-	5	-	-	-	-	-	-	-	-
40-43	91	-	-	-	9	-	-	-	-	-	-	-	-
43-47	95	-	-	-	5	-	-	-	-	-	-	-	-
47-51	75	20	-	-	5	-	-	-	-	-	-	-	-
51-57	75	21	-	-	4	-	-	-	-	-	-	-	-
57-60	41	54	-	-	4	-	-	-	-	-	-	-	-
60-63,5	86	6	-	-	8	-	-	-	-	-	-	-	-
63,5-66	72	28	-	-	-	-	-	-	-	-	-	-	-
66-68,5	67	21	-	-	12	-	-	-	-	-	-	-	-
68,5-74	45	55	-	-	-	-	-	-	-	-	-	-	-
74-79	45	55	-	-	-	-	-	-	-	-	-	-	-
79-85	59	27	-	14	-	-	-	-	-	-	-	-	-
85-90,5	57	27	-	16	-	-	-	-	-	-	-	-	-
90,5-94	61	27	-	12	-	-	-	-	-	-	-	-	-
94-97,5	77	19	-	4	-	-	-	-	-	-	-	-	-
97,5-101	86	6	-	-	8	-	-	-	-	-	-	-	-
101-105	89	-	-	-	11	-	-	-	-	-	-	-	-
105-106	91	-	-	-	9	-	-	-	-	-	-	-	-

*The XRPD patterns indicate alternatively the presence of diopside or clinoenstatite, which are referred here and in the text as clinopyroxene.

**D means that the clay mineral is detected in the sample. Clay minerals were not taken into account in the semi-quantification with the RIR method.

Table A5. Characterization and semi-quantification of mineral phases in samples of the volcanic catchment with XRPD

Sample	Description	Calcite (wt.%)	Alk. Feld. (wt.%)	Analcime (wt.%)	Cpx (wt.%)	Magnetite (wt.%)	Olivine (wt.%)	Volcanic glass
DZ14-10 R1	Volcanic pumice	-	95	-	-	5	-	x
DZ14-10 R2	Cm-size block in ash layers	66	34	-	-	-	-	-
DZ14-10 R3	Cm-size block in ash layers	67	33	-	-	-	-	-
DZ14-10 R4	Cm-size igneous rock in ash layers	-	-	20	72	8	-	-
DZ14-10 R5	Cm-size igneous rock in ash layers	-	15	49	36	-	-	-
DZ14-10 R6	Cm-size igneous rock in ash layers	-	32	-	55	-	13	-
DZ16-8 R1	Ash layers	45	55	-	-	-	-	x
DZ16-8 R2	Ash layers	51	49	-	-	-	-	x
DZ16-8 R3	Volcanic pumice	46	54	-	-	-	-	x
DZ16-8 R4	Volcanic pumice	100	-	-	-	-	-	x
DZ16-8 R5	Cm-size block in ash layers	100	-	-	-	-	-	-
DZ16-8 R6	Cm-size igneous rock in ash layers	-	-	48.5	46.5	5	-	-

x: the baseline strongly affected by noise suggests the predominance of volcanic glass in these samples

Table A6. Elemental composition of samples of the volcanic catchment

Sample	Na (mol.%)	Mg (mol.%)	Al (mol.%)	Si (mol.%)	S (mol.%)	Cl (mol.%)	K (mol.%)	Ca (mol.%)	Fe (mol.%)
<i>DZ16-8</i>									
R2	7.4	1.6	17.7	51.8	0.0	0.3	6.1	8.9	5.6
R3	9.5	0.3	17.8	53.3	0.0	0.3	6.6	7.1	4.8
R4	13.3	0.4	17.4	53.5	0.1	0.8	6.6	3.0	4.5
R6	7.1	10.6	14.0	41.1	0.0	0.1	1.7	11.5	11.2

Table A7. Quantification of the sediment composition (organic matter and mineral phases including clays) in the sediment cores C4, C6, C10, C11 and C13

Depth (cm)	Halite (wt.%)	Alk. Feld. (wt.%)	Saponite-like mineral (wt.%)	Clinopyroxene (wt.%)	Hydromagnesite (wt.%)	Aragonite (wt.%)	Pyrite (wt.%)	Magnetite (wt.%)	O.M. (wt.%)
<i>DZ14-4 C4</i>									
0	2	0	0	4	16	17	0	0	60
2	1	3	1	3	17	11	0	0	65
3	1	4	2	3	13	10	0	0	66
11	1	8	20	0	18	14	0	1	38
20	1	6	12	3	10	16	1	0	52
27	1	12	17	5	8	13	1	1	43
30	2	6	3	9	10	21	1	0	48
35	1	10	18	0	9	15	1	1	45
39	0	15	24	0	2	12	1	1	45
43	0	15	19	0	10	18	1	1	35
48	1	22	21	0	7	13	1	1	35
52	0	18	20	0	5	15	1	1	39
56	1	17	23	0	8	16	1	1	33
<i>DZ14-10 C6</i>									
0	0	6	0	4	15	28	1	0	45
8.5	2	8	0	6	20	27	1	0	35
12	0	7	4	6	26	23	1	0	31
16	1	8	5	6	25	23	1	0	30
20	1	11	5	4	11	24	1	1	42
24	2	15	8	2	11	21	1	1	39
28	1	10	0	5	19	30	1	1	33
32	1	11	8	1	20	27	1	1	31
36	1	15	9	1	19	25	1	1	27
40	1	15	9	2	19	24	1	1	28
46.5	1	12	7	0	19	29	1	1	31
51	1	7	1	8	26	28	1	1	28
55	1	7	0	6	19	32	1	1	34
59	1	9	1	6	11	28	1	1	41
64	2	12	1	7	12	28	1	1	37
69	2	12	0	6	15	28	1	1	35
73	1	14	0	5	13	40	1	1	24
<i>DZ14-10 C10</i>									
0	0	3	6	3	27	20	0	0	41
4	0	3	7	1	20	16	0	0	53
8	0	4	8	0	12	13	0	0	62
12	0	3	3	4	22	20	0	0	47
16	0	3	5	4	25	22	0	0	40
19	0	3	6	4	32	29	0	0	25
23	1	4	6	3	20	21	0	0	43
27	0	6	14	0	17	19	0	0	42
31	1	7	10	0	16	18	0	0	47
35	1	6	12	0	24	27	0	0	29
39.5	1	10	18	0	12	20	1	1	38

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43	0	6	11	3	20	24	0	0	35	
47	1	7	11	5	16	25	1	1	34	
50	1	8	14	6	17	25	1	1	27	
54	1	6	10	13	13	27	1	0	28	
57	1	6	9	11	9	26	1	0	37	
60	1	6	9	8	17	29	1	1	29	
63	1	7	18	4	17	22	1	0	31	
66	1	7	12	7	20	32	1	1	21	
68	2	15	26	0	11	21	1	1	24	
72	0	20	26	0	6	15	1	1	32	
76	1	23	25	0	4	14	1	1	31	
81	0	24	17	0	12	26	1	2	17	
<i>DZ14-10 C11</i>										
0	0	19	0	8	32	16	0	2	22	
2	0	31	0	11	23	16	0	4	15	
6	0	41	0	8	19	15	0	5	12	
11	0	51	0	0	20	14	0	7	7	
16	0	57	0	0	20	10	0	6	7	
21	0	54	0	1	17	9	0	6	12	
27	0	53	0	0	16	10	0	5	15	
<i>DZ16-8 C13</i>										
2	1	0	0	9	8	35	1	0	45	
7	0	7	0	7	19	30	1	0	35	
15	0	4	0	5	25	34	1	0	30	
22.5	0	5	2	9	19	22	1	0	42	
27	0	10	3	12	10	31	2	1	33	
34	0	12	5	10	12	27	1	1	31	
40	0	11	8	10	9	31	2	1	28	
47	0	8	1	7	16	35	1	1	31	
57	0	9	5	6	17	28	1	1	34	
63.5	0	9	6	5	16	20	1	1	41	
68.5	0	14	9	9	14	18	0	1	35	
79	0	14	14	9	16	21	1	1	24	

Table A8. Chemical composition of the lake waters

Survey	pH	Total alkalinity	Mg	Ca	Si
2009 ^{a,b}	9.1-9.4	177.2	3.1	0.33	0.21
2010		241.0	4.5	0.04	0.27
2011		230.3	3.9	0.04	0.25
Oct.2014 ^c		9.2	258.9	4.7	0.05

Cation concentrations are in $\text{mmol}\cdot\text{L}^{-1}$ and total alkalinity in $\text{mmol}\cdot\text{L}^{-1}$ eq. CO_3^{2-}

^aData from Leboulanger *et al.* (2017), except for the dissolved silica concentration measured in this study according to the method of Strickland and Parson (1972), *i.e.* the colorimetry of the reduced silico-molybdc complex. Sensitivity is about $2\ \mu\text{M}\cdot\text{L}^{-1}$ and the precision of $\pm 5\%$.

^bSampling at the end of rainy season

^cData from Gérard *et al.* (2018)

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3 Section A1. Characterization of the volcanic catchment

4 The volcanic catchment is mostly made of volcanic pumices and ash layers (Fig. A1a), containing
5 fragments of solid/igneous rocks of various sizes typically ranging from a few centimeters to several
6 tens of centimeters (Fig. A1b). The XRPD and XRF analyses of volcanic pumices and ash layers
7 indicate the presence of alkaline feldspars and calcite (see Table A6 and A7 for details). The baseline
8 of XRPD patterns is strongly affected by noise, suggesting that volcanic glass is dominant in these
9 samples. The solid blocks found in the ash layers which contain large amounts of calcite (>60wt.%)
10 correspond to fragments of the coral reef, which surrounds the biggest island of Mayotte and has been
11 crossed over by the phreatomagmatic eruption at the origin of the Dziani Dzaha. The igneous rocks are
12 mostly made of alkaline feldspars, clinopyroxene, analcime, and minor amounts of olivine and
13 magnetite.
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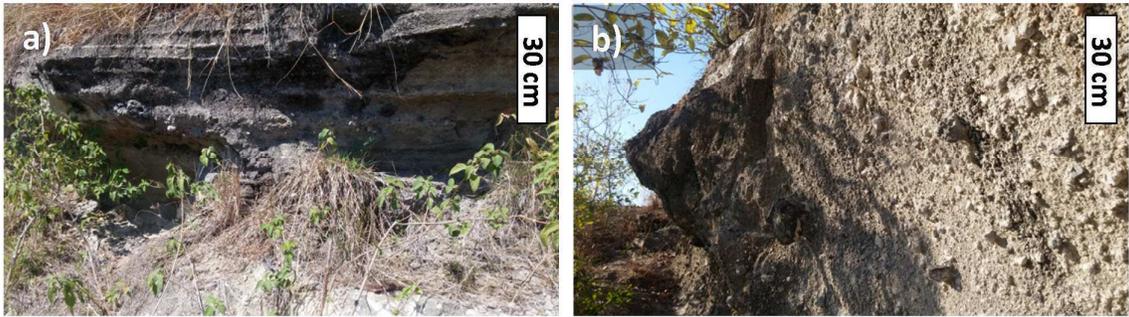
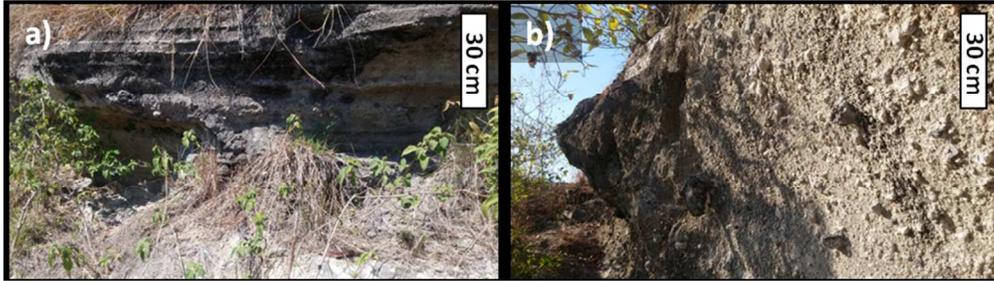


Figure A1. Volcanic catchment: (a) ash layers, (b) fragments of solid/igneous rocks in ash layers.



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