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1 Integrative analysis of the mineralogical and chemical composition of modern
2 microbialites from ten Mexican lakes: what do we learn about their formation?

3

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26 hydromagnesite; kerolite; REE+Y

27

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29

30 **ABSTRACT**

31

32 Interpreting the environmental conditions under which ancient microbialites formed relies upon
33 comparisons with modern analogues. This is why we need a detailed reference framework
34 relating the chemical and mineralogical compositions of modern microbialites to the physical
35 and chemical parameters prevailing in the environments where they form. Here, we measured
36 the chemical, including major and trace elements, and mineralogical composition of
37 microbialites from ten Mexican lakes as well as the chemical composition of the surrounding
38 waters. Saturation states of lakes with different mineral phases were systematically determined
39 and correlations between solution and solid chemical analyses were assessed using multivariate
40 analyses. A large diversity of microbialites was observed in terms of mineralogical
41 composition, with occurrence of diverse carbonate phases such as (Mg-)calcite,
42 monohydrocalcite, aragonite, hydromagnesite, and dolomite as well as authigenic Mg-silicate
43 phases (kerolite and/or stevensite). All lakes harbouring microbialites were saturated or
44 supersaturated with monohydrocalcite, suggesting that such a saturation state might be required
45 for the onset of microbialite formation and that precursor soluble phases such as amorphous
46 calcium carbonate and monohydrocalcite play a pivotal role in these lakes. Subsequently,
47 monohydrocalcite transforms partly or completely to aragonite or Mg-calcite, depending on the
48 lake $(\text{Mg}/\text{Ca})_{\text{aq}}$. Moreover, lakes harbouring hydromagnesite-containing microbialites were
49 saturated with an amorphous magnesium carbonate phase, supporting again the involvement of
50 precursor carbonate phases. Last, authigenic Mg-silicates formed by homogenous or
51 heterogenous nucleation in lakes saturated or supersaturated with a phase reported in the
52 literature as “amorphous sepiolite” and with a H_4SiO_4 concentration superior to 0.2 mM. A
53 strong correlation between the alkalinity and the salinity of all the lakes was observed. The
54 observed large variations of alkalinity between the lakes relate to varying concentration stages
55 of an initial alkaline dilute water, due to a varying hydrochemical functioning. In all cases, the
56 size of microbialites in the lakes correlated positively with salinity, $(\text{Mg}/\text{Ca})_{\text{aq}}$ ratio and
57 alkalinity. The trace element compositions of the microbialites also varied significantly
58 between the lakes. Detrital contamination of the studied microbialites was the major factor
59 affecting their rare earth elements (REE)+Y patterns. In particular, the microbialites highly
60 affected by detrital contamination showed a high (REE+Y) content and flat (REE+Y) patterns.
61 In contrast, some microbialites poorly affected by detrital contamination showed (REE+Y)
62 patterns with features commonly reported for marine microbialites, such as a superchondritic
63 Y/Ho ratio, enrichment in heavy REE and a negative Ce anomaly. This last observation

64 questions the possibility to infer the marine *versus* lacustrine origin of a microbialite only based
65 on (REE+Y) patterns. Overall, while microorganisms can impact nucleation processes and
66 textural arrangements in microbialites, we observe that the hydrogeochemical evolution of
67 lakes exerts a primary control over the onset of microbialite formation and the evolution of their
68 chemical and mineralogical composition. Moreover, while changes of all these chemical and
69 mineralogical features upon diagenesis and metamorphism will need to be assessed, the present
70 study, together with recent meta-analyses of modern microbialites, broadens the set of modern
71 references available for comparisons with geological archives.

72

73 INTRODUCTION

74

75 Microbialites are organo-sedimentary rocks formed by the trapping and binding of
76 detrital sediments and/or the precipitation of authigenic minerals by benthic microbial
77 communities (Burne and Moore, 1987). These rocks are abundant in the geological record and
78 are considered as being among the oldest traces of life (Allwood et al., 2006; Van Kranendonk
79 et al., 2008; Nutman et al., 2016). Both marine and lacustrine microbialites have been found in
80 the geological record (Kamber et al., 2004; Awramik and Buchheim, 2009). Yet, it has been
81 sometimes difficult to determine the environmental conditions in which they formed. For
82 instance, stromatolites from the 2.7 Ga old Tumbiana Formation have been interpreted either
83 as shallow marine (Thorne and Trendall, 2001; Sakurai et al., 2005) or lacustrine (Buick, 1992;
84 Bolhar and Van Kranendonk, 2007; Awramik and Buchheim, 2009; Stüeken et al., 2015)
85 deposits. This calls for establishing diagnostic criteria, which could help discriminate between
86 different formation environments for these sedimentary archives.

87 Unlike their marine counterparts, modern lacustrine microbialites form under a wide
88 diversity of conditions obscuring the search for analogues of ancient lacustrine settings and
89 requesting a good appraisal of this diversity. For example, lakes populated by modern
90 microbialites show a broad range of pH from 7.5 in the Cuatro Ciénegas basin located in
91 Mexico, to 10.5 in Lake Bogoria and Lake Magadi in Kenya (Centeno et al., 2012; Harris et
92 al., 2013). Many of these lakes are hypersaline, with salinity values up to 200 g/l for Lake Big
93 Pond (Eleuthera, Bahamas) (Glunk et al., 2011), while some lakes are characterized by
94 moderate salinity, including Lake Tanganyika with a salinity as low as 0.5 g/l (Harris et al.,
95 2013). Microbialites are formed in lakes showing a large range of $(\text{Mg}/\text{Ca})_{\text{aq}}$ ratios ranging
96 between 0.5 for the Ruidera Pool in Spain (Souza-Egipsy et al., 2006), up to 90 for Lake
97 Walyungup in Western Australia (Coshell et al., 1998). In association with this environmental

98 diversity, modern lacustrine microbialites show a large range of morphologies and microfabrics
99 (*e.g.*, Kempe et al., 1991; López-García et al., 2005; Harris et al., 2013). There is also a broad
100 diversity of mineralogical compositions, including various carbonate phases such as
101 hydromagnesite (*e.g.*, Braithwaite and Zedef, 1994), aragonite and calcite (*e.g.*, Arp et al.,
102 1999a; Guo and Chafetz, 2012), aragonite and dolomite (*e.g.*, Last et al., 2012), or
103 monohydrocalcite (MHC; *e.g.*, Rosen et al., 2004). In addition to carbonates, authigenic Mg-
104 silicates such as smectites (saponite, stevensite), kerolite or sepiolite, have been detected as
105 sometimes abundant phases in several lacustrine microbialites from different localities (Arp et
106 al., 2003; Souza-Egipsy et al., 2005; Reimer et al., 2009; Benzerara et al., 2010; Burne et al.,
107 2014; Zeyen et al., 2015; Pace et al., 2016; Gérard et al., 2018).

108 Overall, there is a need to link the diversity of microbialite features with their formation
109 conditions. For example, the macroscopic morphology, size and spatial distribution of
110 microbialites have been used to infer the distance to the coast, the water lake level, the presence
111 of groundwater seepage or the impact of tectonic activity (*e.g.*, gravity deposits) (Cohen et al.,
112 1997; Sarg et al., 2013; Bahniuk et al., 2015; Bouton et al., 2016). A recent study emphasized
113 the importance of the chemistry and geometry of the substrates and the seasonal variations on
114 the morphology of microbialites (Roche et al., 2019). The macro and/or micro-textures of
115 microbialites have been used to assess the potential involvement of microorganisms in their
116 formation (Arp et al., 1998; Knoll et al., 2013; Theisen et al., 2015). Isotopic compositions
117 (*e.g.*, nitrogen and/or sulfur isotopes) of organic matter (kerogen) and/or bulk composition of
118 ancient microbialites have been used to infer past metabolic activities of diverse
119 microorganisms and/or the environmental conditions prevailing on the early Earth (*e.g.*,
120 Bontognali et al., 2012; Thomazo et al., 2011; Stüeken et al., 2015). Finally, rare earth element
121 (REE) patterns of some ancient stromatolites have been used to determine their formation
122 environment, in particular marine or lacustrine (*e.g.*, Kamber and Webb, 2001; Bolhar and Van
123 Kranendonk, 2007; Siahí et al., 2018). However, REE+Y patterns of modern marine or
124 continental microbialites remain surprisingly scarce in the literature (*e.g.*, Chagas et al., 2016).

125 Several studies have coupled analyses of the mineralogical and chemical composition
126 of microbialites with the lake water chemistry at one single locality/lake (*e.g.*, Lim et al., 2009;
127 Power et al., 2011). Only recently, Chagas et al. (2016) developed a meta-analysis including
128 such data from a larger number (n=21) of lakes. In addition, Valdespino-Castillo et al. (2018)
129 and Iniesto et al. (2021) used a similar approach with a focus on the links between microbial
130 diversity and microbialite or water chemistry, from five and ten locations, respectively,
131 including several lakes in Mexico. These recent studies significantly improve our capability to

132 grasp the relationships between environmental conditions prevailing during microbialite
133 formation and their chemical and mineralogical composition.

134 Here, we present an integrative analysis (defined as a comparative study integrating
135 different data acquired on samples from different locations by a single research group and using
136 a single set of protocols) of microbialites from ten Mexican volcanic lakes located in the trans-
137 Mexican volcanic belt (TMVB) (Ferrari et al., 2012; Sigala et al., 2017). Some of these lakes
138 were already included in the meta-analysis by Chagas et al. (2016). However, the present
139 contribution adds (1) a novel dataset on three lakes in which microbialites had never been
140 described before (Lakes Alberca de Guadalupe, Tecuitlapa and Aljojuca), and (2) new
141 measurements for all sites, including bulk analyses of the major and trace elements (together
142 with REE+Y) concentrations in the microbialites. The structure of prokaryotic and eukaryotic
143 communities associated with the same microbialites was analyzed by Iniesto et al. (2021) based
144 on massive 16S/18S rRNA gene amplicon sequencing. It was found that they all harbor a high
145 diversity of microorganisms. Importantly, despite interlake community variations, a microbial
146 core consisting of 247 operational taxonomic units was shown to be conserved across lake
147 microbialites. Iniesto et al. (2021) suggested that this microbial core might be particularly
148 important for carbonatogenesis. The present study focuses on a complementary piece of
149 information, *i.e.*, relationships between microbialite chemistry/mineralogy and water
150 chemistry. We uncover new relationships between the chemical/mineralogical composition of
151 the lacustrine microbialites and their formation conditions and explore potential scenarios that
152 could account for 1) the conditions necessary for microbialite formation in lakes and 2) the
153 chemical and mineralogical diversity of Mexican lacustrine microbialites.

154

155 **MATERIALS AND METHODS**

156

157 **1. Geological Setting**

158 The ten lakes investigated in this study belong to the trans-Mexican volcanic belt
159 (TMVB), a continental volcanic arc following an East-West orientation located in Central
160 Mexico. It spans over almost 1000 km in length and 20 to 100 km in width, covering an area of
161 about 160 000 km² (Ferrari et al., 2012) (Fig. 1a). The TMVB results from the subduction of
162 the Rivera and Cocos plates beneath North America at the Middle American Trench during the
163 Neogene period (Ferrari et al., 2012). Two types of volcanic rocks are generally described in
164 this zone: (1) calc-alkaline rocks compatible with a subduction environment and (2) alkaline or
165 transitional rocks with compositions similar to oceanic island basalts (Gómez-Tuena et al.,

166 2003). The TMVB hosts numerous monogenetic and shield volcanoes, lava domes and phreato-
167 magmatic vents, sometimes leading to maar formation (Alcocer and Bernal-Brooks, 2010;
168 Siebe et al., 2014). Six studied maar lakes are located on the eastern part of the TMVB in the
169 Cuenca de Oriental basin (Puebla State): four of them (Lakes Alchichica, La Preciosa,
170 Quechulac and Atexcac) are located in the Los Llanos de San Juan region (Fig. 1e) and two of
171 them (Lakes Tecuitlapa and Aljojuca), in the Los Llanos de San Andrés region (Fig. 1f). Four
172 other lakes are located in the central part of the TMVB in the Michoacán-Guanajuato volcanic
173 field (MGVF). Two of them are maars (Lakes La Alberca de los Espinos and Alberca de
174 Guadalupe – also called Alberca de Michoacan –, Fig. 1b and c, respectively) and the other two
175 are lava-dammed basins (Lakes Zirahuén and Pátzcuaro, Fig. 1d). Table 1 summarizes the main
176 known physical and hydrological characteristics of each studied lake.

177 These lakes formed during the Pleistocene between 0.33 Myr ago for Lake Atexcac
178 (Carrasco-Núñez et al., 2007) and 23-20 kyr ago for Lake Alberca de Guadalupe (Siebe et al.,
179 2014). The lakes located in the Cuenca de Oriental Basin are underlain by a Mesozoic limestone
180 basement and by Pleistocene volcanic sequences, mostly basaltic rocks (Armienta et al., 2008).
181 In addition, Lake Atexcac lays on a large andesitic basement (Carrasco-Núñez et al., 2007).
182 The local basement of the lakes located in the Michoacán-Guanajuato volcanic field comprises
183 basalts (Lake Zirahuén) and andesites (Lakes La Alberca de Los Espinos, Alberca de
184 Guadalupe and Pátzcuaro). Investigated lakes are located at an elevation comprised between
185 1985 m (Lake La Alberca de Los Espinos) and 2380 m (Lake Tecuitlapa). Their maximum
186 depth varies between 2.5 m for the shallowest (Lake Tecuitlapa) and ~62 m for Lake
187 Alchichica.

188 All studied lakes are “closed lakes” located within endorheic basins (Alcocer and
189 Bernal-Brooks, 2002; Davies et al., 2004; Armienta et al., 2008). The term “closed lake” refers
190 to a lacustrine water body with a limited drainage basin that normally retains water and allows
191 no surface outflow to external aquatic systems (*e.g.*, Almendinger, 1990). Accordingly, no
192 surface outflow was observed for the closed lakes during our field campaigns whatever the
193 season. Although we do not know their chemical composition, groundwater inflows/outflows
194 very likely exist as suggested by Armienta et al. (2008) for all maar lakes and mentioned by
195 Siebe et al. (2014) for Lake La Alberca de Guadalupe. Groundwater inflow was also inferred
196 for Lake Alchichica (Każmierczak et al., 2011; Zeyen et al., 2019). Hydrological studies of
197 Lake Pátzcuaro (Bischoff et al., 2004) and Lake Alchichica (García Martínez, 2010) also
198 required underground water inflow and outflow to balance the water deficit between
199 evaporation and rainfall.

200

201 **2. Sample collection**

202 Field campaigns were conducted in June 2007, January 2012 and May 2014. Here, we
203 consider as microbialites all carbonate deposits varying from thin encrustations around basaltic
204 pebbles (oncoliths) to well-developed, meter-scale and massive microbialites (mostly
205 thrombolites). Microbialites from Lake Alchichica can be found down to at least 15 m in depth
206 as reported by Saghaï et al. (2016). However, diving was not systematically performed so that
207 depth distribution remains unknown for the other lakes. Several previous studies have
208 investigated microbialites from Lake Alchichica (Kaźmierczak et al., 2011; Couradeau et al.,
209 2011; Couradeau et al., 2013; Gérard et al., 2013; Saghaï et al., 2015; Valdespino-Castillo et
210 al., 2018; Zeyen et al., 2019). Additionally, we previously described microbialites from Lakes
211 La Preciosa, Quechulac, Atexcac, La Alberca de Los Espinos and Pátzcuaro (Zeyen et al., 2015;
212 Zeyen et al., 2019). To complete the analyses previously performed on these 6 lakes, we
213 sampled microbialites at several additional locations on the shores of these lakes. Moreover,
214 we sampled three other lakes populated by microbialites, which to our knowledge, were
215 undescribed to date: Lake Alberca de Guadalupe, Lake Tecuitlapa and Lake Aljojuca. “Living”
216 microbialites (*i.e.*, microbialites covered and populated by a biofilm) were systematically
217 sampled beneath the water level. In Lake Alchichica, samples were collected by scuba diving
218 at different depths: 1, 5, 10 and 15 m depth in January 2012 (Saghaï et al., 2015) and 4 m depth
219 (sample AL66) in June 2007. In addition, “non-living” microbialites (*i.e.*, dry and not covered
220 by a biofilm, sometimes called “fossil” microbialites; *e.g.*, Casanova and Hillaire-Marcel, 1992;
221 Bouton et al., 2016; Zeyen et al., 2019) were systematically sampled above the water level.

222 A summary of the location of aqueous samples and performed analyses is reported in
223 Table SI-1. Surface water samples were collected from the shore of the lakes. Some were also
224 collected at the center of Lake Atexcac (Atx-M) and its north shore (Atx-N) as well as at the
225 center of Lake Alchichica (AL-M) and its west shore (AL-W). In addition, water was sampled
226 with a Niskin bottle in May 2014 in the center of Lake Atexcac at 3, 10, 20 and 30 m depth and
227 in January 2012 and May 2014 in the center of Lake Alchichica at 3, 10, 25, 40 and 55 m depth.
228 Temperature, pH and specific conductance (conductivity normalized at 25°C) of lake surface
229 waters were measured *in situ*. Two hundred milliliters of solution were systematically collected
230 from each lake. Solutions were filtered on the same day using 0.22 µm GF/F filters and kept in
231 sterile tubes. For major cation and ⁸⁷Sr/⁸⁶Sr analyses, 30 and 40 ml, respectively, of filtered
232 solutions were acidified with nitric acid (2%). The remaining 130 ml were used for

233 measurements of alkalinity, anion and orthosilicic acid (H₄SiO₄) concentrations, without pre-
234 acidification.

235

236 3. Chemical analyses of solutions

237 Orthosilicic acid (H₄SiO₄) concentrations were determined by continuous flow
238 colorimetric analyses. For these analyses, water samples from Lake La Preciosa, Quechulac,
239 Tecuitlpa, Aljojuca and Páztcuaro were diluted 10 times. Water samples from Lakes Atexcac,
240 La Alberca de los Espinos and Alberca de Guadalupe were diluted 20, 50 and 100 times,
241 respectively. Concentrations of nitrogen compounds (nitrites NO₂⁻, nitrates NO₃⁻, ammonium
242 NH₄⁺) and phosphates were measured on non-diluted water samples by continuous flow
243 colorimetric analyses. Anion concentrations (fluorides F⁻, chlorides Cl⁻, bromines Br⁻, and
244 sulfates SO₄²⁻) were measured by ion chromatography. Concentrations of major (Ca²⁺, Na⁺,
245 Mg²⁺, K⁺) and minor (Al³⁺, B_T (B(OH)₃ and B(OH)₄⁻), Ba²⁺, Cu²⁺, Fe²⁺, Mn²⁺, Ni²⁺, Sr²⁺, Ti⁴⁺,
246 Zn²⁺) cations were determined by inductively coupled plasma atomic emission spectrometry
247 (ICP-AES). The uncertainty on the concentration measurements of orthosilicic acid, anions and
248 cations was lower than 5%. Salinities were calculated from specific conductance and
249 temperature data, after the method described by Aminot and K  rouel (2004) (Table SI-2).

250 Activities of anions, cations and orthosilicic acid as well as saturation indices of the
251 surface water solutions of the lakes were calculated using the Visual MINTEQ software
252 (Gustafsson, 2011). Table SI-3 summarizes precipitation reactions and solubility constants of
253 the mineral phases included in our calculations and/or used to plot the solubility lines, *e.g.*, Ca-
254 and/or Mg-carbonates (aragonite, calcite, Mg-calcite (Mg_{0.1}Ca_{0.9}CO₃), MHC, vaterite,
255 dolomite, hydromagnesite, amorphous Ca-carbonate (ACC) and amorphous Mg-carbonate),
256 silicates (sepiolite, “amorphous sepiolite”, kerolite, talc, stevensite and amorphous silica) and
257 hydroxyapatite. The temperatures of the lakes measured during sampling (Table SI-2) were
258 systematically considered in the calculation of the saturation indices. Calculations were
259 performed using the Davies method (Davies and Morgan, 1989) without allowing any mineral
260 phase precipitation. The saturation index (*SI*) is defined as the decadic logarithm of the ratio of
261 the ion activity product (*IAP*) over the solubility constant (*K_s*):

$$262 \quad SI = \log (IAP/K_s) \quad (1)$$

263 A solution is supersaturated with respect to a mineral phase when *SI* is positive.

264 Total alkalinities were determined by titration (Gran, 1952) using hydrochloric acid.
265 Commercial mineral water (Evian) was used as a control. The uncertainty on alkalinity

266 measurements was lower than 1%. Alkalinity (*Alk*) is defined by Dickson (1981) as “the number
267 of moles of hydrogen ion equivalent to the excess of proton acceptors (bases formed from weak
268 acids with a dissociation constant $K \leq 10^{-4.5}$, at 25°C and zero ionic strength) over proton donors
269 (acids with $K > 10^{-4.5}$) in one kilogram of sample”, hence:

$$270 \quad Alk = [HCO_3^-] + 2[CO_3^{2-}] + [NH_3] + [H_2BO_3^-] + [H_3SiO_4^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [OH^-] \\ 271 \quad \quad \quad - [HF] - [H_3PO_4] - [H^+] \quad (2)$$

272 with brackets indicating concentrations in mol.kg_{sln}⁻¹. Given the relatively low contributions of
273 N, P, B, and Si species to alkalinity for the lakes considered in the present study (Tables SI-4
274 and SI-5), alkalinity was simplified as:

$$275 \quad Alk = [HCO_3^-] + 2[CO_3^{2-}] \quad (3)$$

276 Concentrations in HCO₃⁻ and CO₃²⁻ could thus be deduced from pH, alkalinity and the pKa of
277 HCO₃⁻/CO₃²⁻ (pKa = 10.32 at 25°C).

278 In order to assess the fractionation of REE+Y between solutions and microbialites, REE
279 + Y concentrations (of the lake solutions) were measured on five lake water samples collected
280 in May 2014 (Alchichica, Atexcac, Quechulac, La Preciosa, La Alberca de Los Espinos) by
281 ICP-MS at the *Service d'Analyse des Roches et Minéraux* (SARM, Centre de Recherches
282 Pétrographiques et Géochimiques, Nancy, France).

283 Finally, strontium isotope ratios (⁸⁷Sr/⁸⁶Sr) of the surface water from 5 lakes sampled in
284 May 2014 were measured: Alchichica (center of the lake), La Preciosa (north-east shore of the
285 lake), Atexcac (center of the lake), La Alberca de Los Espinos (north shore of the lake) and
286 Zirahuén (center of the lake). The automated purification of Sr from lake water samples was
287 performed by high performance ion chromatography (HPLC-Dionex 300) according to the
288 procedure described by Meynadier et al. (2006). Strontium isotope ratios (⁸⁷Sr/⁸⁶Sr) were
289 measured using a Neptune multicollector ICP-MS (Thermo Scientific) at the High-Resolution
290 Analytical Platform (PARI) of the Institut de physique du globe de Paris (IPGP). The strontium
291 isotope ratios were measured three times for each sample, and the reported uncertainty
292 corresponds to the 95% confidence interval calculated using the standard deviation obtained
293 over these three replicates and Student's law.

294

295 **4. Bulk mineralogical analyses of microbialites**

296

297 A quantity of about 10 g for each microbialite sample was finely ground and
298 homogenized in an agate mortar and aliquots of the same powdered sample were used for the

299 different bulk analyses. The surface of microbialite sample (including the dry biofilm) was
300 included in each aliquot except for:

301 1) the non-living microbialite collected in Lake Quechulac. This sample was divided
302 into three samples: the external surface part (Quechulac-4A-2012), the intermediary part
303 (Quechulac-4B-2012) and the internal part (Quechulac-4C-2012).

304 2) the non-living microbialite encrusting a basalt collected in Lake Tecuitlapa. This
305 sample was divided into two samples: the external part (Tec2014-05a) and the intermediate part
306 (Tec2014-05b).

307 These five samples were finely ground separately in an agate mortar and aliquots of each
308 powder sample were used for the different bulk analyses.

309

310 ***4.1. X-ray diffraction***

311 The bulk mineralogical composition of microbialites was determined by x-ray
312 diffraction (XRD). About 1 g of each microbialite sample was deposited on an aluminum
313 sample holder. XRD measurements were performed using a Panalytical X'Pert diffractometer
314 equipped with a cobalt anode (Co-K α). Data were recorded at 40 kV and 40 mA in the
315 continuous-scan mode between 5 and 90° (2 θ) with a step of 0.016° and a total counting time
316 of around 4 h. Diffractograms were analyzed using the PANalytical X'Pert Highscore software
317 for background subtraction, peak finding, and matching with XRD patterns of reference
318 compounds. Reference patterns were obtained from the international crystal structure database
319 (ICSD, Fachinformationszentrum Karlsruhe, Germany; US Institute of Standards and
320 Technology, USA).

321

322 ***4.2. Fourier transform infrared spectroscopy analyses***

323 For Fourier transform infrared (FTIR) spectroscopy analyses, 2.5 mg of microbialite
324 powder and 300 mg of potassium bromide (KBr) were mixed and ground in an agate mortar. A
325 KBr pellet was prepared for each microbialite sample using a vacuum press under 8 tons of
326 pressure for 1 minute. Pellets were placed overnight in a drying oven (95°C) to remove the
327 adsorbed water vapor and were pressed a second time. Transmission spectra were recorded
328 between 400 and 4000 cm⁻¹, using a Nicolet 6700 FTIR spectrometer.

329

330 **5. Microscopy and spectroscopy analyses of microbialites**

331 ***5.1. Raman microspectroscopy and mapping***

332 Raman spectromicroscopy was performed on a polished petrographic thin section of a
333 microbialite from Lake Ajojuca (Aljo2014-02), which was composed of three different Ca-
334 carbonate phases (Mg-calcite, MHC and aragonite) as determined by XRD. For this sample,
335 fluorescence induced by the incident laser was low enough so that it did not prevent Raman
336 analyses. Raman spectra were recorded using a Renishaw InVia spectrometer equipped with a
337 785 nm Renishaw diode laser. The laser was focused on the sample using a DM2500 Leica
338 microscope with a 50× objective (NA= 0.55) to obtain a planar resolution of $\sim 5 \mu\text{m}^2$. The laser
339 power at the sample surface was set at around 1 mW using neutral density filters to avoid
340 damages due to laser-induced heating. The signal was filtered by edge filters and dispersed by
341 a diffraction grating with 1200 grooves/mm and the signal was analyzed with a RENCAM CCD
342 (charge-coupled device) detector. Before each session, the spectrometer was calibrated using a
343 silicon standard. Spectra were collected using the software WIRE 4.1 provided by Renishaw.
344 The streamline technology provided by Renishaw was used to perform dynamic line-scanning
345 Raman mapping on the petrographic section (Bernard et al., 2008). Mosaics were compiled
346 from 40 112 Raman spectra over a $1240 \times 1300 \mu\text{m}^2$ with a stepsize of 6 μm in the x-direction
347 and 6.2 μm in the y-direction. The laser power at the sample surface was set at around 0.5
348 $\text{mW}/\mu\text{m}^2$ when using the line-scanning mode.

349

350 ***5.2. Scanning electron microscopy analyses***

351 Some microbialite samples (ATX-2C1-2012, ATX-2014-13, ATX2014-02; Preciosa05-
352 2012, Pr2014-09, Quechulac1A-2012, AlbEsp2014-01, AL2012-10m, AL2012-12, AL2012-
353 15, Alb2014-02) were sawed to obtain ~ 5 mm thick sections. They were polished with diamond
354 polishing paste with a grain size down to a $\frac{1}{4}$ of a micrometer. Thin-sections were rinsed with
355 two consecutive ultrasonic cleaning baths with 100% ethanol, then milliQ water. Finally,
356 polished sections were dried overnight in an evacuated desiccator. Samples were mounted on
357 2.5 cm wide aluminum stubs using double-sided carbon tape. Some microbialite samples were
358 embedded in resin (AL13, AL66, AL2014-13, AL2014-15, AlbEsp2014-01, Patz2014-02,
359 Aljo2014-02). For this purpose, microbialite fragments were fixed in a 2.5% formaldehyde
360 solution (methanol free, ultra pure; Polysciences, Inc.) for 4 h at 6°C, then washed 3 times in a
361 phosphate-buffered saline (PBS) solution and finally stored in (1/1) ethanol/PBS at 20°C.
362 Samples were then dehydrated through a graded series of ethanol solutions, each during 30 min
363 (ethanol/milliQ water volume ratios at 15, 30, 50, 70, 90, and 99%), and during 12 h in an
364 ethanol/water volume ratio of 99%. Samples were progressively embedded in a hard grade LR-
365 white resin (Polysciences, Inc.) by incubating the samples at 6°C for 18 h in (1) a 1:2 mixture

366 of LR-white:ethanol, then (2) a 2:1 mixture of LR-white:ethanol and (3) pure LR-white resin.
367 After 1 h at room temperature, samples were embedded in pure LR-white resin for 1 h at 40°C
368 and for 24 h at 60°C. After polymerization, transverse sections were cut with a diamond wire
369 to obtain ~2 mm thick sections and polished with diamond paste down to a ¼ of a micrometer.
370 After rinsing, thin sections were dried overnight in an evacuated desiccator. Samples were
371 mounted on 1.25 cm wide aluminum stubs using double-sided carbon tape before carbon
372 coating.

373 Scanning electron microscopy (SEM) analyses were performed using a Zeiss Ultra 55
374 field emission gun SEM. Backscattered electron (BSE) images were acquired using an angle
375 selective backscattered (AsB) detector at an accelerating voltage of 15 kV, a working distance
376 of ~7.5 mm and a 60 µm aperture at high current. The elemental composition of mineral phases
377 was determined by energy dispersive X-ray spectrometry (EDXS) using an EDS QUANTAX
378 detector. EDXS data were analyzed using the ESPRIT software package (Bruker).

379

380 **6. Bulk chemical analyses of microbialites**

381 Concentrations of major elements, total organic carbon, total sulfur and trace elements
382 were measured on 32 microbialite samples at the *Service d'Analyse des Roches et Minéraux*
383 (SARM, Centre de Recherches Pétrographiques et Géochimiques, Nancy, France). About two
384 grams of ground powder were used for these analyses. The uncertainties for each analytical
385 method were deduced from relative standard deviations calculated on a minimum of 30
386 measurements of reference geochemical standards. Major element analyses were performed
387 using an ICP-AES ICap 6500 (Thermo Fischer) after alkali fusion of rock samples with LiBO₂
388 followed by dissolution in HNO₃. The uncertainties on the major element measurements were
389 between 1% and 25% depending on their concentrations. Organic carbon and total sulfur
390 contents were determined using a Horiba EMIA320V2 carbon/sulfur analyzer. The
391 uncertainties on organic carbon measurements were lower than 5% for the highest
392 concentrations (2.55 at.%), lower than 10 % TOC values between 0.7 and 1.47 at.% and lower
393 than 15% for TOC lower than 0.69 at.%. The uncertainty on total sulfur measurements were
394 lower than 10 % for S contents > 0.37 at.%, lower than 15% for S contents between 0.07 to
395 0.18 at.% and lower than 20 at.% for the lowest values.

396 A normative abundance (in wt.%) of the mineral phases in microbialites the least
397 affected by detrital contamination (*i.e.*, authigenic-dominated microbialites) was assessed based
398 on their bulk chemical compositions (mainly Mg, Ca and Si concentrations). For this purpose,
399 we considered the following stoichiometries for the main phases detected by XRD, FTIR and

400 optical and scanning electron microscopy: CaCO_3 for aragonite, $\text{Mg}_{0.1}\text{Ca}_{0.9}\text{CO}_3$ for Mg-calcite,
401 $\text{CaCO}_3 \cdot \text{H}_2\text{O}$ for MHC, $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ for hydromagnesite, $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot \text{H}_2\text{O}$ for
402 kerolite and $\text{FeMg}_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot \text{H}_2\text{O}$ for Fe-rich kerolite. For these estimations, the
403 stoichiometry of Mg-calcite and dehydrated Fe-rich kerolite were chosen arbitrarily. We
404 assumed that all silicon was associated with kerolite since amorphous silica was not observed
405 by microscopy. While some of these assumptions might not be totally accurate, this approach
406 provides an approximate assessment of the bulk mineralogical composition of the microbialites.
407 For samples having an Al content higher than 0.49 wt% (*i.e.*, microbialites from Lakes Aljojuca,
408 Pátzcuaro, Alberca de Guadalupe and Tecuitlapa, as well as some of the microbialites from
409 Lakes La Preciosa, Atexcac and Alchichica), the normative abundance of the mineral phases
410 was not possible to assess.

411 Trace element analyses, including REE+Y, were performed using an ICP-MS Thermo
412 Elemental X7 following the same procedure as in Carignan et al. (2001) after rock
413 decomposition using alkali fusion. REE+Y data were normalized against the Post-Archean
414 Australian Shale (PAAS) REE+Y pattern (Pourmand et al., 2012). Y was inserted in the pattern
415 between Dy and Ho because of its intermediate ionic radius (Bau and Dulski 1996). In order to
416 characterize the REE+Y patterns of microbialites, the following shale normalized anomalies
417 were calculated: Ce/Ce^* , La/La^* , Eu/Eu^* , Gd/Gd^* and Pr/Pr^* . The shale-normalized Yb/Nd
418 ratio was used to describe the heavy rare earth elements (HREE) enrichment of microbialites.
419 More details about the calculations are available in Text SI-1 in Supplementary Information.

420

421 7. Statistical analyses

422 Statistical analyses of the chemical composition of lake solutions and microbialites were
423 performed using the R software (R Core Team, 2015).

424 Twenty-five variables were considered for the aqueous chemistry: temperature, pH,
425 conductivity (noticed as C_{25}), salinity, alkalinity, Mg/Ca, concentrations (expressed in mmol.l^{-1})
426 of Al, B, Ba, Ca, K, Mg, Na, Sr, Zn, H_4SiO_4 , PO_4 , NH_4 , NO_3 , F, Cl, SO_4 , Br, CO_3 and HCO_3 .
427 First, strength and direction of the pairwise monotonic relationships between the 25 aqueous
428 variables on 31 aqueous samples were evaluated by the Spearman's correlation coefficient
429 (values ranging from -1 to +1). The statistical significance of each correlation was assessed and
430 indicated by a p -value: correlations were considered as significant when the Spearman's
431 correlation coefficient (r_s) followed the relationship: $|r_s| \geq 0.6$ and/or when the p -value (p) was
432 lower than 1.67×10^{-4} (Bonferroni correction corresponding to a false positive error rate lower

433 than 5% per test). Pairwise relationships of the variables were drawn using the R package
434 Performance Analytics (Peterson and Carl, 2014).

435 Sixty-three variables were considered to describe the bulk chemical composition of
436 microbialites: (i) concentrations of the 10 major elements (expressed in wt.%): Si, Al, Fe, Mn,
437 Mg, Ca, Na, K, Ti, P; (ii) concentrations of 33 trace elements (expressed in ppm): As, Ba, Ce,
438 Co, Cs, Dy, Er, Eu, Ga, Gd, Ge, Hf, Ho, La, Lu, Nb, Nd, Pb, Pr, Rb, Sm, Sr, Ta, Tb, Th, Tm,
439 U, V, Y, Yb, Zr and C_{org} , S_{tot} (expressed in at.%); and finally (iii) a total of 20 parameters
440 characterizing the REE+Y patterns of microbialites: three La/La* anomalies, three Ce/Ce*
441 anomalies, two Gd/Gd* anomalies, two Eu/Eu* anomalies, one Pr/Pr* anomaly, Y/Ho ratio,
442 the sum of rare earth elements including Y (noted as ΣREE), $(Yb/Nd)_{SN}$, $(La/Yb)_{SN}$, $(Pr/Yb)_{SN}$,
443 $(Nd/Yb)_{SN}$, non-normalized Nd/Yb, $(Sm/Yb)_{SN}$ and $(Pr/Sm)_{SN}$ (Text SI-1 in Supplementary
444 Information).

445 In order to identify microbialites significantly affected by detrital contamination *versus*
446 authigenic-dominated microbialites, we performed a clustering on latent (directional) variables
447 using the R package ClustVarLV (Vigneau et al. 2015). We identified a group of elements
448 linearly correlated with Al, an element classically considered as the main conservative proxy of
449 detrital silicates (Sageman and Lyons, 2003). We performed a standardized principal
450 component analyses (PCA) on the entire group of 32 microbialites samples described by these
451 variables (potentially indicative of detrital contamination) using the R package FactoMineR (Lê
452 et al., 2008). Then, considering the group of authigenic-dominated microbialites, we evaluated
453 the pairwise monotonic relationships between the 63 solid variables by the Spearman's
454 correlation coefficient (values ranging from -1 to +1) and performed two PCA using (i) the 63
455 variables and (ii) the 20 variables describing the REE+Y patterns of microbialites. Pairwise
456 correlations were considered as significant when $|r_s| \geq 0.6$ and/or $p \leq 2.56 \times 10^{-5}$ (Bonferroni
457 correction corresponding to a false positive error rate lower than 5% per test). We performed
458 pairwise comparisons of variance of REE+Y patterns of microbialites between groups of
459 samples according to their detrital contamination.

460 Finally, we tested correlations between microbialite bulk chemical composition and lake
461 water geochemistry. For this purpose, the strength and direction of the pairwise monotonic
462 relationships were evaluated between 24 aqueous variables (listed above without Zn because it
463 was not measured in microbialites) and 63 solid variables on 28 microbialite samples with their
464 corresponding waters by the Spearman's correlation coefficient (values ranging from -1 to +1).
465 Correlations were considered as significant when $|r_s| \geq 0.6$ and/or $p \leq 3.31 \times 10^{-5}$ (Bonferroni
466 correction corresponding to a false positive error rate lower than 5% per test). For this analysis,

467 we considered only microbialite samples for which a corresponding water sample was
468 available. We excluded microbialites sampled in June 2007 (AL13, AL69-2m, AL60-6m and
469 AL54-11m), as water samples were not analyzed with the same methods during this field
470 campaign (Każmierczak et al., 2011).

471

472 **RESULTS**

473

474 **1. Geochemical diversity of the studied Mexican lakes**

475 The complete set of aqueous geochemical data for the 10 lakes is reported in Table SI-
476 4. Ionic balances were always lower than 10% supporting the consistency of the ICP-AES,
477 continuous flow colorimetry, ion chromatography and alkalinity measurements. All the lakes
478 had an alkaline pH between 8.4 and 9.6. Water temperatures measured in May 2014 ranged
479 between 19°C (Lake La Preciosa) and 29°C (Lake Pátzcuaro). The salinities varied among the
480 lakes: Lakes Zirahuén and Alberca de Guadalupe showed salinities of 0.1 and 0.2 psu,
481 respectively, and were considered as freshwater lakes following Hammer (1986). Lakes
482 Quechulac, Pátzcuaro, La Alberca de Los Espinos, Aljojuca, La Preciosa, and Tecuitlapa were
483 subsaline with salinities comprised between 0.5 and 2.7 psu. Lake Atexcac and Lake Alchichica
484 were hyposaline with salinities of 7.4 and 8.3 psu, respectively. Sodium concentrations were
485 positively correlated with salinities ($r_s=0.90$) (Fig. SI-1). Therefore, sodium concentrations
486 were also diverse in these lacustrine systems varying between 0.35 mM in Lake Zirahuén and
487 102.88 mM in the surface water of Lake Alchichica as measured in May 2014. Overall, studied
488 lakes showed a large range of alkalinity: from 1.23 mM for Lake Zirahuén to 49.40 mM for
489 Lake Tecuitlapa. The Mg/Ca ratio of the lakes varied between 1 (Lake Zirahuén) and 90 (Lake
490 Alchichica in May 2014). The concentration of orthosilicic acid (H_4SiO_4) in May 2014 was
491 significantly higher in Lake Alberca de Guadalupe (1.8 mM) and Lake Atexcac (1.1 mM) than
492 in the other lakes (Table SI-4). While pH, magnesium and orthosilicic acid activities were
493 relatively constant through time in Lakes Quechulac, Atexcac and La Preciosa, the H_4SiO_4
494 activity varied in Lake Alchichica between January 2012 (0.0046 mM in the center and 0.2863
495 mM on the western shore) and May 2014 (0.0013 mM in the center and 0.0254 mM on the
496 western shore) (Table SI-4).

497 Several earlier studies monitored the chemical composition of surface water in some of
498 these lakes at different periods during the year (Vilaclara et al., 1993; Armienta et al., 2008;
499 Kaźmierczak et al., 2011; Sigala et al., 2017). A comparison with the present data suggests that
500 the solution chemistry of these lakes have remained relatively constant with the notable

501 exception of calcium concentrations. For example, the calcium concentration in the center of
502 Lake Alchichica differed by more than a factor of 2 between May 2014 (~0.19 mM) and January
503 2012 (~0.46 mM) (Table SI-4). Similarly, the calcium concentration in Lake La Preciosa was
504 2.4 times higher in January 2012 (~0.61 mM) than in May 2014 (~0.25 mM). Moreover, spatial
505 variations were also detected in Lake Alchichica, where the Ca concentration on the western
506 shore (~0.90 mM in January 2012) was significantly higher than in the center of the Lake (~0.46
507 mM in January 2012). These temporal and spatial variations of calcium concentrations in Lake
508 Alchichica may be due to (i) the seasonal mixing of the lake in December/January bringing
509 deep Ca to shallower depth; (ii) groundwater inflow; (iii) photosynthetic activity and associated
510 carbonate precipitation, which may locally reduce Ca concentration. No strong evidence allows
511 to decipher between these three non-exclusive hypotheses.

512 Two groups of lakes could be distinguished based on their Sr isotope ratios (Table 2):
513 Lakes Alchichica, La Preciosa and Atexcac had higher $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.706888 ± 0.000004 ,
514 0.706962 ± 0.000021 and 0.706998 ± 0.000040 , respectively), than Lakes La Alberca de Los
515 Espinos and Zirahuén (0.703914 ± 0.000020 and 0.704514 ± 0.000024 , respectively).

516 Correlations between aqueous geochemistry parameters of Mexican lakes were
517 systematically assessed (Fig. SI-1). Here, we only considered the strongest and statistically
518 significant correlations with a Spearman's correlation coefficient $|r_s| > 0.6$ and a corrected p-
519 value lower than 5% per test (owing to Bonferroni correction for multiple testing). Alkalinity,
520 $[\text{Na}^+]$, salinity, conductivity (C_{25}), $[\text{HCO}_3^-]$, $[\text{CO}_3^{2-}]$, $[\text{K}^+]$ and $[\text{SO}_4^{2-}]$ were all positively
521 correlated ($r_s \geq 0.74$). In particular, a strong positive correlation between alkalinity and sodium
522 concentration ($r_s = 0.79$) was observed. Since Na^+ and HCO_3^- are among the major cations and
523 anions in the studied lakes, this warrants charge balance. The positive correlation between
524 alkalinity, $[\text{HCO}_3^-]$ and $[\text{CO}_3^{2-}]$ was an obvious result from (1) the equilibrium between $[\text{HCO}_3^-]$
525 and $[\text{CO}_3^{2-}]$ and (2) the relationship between $[\text{HCO}_3^-]$, $[\text{CO}_3^{2-}]$ and alkalinity (*i.e.*, $\text{Alk} = [\text{HCO}_3^-]$
526 $+ 2[\text{CO}_3^{2-}]$) (Table SI-5). The $(\text{Mg}/\text{Ca})_{\text{aq}}$ ratio was positively correlated with alkalinity
527 ($r_s = 0.67$), $[\text{HCO}_3^-]$ ($r_s = 0.78$), SO_4^{2-} ($r_s = 0.78$) and $[\text{Br}^-]$ ($r_s = 0.66$). Alkali metal (potassium and
528 sodium) concentrations were positively correlated with each other ($r_s = 0.92$). High positive
529 correlations were observed between $[\text{Mg}^{2+}]$, $[\text{Cl}^-]$, $[\text{Br}^-]$ and $[\text{B}]_{\text{T}}$ (*i.e.*, $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$) (r_s
530 ≥ 0.89). Strontium concentration was positively correlated with $[\text{Ca}^{2+}]$ ($r_s = 0.86$) and negatively
531 correlated with the $(\text{Mg}/\text{Ca})_{\text{aq}}$ ratio ($r_s = -0.78$).

532 Saturations of the surface solutions of all lakes with respect to several carbonate phases
533 were best visualized in a solubility diagram, where the logarithms of $a(\text{Mg}^{2+})$ or $a(\text{Ca}^{2+})$ were
534 plotted against the log of $a(\text{CO}_3^{2-})$ (Fig. 2). Values of these saturation indices were also reported

535 in Table SI-6. All lakes, but Lake Zirahuén, were saturated or supersaturated with respect to
536 MHC. Lake Quechulac and Lake La Preciosa samples collected in 2014 lied exactly on the
537 solubility line of MHC as defined by Fukushi and Matsumiya (2018), while other solutions
538 were at a higher saturation. Lake Zirahuén was significantly lower, close to saturation with
539 aragonite (Fig. 2). Considering $a(\text{Mg}^{2+})$, Lake Alchichica surface solutions were all
540 supersaturated with an amorphous pure Mg-carbonate phase. Atexcac water sample collected
541 in 2012 was at saturation with amorphous Mg-carbonate, whereas the water sample collected
542 in 2014 as well as all other lake waters were undersaturated with amorphous Mg-carbonate
543 (Fig.2). Moreover, all the other lakes were also undersaturated with respect to hydromagnesite
544 (Table SI-6).

545 Saturations of the solutions with respect to authigenic silicate phases were best grasped
546 in a solubility diagram, where the logarithm of the $a(\text{Mg}^{2+})/a(\text{H}^+)^2$ activity ratio was plotted
547 against the log of $a(\text{H}_4\text{SiO}_4)$ of the solutions (Fig. 3). Lake Zirahuén was undersaturated with
548 respect to all reported low-temperature Mg-silicates such as sepiolite, kerolite, talc and
549 stevensite. One sample of Lake Alchichica was saturated with talc, while other samples from
550 this lake were saturated or supersaturated with kerolite and stevensite, and only one sample
551 collected in 2012 on the west shore of the lake was supersaturated with “amorphous sepiolite”,
552 as defined by Wollast et al. (1968). One sample from Quechulac collected in the center of the
553 lake in 2012 was understurated with respect to amorphous sepiolite. All other lakes were
554 saturated or supersaturated with amorphous sepiolite. Lake Alberca de Guadalupe and one
555 sample of Lake Atexcac collected in 2012 lied above the critical supersaturation line for
556 homogenous nucleation of Mg-silicates as defined by Tosca et al. (2011) and Tosca and
557 Masterson (2014). All lakes lied below the solubility line of amorphous silica.

558

559 **2. Microbialite occurrence in modern Mexican lakes**

560

561 No microbialite was found around the shores of Lake Zirahuén, while some
562 microbialites were observed in the other nine lakes (Fig. SI-2). Living microbialites had varying
563 sizes and extents depending on the lakes. For example, microbialites appeared as calcified
564 crusts around volcanic rocks, measuring several hundreds of micrometers in thickness in Lake
565 Alberca de Guadalupe (Fig. SI-2r-s) and few centimeters in thickness in Lake Aljojuca (Fig.
566 SI-2 k-l), Lake Tecuitlapa (Fig. SI-2m-n-o) and Lake Pátzcuaro (Fig. SI-2 t). In contrast, they
567 appeared as meter-sized mounds with various morphologies in Lake Quechulac (Fig. SI-2i-j),
568 Lake La Preciosa (Fig. SI-2f-g-h), Lake Atexcac (Fig. SI-2d-e) and Lake Alchichica (Fig. SI-

569 2a-b-c). Microbialites from Lake Quechulac were observed on a small island at the center of
570 the lake but were absent from the shores of the lake. Microbialites from Lake Pátzcuaro were
571 stromatolitic, *i.e.*, showing macroscopic laminations (Fig. SI-2t). Microbialites from the other
572 lakes showed a clotted thrombolitic fabric. Microbialites in Lake Alchichica formed a massive
573 continuous reef along the shoreline.

574

575 **3. Mineralogical diversity of Mexican lacustrine microbialites**

576

577 The bulk mineralogical composition of the microbialites was assessed by XRD and
578 FTIR (Figs. SI-3 and SI-4). The distribution and texture of mineral phases were characterized
579 by optical microscopy and/or Raman microspectroscopy and/or scanning electron microscopy.
580 Microbialites showed various mineralogical compositions as summarized in Tables 3 and SI-7.

581

582 ***3.1. Carbonate phases: identity, texture and textural relationships***

583

584 Diverse carbonates were detected in the microbialites: (Mg-)calcite, MHC
585 ($\text{CaCO}_3 \cdot \text{H}_2\text{O}$), aragonite, dolomite and hydromagnesite [$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$]. No ACC
586 phase was detected by these bulk methods. Massive occurrences of hydromagnesite were
587 observed in Lake Alchichica microbialites, appearing in a rosette-like texture, whereas this was
588 more occasional in Lake Atexcac (Fig. SI-3a and Table SI-7). Dolomite was observed as a
589 minor phase in one living microbialite from Lake Atexcac (ATX2014-13). It appeared as fine-
590 grained crystals located close to some feldspar and aragonite grains. Based on the relative
591 intensity of the XRD peaks and as supported by bulk chemical analyses (Table SI-8), we
592 inferred that microbialites from Lakes Alchichica, Atexcac, La Preciosa and Quechulac all
593 contained abundant aragonite (Fig. SI-3a-b), while microbialites from Lakes Aljojuca,
594 Tecuitlapa and Pátzcuaro contained mostly (Mg-)calcite and/or MHC with minor amounts of
595 aragonite only (Fig. SI-3c). Last, microbialites from Lake La Alberca de Los Espinos and Lake
596 Alberca de Guadalupe contained MHC and/or (Mg-)calcite only, with no aragonite (Fig. SI-
597 3c). Microbialites from Lake Pátzcuaro (Patz2014-02) showed macroscopic laminations. These
598 laminations corresponded to alternations of Mg-calcite, aragonite and Mg-silicates as observed
599 by SEM and optical microscopy (Fig. 4a-b). Although MHC was detected by XRD in
600 microbialites from Lake Pátzcuaro based on a small peak at 23.9° (2θ) (Fig. SI-3c), it was not
601 observed by SEM. Aragonite was mainly distributed as large nodules measuring several
602 hundreds of micrometers (Fig. 4c-d-e-f) particularly in microbialites with high amounts of

603 authigenic Mg-silicates or hydromagnesite such as in Lakes La Preciosa, Atexcac and
604 Alchichica. In these nodules, aragonite mostly showed a micritic texture but was sometimes
605 acicular as observed in microbialites from Lakes La Preciosa, Atexcac, Alchichica and
606 Quechulac.

607 The co-existence of (Mg-)calcite and MHC in microbialites from Lake Aljojuca
608 (Aljo2014-02), as revealed by XRD (Fig. SI-3c), was further investigated by SEM and Raman
609 microspectroscopy to assess their textural relationship (Fig. 5). MHC was identified by Raman
610 microspectroscopy based on a main band at 1068 cm^{-1} (Fig. 5a-b) corresponding to the ν_1
611 internal symmetric stretching of the C-O bonds in the carbonate group (Zhang et al., 2013).
612 This stretching mode in Mg-calcite was shifted to higher wavenumbers. Its exact position
613 depends on the Mg content (Bischoff et al., 1985; Perrin et al., 2016). In the present case, it
614 appeared at a varying energy position between 1087.3 and 1090.1 cm^{-1} (Fig. 5a-b). Following
615 Perrin et al. (2016), the Mg content of Mg-calcite therefore varied between ~5 and 19 mol% of
616 MgCO_3 . In Lake Aljojuca microbialites, Mg-calcite was distributed as nodules possibly
617 growing at the expense of a matrix composed of MHC (Fig. 5 a-c-d). SEM observations (in the
618 backscattered electron mode) of microbialites from Lake Tecuitlapa and Aljojuca showed that
619 Mg-calcite appeared brighter than MHC (Fig. 5e-f-g).

620 Interestingly, biomorphs possibly resulting from the encrustation of diverse bacterial or
621 eukaryotic cells were repeatedly observed as entombed within the carbonate phases, especially
622 aragonite, MHC and Mg-calcite. Microfossils were mainly associated with aragonite in
623 microbialites from Lake Alchichica (Fig. 6a-b-c-d), Lake Atexcac (Fig. 6e-f), Lake La Preciosa
624 (Fig. 6g) and Lake Quechulac (Fig. 6h). MHC locally contained dense clusters of encrusted
625 cells measuring $\sim 8\text{ }\mu\text{m}$ in width as observed in Aljojuca microbialites (Fig. 6i). Sometimes,
626 MHC also contained particularly well-preserved diatom fossils as observed in the microbialites
627 from Lake Tecuitlapa (Fig. 5f). Dense clusters of filamentous microfossils entombed in Mg-
628 calcite and MHC were observed in the microbialites from Lake La Alberca de Los Espinos
629 (Fig. 6j). To a lesser extent, some microfossils of diatoms and coccoid-shaped cells were
630 observed in association with Mg-calcite in a living microbialite from Lake Alberca de
631 Guadalupe (Fig. 6l). Microbial communities associated with these microbialites are very
632 diverse (Iniesto et al., 2021) and no taxonomical affiliation of the observed fossils could be
633 straightforwardly achieved.

634

635 ***3.2. Identity and micro-texture of authigenic Mg-silicates***

636

637 Poorly-crystalline Mg-silicates were detected by XRD based on broad peaks at 4.58-
638 4.55 Å (22.8° 2 Θ), 2.60-2.58 Å (42.3° 2 Θ) and 1.54 Å (72.1° 2 Θ) (Fig. SI-3b and c) in
639 microbialites from Lakes Pátzcuaro, Atexcac, La Preciosa, Tecuitlapa and La Alberca de Los
640 Espinos. These peaks correspond to two dimensional *hk* diffraction bands (02,11), (13,20) and
641 (06,33), respectively, characteristic of poorly ordered layer silicates such as kerolite (an
642 hydrated talc), with the general formula (Mg₃Si₄O₁₀(OH)₂·nH₂O), and/or trioctahedral smectite,
643 such as stevensite: (Ca_{0.5},Na)_{0.33}(Mg,Fe²⁺)₃Si₄O₁₀(OH)₂·n(H₂O) (Brindley et al., 1955; Brindley
644 et al., 1977). Based on the Si-O-Si stretching at 1024 cm⁻¹ and the Mg₃-OH stretching around
645 3680 cm⁻¹, FTIR analyses were more sensitive than XRD to the presence of these phases and
646 allowed detecting them in additional microbialites such as Lake Quechulac (Zeyen et al., 2015)
647 and Lake Alberca de Guadalupe. In contrast, these phases were not detected at all by XRD and
648 FTIR in microbialites from Lake Aljojuca and Lake Alchichica (*i.e.*, AL2012-12) (Figs. SI-3
649 and SI-4). Consistently, kerolite and/or stevensite was observed by optical and scanning
650 electron microscopies in most of the studied microbialites except those from Lake Aljojuca and
651 most of the samples from Lake Alchichica (Figs. 4 and 7). Kerolite and/or stevensite were only
652 observed in minor amount in one sample from the North-West shore of Lake Alchichica
653 (AL2014-13). In microbialites from the other lakes, kerolite/stevensite was mainly distributed
654 as large homogeneous fractured (indicative of its hydrated nature) patches measuring up to
655 several hundreds of micrometers (Figs. 4c-e and 7). Moreover, we observed in all microbialites
656 containing kerolite/stevensite, an intimate association between kerolite/stevensite and
657 biomorphs (Fig. 7). This supported the previous conclusion that these phases are authigenic
658 (Zeyen et al., 2015 and 2019). Interestingly, some of the Mg-silicate seemed to be partly
659 replaced by carbonates (Fig. 7e-g-h-i).

660

661 **3.3. Additional mineral phases**

662 In addition to carbonate and silicate phases, several microbialites from Lake Alchichica
663 contained Fe-bearing layered double hydroxides (LDH), belonging to the iowaite
664 (Mg₆Fe³⁺₂(OH)₁₆Cl₂·4H₂O) – pyroaurite (Mg₆Fe³⁺₂(OH)₁₆CO₃·4H₂O) group. This phase was
665 evidenced by peaks at 7.65 Å (13.4° 2 Θ) and 3.76 Å (27.6° 2 Θ) in the XRD patterns, consistent
666 with the (003) and (006) Bragg reflections of LDHs, respectively (Fig. SI-3a) (Turvey et al.,
667 2018; Zeyen et al., 2019). In addition, non-authigenic phases were detected by XRD and
668 observed by SEM as well. Na-feldspar (albite) appeared as a major phase in the Alberca de
669 Guadalupe microbialite. Albite also appeared as an abundant phase in Tec2014-06 and Pr2014-
670 03 (Fig. SI-3d). Finally, this mineral phase was detected as a minor phase in Aljo2014-01,

671 Aljo2014-02 and Tec2014-05b. Anorthite (Ca-feldspar) was detected as a minor phase in
672 AL60-6m, Preciosa05-2012, Preciosa06-2012, ATX2014-13. Last, illite (with the general
673 formula $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$) was detected in the AL2012-10m
674 microbialite sample only (Fig. SI-3a). Assuming that all K was in orthose, all Na in albite and
675 that all Al was in the feldspar phases (albite $NaAlSi_3O_8$, anorthite $CaAl_2Si_2O_8$ and orthose
676 $KAlSi_3O_8$), we could estimate that these detrital phases represented 21-22% of the total mass
677 of the microbialites *versus* 78-79% for authigenic phases (carbonate $CaCO_3$ and Mg-silicates)
678 in the three microbialites samples highly affected by detrital contamination (Pr2014-03,
679 Tec2014-05b and LaAlb2014-02, see below). This number was an underestimation of the
680 proportion of the detrital phases in these microbialites since it did not take into account quartz,
681 which was detected in LaAlb2014-02 and Pr2014-03 by XRD, as well as other potential non-
682 Al-bearing detrital phases (Fig. SI-3d).

683

684 ***3.4. Variations of the mineralogical composition of the microbialites within a single*** 685 ***lake***

686 Some variations of the mineralogical abundance were detected among microbialites
687 from the same lake. For example, living microbialites located on the north shore of Lake
688 Atexcac were mainly composed of Mg-silicates and aragonite (ATX-2C1-2012, ATX2014-02,
689 ATX2014-07), while one living microbialite from the south shore was mainly composed of
690 aragonite and contained minor amounts of Mg-silicates only (ATX2014-13). Similarly, living
691 microbialites located on the north shore of Lake Alchichica (AL13, AL66, AL69-2m, AL60-
692 6m, AL2012-1m, AL2012-5m, AL2012-10m, AL2012-15m) were composed of 56 to 88% of
693 hydromagnesite with lesser amounts of aragonite, whereas, some living and non living
694 microbialites located on the west shore of the lake (AL2012-17, AL2014-13, AL2014-15), were
695 composed of 74 to 98% of aragonite with minor amounts of hydromagnesite (Table SI-8). Only
696 two living microbialites located on the west shore of Lake Alchichica (AL2012-12 and
697 AL2014-12) contained mainly hydromagnesite (77% for AL2014-12) and to a lesser extent,
698 aragonite.

699 Moreover, several non-living microbialites had mineralogical compositions differing
700 from living microbialites. For instance, a non-living microbialite sampled on the northeastern
701 shore of Lake Pátzcuaro (Patz2014-01) was composed of Mg-calcite only, while the living
702 microbialite collected in the same area (Patz2014-02) contained Mg-calcite as well as aragonite,
703 MHC and Mg-silicates (Table SI-7). Similarly, a non-living microbialite from the west shore
704 of Lake Alchichica (AL2012-15) was composed of aragonite and some Mg-poor calcite,

705 whereas living microbialites from this area (AL2014-15) were mainly composed of aragonite
706 and hydromagnesite (Tables SI-7 and SI-8).

707

708 **4. Bulk chemical composition of microbialites**

709

710 ***4.1. Identification of an authigenic-dominated microbialites group***

711

712 Bulk chemical analyses of major and trace elements were performed on 32 microbialite
713 samples (Tables SI-9, SI-10 and SI-11). The clustering on latent variables (Fig. 8a) revealed
714 the existence of a group of 8 strongly positively correlated chemical elements ($r_s \geq 0.72$),
715 including the alkali metals K and Rb (large ion lithophile elements), high field strength elements
716 (HFSE; Nb, Ta, Hf and Zr), Al and Ga. Na and Th were correlated to a lesser extent to these 8
717 variables ($r_s \geq 0.85$). Enrichment in those 8 elements is typical of detrital minerals such as
718 feldspars or pyroxenes. A principal component analysis (PCA) was performed using these 8
719 variables on the 32 microbialite samples (Fig. 8b). From this analysis, it was possible to
720 distinguish 3 groups of samples: a group of samples highly affected by detrital contamination,
721 an intermediate group of microbialites moderately affected by detrital contamination and a third
722 group containing authigenic-dominated microbialites (summary in Table SI-7 and Text SI-2 in
723 Supplementary Information). This classification was supported by XRD and SEM analyses.
724 The three microbialite samples Pr2014-03, Tec2014-05b and LaAlb2014-02 clustered together
725 and were particularly enriched compared to the other samples in the 8 above-mentioned
726 chemical elements (Fig. 8b), with Al concentrations of 3.73 ± 0.19 , 3.57 ± 0.18 and 3.46 ± 0.17
727 wt.%, respectively (Table SI-9). There were some variations between these three samples:
728 microbialite sample LaAlb2014-02 was particularly enriched in Ta and Nb (Table SI-10; Fig.
729 8b). Pr2014-03 sample was specifically enriched in Rb and Ga (Table SI-10; Fig. 8b). Tec2014-
730 05b sample was distinctly enriched in Zr and Hf (Table SI-10; Fig. 8b).

731 Eleven other microbialites, defined as “intermediately affected by detrital
732 contamination” (Preciosa-05-2012, Preciosa-06-2012, Tec2014-05a, Aljo2014-02, Patz-2014-
733 02, AL54-11m, AL60-6m, AL2012-10m, AL2012-15, ATX-2C1-2012 and ATX2014-13)
734 grouped together in the PCA analysis and were also enriched in these 8 elements, but to a lesser
735 extent. These samples contained relatively high amounts of Al ranging from 0.49 ± 0.07 wt.%
736 for Preciosa-06-2012 to 1.15 ± 0.06 wt.% for Aljo2014-02.

737 Last, on the PCA biplot, we identified a group of 18 microbialites characterized by low
738 concentrations of K, Rb, Nb, Ta, Hf, Zr, Al and Ga: AL13, AL69-2m, AL2012-1m, AL2012-

739 5m, AL2012-15m, AL2012-12, AL2012-17, AL2014-13, AL2014-15, ATX2014-07, Pr2014-
740 01, Pr2014-02, Pr2014-09, AlbEsp2014-01, Quechulac1A-2012, Quechulac4A-2012,
741 Quechulac4B-2012 and Quechulac4C-2012 (Fig. 8b). This group contained Al concentration
742 lower than 0.27 ± 0.03 wt.% (Table SI-9) and these samples were considered here as authigenic-
743 dominated.

744

745 **4.2. Mg-Ca-Si contents of microbialites**

746

747 Calcium (Ca mass content ranged between 13.9 and 94.9 %, average 57.2 %),
748 magnesium (between 1.3 and 80.8 %, average 26.0 %), and silicon (between 0.7 and 38.5 %, average 12.2 %), were the most abundant chemical elements in all microbialites, followed by
749 aluminum, iron and sodium, depending on samples. Except for the 3 microbialite samples the
750 most affected by detrital contaminations, the 29 others microbialites were plotted in a ternary
751 Ca-Mg-Si diagram (Fig. 9). They were distributed along two main trends: 1) most of the
752 microbialites from Lake Alchichica were distributed along the Ca-Mg line, consistent with the
753 observations that they mostly contained aragonite and hydromagnesite in varying proportions.
754 AL54-11m, AL60-6m, AL2012-10 and AL2012-15 samples, which all appear as
755 “intermediately” contaminated, departed from this trend because of their relatively higher Si
756 content (2.46 ± 0.07 , 2.56 ± 0.08 , 3.83 ± 0.08 and 1.86 ± 0.09 wt.%, respectively). 2)
757 Microbialites from Lakes Quechulac, La Alberca de Los Espinos, La Preciosa, Atexcac,
758 Tecuitlapa and Pátzcuaro scattered along a second trend between the Ca pole and a pole
759 consisting of a Mg:Si mixture of about 41:59 (in wt.%/wt.%), very close to the 3:4 Mg:Si
760 stoichiometry of kerolite and stevensite. As supported by XRD and FTIR, this second trend
761 corresponded to a mixture of varying proportions of Ca-carbonates (aragonite, calcite and
762 MHC) and an authigenic Mg-silicate (kerolite and/or stevensite). ATX-2C1-2012 departed
763 from this second trend and was closer to the Mg end member, consistent with the fact that it
764 also contained hydromagnesite as shown by XRD analyses (Fig.SI-3b). Preciosa05-2012,
765 Aljo2014-02 and ATX2014-13 samples, which were “intermediately” contaminated, slightly
766 departed from this trend and contained more Si mainly due to the presence of detrital phases
767 (Ca-containing feldspar). The Si *versus* Mg contents of these microbialites (except ATX-2C1-
768 2012) were plotted and a strong positive correlation was observed ($R^2=0.93$) (Fig. SI-5). The
769 correlation slope was equal to 0.70 ± 0.07 (wt.%/wt.%) corresponding to 0.81 ± 0.07
770 (at.%/at.%), very close to the theoretically expected atom Mg/Si stoichiometry (0.75) of kerolite
771 and stevensite (Fig. SI-5).
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4.3. Statistical analyses of the chemical compositions of the microbialites

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A statistical analysis of the dataset was performed on the group of 18 authigenic-dominated microbialites to assess potential correlations between the variables describing the chemical composition of the studied microbialites. Several monotonic associations were detected between major and trace elements composing these microbialites considering $|r_s| \geq 0.6$ and a corrected p-value lower than 5% per test (Fig. SI-6). The diagram of pairwise correlations revealed an expected positive correlation between the alkaline earth elements Ca and Sr ($r_s=0.84$), all strongly anti-correlated with Mg. Out of the 18 samples, a group of nine samples (Pr2014-09, Pr2014-01, Pr2014-02, Preciosa06-2012, Preciosa05-2012, Al2014-15, AL13, Quechulac1A-2012 and Quechulac4C-2012), showed a linear positive correlation between S_{tot} and C_{org} content (R^2 of 0.99). The S_{tot}/C_{org} atomic ratio was 0.188 ± 0.009 (Fig. SI-7).

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A principal component analysis was performed on the complete dataset of 63 variables describing the group of 18 authigenic-dominated microbialites (Fig. 10). The AlbEsp2014-01 and ATX2014-07 microbialite samples significantly contributed to the first axis (explaining 34.5% of the total variability), while the Pr2014-01, Pr2014-02 and AL2012-17 microbialite samples significantly contributed to the second axis (explaining 21.8% of the total variability). On the first axis, the AlbEsp2014-01 microbialite sample was particularly enriched in REE+Y with the sum of the REE+Y reaching 12.22 ppm (Table SI-11). In addition, this microbialite sample was particularly concentrated in Mn (0.464 ± 0.03 wt.%) and P (0.27 ± 0.02 wt.%) (Table SI-9). Last, this sample was one of the most enriched in organic carbon (1.04 ± 0.1 at.%) in the group of authigenic-dominated microbialites (Table SI-9). On the second axis, the AL2012-17 microbialite showed a particularly high Y/Ho ratio, reaching a value of 58 and also departed from the other samples based on its high Eu positive anomaly reaching ~ 9 as well as a high positive Gd anomaly (expressed as $Gd/(2Tb-Dy)$) reaching 1.81 (Text SI-1). Moreover, sample AL2012-17 had the highest Fe content (2.49 ± 0.5 wt.%) and a high Sr concentration (equal to 3,441 ppm) in the group of authigenic-dominated microbialites. Last but not least, Pr2014-09 and AL2012-17 microbialites were marked by a pronounced $(Yb/Nd)_{SN}$ anomaly reaching 4.73 and 4.13, respectively, highlighting their HREE enrichment (Fig. 10 and Texts SI-1 and SI-3). Additional interesting but less robust correlations were observed: for example, a positive correlation was observed between the Eu and Ca contents ($r_s=0.75$) in authigenic-dominated microbialites (Fig. SI-6 and Text SI-4).

807 **4.4. REE+Y patterns of microbialites**

808

809 Mexican microbialites exhibited a wide range of REE contents, with the sum of
810 REEs+Y (noted Σ REE) content varying from 1.18 ppm up to 65 ppm (Table SI-11). The Σ REE
811 content of microbialites was positively correlated with their Al content ($r_s=0.81$) (Text SI-3).

812 A PCA was performed on the group of authigenic-dominated microbialites considering
813 the set of 20 variables describing REE+Y patterns of microbialites (Text SI-3). This allowed to
814 discriminate four main types of REE patterns. (i) Patterns such as the ones of AL2012-17 and
815 Pr2014-09 microbialites showed high positive Eu/Eu* anomalies, Gd/Gd* positive anomalies,
816 a high enrichment in HREE as well as a very high Y/Ho ratio (Fig. 11a). (ii) Patterns such as
817 the ones of samples Pr2014-01 and Pr2014-02 were flat, i.e., showed (Nd/Yb)_{SN}, (Pr/Yb)_{SN},
818 (Pr/Sm)_{SN} and (Sm/Yb)_{SN} ratios close to 1 (Fig. 11b). (iii) Patterns of AL2012-5m showed a
819 positive Ce/Ce* anomaly (Fig. 11c). (iv) Patterns of AlbEsp2014-01, Quechulac-4A-2012 and
820 AL2012-15m had a high Σ REE as well as a strong negative Ce/Ce* anomaly and a strong
821 positive Pr/Pr* anomaly (Fig. 11d). Importantly, the lower the Al concentrations in
822 microbialites, the higher the anomalies in Eu, Ce, Pr, La and/or Gd and the HREE to LREE
823 enrichment (Text SI-3). Finally, the Y/Ho ratio of microbialites also depended on the Al content
824 of microbialites. Al-rich microbialites showed a chondritic Y/Ho ratio (26-28), while Al-poor
825 microbialites had a more variable Y/Ho up to 58.0 for AL2012-17 (Text SI-3).

826

827 **5. Relationships between microbialite composition/occurrence and aqueous geochemistry**

828

829 Relationships between the microbialite composition and aqueous geochemistry are
830 shown on a Spearman pairwise correlations diagram (Fig. SI-8). A strong positive correlation
831 was observed between $[\text{Sr}^{2+}]_{\text{aq}}$ and the P content of microbialites ($r_s=0.9$) (Fig. 12). Moreover,
832 fractionations of REEs were detected between solutions and microbialites (Text SI-4). In
833 general, microbialites incorporated more LREE compared to the ambient solutions within
834 which they formed. Microbialites from Lake Quechulac, Lake La Preciosa, Lake Atexcac, and
835 the north shore of Lake Alchichica showed relatively similar solid/solution fractionation
836 patterns with a strong >1 fractionation for Ce and a weaker >1 fractionation for Pr and Nd (*i.e.*,
837 microbialites incorporated more Ce, Pr and Nd compared to the ambient solutions) (Fig. SI-4-
838 1). Last, microbialite from Lake La Alberca de Los Espinos showed high solid/solution
839 fractionations for Nd (Text SI-4).

840 As mentioned earlier, the alkalinity of the lakes was positively correlated with their Na
841 content ($r_s=0.79$) and by extension their salinity ($r_s=0.71$) (Fig. 13) as well as the $(\text{Mg}/\text{Ca})_{\text{aq}}$
842 ratio (Fig. 14a) ($r_s=0.67$ between alkalinity and $[\text{Mg}/\text{Ca}]_{\text{aq}}$ and $r_s=0.63$ between salinity and
843 $[\text{Mg}/\text{Ca}]_{\text{aq}}$). Salinity was positively correlated with $[\text{Mg}]_{\text{aq}}$ ($r_s=0.59$) (Fig. 14b). Alkalinity-
844 salinity- $(\text{Mg}/\text{Ca})_{\text{aq}}$ were also qualitatively correlated with the occurrence (abundance and size)
845 of microbialites (Fig. 13). Indeed, no microbialite was observed in Lake Zirahuén, where
846 alkalinity was the lowest (~ 1.2 mM). At a higher alkalinity of ~ 4.3 mM such as in Lake Alberca
847 de Guadalupe, very small microbialites consisted in thin crusts measuring around several
848 hundreds of micrometers in thickness around basaltic blocks. At alkalinities higher than ~ 7.6
849 mM such as in Lakes La Alberca de Los Espinos, Pátzcuaro, Aljojuca, La Preciosa and
850 Tecuitlapa, living microbialites were well developed along the shore of the lakes. Last,
851 microbialites formed massive and almost continuous reefs at an alkalinity higher than 31 mM
852 such as in Lake Atexcac and Lake Alchichica.

853

854 DISCUSSION

855

856 1. Origins of the chemical variability of the lakes

857 Alkalinity was positively correlated with the salinity of the lakes (Fig. 13). Such a
858 correlation can be viewed as the direct effect of electroneutrality and the fact that Na^+ and
859 HCO_3^- are major ionic species. Several of the continental (Lake Van, Pavilion Lake,
860 Fayetteville Green Lake, Bacalar, Cuatro Ciénegas) and/or volcanic (Salda, Vai Si'I and Vai
861 Lahi) lakes studied by Chagas et al. (2016) also plotted on the same positive correlation. In
862 contrast, coastal lakes (*i.e.*, Big Pond, Laguna Pirata, Clifton, Lagoa Vermelha, Kirimati-Lake
863 21, Walyungup and Fellmongery), with a higher salinity, did not plot on this positive
864 correlation. This can be explained by the fact that coastal lakes have an important seawater
865 input increasing their $[\text{Na}^+]$ and $[\text{Cl}^-]$ relatively to their $[\text{HCO}_3^-]$.

866 One question relates to the origin of the broad variations of salinity (0.35 mM-102.88
867 mM) and alkalinity (1.3 mM-43.0 mM) among the Mexican lakes studied here. Lakes and ponds
868 in the Pantanal wetland in Brazil show similar correlated variations of alkalinity and salinity
869 over an even broader range (Furian et al., 2013). They were explained as the result of varying
870 concentration stages of the same initial dilute water. Following the concept of chemical divide,
871 when dilute waters feeding lakes have a dissolved inorganic carbon (DIC) concentration higher
872 than the concentrations of alkaline earth metals (Ca^{2+} and Mg^{2+}), they evolve upon evaporation
873 into increasingly alkaline brines with decreasing relative concentrations of Ca^{2+} then Mg^{2+}

874 (Pecoraino et al., 2015). This also explains why alkalinity increases correlatively with $[\text{Na}^+]_{\text{aq}}$
875 and $(\text{Mg}/\text{Ca})_{\text{aq}}$ upon evaporation (Gac et al., 1977; Al-droubi et al., 1980; Darragi and Tardy,
876 1987). Dilute waters feeding Mexican lakes most often comprise rainfall and groundwater only.
877 The composition of groundwaters is controlled by the weathering of surrounding bedrocks and
878 in particular their $\text{DIC}/([\text{Ca}^{2+}]+[\text{Mg}^{2+}])$ ratios will depend on the petrological composition of
879 the bedrock (e.g., basaltic/andesitic rocks *versus* carbonates; Gaillardet et al., 1999). Some
880 variations were observed in the nature of the bedrock sourcing Mexican lakes. Indeed, Lake La
881 Alberca de los Espinos and Lake Zirahuén showed low $^{87}\text{Sr}/^{86}\text{Sr}$ values close to 0.7040. This
882 was within the 0.7037-0.7047 range for $^{87}\text{Sr}/^{86}\text{Sr}$ values measured by Verma (1999) on basaltic
883 andesites, andesites and dacites from the Sierra de Chichinautzin, located south of Mexico City
884 in the TMVB. This suggested that both lakes were mostly fed by the weathering of
885 basaltic/andesitic rocks, consistently with the rocks outcropping around these lakes (Davies et
886 al., 2004; Siebe et al., 2014). This kind of petrology typically generates high
887 $\text{DIC}/([\text{Ca}^{2+}]+[\text{Mg}^{2+}])$ dilute waters (Pecoraino et al., 2015). In contrast, Lakes Alchichica, La
888 Preciosa and Atexcac had significantly more radiogenic dissolved Sr (*i.e.*, $^{87}\text{Sr}/^{86}\text{Sr}$ values close
889 to 0.7070) suggesting that they were fed by the dissolution of both basalts and carbonate rocks
890 (Verma, 2000; Gómez-Tuena et al., 2007). Again, this is consistent with the presence of a
891 limestone bedrock outcropping within the Cretaceous Cuenca de Oriental basin (Reyes Cortés,
892 1979; Caballero et al., 2003; Carrasco-Núñez et al., 2007; Armienta et al., 2008). In that case
893 the $\text{DIC}/([\text{Ca}^{2+}]+[\text{Mg}^{2+}])$ of the dilute waters might be lower. However, in both cases, volcanic
894 CO_2 outflows may be an additional parameter increasing the $\text{DIC}/([\text{Ca}^{2+}]+[\text{Mg}^{2+}])$ ratio of
895 groundwater, hence favoring an alkaline-type evolution of the lakes as shown by Milesi et al.
896 (2020) for Lake Dziani Dzaha. Although we did not measure the isotopic composition of DIC,
897 which may offer a definitive answer to this question, we observed that most Mexican lake
898 solutions, except Lakes Zirahuén, Alberca de Guadalupe and Tecuitlapa, were equilibrated with
899 a pCO_2 higher than the atmospheric pCO_2 (Table SI-12). This suggests that volcanic CO_2 may
900 play an additional role in maintaining a high DIC in these lakes (Pecoraino et al. 2015). In any
901 case, all studied Mexican lakes plotted in the alkaline domain of a Ca^{2+} , SO_4^{2-} , $\text{HCO}_3^- + \text{CO}_3^{2-}$
902 (all expressed in equivalent/L) ternary diagram (“Spencer diagram”, Fig. SI-9), supporting the
903 idea that they indeed evolve toward more alkaline conditions over increasing evaporative
904 concentration.

905 Mercedes-Martin et al. (2019) developed a hydrochemical model shedding light on
906 the hydrological parameters that may control varying concentration factors, hence explaining
907 why some Mexican lakes may eventually have higher alkalinities/salinities/ $(\text{Mg}/\text{Ca})_{\text{aq}}$ than

908 others. One of their model focused on closed lakes and allowed a stationary water level for the
909 lake by balancing groundwater input with outputs by evaporation and leakage to the lake bottom
910 aquifer. Therefore, in this case, varying concentration factors cannot be assessed in the field
911 based on an apparent water level decrease. They showed that in this model the major parameters
912 controlling the concentration factor were the rate of solute input to the lake and the rate of
913 leakage to groundwater systems. Similarly, Furian et al. (2013) proposed that the varying
914 concentration stages of Pantanal ponds depended on their hydrological functioning, itself
915 controlled by the presence/absence of low permeability soils as barriers to input/output water
916 movements. In conclusion, the hydrology of the lakes controls their concentration stage.
917 Because feeding dilute waters are relatively alkaline, they become even more alkaline, more
918 saline and show an increasing $(\text{Mg}/\text{Ca})_{\text{aq}}$ upon concentration. Unfortunately, we do not
919 presently have all hydrochemical parameters allowing to model the varying concentration
920 stages of all studied Mexican lakes, but at least, assuming a similar initial Cl^- concentration for
921 all the lakes, we can infer that the concentration factor is more than 500 times higher in Lake
922 Alchichica than in Lake Zirahuén.

923 As an exception, Lake Tecuitlapa departed from the correlation between salinity and
924 (i) $(\text{Mg}/\text{Ca})_{\text{aq}}$ and (ii) $[\text{Mg}^{2+}]_{\text{aq}}$, with a marked relative Mg depletion (Fig. 14). This lake showed
925 the highest pH (9.6) and the highest alkalinity (49.40 mM) among the studied lakes. The
926 particular high pH and alkalinity of Lake Tecuitlapa might be of biological origin since this
927 lake is characterized as hypertrophic (Sigala et al., 2017) with high $[\text{PO}_4^{3-}]_{\text{aq}}$ and total dissolved
928 N species concentrations (Table SI-4) and high photosynthetic biomass was observed (Fig. SI-
929 2). Other studies similarly suggested that high primary production levels can contribute to a
930 high pH and alkalinity (López-Archilla et al., 2004; Milesi et al., 2019; Milesi et al., 2020).
931 Chagas et al. (2016) also reported a positive correlation between salinity and $[\text{Mg}^{2+}]_{\text{aq}}$ in twenty-
932 one lakes with the departure of one lake (Lake Van located in Turkey) showing a marked Mg
933 depletion relative to its high salinity, similarly to Lake Tecuitlapa in the present study. Lake
934 Van showed the highest alkalinity (~150 mM) and the highest pH (9.9) among the lakes studied
935 by Chagas et al. (2016). They suggested that Lake Van's depletion in Mg was the consequence
936 of its high alkalinity and the availability of CO_3^{2-} ions to react with cations. However, although
937 diverse carbonate phases were observed in Tecuitlapa microbialites, these did not contain
938 particularly insoluble Mg-rich phases that might drag the concentration of Mg downward
939 compared to other lakes. Alternatively, Reimer et al. (2009) explained the Mg^{2+} depletion in
940 Lake Van by abundant Mg-silicate precipitation. Here, Mg-silicates were detected in Lake
941 Tecuitlapa microbialites but also in microbialites from other lakes without any relative

942 depletion in $[Mg^{2+}]_{aq}$ relative to their salinity. Another possibility could be that some saline,
943 Ca-rich and Mg-poor water may feed Lake Tecuitlapa, relatively decreasing its Mg
944 concentration. Lastly, since Lake Tecuitlapa contains a high biomass and Mg^{2+} is an important
945 cofactor in many enzymes, cells might be an important sink of Mg, decreasing its concentration
946 in solution. Only future studies addressing the hydrology of this lake will be able to test those
947 different hypotheses.

948

949 **2. Relationships between microbialites and lake aqueous geochemistry**

950 The chemical compositions of lake solutions were measured on samples collected at a
951 specific time. By contrast, microbialites form over a certain time and therefore integrate
952 potential solution chemistry variations that we may not see. Accordingly, we evidenced some,
953 yet limited chemical variations over time in lake solutions as further discuss below. Chemical
954 conditions may also vary spatially within a lake, with depth and possibly locally where a
955 microbialite forms and again, this cannot be tracked by reporting the bulk chemistry of the
956 lakes. Several sampling at different places in one lake consistently showed some chemical
957 variations, which, again, were limited. Therefore, we assumed that these variations were most
958 of the times small in comparison with the large chemical variations between the lakes. This is
959 supported by clear first order relationships evidenced between lake aqueous geochemistries and
960 microbialites that we discuss in this section.

961

962 **2.1. Geochemical conditions for the formation of microbialites and carbonate** 963 **precipitation pathways**

964

965 We observed a correlation between the alkalinity/salinity and the occurrence,
966 abundance, and size of microbialites in Mexican lakes (Fig. 13): no microbialite at the lowest
967 alkalinity and lowest salinity (Lake Zirahuén); thin carbonates crusts at intermediate
968 alkalinities/salinities (Lake Alberca de Guadalupe); larger microbialites at higher
969 alkalinities/salinities (Lakes La Preciosa and Aljojuca); finally, massive microbialitic reefs at
970 the highest alkalinities/salinities (*e.g.*, Lakes Atexcac and Alchichica). A minimum alkalinity
971 between 1.23 and 4.28 mM and a minimum salinity between 0.08 and 0.21 g/L seem required
972 for the formation of microbialites. This corresponded to lakes with a $SI_{Mg-calcite}$ higher than 1.11.
973 This value is in accordance with the threshold of 1.0 required for cyanobacterial calcification
974 by calcite, as established by Arp et al. (2001). Therefore, based on the hypothesis that alkalinity
975 increases with concentration factor, the onset of microbialite formation may appear as a

976 milestone in the hydrochemical history of a lake, starting only after the achievement of a
977 minimum alkalinity and/or salinity value.

978 The analysis of a solubility diagram, where the logarithms of $a(\text{Mg}^{2+})$ or $a(\text{Ca}^{2+})$ were
979 plotted against the log of $a(\text{CO}_3^{2-})$ offered deeper insight into what may control carbonate
980 precipitation in Mexican lakes (Fig. 2). Similarly to what Fukushi and Matsumiya (2018)
981 evidenced in other alkaline lakes, we observed that several Mexican lakes (Quechulac, La
982 Preciosa and Atexcac) plot along/close to the solubility line of MHC, supporting the idea that
983 the $a(\text{Ca}^{2+})/a(\text{CO}_3^{2-})$ ratio in these lakes is controlled by the precipitation of this phase. All other
984 lakes but Zirahuén plot above the solubility line of MHC by about 0.5 log unit. Interestingly,
985 Fukushi and Matsumiya (2018) also observed that several alkaline lakes were similarly
986 supersaturated with MHC. This may suggest that additional precursor phases more soluble than
987 MHC control the $a(\text{Ca}^{2+})/a(\text{CO}_3^{2-})$ ratio in these lakes. Chaka et al. (2018) mentioned that MHC
988 is unlikely to precipitate primarily from a solution but results from the transformation of ACC
989 precursor. Rodriguez-Blanco et al. (2014) and Blue et al. (2017) also concurred that MHC is a
990 metastable intermediate between ACC and anhydrous Ca-carbonate phases such as calcite and
991 aragonite. While all Mexican lakes plot below the solubility line of ACC as determined by
992 Brecevic and Nielsen (1989), Mergelsberg et al. (2020) noticed that ACC with a lower
993 solubility exists. Overall, it is therefore possible that Mexican lakes plot close to the solubility
994 line of such a less soluble ACC phase. Alternatively, heterogenous nucleation of ACC, *e.g.*, on
995 cell surfaces or exopolymeric substances may as well occur at a lower $(\text{Ca}^{2+})(\text{CO}_3^{2-})$ product
996 than the ACC solubility line by Brecevic and Nielsen (1989). Following an Ostwald step rule,
997 when conditions are thermodynamically favored, the most soluble phases precipitate first since
998 they are kinetically favored (Chaka, 2018). Then they transform to less soluble, more
999 thermodynamically stable phases, either by dissolution-precipitation or solid-state
1000 transformation. Considering all these facts, we therefore suggest the following precipitation
1001 sequence for Ca-carbonates in Mexican lakes: (i) first, there is a homogeneous and/or
1002 heterogenous nucleation of ACC, which may control the $a(\text{Ca}^{2+})/a(\text{CO}_3^{2-})$ of many of the lakes.
1003 No ACC was detected in Mexican microbialites by bulk XRD and FTIR measurements.
1004 Benzerara et al. (2006) reported ACC in Lake Van microbialites, but this was achieved by
1005 precise TEM analyses and ACC clearly remain difficult to detect in association with other
1006 abundant, crystalline phases. Moreover, ACC might be so reactive that it transforms instantly,
1007 which adds to the difficulty to detect it. (ii) Then, ACC transforms to MHC. (iii) Third, MHC
1008 transforms to calcite or aragonite depending on the aqueous Mg/Ca ratio prevailing in the lake

1009 solution (Figs. 14 and 15). This latter transformation is not complete in some lakes as we detect
1010 MHC in some microbialites (see below).

1011 Only Lake Zirahuén lied much below the MHC solubility line, close to the aragonite
1012 and calcite solubility lines (Fig. 2). We did not observe any microbialite in this lake. This
1013 suggests that saturation with anhydrous carbonate (*i.e.*, aragonite, calcite) is insufficient for the
1014 detectable formation of microbialites and that (super)saturation with MHC might be necessary
1015 for this to happen.

1016 Fukushi and Matsumiya (2018) also observed a correlation between $a(\text{Mg}^{2+})$ and
1017 $a(\text{CO}_3^{2-})$ in several alkaline lakes, corresponding to the solubility of amorphous magnesium
1018 carbonates and therefore suggested that this phase controls the $a(\text{Mg}^{2+})/a(\text{CO}_3^{2-})$ in these lakes.
1019 This appears to be valid for Lake Alchichica (and to a lesser extent Lake Atexcac), in which
1020 solution waters are supersaturated with respect to hydromagnesite (Table SI-6) and
1021 microbialites contain hydromagnesite (Fig. 2). Chaka (2018) mentioned that hydromagnesite is
1022 unlikely to precipitate primarily from water and that this goes through transient more hydrated
1023 and more soluble precursor phases such as nesquehonite and dypingite. Overall, we can propose
1024 the following mineral precipitation sequence in Lake Alchichica: (i) there is precipitation of an
1025 amorphous magnesium carbonate, which then (ii) transforms to nesquehonite and which (iii)
1026 ultimately transforms to hydromagnesite. All the other lakes, except Atexcac, lie much lower
1027 than the amorphous Mg-carbonate solubility line (named AMC2 as determined by Fukushi and
1028 Matsumiya (2018)). Therefore, in these lakes, the $a(\text{Mg}^{2+})/a(\text{CO}_3^{2-})$ ratio is likely impacted by
1029 other mineral phases, possibly the authigenic Mg-silicates that were found pervasively, and/or
1030 Ca-carbonates. All these other lakes are moreover undersaturated with hydromagnesite and
1031 therefore, the formation of this phase is eventually not expected in these lakes. Last, in Lake
1032 Atexcac, waters were sometimes on, sometimes below the solubility line of amorphous Mg-
1033 carbonate (AMC2, Fig. 2). These variations of the chemical composition of the lake, possibly
1034 due to some hydrological variations (*e.g.*, higher concentration stages) may explain the limited
1035 amounts of hydromagnesite and abundant authigenic Mg-silicates in Lake Atexcac
1036 microbialites.

1037

1038 **2.1.1. Relationship between the aqueous Mg/Ca ratio and the carbonate** 1039 **mineralogy of microbialites**

1040

1041 The identity of the carbonate phases (Mg-calcite, MHC, aragonite, hydromagnesite)
1042 composing living Mexican microbialites was clearly correlated with the $(\text{Mg}/\text{Ca})_{\text{aq}}$ ratio of the

1043 lakes (Figs. 14 and 15). Müller et al. (1972) observed a similar empirical relationship based on
1044 the study of authigenic (non microbialitic) sediments collected from twenty-five lakes. The
1045 thresholds they inferred were about the same as in our study, except for the onset of
1046 hydromagnesite precipitation that they did not observe in the field but simulated by laboratory
1047 experiments. Based on these experiments, they suggested that hydromagnesite precipitated at
1048 $(\text{Mg}/\text{Ca})_{\text{aq}} > 500$. Chagas et al. (2016) also reported a similar relationship between the identity
1049 of the carbonate phases composing microbialites and the $(\text{Mg}/\text{Ca})_{\text{aq}}$ ratio of the lakes based on
1050 a compilation of data from twenty-one lakes. These authors also noted departures from this
1051 relationship for lakes where local groundwater discharges influenced the mineralogy of the
1052 microbialites, such as in Lake Van (Kempe et al., 1991). Chagas et al. (2016) suggested that
1053 $[\text{Mg}^{2+}]_{\text{aq}}$ was a good predictor for the presence of high Mg-calcite and MHC in microbialites.

1054 As explained above, the formation of hydromagnesite may require Mg^{2+} and CO_3^{2-}
1055 activities high enough so that solution activity products are above the solubility line of
1056 amorphous magnesium carbonate. The $(\text{Mg}/\text{Ca})_{\text{aq}}$ ratio would thus appear as an indirect
1057 predictor of hydromagnesite formation, because it is generally correlated with DIC, hence CO_3^{2-}
1058 activity, and Mg^{2+} concentration. The control of the identity of the anhydrous Ca-carbonate
1059 phases composing microbialites appears different. Since ACC and/or MHC might be the same
1060 precursors for all lakes, we propose that the control by $(\text{Mg}/\text{Ca})_{\text{aq}}$ operates on the transformation
1061 of the precursor phases into the most stable phases. At a $(\text{Mg}/\text{Ca})_{\text{aq}}$ ratio higher than 10, MHC
1062 transforms completely to aragonite (Fig. 15). At a lower $(\text{Mg}/\text{Ca})_{\text{aq}}$, MHC transforms partially
1063 to Mg-calcite or aragonite. Overall, this scenario is consistent with the claim that MHC might
1064 be a widespread metastable intermediate in the formation of anhydrous calcium carbonates and
1065 that it has been observed as an intermediate between ACC and aragonite or (Mg-)calcite
1066 (Chaka, 2018). Interestingly, it has also been argued that because of its unique structure, MHC
1067 is relatively more stable than other hydrated Ca or Mg carbonate phases, and its transformation
1068 to anhydrous carbonates occurs through dissolution-precipitation only. By contrast, other
1069 hydrated phases may undergo solid state transformations upon dehydration (Chaka, 2018). This
1070 may explain why some MHC may be preserved when they are kept away from dissolution, and
1071 how $(\text{Mg}/\text{Ca})_{\text{aq}}$ may direct the transformation of MHC to (Mg-)calcite or aragonite through
1072 dissolution-precipitation. Indeed, since $[\text{Mg}^{2+}]_{\text{aq}}$ inhibits calcite precipitation (Berner, 1975;
1073 Deleuze and Brantley, 1997; Pokrovsky, 1998; Bots et al., 2011), the kinetics of aragonite
1074 precipitation becomes relatively faster than that of calcite when the Mg content of Mg-calcite
1075 exceeds ~18 mol% (Davis et al., 2000).

1076 Several parameters can modify the $(\text{Mg}/\text{Ca})_{\text{aq}}$ thresholds between the domains of
1077 dominance of the different carbonate phases. For instance, $[\text{SO}_4^{2-}]_{\text{aq}}$ may decrease calcite
1078 precipitation rate relative to aragonite (Walter, 1986; Bots et al., 2011) so that high $[\text{SO}_4^{2-}]_{\text{aq}}$
1079 may favor the dominance of aragonite. Here, deconvoluting the impact of $(\text{Mg}/\text{Ca})_{\text{aq}}$ *versus*
1080 $[\text{SO}_4^{2-}]_{\text{aq}}$ was difficult since both parameters were positively correlated ($r_s=0.78$). As an
1081 exception, Lake Tecuitlapa had a lower $(\text{Mg}/\text{Ca})_{\text{aq}}$ ratio (3 *versus* 5.3 to 10.4) but a higher $[\text{SO}_4^{2-}]_{\text{aq}}$
1082 (1.6 *versus* 0.2 mM) than Lake Quechulac. Lake Tecuitlapa microbialites were mainly
1083 composed of Mg-calcite and MHC, while Lake Quechulac microbialites were composed of
1084 aragonite only. In that case, the $(\text{Mg}/\text{Ca})_{\text{aq}}$ ratio was therefore the dominant controlling
1085 parameter, consistently with what was reported by Bischoff and Fyfe (1968).

1086 Finally, we observed deviations from this global relationship between the identity of the
1087 carbonate phases and the $(\text{Mg}/\text{Ca})_{\text{aq}}$ ratio in non-living microbialites. Some of these deviations
1088 may indicate the impact of diagenesis as suggested by the detection of Mg-poor calcite in fossil
1089 microbialites of Lake Alchichica (*e.g.*, AL2012-15). Calcite may result from meteoric alteration
1090 of aragonite by dissolution/reprecipitation (*e.g.*, De Boever et al., 2017). In this case,
1091 hydromagnesite seems to be leached out. How Mg-silicates are affected by meteoric alteration
1092 remains to be understood. In other cases, the deviations may be due to past variations of the
1093 $(\text{Mg}/\text{Ca})_{\text{aq}}$ ratio of the lakes. In this scenario, the carbonate mineralogy of non-living
1094 microbialites recorded in most cases lower $(\text{Mg}/\text{Ca})_{\text{aq}}$ past values: *e.g.*, the non-living
1095 microbialite of Lake Pátzcuaro was composed of Mg-calcite only, while the living microbialite
1096 contained Mg-calcite, MHC and aragonite; non-living microbialites in Lake Alchichica
1097 contained aragonite and calcite, while living ones contained aragonite and hydromagnesite.
1098 Overall, one may infer an increasing net concentration factor over time, which increases the
1099 alkalinity as well as the $(\text{Mg}/\text{Ca})_{\text{aq}}$ ratio of the lakes, as discussed above. After the onset of
1100 microbialite formation, this would result in the successive formation of living microbialites,
1101 which are first composed of Mg-calcite, then aragonite and finally hydromagnesite along with
1102 the alkalinity, salinity and aqueous Mg/Ca gradients (Figs. 13-16).

1103

1104 **2.1.2. Occurrence of monohydrocalcite and its environmental significance**

1105

1106 Based on the (super)saturation of all Mexican microbialites-harbours lakes with
1107 respect to MHC and consistently with several recent theoretical, field and experimental studies
1108 (*e.g.*, Chaka, 2018; Fukushi and Matsumiya, 2018; Fukushi et al., 2020), MHC is interpreted
1109 as a precursor phase in Mexican lakes. It is sometimes transient, transforming into aragonite

1110 and/or Mg-calcite. Sometimes, it is preserved in several microbialites. Microbialites from Lakes
1111 Tecuitlapa and Aljojuca offer some textural examples of MHC replacement by Mg-calcite (Fig.
1112 5). MHC was observed in the living microbialites from Lake La Alberca de Los Espinos
1113 ((Mg/Ca)_{aq}=2.8), Lake Pátzcuaro ((Mg/Ca)_{aq}=3.0) and Lake Tecuitlapa ((Mg/Ca)_{aq}=3.0) as the
1114 second most abundant carbonate phase after (Mg-)calcite. MHC was the main mineral phase in
1115 living microbialites from Lake Aljojuca ((Mg/Ca)_{aq}=6.8) but was absent from microbialites in
1116 Lake Quechulac ((Mg/Ca)_{aq}=10.4) (Fig. 15; Table 3).

1117 MHC has been frequently found in lacustrine deposits (Domagalski et al., 1989),
1118 including microbialites (Kharaka et al., 1984; Rosen et al., 2004; Last et al., 2010), sometimes
1119 partially replaced by Mg-calcite (Spencer, 1977). This mineral phase has also been shown to
1120 be preserved in ancient (> 1000 years) lacustrine sediments (Stoffers and Fischbeck, 1974).
1121 Chagas et al. (2016) proposed that MHC formed in lakes with Mg concentration higher than
1122 37.5 mM. Taylor (1975) argued that a pH higher than 8.6 and a Mg/Ca ratio higher than 10
1123 favored the precipitation of MHC, whereas Fukushi et al. (2011) reported that a pH higher than
1124 8 and a (Mg/Ca)_{aq} ratio higher than 4 could favor this process. Loste et al. (2003) experimentally
1125 showed the precipitation of MHC at Mg/Ca ratios higher than 3, but in association with other
1126 carbonate phases. Here, we suggest that the precipitation of MHC is determined by (Ca²⁺) and
1127 (CO₃²⁻) activities being above the solubility line of MHC. Then, MHC secondarily transforms
1128 partly or completely to more stable anhydrous Ca-phases by dissolution-precipitation.
1129 Therefore, in Mexican microbialites, the control on MHC presence/absence may relate to the
1130 efficiency/kinetics/inhibition of its transformation to (Mg-)calcite or aragonite.

1131 Rodriguez-Blanco et al. (2014) consistently proposed that some (Mg-)calcite and
1132 aragonite found in the geological record may be of secondary origin, resulting from the
1133 transformation of a primary metastable MHC phase. Finding past traces of MHC in ancient
1134 microbialites might therefore be challenging. Whether preservation of MHC, observed in non-
1135 living microbialites from Lake Aljojuca and Lake Tecuitlapa, may be favored by high
1136 concentrations of orthosilicic acid as suggested by Zhang et al. (2013) and/or phosphates
1137 (Fukushi et al., 2011) will require further investigations. An additional preservation pathway
1138 may involve microorganisms. We observed microcrystalline MHC associated with dense
1139 clusters of filamentous microfossils in microbialites from Lakes Tecuitlapa and Aljojuca.
1140 Similarly, MHC was observed as the organomineralization by-product of anoxygenic
1141 phototrophic bacteria (Bundeleva et al., 2012). These authors suggested that organic matter
1142 such as exopolymeric substances (EPS) may preserve MHC from recrystallisation into more

1143 stable carbonates. Future experimental studies exploring the chemical and biological pathways
1144 favoring the preservation of MHC will be crucial.

1145

1146 **2.1.3. Sr enrichment within microbialites and its relationships with** 1147 **carbonate mineralogy**

1148

1149 There was a positive linear correlation between the Sr and Ca microbialite contents
1150 ($r_s=0.84$). Only AlbEsp2014-01 outlied this relationship. Authigenic-dominated microbialites
1151 showed a Sr/Ca ratio of 0.009 ± 0.002 . We calculated the solid/liquid partition coefficient of Sr
1152 normalized to Ca (for the samples collected in 2014 and authigenic-dominated):
1153 $(\text{Sr/Ca})_{\text{mic}}/(\text{Sr/Ca})_{\text{aq}}=2.4 \pm 0.7$, indicating an enrichment of Sr in the microbialites compared to
1154 the solutions relatively to Ca. Tesoriero and Pankow (1996) measured a partition coefficient of
1155 0.021 between Sr/Ca in calcite *versus* Sr/Ca in the solution at 25°C. Dietzel et al. (2004)
1156 measured a partition coefficient of 1.19 at 25°C in aragonite. Here, we therefore observed a
1157 relative enrichment of Sr over Ca between the solid and the solution that is not explained by
1158 the precipitation of calcite and/or aragonite alone. Some hypotheses can be explored to explain
1159 this enrichment but they will need to be investigated in the future. On the one hand, other
1160 mineral phases, such as sulfates, may contribute, although they are at low concentration in the
1161 studied microbialites and the S content does not correlate with that of Sr ($r_s=0.2$). Alternatively,
1162 some biological processes may play a role in such a fractionation. Extracellular bioprecipitation
1163 of carbonates has been reported to induce fractionation but they appear lower than the one
1164 measured here. For example, the bacterium *Sporosarcina pasteurii* induces extracellular
1165 precipitation of $(\text{Ca,Sr})\text{CO}_3$ via ureolysis (Lauchnor et al., 2013), with a solid/liquid partition
1166 coefficient of 0.38-1.00. In a similar study, Mitchell and Ferris (2005) found a Sr partition
1167 coefficient to be 0.46 at 20 °C in carbonates formed by the ureolytic *Bacillus pasteurii*.
1168 Alternatively, Cam et al., (2016) and Blondeau et al. (2018) showed a very high Sr over Ca
1169 enrichment in intracellular carbonates formed by *Gloeomargarita lithophora*, a cyanobacterium
1170 isolated from Lake Alchichica (Couradeau et al., 2013) and found in other lakes as well (Ragon
1171 et al., 2014). Whether ACC formed by these bacteria may eventually feed at least some of the
1172 extracellular carbonate phases forming Mexican microbialites in trace elements such as Sr will
1173 have to be explored.

1174

1175 **2.2. Geochemical conditions allowing authigenic Mg-silicates precipitation and** 1176 **proxies for $[\text{H}_4\text{SiO}_4]_{\text{aq}}$ of ancient lakes**

1177

1178 All lakes harboring microbialites were supersaturated with respect to hydrated Mg-
1179 silicates such as kerolite, sepiolite or stevensite except at the center of Lake Alchichica (AL-
1180 M) (Fig. 3 and Table SI-6). However, hydrated Mg-silicates were systematically observed as
1181 authigenic phases, except in microbialites from Lake Aljojuca and in most of the samples from
1182 Lake Alchichica (Table SI-7). More soluble phases, such as the “amorphous sepiolite” as
1183 defined by Wollast et al. (1968), thus appear as better predictors of authigenic silicate formation
1184 since it better accounts for the absence of Mg-silicates in Alchichica samples (Fig. 3). Two
1185 lakes (Lakes Alberca de Guadalupe and Atexcac) were located above the critical
1186 supersaturation line for homogenous nucleation as defined by Tosca et al. (2011) and Tosca
1187 and Masterson (2014). It is therefore thermodynamically and kinetically possible that
1188 authigenic silicate phases precipitate spontaneously, without any biological mediation in these
1189 lakes. All other lakes harbouring authigenic-silicate-containing microbialites lie below this line
1190 and on or above the solubility line of “amorphous sepiolite” (Fig. 3). Two hypotheses can be
1191 formulated: (i) The phase forming in Mexican microbialites is closer in solubility to the
1192 “amorphous sepiolite” phase formed in Wollast et al. (1968)’s experiments and this phase is
1193 different and less soluble than the phase formed in Tosca et al. (2011)’s experiments. Such a
1194 difference between the phases formed in both studies was discussed by Tosca et al. (2011) and
1195 may relate to the source of Si that was used in these experiments (*i.e.*, sodium metasilicate
1196 nonahydrate *versus* tetraethyl orthosilicate). (ii) Authigenic silicates in Mexican microbialites
1197 are similar to the ones forming in Tosca et al. (2011)’s experiments but they nucleate
1198 heterogeneously, hence at a lower ionic activity product than the critical supersaturation line
1199 for homogeneous nucleation. Microscopy observations of biofilms entombed within Mg-
1200 silicates in Mexican microbialites support the possibility of such an extensive heterogenous
1201 nucleation (Zeyen et al., 2015). Only a better understanding of the structural controls over the
1202 solubility of these phases will help to decipher between these two hypotheses. Surprisingly, the
1203 saturation index with respect to kerolite in Lake Aljojuca ($SI_{\text{kerolite}}=4.82$; $[\text{H}_4\text{SiO}_4]_{\text{aq}}=0.16$ mM)
1204 was higher than *e.g.*, in Lake Pátzcuaro ($SI_{\text{kerolite}}=4.17$; $[\text{H}_4\text{SiO}_4]_{\text{aq}}=0.37$ mM), although
1205 authigenic Mg-silicates were detected and observed in Lake Pátzcuaro microbialites but not in
1206 Lake Aljojuca microbialites. The origin of this discrepancy remains to be understood.

1207 Lakes do not plot along a single line in the solubility diagram for authigenic Mg-
1208 silicates, meaning that the solubilities of these phases may not control the activities of the
1209 dissolved chemical species, at least not in all lakes. Then, what controls H_4SiO_4 activity in the
1210 lakes remains an open question. The nature of the weathered protolith and variations of silicate

1211 weathering intensity may be prime parameters. The biomineralization activity of diatoms in the
1212 lakes may also play an important role. Indeed, diatoms actively take up H_4SiO_4 from the water
1213 (Milligan and Morel, 2002) and precipitate opaline silica even in those Mexican lakes that are
1214 undersaturated with respect to amorphous silica. Here, similarly to what has been shown in the
1215 oceans (Conley et al., 2017), it is possible that diatom populations decrease $[\text{H}_4\text{SiO}_4]_{\text{aq}}$ to
1216 different extents between lakes and/or at different time of the year in a given lake, explaining
1217 the observed temporal variations of $[\text{H}_4\text{SiO}_4]_{\text{aq}}$. Upon diatom death, especially in lakes where
1218 solutions are undersaturated with respect to amorphous silica, H_4SiO_4 is expected to be
1219 “recycled” back to the solution. The maintenance of an out-of-equilibrium state regarding the
1220 precipitation of Mg-silicates suggests that either the input of H_4SiO_4 to the lakes by diatom
1221 dissolution and/or weathering processes may be constantly higher than the removal of Si by the
1222 kerolite/stevensite precipitation. However, at least in some cases, H_4SiO_4 appears to be retained
1223 in microbialites rather than released back to solution. Indeed, we observed that diatoms may
1224 serve as loci for Mg-silicate precipitation, producing diatoms fossilized by Mg-silicates
1225 (kerolite/stevensite) in the microbialites from Lakes Atexcac and Alberca de Guadalupe. This
1226 process called “reverse weathering” was also observed by Badaut and Risacher (1983) and
1227 Bentz and Peterson (2020) in Andean saline lakes.

1228 We observed Al-poor Mg-silicates as a predominant authigenic phase in Mexican lakes.
1229 Gérard et al. (2018) also detected Al-poor Mg-silicates as a predominant phase in microbialites
1230 from Lake Dziani. In contrast, Milesi et al. (2019) and Milesi et al. (2020) observed a Mg-rich
1231 aluminosilicate as a predominant phase in the sediments of Lake Dziani. Milesi et al. (2019)
1232 proposed that the dissolution of detrital silicates and hydromagnesite in sediments provided Al,
1233 Si and Mg, and favored the precipitation of a Mg-rich aluminosilicate phase. Unfortunately, we
1234 did not analyze the mineralogical composition of the sediments in Mexican lakes to assess how
1235 systematic the dichotomy observed in Lake Dziani might be. This will be important to assess
1236 since Millot (1970) proposed that Al-rich clay minerals preferably form at basin margins by
1237 heterogenous nucleation on detrital Al-silicates, whereas homogenous nucleation of Al-poor
1238 Mg-silicates (such as stevensite) occurs preferentially towards the basin center where detrital
1239 materials are at a lower amount. The paleoenvironmental significance of this relationship may
1240 however not be attested in small-scale basins. In any case, we underline that the presence of Al-
1241 poor Mg-silicates in Dziani and Mexican microbialites vs. Mg-aluminosilicates in Dziani
1242 sediments is supported by the phase equilibria mentioned above. Indeed, Mg-aluminosilicates
1243 (such as saponite or montmorillonite) are less soluble than amorphous sepiolite and can
1244 therefore precipitate at a lower ionic activity product (Tosca, 2015). Pore waters in Dziani

1245 sediments have an ionic activity product lower than the solubility line of amorphous sepiolite
1246 but equal/higher than that of Mg aluminosilicates. In contrast, Dziani and most Mexican lake
1247 waters are saturated or supersaturated with amorphous sepiolite, thus allowing precipitation of
1248 Al-poor Mg silicates. One major parameter explaining this difference is that Dziani sediment
1249 pore waters have a lower H_4SiO_4 activity than Dziani and Mexican lake waters. As mentioned
1250 above, the determinism of H_4SiO_4 activity remains to be explored.

1251 Last, similarly to MHC, the long-term preservation of authigenic Mg-silicates in the
1252 fossil record can be discussed. Early secondary replacement of Mg-silicates by (Mg-)calcite
1253 and/or aragonite was observed by SEM in Lake Alberca de Guadalupe, Lake Atexcac, Lake
1254 Quechulac and Lake La Preciosa (Fig. 7). This suggests that a carbonation reaction transforms
1255 the silicates, which might be very fast due to their poor crystallinity. Tosca and Wright (2015)
1256 addressed in detail several additional processes susceptible to destabilize authigenic Mg-silicates
1257 upon diagenesis. They showed that Mg-silicates may dissolve due to organic carbon
1258 degradation by *e.g.*, methanogenesis, which decreases pore solution pH and drives solutions
1259 out of Mg-silicate stability zone. Moreover, cation migration to octahedral vacancies in these
1260 silicates generate protons, which in turn may result in their dissolution (Komadel et al., 2005;
1261 Tosca and Wright, 2015). In addition, potential magmatic CO_2 degassing could increase the pH
1262 of the pore water of the sediments (Milesi et al., 2020) which could eventually lead to the Mg-
1263 silicate destabilization upon diagenesis. Yet, Mg-silicates are sometimes preserved in the
1264 geological record (Tettenhorst and Moore 1978; Tosca et al., 2011), urging their systematic
1265 search in ancient microbialites.

1266

1267 **2.3. Local processes: evidence for microbial influence**

1268 The above discussion identifies large-scale chemical and hydrological parameters
1269 controlling the formation of microbialites and their mineralogical composition. However, this
1270 should not be considered as a negation of the role of biology, which may catalyze precipitation
1271 and/or “mold” mineral textures. We discuss several aspects of this below.

1272

1273 *Carbonates*

1274 Arp et al. (2001) suggested that DIC controls biologically-mediated carbonate
1275 precipitation pathways: at high DIC and pH (*e.g.*, soda lakes), carbon removal by cyanobacterial
1276 photosynthesis induces only a minor rise in calcite supersaturation in the entire lake, because
1277 of the large buffering of pH by DIC. If local pH increase is the biological driver of nucleation,
1278 $CaCO_3$ may therefore not precipitate preferentially on cells in these lakes but instead

1279 homogenous CaCO_3 nucleation may occur everywhere. In contrast, in low-DIC water,
1280 photosynthesis results in a strong rise in calcite supersaturation ($\Delta\text{SI}_{\text{calcite}} = 0.3 - 0.5$), and Ca-
1281 carbonate precipitation occurs preferentially around the cells, thereby inducing the formation of
1282 calcimicrobes in the rock record. As mentioned previously, this model should be reconsidered
1283 by focusing on local saturations with precursor phases (*e.g.*, ACC and/or MHC) instead of
1284 calcite. For example, microorganisms may impact not only the nucleation of the precursor
1285 phases but also the different transformation steps to the final most stable phases found in
1286 microbialites. Moreover, we observed fossilized bacteria (calcimicrobes) in association with
1287 (Mg-)calcite, MHC, or aragonite in microbialites from all the studied lakes including those with
1288 high DIC. As already mentioned by Gérard et al. (2013) and Couradeau et al. (2013), this
1289 contradicts the idea that calcimicrobes cannot form in high-DIC environment. However, these
1290 observations might be reconciliated with Arp et al (2001)'s model by considering that while the
1291 alkalinity engine driven by cyanobacterial photosynthesis plays a minor role in high-DIC
1292 environments, heterogeneous nucleation of carbonate phases on *e.g.*, cyanobacterial sheaths
1293 may play an important role, hence partly localizing precipitation around cells (Giuffrè et al.,
1294 2013).

1295 Moreover, it has been reported that some microorganisms may orient mineral
1296 precipitation towards one carbonate phase at the expense of another, such as the cells of the
1297 cyanobacterial *Pleurocapsales* and *Chroococcales* orders, which were shown to induce the
1298 precipitation of aragonite in a hydromagnesite-dominated environment (Gérard et al., 2013;
1299 Couradeau et al., 2013; Saghaï et al., 2015). Future studies should be directed to determining
1300 whether such microorganisms may be present in all the studied lakes and may systematically
1301 favor aragonite over hydromagnesite nucleation or if this biological influence is only a
1302 parameter of lower importance.

1303

1304 *Mg-silicates*

1305 The microbial mediation of authigenic Mg-silicate precipitation has been increasingly
1306 suggested in various environments based on the observation of close spatial associations
1307 between cells and these phases (Léveillé et al., 2002; Arp et al., 2003; Souza Eglypsy et al.,
1308 2005; Burne et al., 2014; Zeyen et al., 2015; Pace et al., 2016; Gérard et al., 2018). Léveillé et
1309 al. (2002) argued that the precipitation of authigenic Mg-silicates, at least in part, results from
1310 the binding effect of the EPS concentrating ions (Mg and silica) from solution and serving as
1311 nucleation sites for kerolite precipitation. This mechanism was also favored by Pace et al.,
1312 (2016). Zeyen et al (2015) observed an intimate and pervasive association of EPS with Mg-

1313 silicates, down to the nm-scale, also supporting the importance of these polymers in mineral
1314 precipitation. An additional question relates on how EPS could fractionate Mg, Si and Al. Burne
1315 et al. (2014) proposed that Mg-silicate formation is promoted by high local silica activity from
1316 dissolving diatoms. As described above, spontaneous homogeneous nucleation is possible in
1317 two Mexican lakes. In other lakes, it remains to understand if the spontaneous nucleation of a
1318 phase with a solubility close to that of amorphous sepiolite is possible. In this case, the
1319 involvement of microbes may not be strictly necessary for the precipitation of this phase in
1320 Mexican microbialites. Otherwise, we observe in the solubility diagram of Mg-silicates
1321 evidence of heterogeneous nucleation of a phase with a solubility similar to that measured by
1322 Tosca et al. (2011) and this might be catalyzed, at least in part, by microorganisms.

1323

1324 *P-rich phases*

1325 The present study highlighted a positive linear correlation between the P content of the
1326 studied microbialites and the $[Sr]_{aq}$ of the corresponding lakes (Figs. 12 and SI-8). $[Sr]_{aq}$ was
1327 also positively correlated with $[Ca]_{aq}$, which can be explained by the similar chemical behavior
1328 of both elements. The correlation between the P content of the studied microbialites and $[Sr]_{aq}$
1329 may suggest that (i) some of the phosphorus in the microbialites is in the form of Ca-phosphate
1330 mineral phases and (ii) this phosphate mineral reservoir is relatively bigger at lower $(Mg/Ca)_{aq}$
1331 ratio and lower alkalinity, *i.e.*, where the precipitation of Ca-phosphate may be favored
1332 relatively to that of carbonate phases. Consistently, it can be noted that the saturation index with
1333 respect to hydroxyapatite was the highest under these conditions (Table SI-6). Recently, Toner
1334 and Catling (2019) highlighted a positive correlation between $[PO_4^{3-}]_{aq}$ and dissolved inorganic
1335 carbon (DIC) in different North American and African lakes. These authors explained that this
1336 positive correlation resulted from the precipitation of Ca-carbonates in highly alkaline lakes,
1337 which acted as a sink for Ca^{2+} , which therefore did not precipitate with P, resulting in its
1338 accumulation in the water column. In this present study, we did not observe such a correlation,
1339 possibly because $[PO_4^{3-}]_{aq}$ measurements were not precise enough. Alternatively, the removal
1340 of phosphorus via biotic mechanisms may have a strong impact on the PO_4^{3-} concentration in
1341 these lacustrine systems. Interestingly, statistical analyses highlighted the fact that there is a
1342 positive correlation between P and Mn contents of microbialites. These elements are also
1343 correlated with the C_{org} content of microbialites. Especially, the living microbialite sample from
1344 Lake La Alberca de Los Espinos showed the highest concentrations in P, Mn and C_{org} . It is not
1345 clear if Mn and P are part of the same phase within this microbialite, but the incorporation of

1346 these two nutrients could be mediated by the activity of microorganisms. The speciation of P
1347 in these microbialites will need further investigations using, *e.g.*, spectro(micro)scopy tools.

1348

1349 *S-rich organic molecules*

1350 We observed a positive correlation between the organic carbon and total sulphur
1351 contents for 9 microbialite samples, with a $S_{\text{tot}}/C_{\text{org}}$ atomic ratio equal to 0.188 ± 0.009 (Fig.
1352 SI-7). This correlation may be consistent with S being associated with organic carbon in
1353 microbialites. However, the measured S/C ratio is significantly higher than the mean S/C ratio
1354 of 0.012 (at./at.) with a range of 0.006 – 0.032 (at./at.) measured on 8 types of natural and
1355 cultured bacteria by Fagerbakke et al. (1996). Heldal et al. (2003) measured even lower ratios
1356 between 0.003 and 0.009 (at./at.) for marine *Synechococcus* and *Prochlorococcus* strains. One
1357 possibility is that organic matter entombed within microbialites becomes sulfurized, a process,
1358 which would increase the S/C ratio as this has been observed in 2.72 Ga old microbialites (Lepot
1359 et al., 2009). Atomic S/C ratio of organic matter globules from these ancient microbialites reach
1360 up to 0.042 (Lepot et al., 2019). The presence of sulfurized organic compounds (thiopenes) was
1361 also observed in modern freshwater microbialites from Cuatro Ciénegas (Mexico) (Nitti et al.,
1362 2012). Alternatively, some S may be in the form of sulfates within carbonate phases or sulfide
1363 phases explaining the departure of some samples towards compositions richer in S. A major
1364 obstacle to address these questions deals with the speciation of S in these samples, which would
1365 need to be assessed in the future to discriminate between these different possibilities.

1366

1367 **3. REE+Y patterns of authigenic-dominated microbialites**

1368

1369 REE+Y patterns of ancient chemical sediments have often been used as proxies to identify
1370 their depositional environments (Van Kranendonk et al., 2003; Bolhar and Van Kranendonk,
1371 2007; Awramik and Buchheim, 2009; Zhao and Zheng, 2017; Eltom et al., 2017) and
1372 reconstruct the geochemistry of ancient seawater (Kamber and Webb, 2001; Kamber et al.,
1373 2004; Bolhar et al., 2004; Bolhar and Van Kranendonk, 2007; Frimmel, 2009; Riding et al.,
1374 2014; Kamber et al., 2014). However, as also reported before, we observe that detrital
1375 contaminations strongly affects microbialite REE+Y patterns and blurs this message. As a
1376 result, REE+Y patterns of Mexican microbialites highly affected by detritism hold no
1377 information on their formation environments (Text SI-3). These microbialites showed: (i) a
1378 high total REE+Y contents, above 12.2 ppm; (ii) a flat REE pattern and less marked REE
1379 anomalies, and finally (iii) a low Y/Ho ratio (close to that of chondrites). By contrast, although
1380 authigenic-dominated microbialites also showed some hints of contamination (Text SI-3), some

1381 variations were observed in their REE+Y patterns, which may be indicative of the conditions
1382 under which they form. REE+Y patterns of Mexican authigenic-dominated microbialites
1383 showed (i) a relatively higher proportion of HREE, (ii) relatively high (positive or negative)
1384 anomalies in Eu, Ce, La, Gd and Pr and (iii) a high Y/Ho ratio. The possible origins of these
1385 signatures are discussed in Supplementary Data. However, whatever their origins, it is
1386 particularly interesting to observe that these signatures have been classically attributed to
1387 microbialites formed in seawater. The REE+Y pattern of marine microbialites from the Heron
1388 Reef, Great Barrier Reef has been used as a modern reference for marine microbialites (Webb
1389 and Kamber, 2000). Similarly to modern seawater, they showed HREE enrichment with
1390 $(Nd/Yb)_{SN} = 0.236 \pm 0.026$, negative Ce and positive La and Gd anomalies, and a uniformly
1391 superchondritic Y/Ho ratio (56.17 ± 2.66). Similar features were observed in Messinian
1392 carbonates from Calcare di Base (Sicily) by Guido et al. (2011): a HREE enrichment with
1393 $(Nd/Yb)_{SN}$ of 0.5; positive La, Gd, Eu and Y anomalies, a negative Ce anomaly and a
1394 superchondritic Y/Ho ratio of 57.1. This led the authors to conclude about a marine origin of
1395 these carbonates. However, here we demonstrate that some of the modern Mexican lacustrine
1396 microbialites also show similar REE+Y patterns, despite their freshwater origin: a HREE
1397 enrichment (mean value $Nd/Yb_{SN} = 0.56$, $SD = 0.19$), La, Gd, Eu positive anomalies, Ce
1398 negative anomalies and a superchondritic Y/Ho value (reaching up to 58). Many continental
1399 waters exhibit REE+Y patterns that closely resemble those of modern seawater (Johannesson
1400 et al., 2006). Overall, this calls for a careful reassessment of the criteria discriminating between
1401 marine and freshwater environments and a better understanding of the diversity of the
1402 processes, including the role of microbes, involved in the fractionation of REE+Y in these
1403 systems.

1404

1405 **CONCLUSION**

1406

1407 Ten alkaline Mexican lakes showed correlated salinities, alkalinities and $(Mg/Ca)_{aq}$
1408 ratios varying over a broad range. These environmental parameters controlled the
1409 presence/absence and size/amount of microbialites in the lakes, as well as their mineralogical
1410 composition as illustrated by Figure 16. A minimum alkalinity between 1.23 and 4.28 mM and
1411 a salinity between 0.08 and 0.21 g/L appeared necessary for the formation of microbialites. This
1412 may more accurately relate to the achievement of saturation levels of the solutions close or
1413 above the solubility of MHC. A precipitation pathway for Ca-carbonate phases is inferred: ACC
1414 may precipitate first before transforming to MHC, which itself transforms partly or completely

1415 to Mg-calcite or aragonite, depending on the $(\text{Mg}/\text{Ca})_{\text{aq}}$ of the solution. Moreover, when (Mg^{2+})
1416 and (CO_3^{2-}) activities are higher than the solubility of amorphous magnesium carbonate, Mg-
1417 carbonates precipitate and transform ultimately to hydromagnesite. The occurrence of
1418 authigenic Mg-silicates was decoupled from this global trend. Such phases were detected in
1419 microbialites from lakes saturated or supersaturated with a phase reported in the literature as
1420 “amorphous sepiolite” and with a concentration of orthosilicic acid higher than 0.2 mM.
1421 Overall, by identifying the primary mineralogy of a microbialite, one may obtain information
1422 on several chemical conditions prevailing in the lake where these microbialites formed.
1423 Moreover, since higher salinity-alkalinity- $(\text{Mg}/\text{Ca})_{\text{aq}}$ result from an increasing concentration of
1424 alkaline lakes, we can propose an integrated evolutionary scenario in which microbialite
1425 formation evolves with the changing lake hydrochemistry, which itself depends on the
1426 hydrological functioning of the lake. As the concentration stage of an alkaline lake increases,
1427 salinity/alkalinity increases and, at some point, microbialites start to form. Upon further
1428 concentration, the $(\text{Mg}/\text{Ca})_{\text{aq}}$ ratio increases and the mineralogy of the microbialites shifts from
1429 Mg-calcite to aragonite and eventually hydromagnesite appears as well. In parallel, microbialite
1430 formation populating the lakes become more massive (Fig. 16).

1431 The trace element composition of microbialites also offers additional information. High
1432 concentrations in Al, Ga, Nb, Ta, K, Rb, Hf and Zr were diagnostic of microbialite
1433 contamination by detrital particles. This resulted in high REE+Y contents of these microbialites
1434 together with a flat REE+Y pattern. In contrast, lacustrine authigenic-dominated microbialites
1435 showed an HREE enrichment, and marked REE anomalies with, in particular, a positive Eu
1436 anomaly, a negative Ce anomaly and a high Y/Ho ratio. Therefore, these characteristics, used
1437 in past studies as diagnostic of a marine origin, can also be found in some lacustrine
1438 microbialites, questioning their diagnostic value for marine settings.

1439 This study suggests that the abundance and the mineralogical and chemical composition
1440 of lacustrine microbialites can be predicted at a first order based on the global physico-chemical
1441 and hydrological conditions prevailing in the lake. However, these physicochemical conditions,
1442 while being necessary, might not always be sufficient and other processes may explain some of
1443 the observed variability across microbialites within a single lake. This is the case of
1444 groundwater vents, and/or the presence of certain microorganisms influencing local conditions
1445 and precipitation of specific mineral phases. Moreover, since the global physico-chemical
1446 conditions prevailing in a lake may influence the taxonomic and functional diversity of
1447 microbial communities and vice-versa, this relationship between environmental parameters and
1448 the composition of microbialites does not preclude the importance of biology. Future integrative

1449 (meta-)analyses of taxonomic and functional diversity of microbial populations in addition to
1450 solution geochemistry, microbialite mineralogical and chemical composition in different lakes
1451 may reveal some of these connections. The general rules exposed here offer a new framework
1452 for a better interpretation of the paleo-environmental conditions under which ancient lacustrine
1453 microbialites formed. Last, for this purpose, the diversity of transformations occurring upon
1454 diagenesis and/or metamorphism of the phases composing modern microbialites, including
1455 monohydrocalcite and Mg-silicates, will be crucial to assess.

1456

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1478

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- 1949

1950 **FIGURE CAPTIONS**

1951

1952 **Figure 1.** Geographic location of the ten studied lakes. (a) Geological map representing the
1953 location of the trans-Mexican volcanic belt (TMVB, green area) from Ferrari et al. (2012) and
1954 the location of studied lakes marked by red squares. (b-f) Google Earth images of the lakes.
1955 Blue, yellow and red circle symbols correspond to microbialite sampling areas in June 2007,
1956 January 2012 and May 2014, respectively. No dot for Lake Zirahuén because this lake was not
1957 populated by microbialites; solutions have been sampled in the center of the lake. AH: Anegada
1958 high; LTVF: Los Tuxtlas volcanic field.

1959

1960 **Figure 2.** Solubility diagram in the $\log[a(\text{CO}_3^{2-})] - \log[a(\text{Ca}^{2+})]$ (in red) or $-\log[a(\text{Mg}^{2+})]$ (in
1961 black) space determined at 25°C. All surface waters are plotted after correction of their
1962 temperature variations. The solubilities of calcite and aragonite were defined by Plummer and
1963 Busenberg (1982); the solubility of amorphous Ca-carbonate (ACC) was measured by Brecevic
1964 and Nielsen (1989). The solubilities of monohydrocalcite (MHC) and amorphous Mg-carbonate
1965 (AMC2) were determined by Fukushi and Matsumiya (2018). AMC2 corresponds to a phase
1966 precipitating during the late-stage of the precipitation of AMC (Fukushi and Matsumiya, 2018)
1967 Diamond symbols stand for water solutions sampled in Lakes Quechulac (Q), La Preciosa (LP),
1968 Atexcac (Atx-N) and Alchichica (AL-M and AL-W) in January 2012. Circle symbols
1969 correspond to solutions sampled in Lakes Alberca de Guadalupe (Alb), Pátzcuaro (P),
1970 Tecuitlapa (T), La Alberca de Los Espinos (AE), Aljojuca (Alj), Zirahuén (Z), Alchichica (AL-
1971 M), Quechulac (Q), Atexcac (Atx-M) and La Preciosa (LP) in May 2014.

1972

1973 **Figure 3.** Solubility diagram in the $\log[a(\text{Mg}^{2+})/a(\text{H}^+)^2] - \log[a(\text{H}_4\text{SiO}_4)]$ space determined at
1974 25°C. All surface waters are plotted after correction of their temperature variations. The
1975 equilibrium solubilities of talc (Jones and Galan, 1988), amorphous sepiolite (Wollast et al.,

1976 1968), stevensite (Decarreau, 1983), kerolite and sepiolite (Stoessell, 1988), are indicated as
1977 oblique lines. Vertical dashed lines indicate the equilibrium solubility of quartz and amorphous
1978 silica (Truesdell and Jones, 1974). The Mg-saponite-montmorillonite equilibrium was
1979 estimated by Tosca (2015) using thermodynamic data estimated from Weaver and Beck (1977).
1980 The “critical saturation” line results from experiments conducted by Tosca et al., (2011) and
1981 Tosca and Masterson (2014) and relates to homogeneous nucleation of Mg-silicate phases from
1982 solution. Diamond symbols stand for water solutions sampled in Lakes Quechulac (Q), La
1983 Preciosa (LP), Atexcac (Atx-N) and Alchichica (AL-M and AL-W) on January 2012. Circle
1984 symbols correspond to water solutions sampled in Lakes Alberca de Guadalupe (Alb),
1985 Pátzcuaro (P), Tecuitlapa (T), La Alberca de Los Espinos (AE), Aljojuca (Alj), Zirahuén (Z),
1986 Alchichica (AL-M and AL-W), Quechulac (Q), Atexcac (Atx-M and ATX-N) and La Preciosa
1987 (LP) on May 2014. Red symbols stand for lakes where kerolite/stevensite were not observed
1988 nor detected within microbialites, whereas green symbols stand for lakes where microbialites
1989 contained kerolite/stevensite. The ‘Mg-silicates’ vertical solid line corresponds to the $[H_4SiO_4]$
1990 threshold over which kerolite/stevensite precipitation was observed for the studied
1991 microbialites.

1992

1993 **Figure 4.** Textures of mineral phases observed in Mexican microbialites by light microscopy.
1994 (a) Plane-polarized light photomicrograph of Pátzcuaro microbialite sample (Patz2014-01)
1995 showing a stromatolite-type texture with laminations. (b) Cross-polarized light
1996 photomicrograph of the same area showing the presence of a poorly crystalline phase,
1997 interpreted here as kerolite and/or stevensite (K/S) and a layer of Mg-calcite (MgC). (c) Plane-
1998 polarized light photomicrograph of La Preciosa microbialite sample (LP2014-08) showing
1999 aragonite dark nodules (A) surrounded by a brighter brown kerolite and/or stevensite matrix
2000 (K/S). (d) Cross-polarized light photomicrograph of the same area revealing the poor

2001 crystallinity of kerolite and/or stevensite and the acicular texture of aragonite apparent on the
2002 edges. (e-f) Plane-polarized and cross-polarized light photomicrographs of Atexcac
2003 microbialite sample (ATX-2C1-2012) showing a matrix of kerolite (K/S) and/or stevensite and
2004 the aragonite nodules (A).

2005

2006 **Figure 5.** Distribution and texture of Mg-calcite and monohydrocalcite in microbialites from
2007 Lakes Aljojuca and Tecuitlapa (Aljo214-02 and Tec2014-06). (a) Plane polarized light
2008 photomicrograph of the Aljojuca microbialite sample showing alternations between 2 phases:
2009 a dark phase (Mg-calcite) distributed as a large nodule possibly growing within a bright matrix
2010 (monohydrocalcite). (b) Raman spectra of (1) Mg-calcite showing a ν_1 band at 1090.1 cm^{-1} , (2)
2011 Mg-calcite showing a ν_1 band at 1087.3 cm^{-1} , (3) monohydrocalcite (MHC) with a ν_1 band at
2012 1068.6 cm^{-1} corresponding to the bright matrix. In these spectra, the bands below 400 cm^{-1}
2013 correspond to lattice mode vibrations and the band around 750 cm^{-1} to the in-plane bend (ν_4) of
2014 C-O bonds. (c) Plane polarized light photomicrograph overview of the studied area with a
2015 predominance of MHC in the Aljojuca microbialite. (d) Dynamic line-scanning Raman
2016 mapping of the area marked by a rectangle on (c) showing the correlation index for each
2017 spectrum with the reference spectra of MHC (green) and Mg-calcite (red). Bright colors
2018 indicate a greater correlation between the sampled spot and the references. Black pixels
2019 correspond to the glue used for sample preparation and/or organic matter (e) SEM image of the
2020 Aljojuca microbialite in the backscattered electron mode with MHC (dark phase) and Mg-
2021 calcite (white nodules). (f) SEM image of the Tecuitlapa microbialite in the backscattered
2022 electron mode showing a chemical contrast between MHC (darker phase), which embeds a
2023 diatom microfossil on the left (arrow), and the brighter Mg-calcite phase. (g) EDXS spectra of
2024 (1) Mg-calcite and (2) MHC in Aljojuca microbialite (outlined in (e)), and (3) Mg-calcite and
2025 (4) MHC in Tecuitlapa microbialite (outlined in (f)).

2026

2027 **Figure 6.** Biomorphs entombed within carbonates in Mexican microbialites. **(a-l)** SEM images
2028 in the backscattered electron mode of microbialites from Lakes Alchichica (AL), Atexcac
2029 (ATX), La Preciosa, Quechulac, Aljojuca (Aljo), La Alberca de Los Espinos (AlbEsp),
2030 Tecuitlapa (Tec), Alberca de Guadalupe (LaAlb). Abbreviations for the mineral phases are: A:
2031 aragonite; C: calcite, Mg-C: magnesian calcite, MHC: monohydrocalcite, H: hydromagnesite,
2032 K/S: kerolite/stevensite.

2033

2034 **Figure 7.** Frequent associations between Mg-silicates (kerolite and/or stevensite) and
2035 biomorphs (indicated by dashed red arrows). SEM images taken in the backscattered electron
2036 mode of microbialites from Lakes **(a)** La Preciosa (Preciosa05-2012), **(b)** La Preciosa (Pr2014-
2037 09), **(c)** Quechulac (Quechulac-1A-2012), **(d)** Atexcac (ATX-2C1-2012) and **(e)** (ATX2014-
2038 13) **(f)** La Alberca de los Espinos (AlbEsp2014-01), **(g)** Alberca de Guadalupe (LaAlb2014-
2039 02), **(h)** Pátzcuaro (Patz2014-02) and **(i)** Tecuitlapa (Tec2014-06). Abbreviations for the
2040 mineral phases are: A: aragonite; Mg-C: magnesian calcite, MHC: monohydrocalcite, H:
2041 hydromagnesite, K/S: kerolite/stevensite.

2042

2043 **Figure 8.** Classification of three groups of samples according to their detrital contamination.
2044 **(a)** Dendrogram of the hierarchical relationships between 43 variables representing major and
2045 trace elements (represented as tree leaves) describing the 32 microbialite samples. The order by
2046 which the leaves are connected in the dendrogram is directly related to the strength of the linear
2047 correlation between the variables: the smaller the vertical distance between two leaves and the
2048 node connecting them, the stronger the correlation between the two corresponding variables.
2049 Optimal grouping of correlated variables was inferred. The group composed by Al and seven
2050 variables linearly correlated to Al is highlighted. **(b)** PCA analyses with biplot of variables

2051 (vectors represented by arrows) and samples (dots). Each axis (or principal component) is a
2052 linear combination of variables defined in order to maximize the spatial discrimination of
2053 samples; coordinates of vectors on each axis indicate the coefficient of the variables in the linear
2054 combination. Longer the orthogonal projection of an arrow on a given axis, stronger the
2055 contribution of the variable to this axis. Smaller the angle between arrows, stronger the positive
2056 linear correlation between corresponding variable. Orthogonal arrows indicate no correlation,
2057 while arrows pointing in opposite directions indicate a negative correlation. The samples are
2058 plotted in two dimensions using their projections onto the first two principal components. The
2059 part of the total sample variability explained by each axis is indicated in the axis titles.
2060 Three major groups of samples are highlighted: -HDC: three samples highly affected by detrital
2061 contamination (red squares); -IDC: eleven samples intermediately affected by detrital
2062 contamination (green diamonds) and -LDC: eighteen samples the least affected by detrital
2063 contamination (=authigenic-dominated) microbialites (blue dots).

2064

2065 **Figure 9.** Ternary Mg-Ca-Si diagram reporting bulk chemical composition (wt.%) of studied
2066 microbialites except the 3 microbialite samples affected by strong detrital contamination
2067 (Pr2014-03, LaAlb2014-02 and Tec2014-05b). Arrows correspond to: (1) the hydromagnesite-
2068 aragonite trend followed by Alchichica microbialites and (2) a trend between an aragonite
2069 and/or (low Mg-)calcite and/or monohydrocalcite, and a Mg-silicate endmember (noted 2 on
2070 the Mg-Si axis) corresponding to microbialites from the other lakes. The sample ATX-2C1-
2071 2012 departs from this trend because in addition to aragonite and Mg-silicate, it is composed
2072 of hydromagnesite.

2073

2074 **Figure 10.** PCA performed on the group of 18 authigenic-dominated microbialites, (a) PCA
2075 variables factor map representing the complete dataset of 63 variables describing the

2076 microbialite bulk chemistry. **(b)** PCA plot with samples plotted in two dimensions using their
2077 projections onto the first two principal components. More guidance can be found in the caption
2078 of Figure 8.

2079
2080 **Figure 11.** REE+Y patterns of some of the authigenic-dominated microbialites. Four main
2081 signatures are observed as highlighted by PCA (Figure SI-9). **(a)** REE+Y patterns showing high
2082 positive Eu/Eu* anomalies, Gd/Gd* positive anomalies, high Yb/Nd_{SN} ratio revealing an
2083 enrichment in HREE and a very high Y/Ho ratio; **(b)** REE+Y pattern showing the absence of
2084 Ce anomaly and a particular low (Σ REE+Y) content; **(c)** REE+Y patterns showing high
2085 Σ REE+Y and marked negative Ce/Ce* anomalies; **(d)** relatively flat REE+Y patterns.

2086
2087 **Figure 12.** Scatter plot of aqueous Sr content of the lakes *versus* P content of microbialites
2088 showing a positive correlation ($r_s=0.9$). Samples with high detrital contamination (red squares);
2089 intermediately contaminated samples (green diamonds); authigenic-dominated samples (blue
2090 dots).

2091
2092 **Figure 13.** Scatter plot (log-log) of the alkalinity *versus* the salinity of the lakes normalized to
2093 the Lake Zirahuen's salinity. The degree of microbialite occurrence is documented in red. These
2094 alkalinity and salinity data correspond to samples collected in May 2014. The dashed blue line
2095 indicates the positive correlation. The regression coefficient (R^2) of the plot is equal to 0.89.

2096
2097 **Figure 14.** Scatter plot (log-log) of the salinity *versus* **(a)** $(\text{Mg}/\text{Ca})_{\text{aq}}$ and **(b)** $[\text{Mg}]_{\text{aq}}$. Positive
2098 correlation are observed between salinity *versus* aqueous Mg/Ca and aqueous Mg
2099 concentrations. Lake Tecuitlapa (T) is below the two trends. Abbreviations for the carbonate
2100 phases are: Mg-calcite (MgC); monohydrocalcite (MHC); aragonite (A); hydromagnesite (H).

2101

2102 **Figure 15.** Scatter plot of $(\text{Mg}/\text{Ca})_{\text{aq}}$ and $[\text{Mg}]_{\text{aq}}$. The carbonate microbialite mineralogy for
2103 each lake is reported in square brackets. Lakes: Zirahuén (Z), Alberca de Guadalupe (Alb), La
2104 Alberca de Los Espinos (AE), Pátzcuaro (P), Tecuitlapa (T), Aljojuca (Alj), Quechulac (Q), La
2105 Preciosa (LP), center (Atx-M) and north side (Atx-N) of Lake Atexcac, west side (AL-W) and
2106 center (AL-M) of Lake Alchichica. Abbreviations for the carbonate phases are: Mg-calcite
2107 (MgC); monohydrocalcite (MHC); aragonite (A); hydromagnesite (H).

2108

2109 **Figure 16.** Model of lake evolution over time. Microbialites start emerging at a certain stage of
2110 evaporation and/or weathering of the lake (when $[\text{Na}^+]_{\text{aq}}$ and alkalinity become higher than
2111 certain threshold values). Then microbialite mineralogy changes according to key parameters
2112 such as the aqueous (Mg/Ca) , which controls carbonate mineralogy, and aqueous $[\text{H}_4\text{SiO}_4]$
2113 controlling the precipitation of authigenic Mg-silicate.

TABLES

Lake	General location	Sampling location (January 2012 / May 2014)	Elevation (masl)	Lake type	Lake basement
La Preciosa	Los Llanos de San Juan region, eastern TMVB	19° 22' 32.70"N; 97° 23' 12.14"W / 19° 22' 09.80"N; 97° 23' 00.26"W	2330	Triple phreatic explosion maar	limestone, basalts
Quechulac	Los Llanos de San Juan region, eastern TMVB	19° 22' 31.56"N; 97° 21' 18.29"W / Ø	2330	Phreatic explosion maar	limestone, basalts
Atexcac	Los Llanos de San Juan region, eastern TMVB	19° 20' 08.27"N; 97° 27' 10.24"W / 19° 20' 08.27"N; 97° 27' 10.24"W	2360	Phreato-magmatic explosion maar	limestones, andesites, basalts
Alchichica	Los Llanos de San Juan region, eastern TMVB	19° 25' 12.32"N; 97° 24' 11.79"W / 19° 25' 00.76"N; 97° 24' 41.64"W	2320	Phreatic explosion maar	limestone, basalts
Aljojuca	Los Llanos de San Andrés, eastern TMVB	Ø / 19° 05' 36.27"N; 97° 31' 50.91"W	2379	Phreatic explosion maar	limestone, basalts
Tecuitlapa	Los Llanos de San Andrés, eastern TMVB	Ø / 19° 07' 29.35"N; 97° 32' 35.30"W	2380	Phreato-magmatic explosion maar	limestone, basalts
La Alberca de Los Espinos	Zacapu Basin, MGVF, central TMVB	Ø / 19° 54' 29.20"N; 101° 46' 02.90"W	1985	Phreato-magmatic explosion maar	andesite xenoliths
Alberca de Guadalupe	Zacapu Basin, MGVF, central TMVB	Ø / 19° 48' 21.11"N; 101° 27' 10.91"W	2066	Phreato-magmatic explosion maar	andesites, ignimbrite clasts
Pátzcuaro	El Estribo volcanic complex, MGVF, central TMVB	Ø / 19° 40' 08.30"N; 101° 33' 44.40"W	2044	Lava-dammed basin associated with fractures	andesites
Zirahuén	Highland Michoacán, MGVF, central TMVB	Ø / 19° 26' 18.21"N; 101° 44' 40.03"W	2082	Lava-dammed endorheic basin	basalts

Lake	Water type	Mixing Type	Max depth (m)	Inflow/ outflow	Age	Microbialite Description	References
La Preciosa	Bic-Mg	Warm monomictic	46	ND	Pleistocene	Living and non-living microbialites	Armienta et al., 2008; Sigala et al., 2017
Quechulac	Bic-Mg	Warm monomictic	40	ND	Pleistocene	Living and non-living microbialites	Armienta et al., 2008; Sigala et al., 2017
Atexcac	Cl(+HCO ₃)-Na	Warm monomictic	39	ND	~ 0.33 Myr	Living and non-living microbialites	Carrasco-Núñez et al., 2007; Armienta et al., 2008
Alchichica	Cl(+HCO ₃)-Na	Warm monomictic	62	Groundwater inflow on the W shore	Pleistocene	Living and non-living microbialites	Armienta et al., 2008; Sigala et al., 2017; Zeyen et al., 2019
Aljojuca	Na-Bic	Warm monomictic	51	ND	Pleistocene	Basalts encrusted by living and non-living microbialites	Armienta et al., 2008; Sigala et al., 2017
Tecuitlapa	Na-Bic	Warm polymictic	2.5	ND	Pleistocene	Basalts encrusted by living and non-living microbialites	Armienta et al., 2008; Sigala et al., 2017
La Alberca de Los Espinos	Bic(+Cl)-Na	Warm monomictic	30	ND	~ 25 kyr	Living and non-living microbialites	Siebe et al., 2014
Alberca de Guadalupe	Bic-Mixed(Na-Mg)	Warm polymictic	9	Groundwater inflow on the E shore	~23 -20 kyr	Andesites finely encrusted by living and non-living microbialites	Siebe et al., 2014
Pátzcuaro	Na-Bic	Warm polymictic	9	Groundwater inflows along the S shore and the N shore	> ~30 kyr	Andesites encrusted by living and non-living microbialites	Bischoff et al., 2004 ; Israde-Alcántara et al., 2005; Pola et al., 2015 ; Sigala et al., 2017
Zirahuén	Bic-Mixed(Na-Ca-Mg)	Warm monomictic	40	Inflows from rivers Río de la Palma and Arroyo Zirahuén	Late Pleistocene (100-11 Kyr)	No microbialites	Davies et al., 2004; Armienta et al., 2008. Sigala et al., 2017

Table 1.

Location, elevation, type of lake, geology, water type, mixing type, maximum depth, documented inflow and outflow, age and microbialite type of the studied lakes. Meaning of the abbreviations: TMVB: trans-Mexican volcanic belt; MGVF: Michoacán-Guanajuato volcanic field. masl: meters above sea level. Ø: no sample was collected during this field campaign.

Lake surface water	$^{87}\text{Sr}/^{86}\text{Sr}$	95% confidence interval
Alchichica – AL2014_0m_M	0.706888	0.000004
La Preciosa – Preciosa2014-0m	0.706962	0.000021
Atexcac – ATX2014_0m_M	0.706998	0.000040
La Alberca de Los Espinos – AlbEsp2014_0m	0.703914	0.000020
Zirahuén –Zirahuen2014_0m	0.704514	0.000024

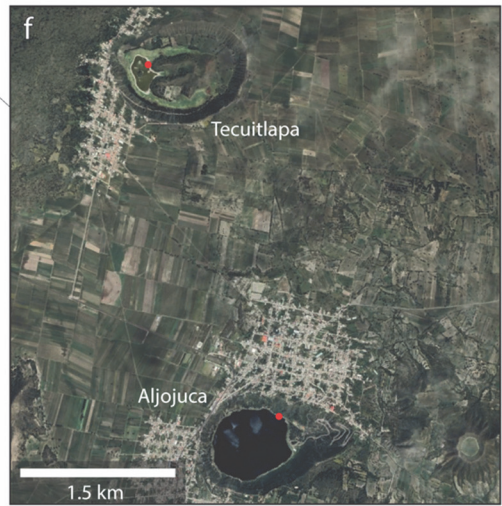
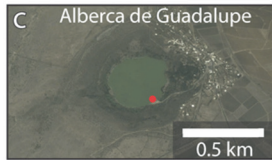
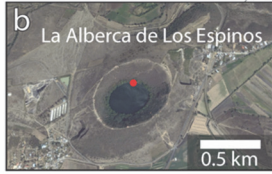
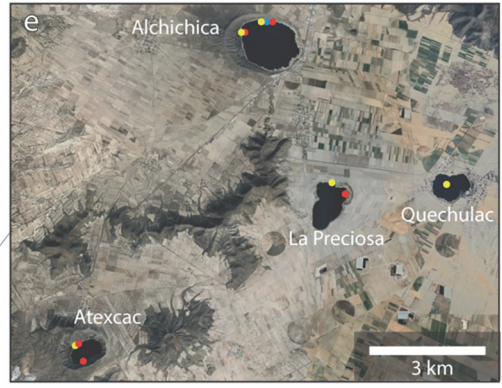
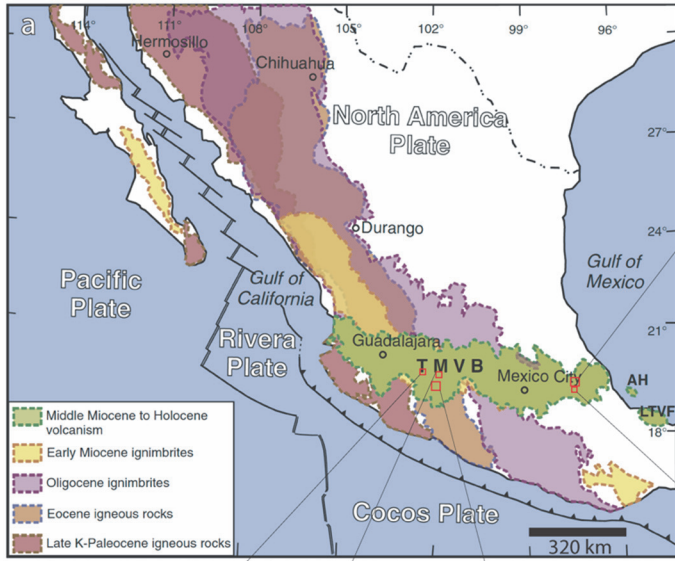
Table 2.

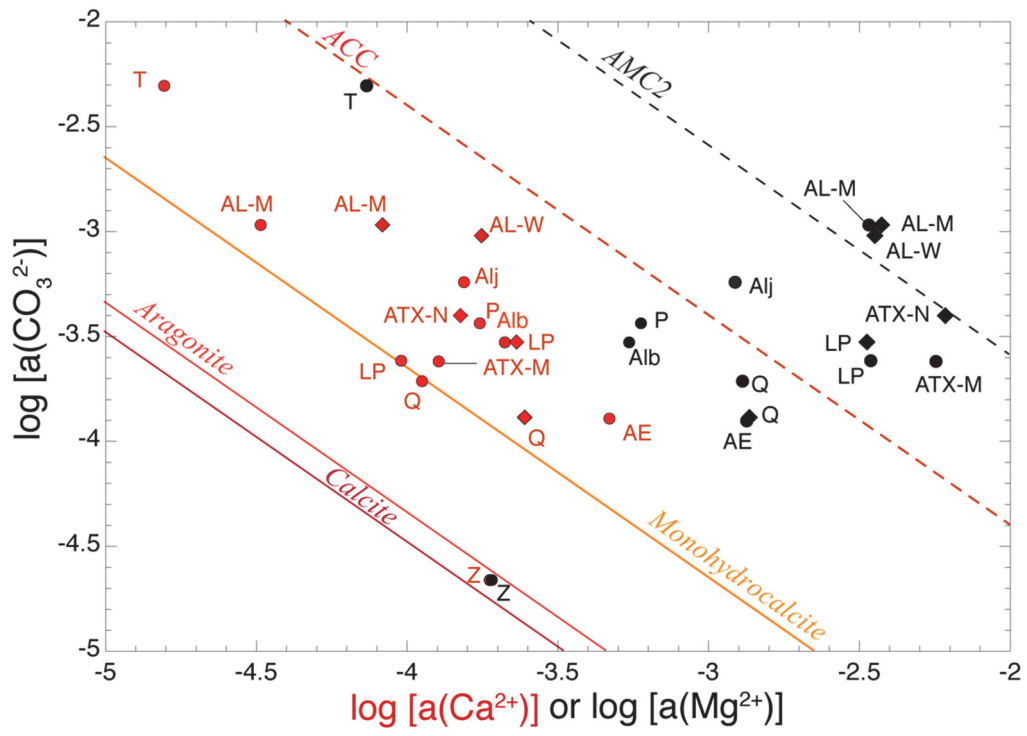
Strontium isotopic compositions of five lake surface waters sampled in May 2014.

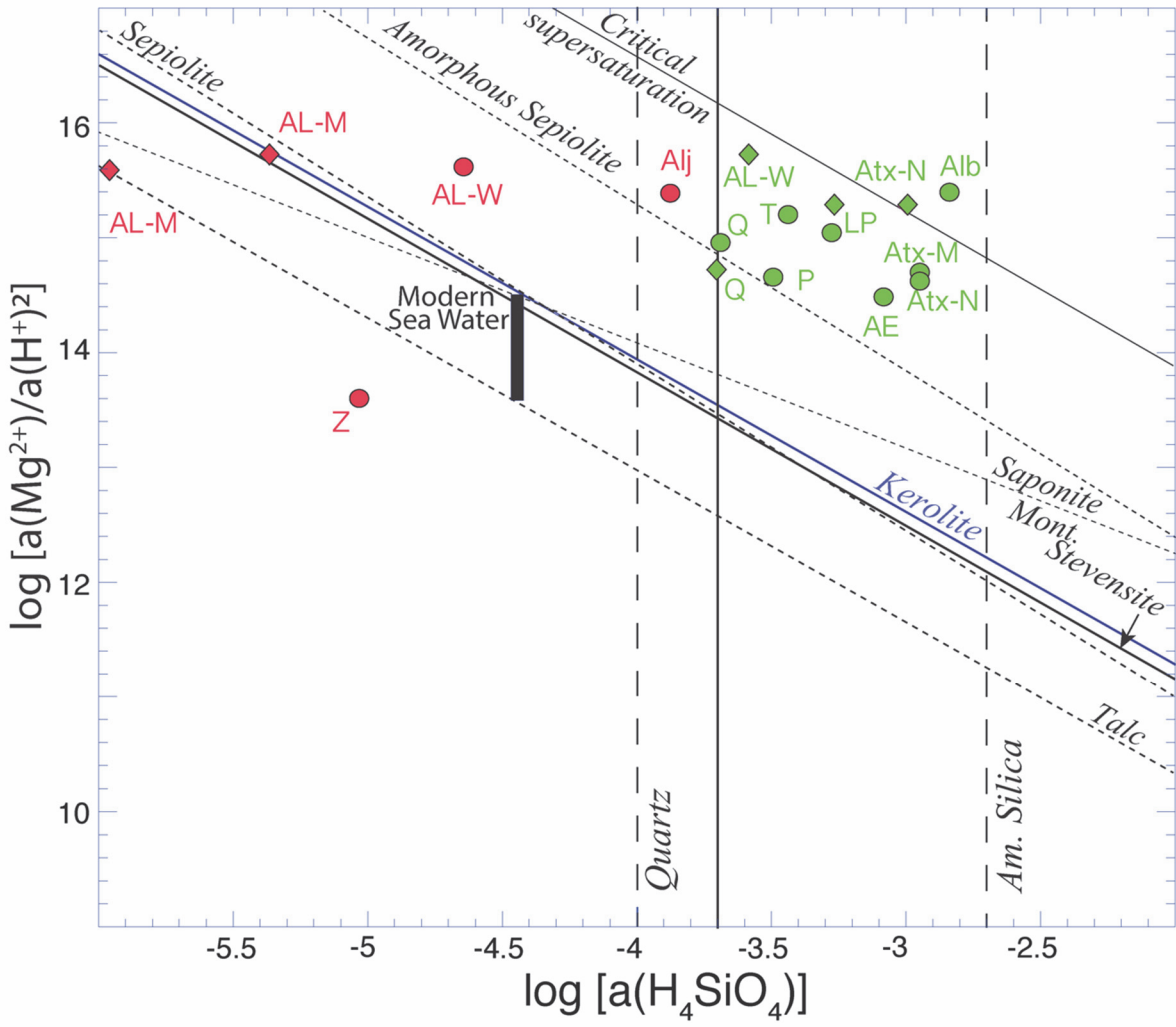
Lake	Main phases
La Preciosa	A – K/S
Quechulac	A – K/S
Atexcac	A – K/S and K/S –A
Alchichica	H – A and A – H
Aljojuca	MHC – (Mg-)C – A
Tecuitlapa	(Mg-)C – MHC – A – K/S
La Alberca de Los Espinos	(Mg-)C – MHC – K/S
Alberca de Guadalupe	(Mg-)C – K/S
Pátzcuaro	(Mg-)C – MHC – A – K/S
Zirahuén	Ø

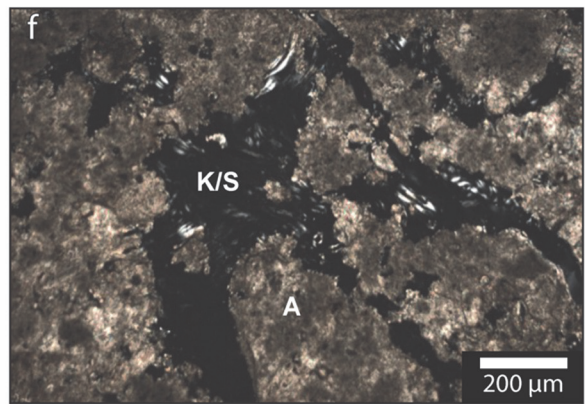
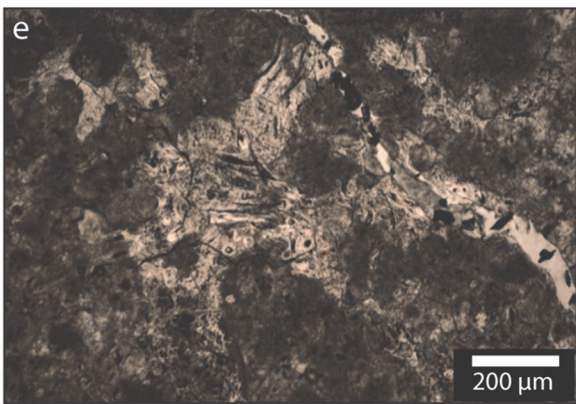
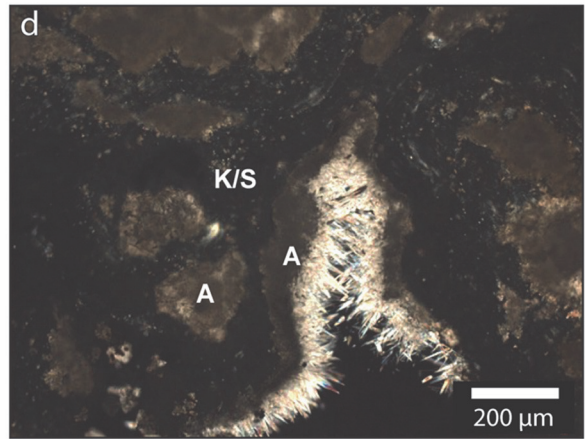
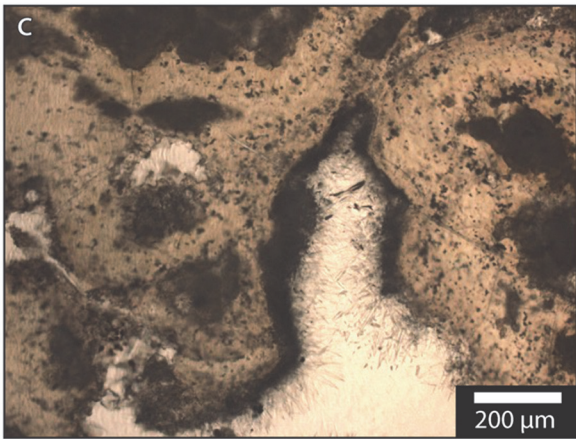
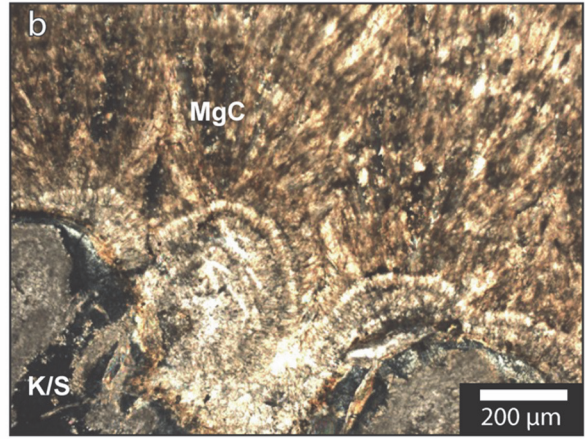
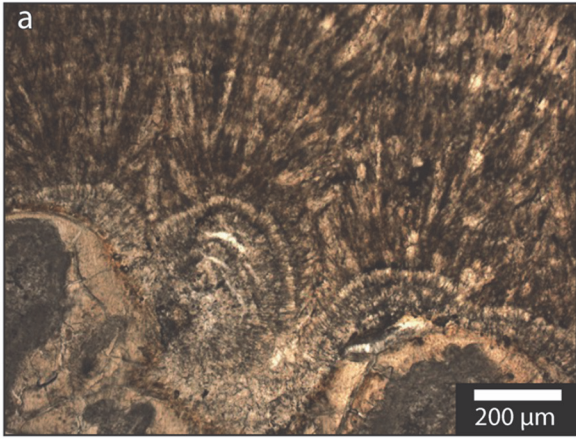
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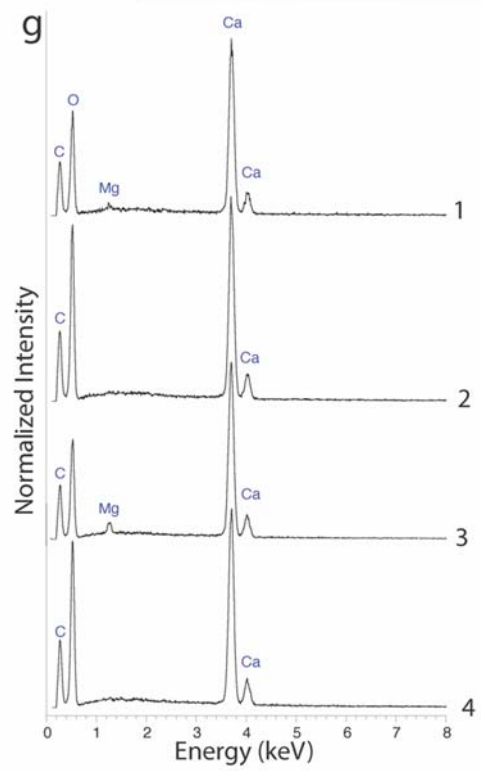
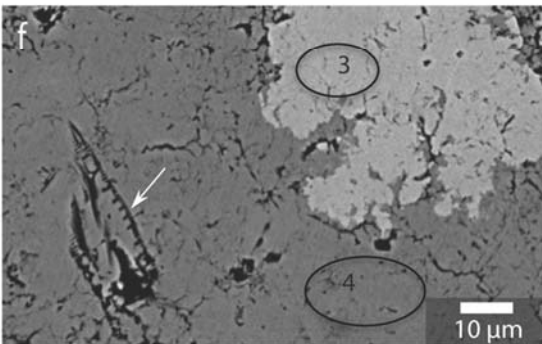
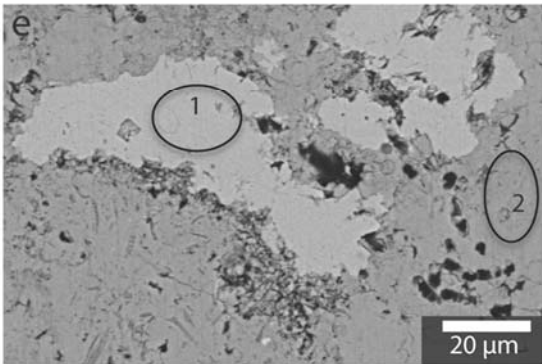
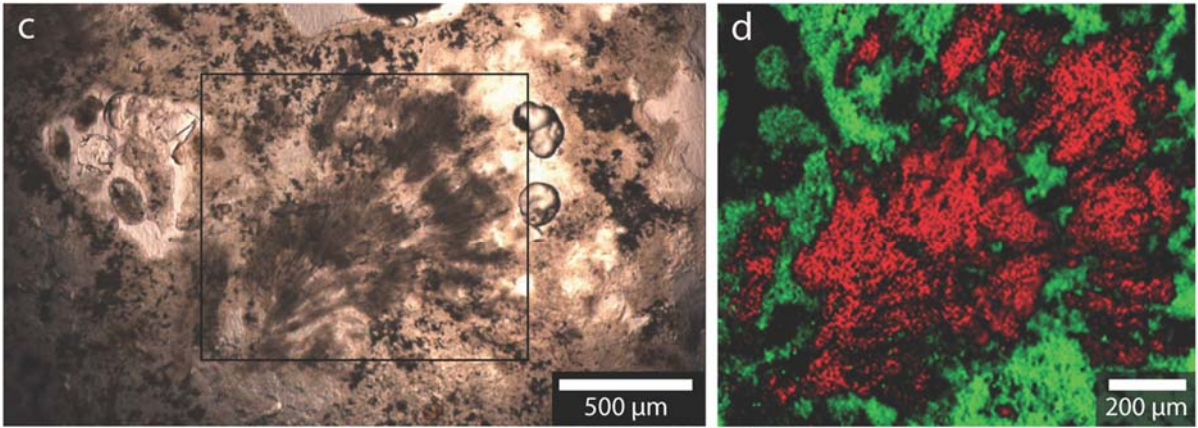
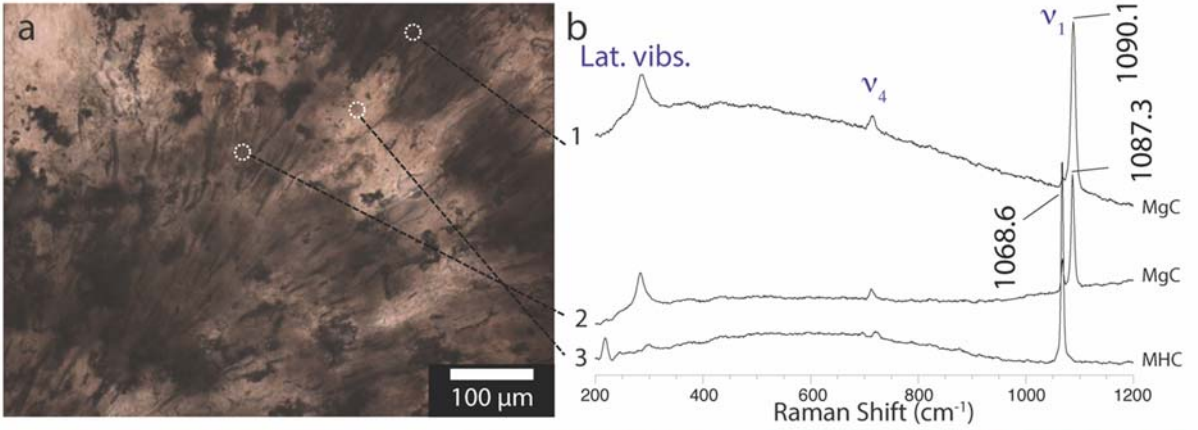
List of the main mineral phases of the microbialites in decreasing order of abundance, as detected by XRD and FTIR and/or observed by optical and scanning electron microscopy. This table was derived from results obtained on living microbialites. Lake Zirahuén has no living or non-living microbialites (Ø). ((Mg-)C: (Mg-)calcite; MHC: Monohydrocalcite; A: Aragonite; H: Hydromagnesite; K/S: Kerolite and/or Stevensite).

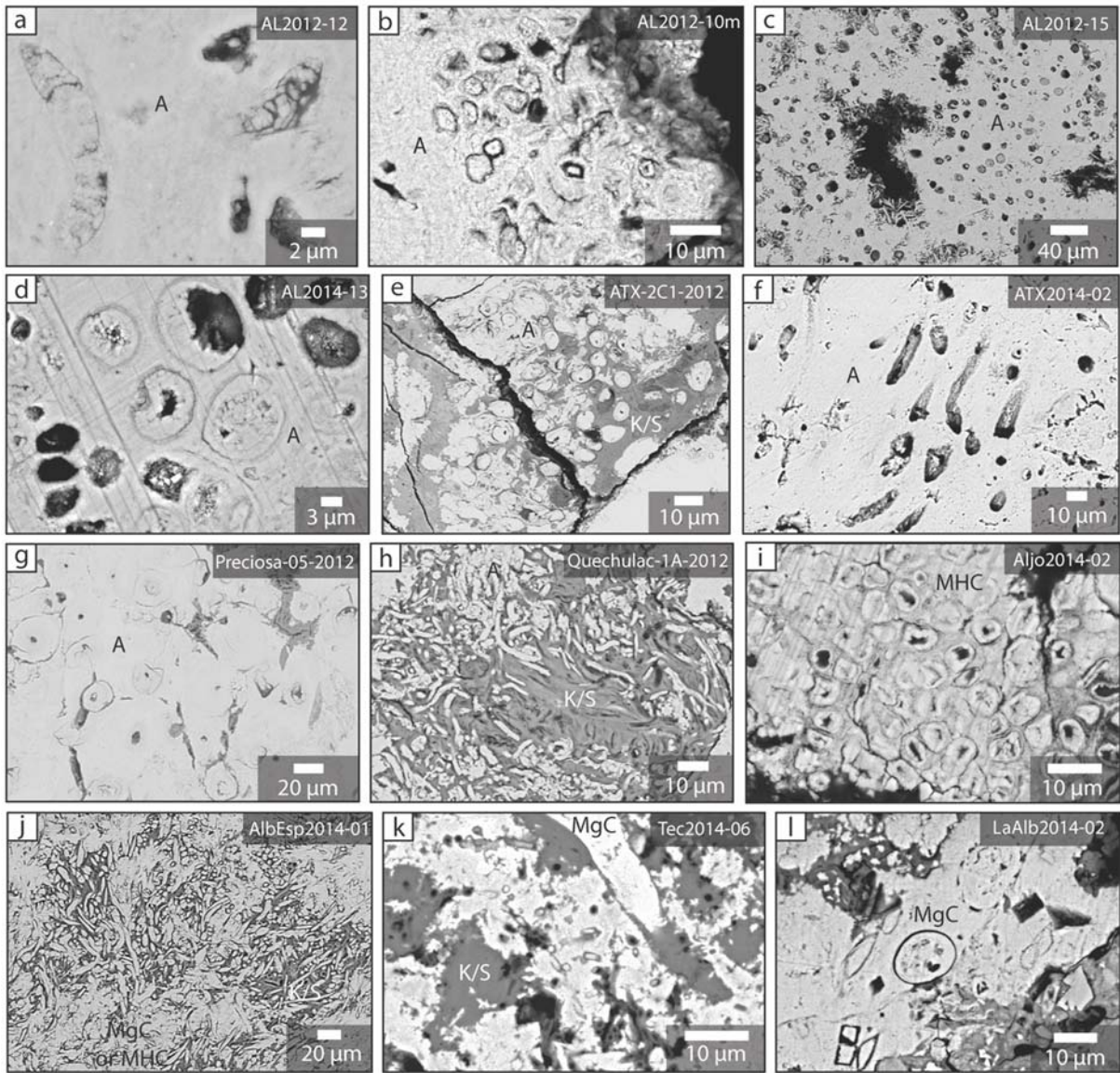


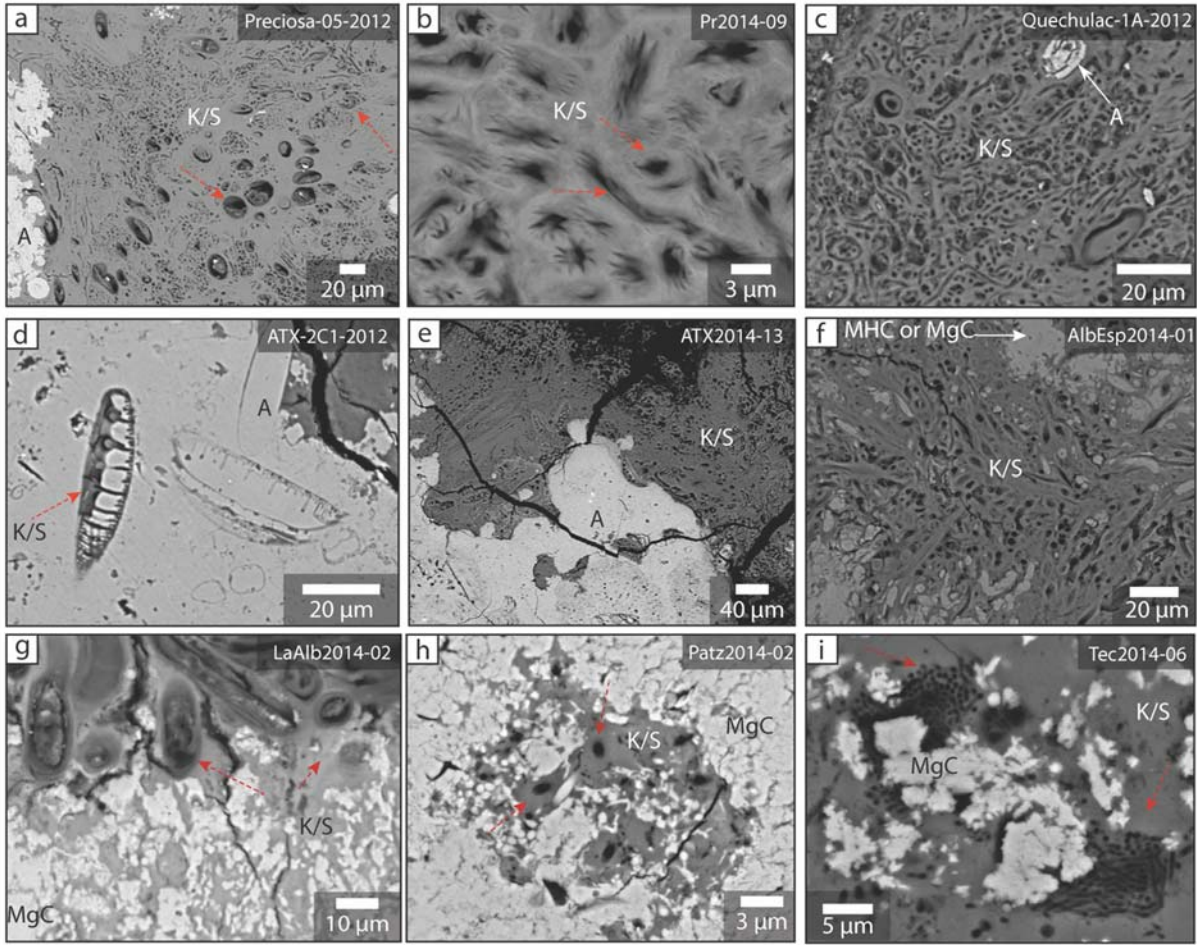


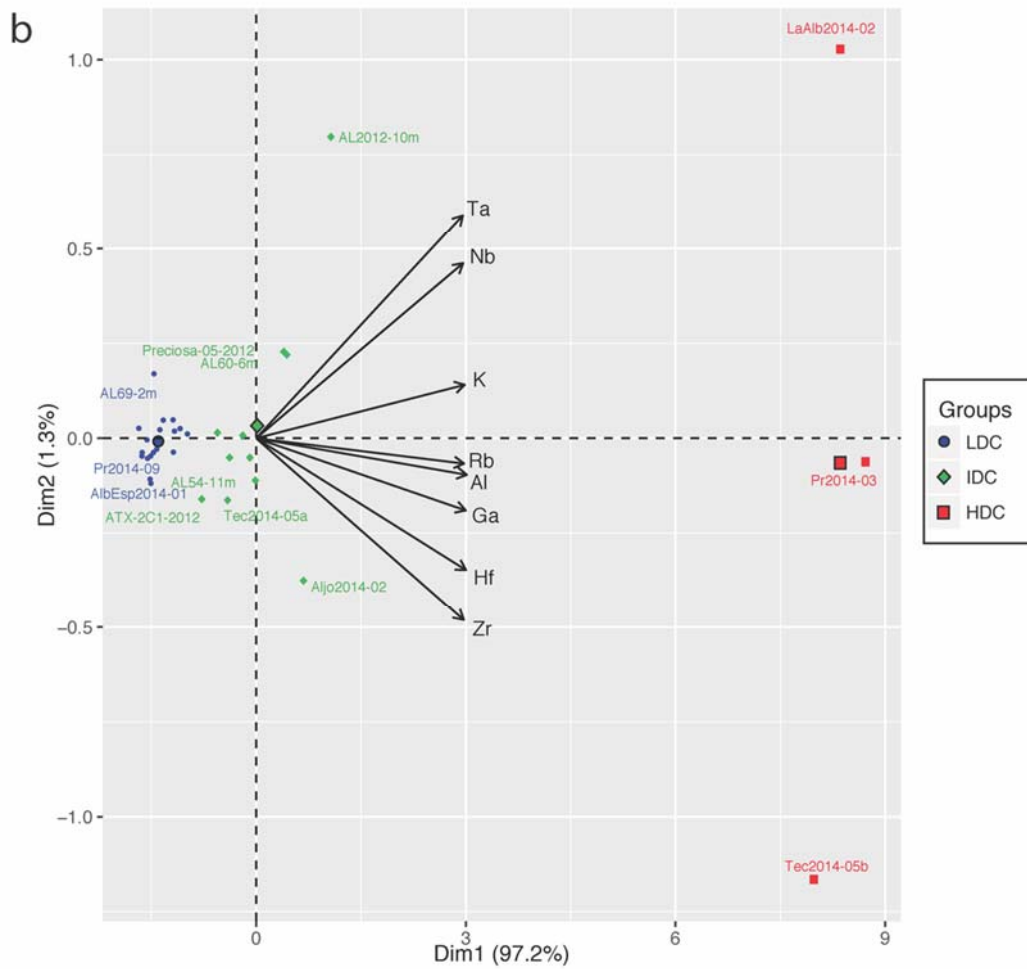
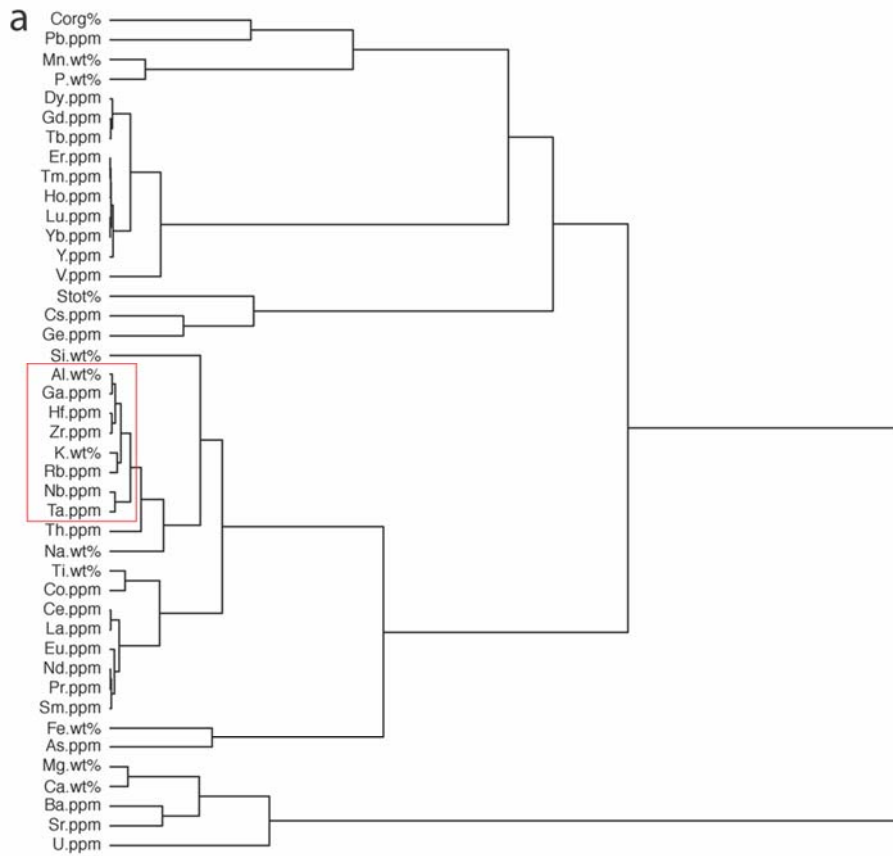


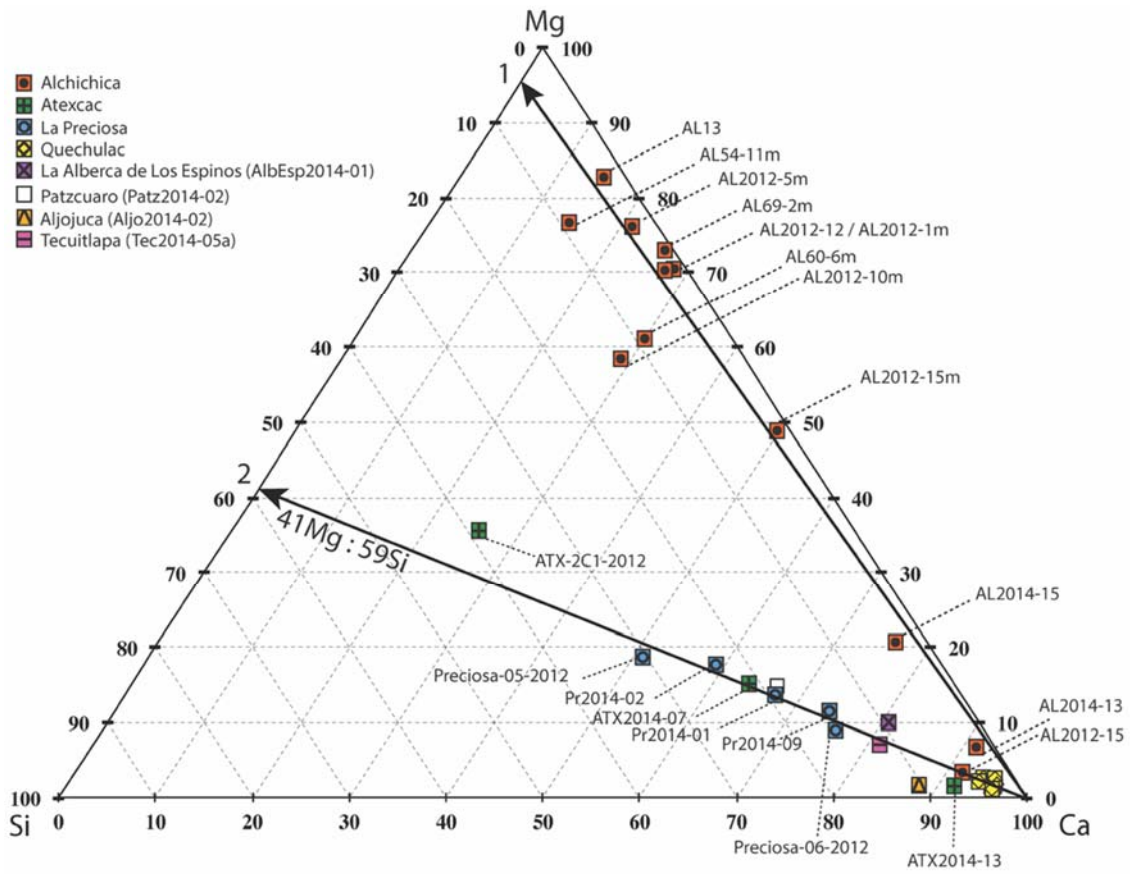


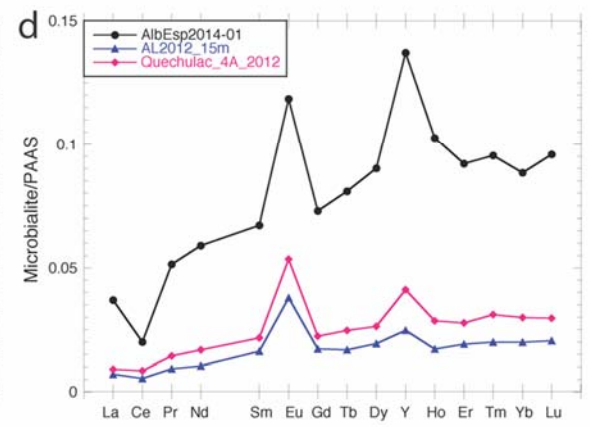
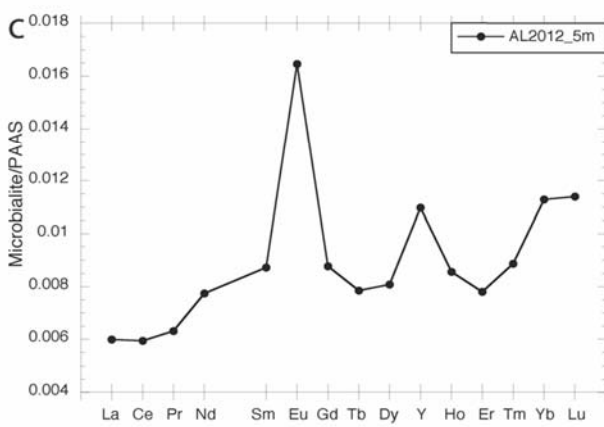
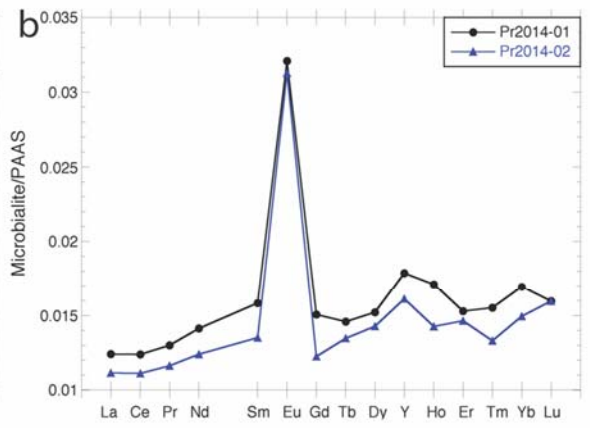
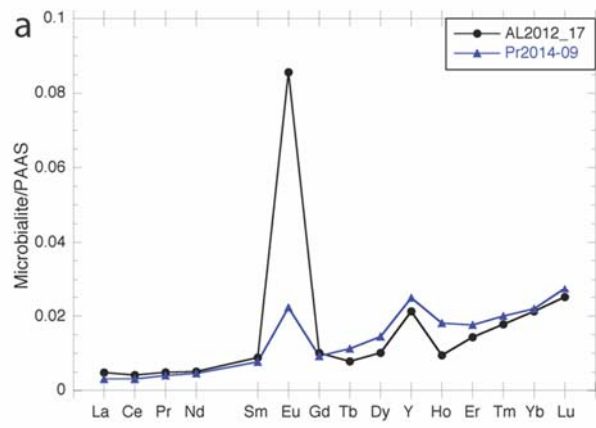


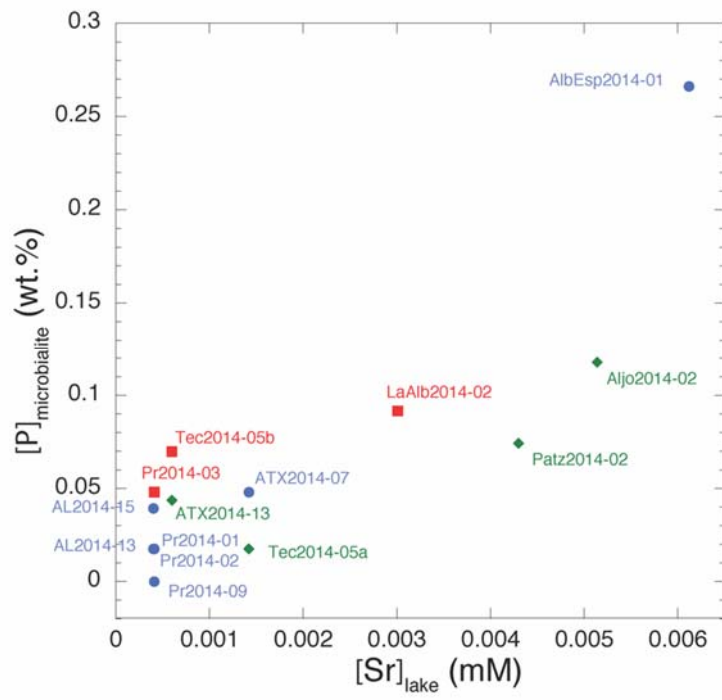


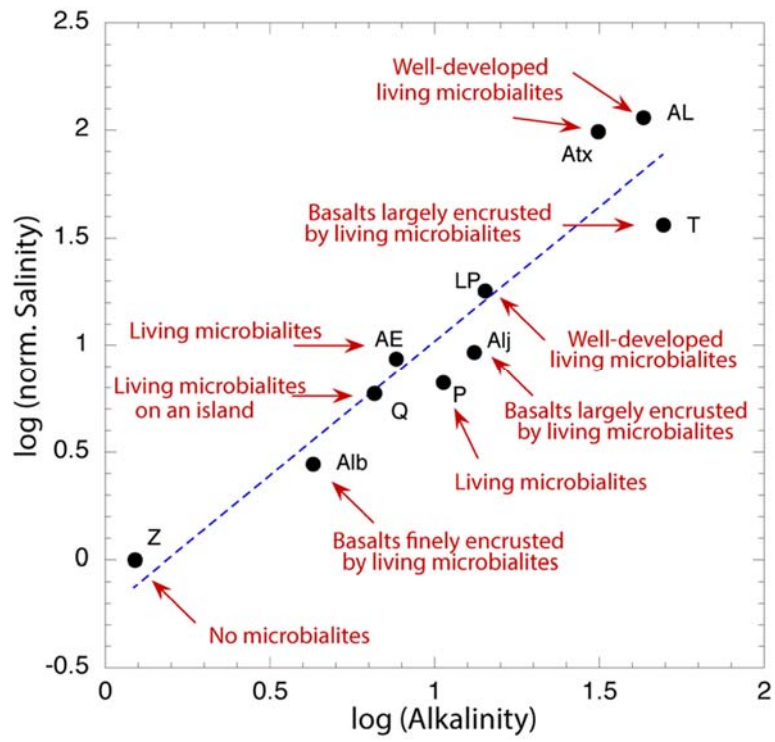


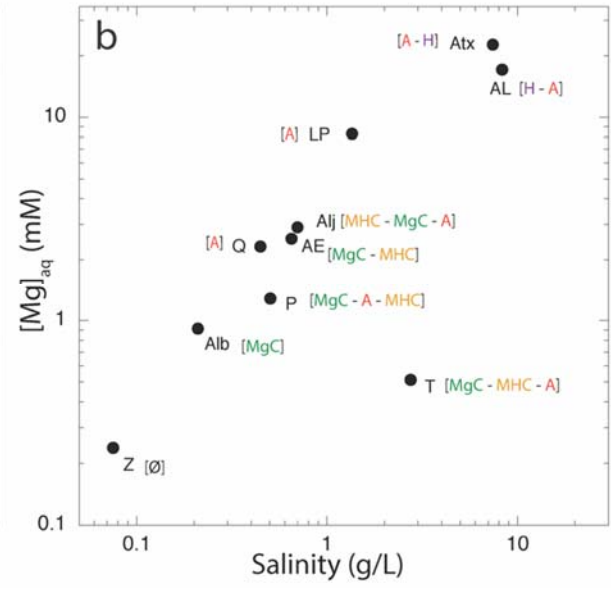
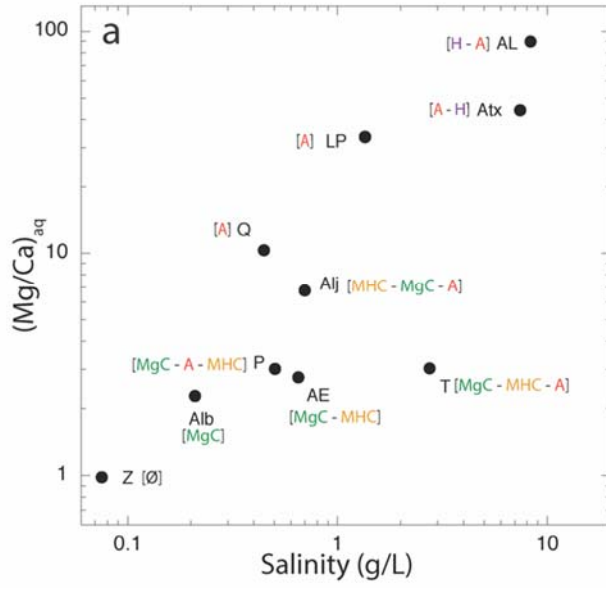


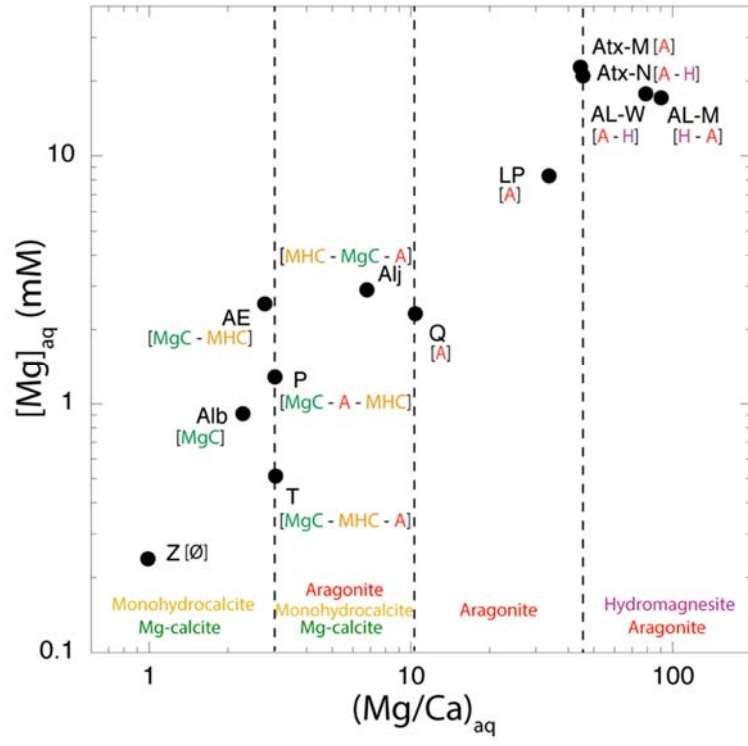


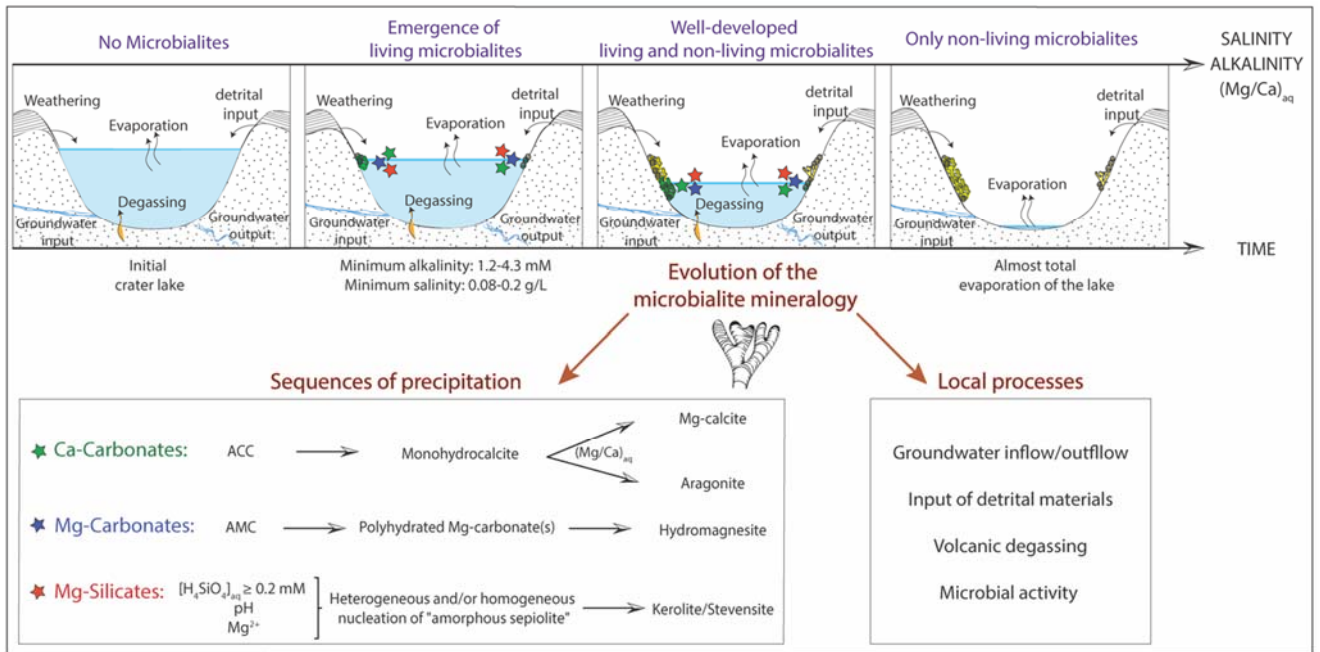












Supporting Information in:

Integrative analysis of the mineralogical and chemical composition of modern microbialites from ten Mexican lakes: what do we learn about their formation?

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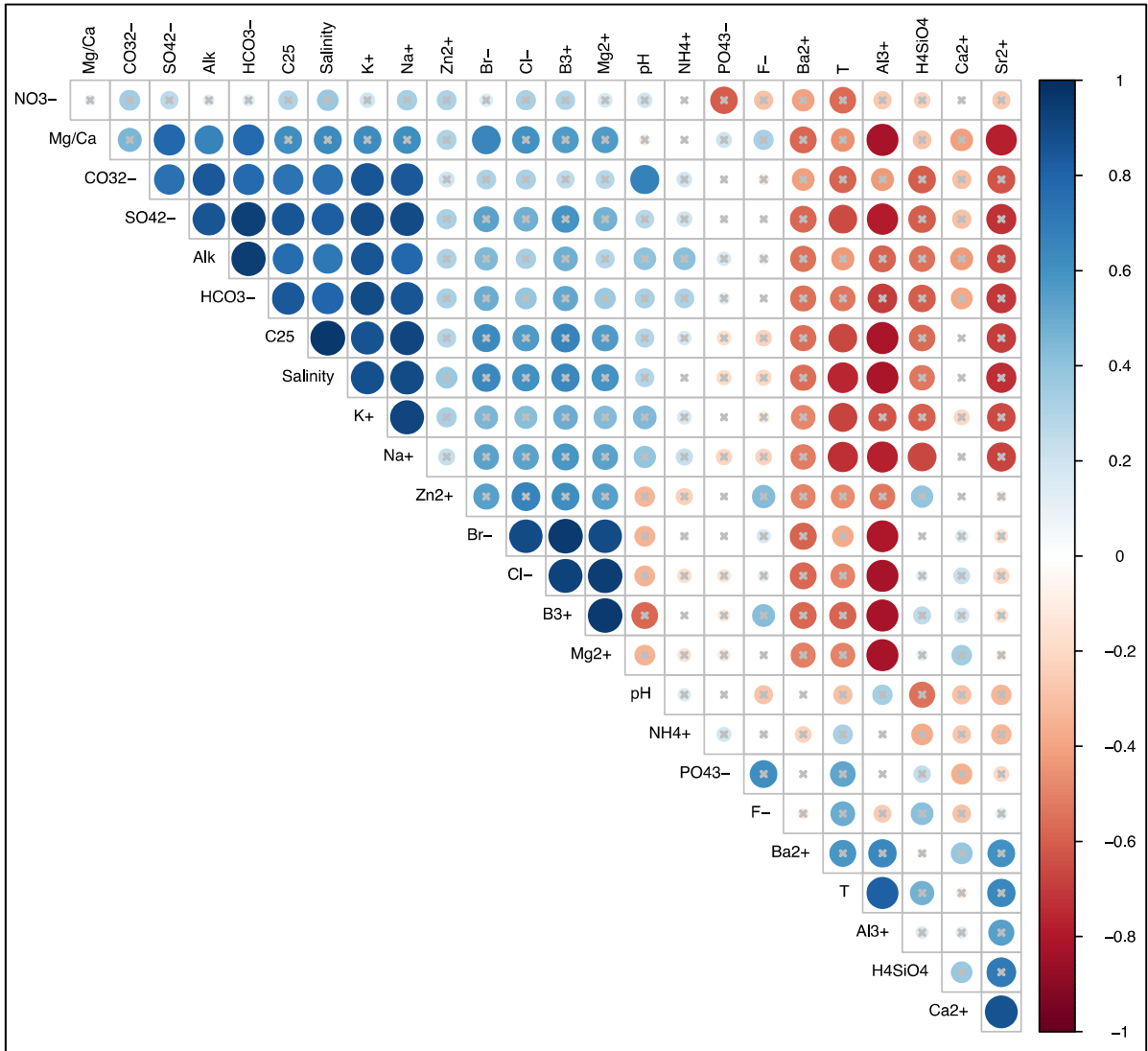
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Keywords: microbialites; crater lake; alkalinity; monohydrocalcite; (Mg-)calcite; aragonite; hydromagnesite; kerolite; REE+Y

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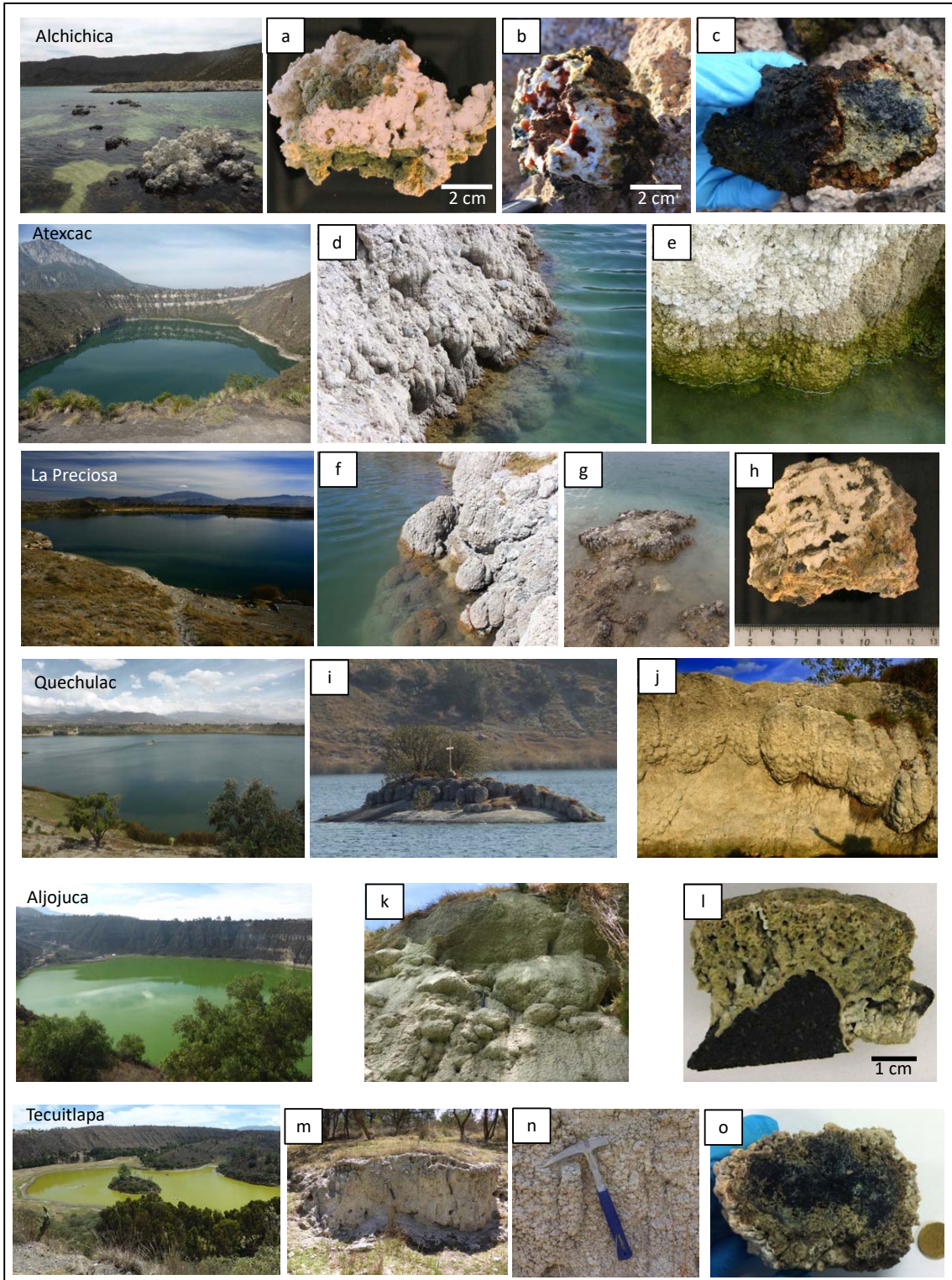


Figure SI-2. Overviews of the studied lakes and photographs of the microbialites

Lakes Alchichica (**a, b, c**), Atexcac (**d, e**), La Preciosa (**f, g, h**), Quechulac (**i, j**), Aljojuca (**k,l**), Tecuitlapa (**m, n, o**), La Alberca de los Espinos (**p, q**), Alberca de Guadalupe (**r, s**), Pátzcuaro (**t**), and Zirahuén.

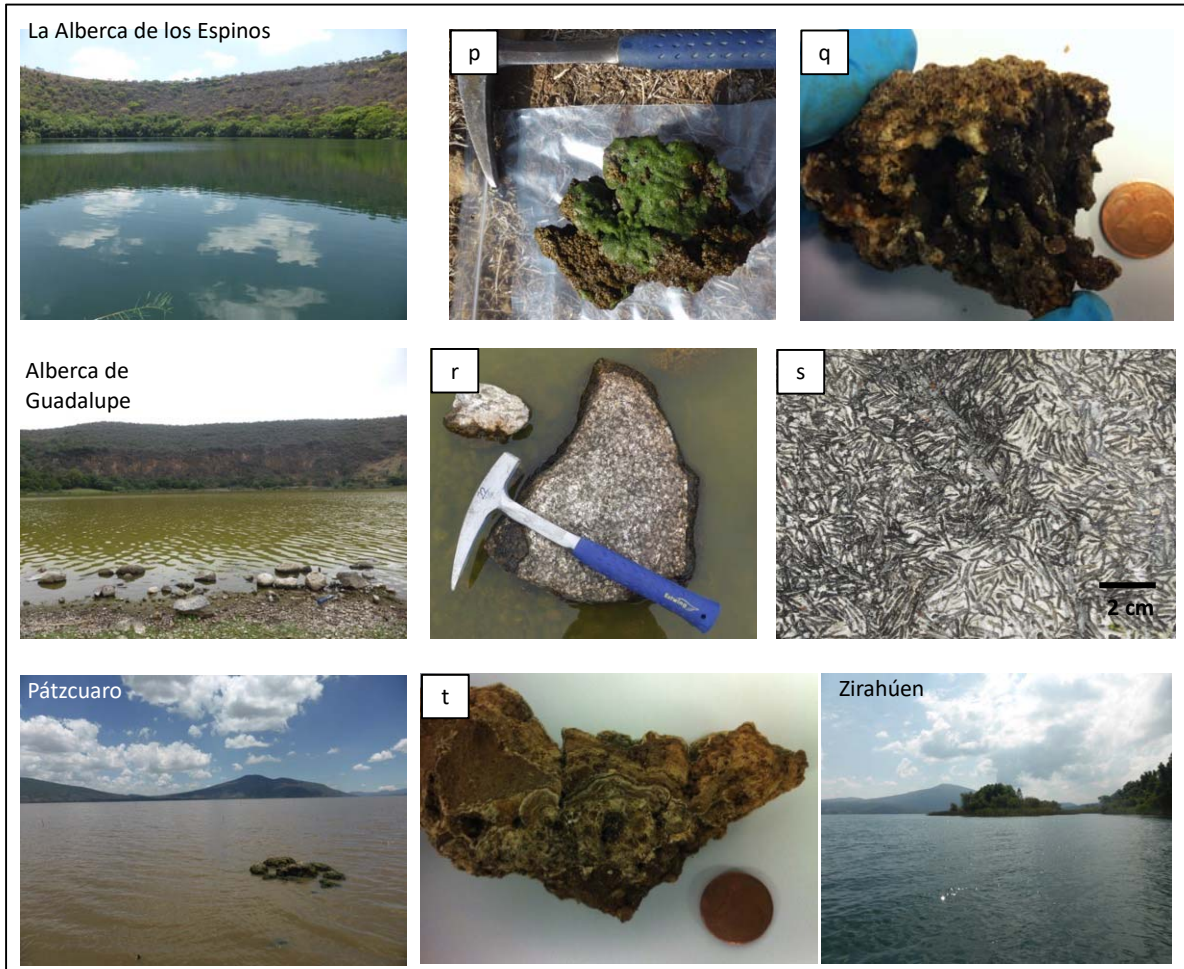


Figure SI-2. Continued

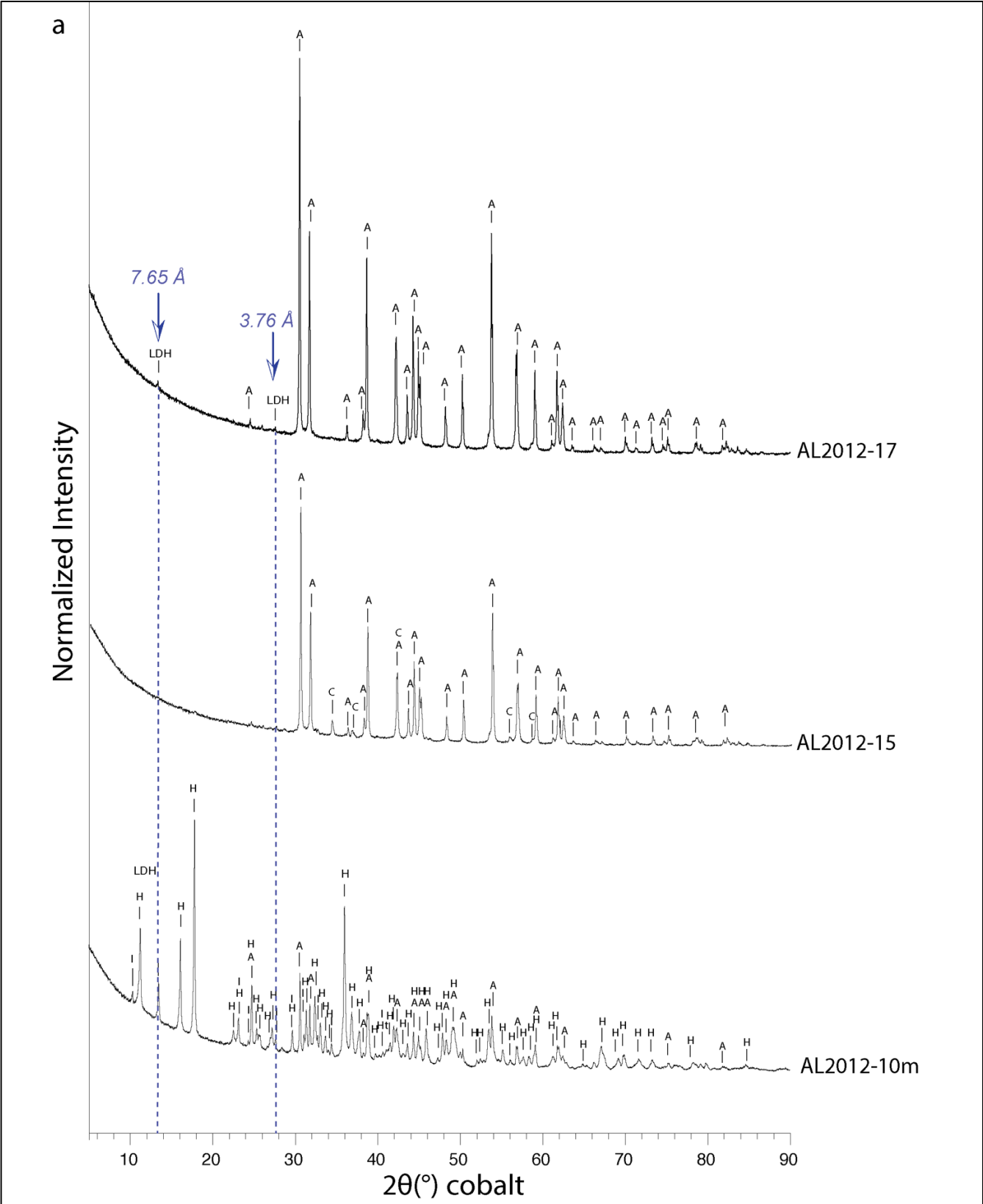


Figure SI-3. Powder x-ray diffraction patterns of some of the studied microbialites

(a) Microbialites mainly composed of aragonite and/or hydromagnesite, (b) microbialites mainly composed of aragonite and Mg-silicates, (c) microbialites mainly composed of Mg-calcite and/or monohydrocalcite, (d) microbialites affected by high detrital contamination. Abbreviations for the phases are: H: hydromagnesite; A: aragonite; C: calcite; MC: monohydrocalcite; D: dolomite; K/S: kerolite and/or stevensite; LDH: layered double hydroxide; I: illite; An: anorthite; Ab: albite; Q: quartz; Px: pyroxene.

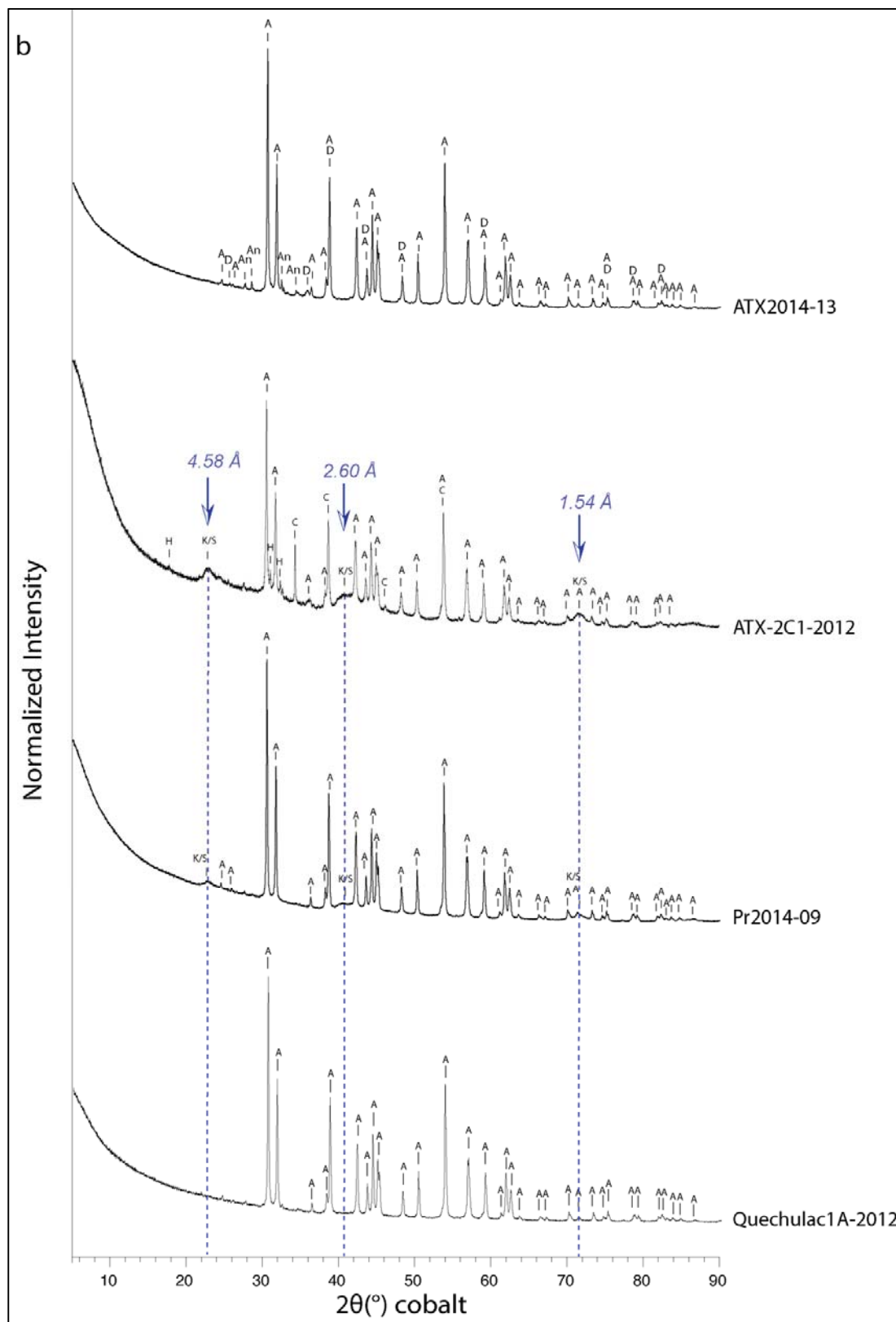


Figure SI-3. Continued

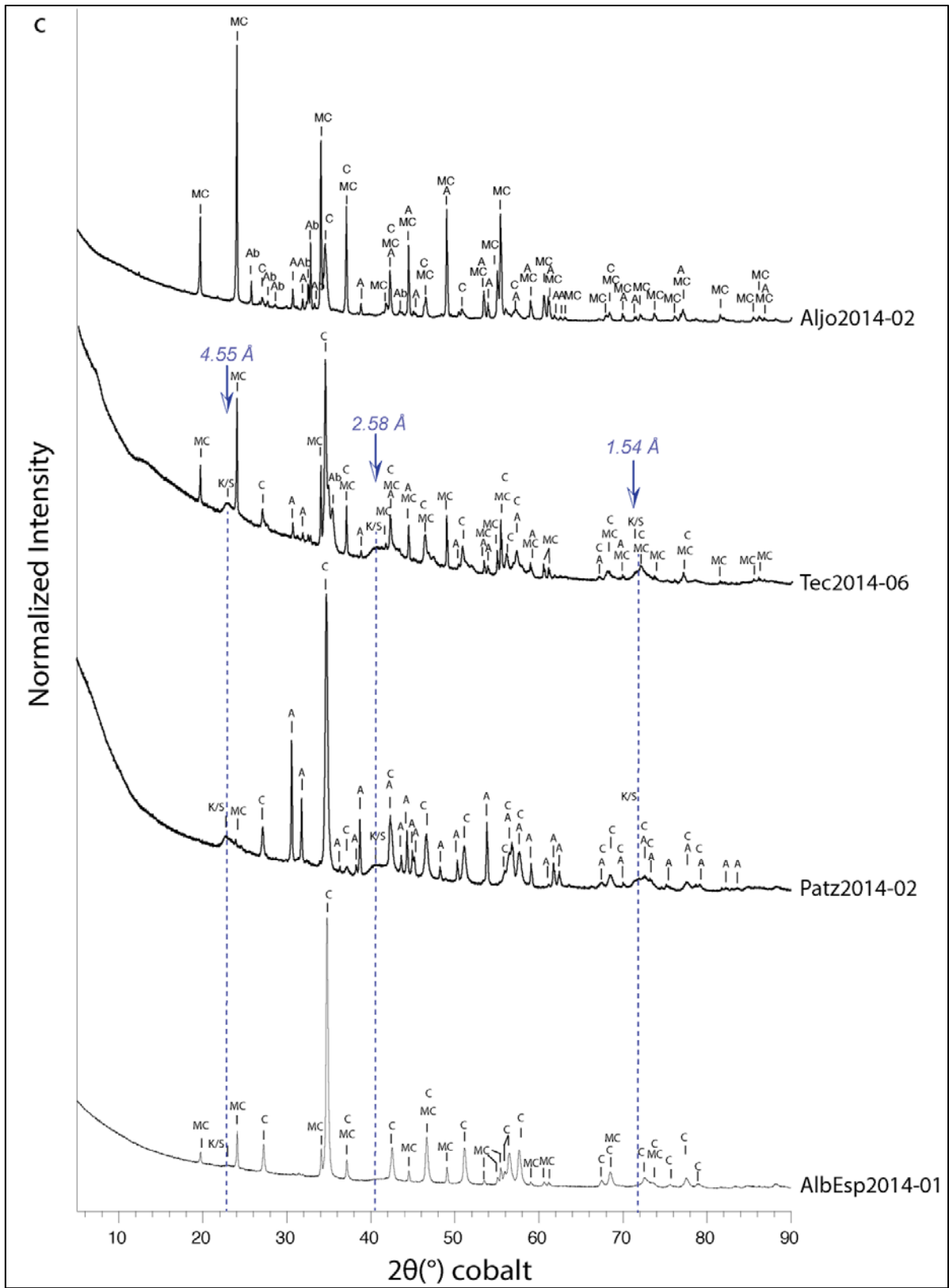


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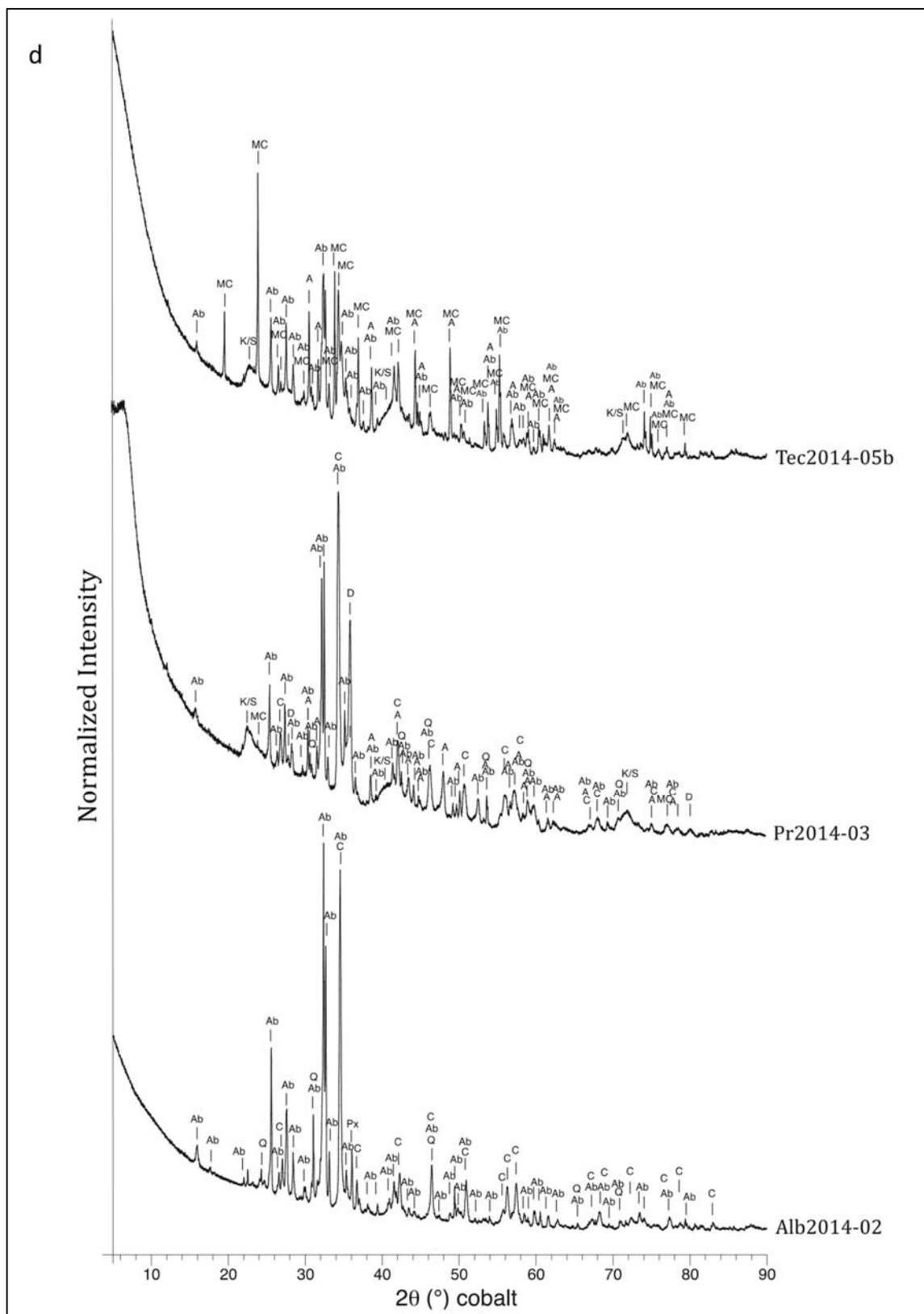


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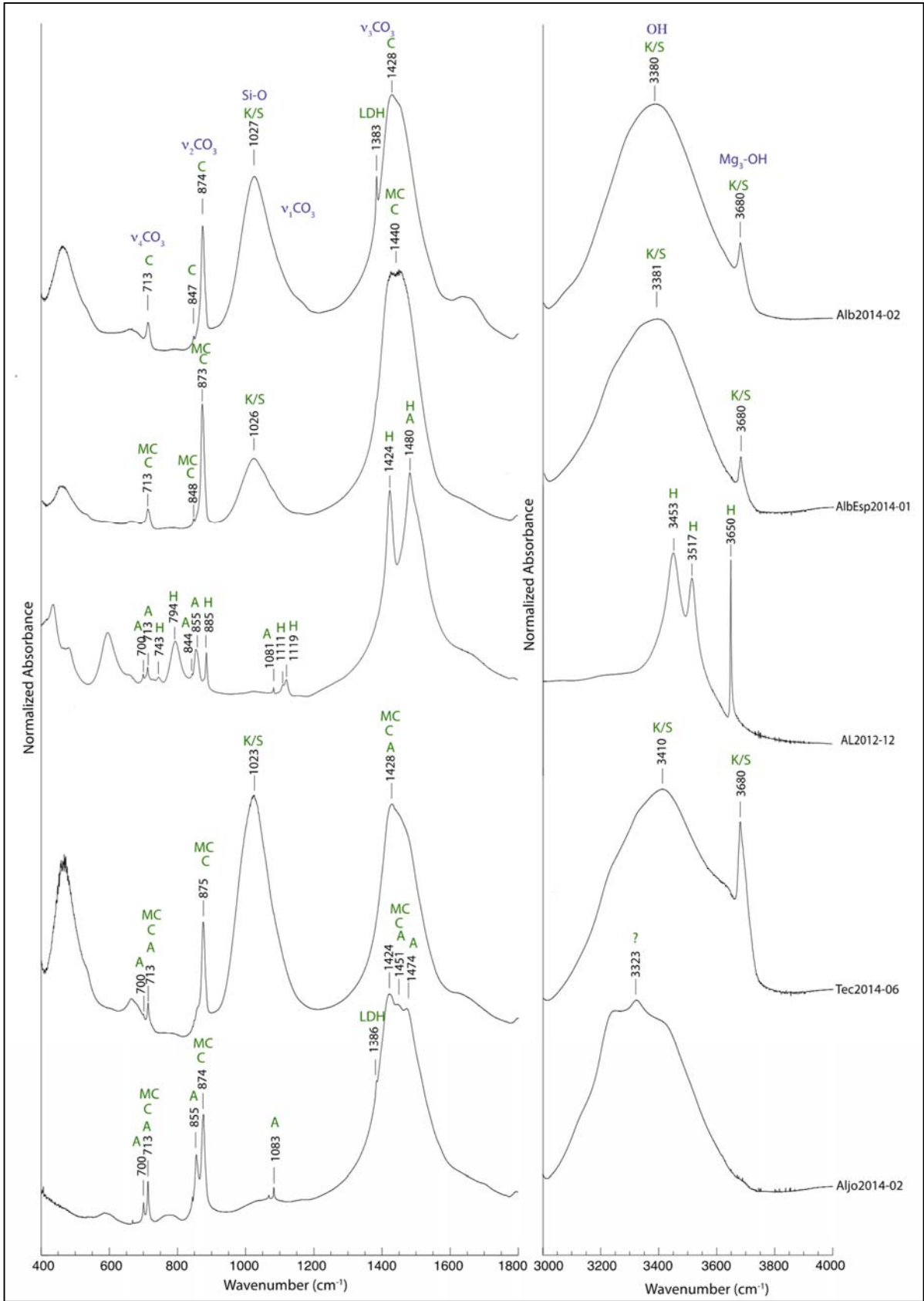


Figure SI-4. FTIR spectra of some of the studied microbialites

Microbialites from Lakes Alberca de Guadalupe (Alb), La Alberca de Los Espinos (AlbEsp), Alchichica (AL), Tecuitlapa (Tec) and Aljojuca (Aljo). Phase indexations are in green; FTIR band indexation are in purple. Abbreviations for the phases are: H: hydromagnesite; A: aragonite; C: calcite; MC: monohydrocalcite; K/S: kerolite and/or stevensite; LDH: layered double hydroxide.

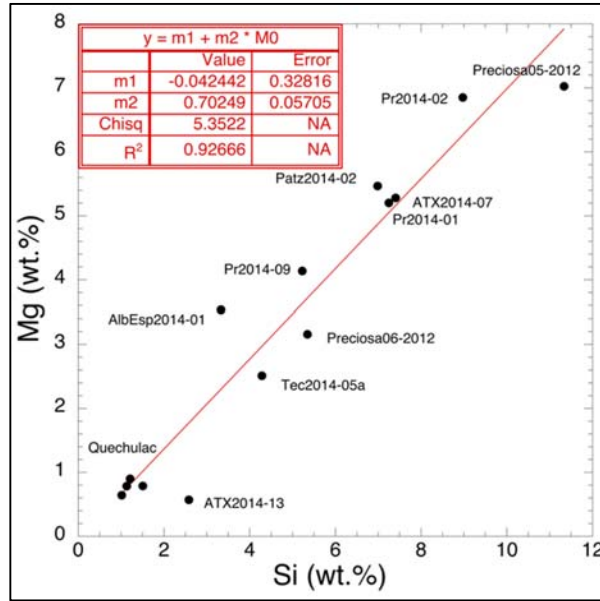


Figure SI-5. Silicon vs. magnesium contents of the microbialites

Silicon *versus* magnesium contents (wt.%) of the microbialites the least (authigenic-dominated) and intermediately affected by detrital contamination and containing kerolite and/or stevensite (excluding ATX-2C1-2012 which also contained hydromagnesite). The regression coefficient (R^2) of this plot is equal to 0.93. The slope of the regression line is 0.70 ± 0.06 in wt.%/wt.% (corresponding to 0.81 ± 0.07 at.%/at.%), close to the stoichiometry of kerolite and stevensite (*i.e.*, 0.75 in atomic ratio).

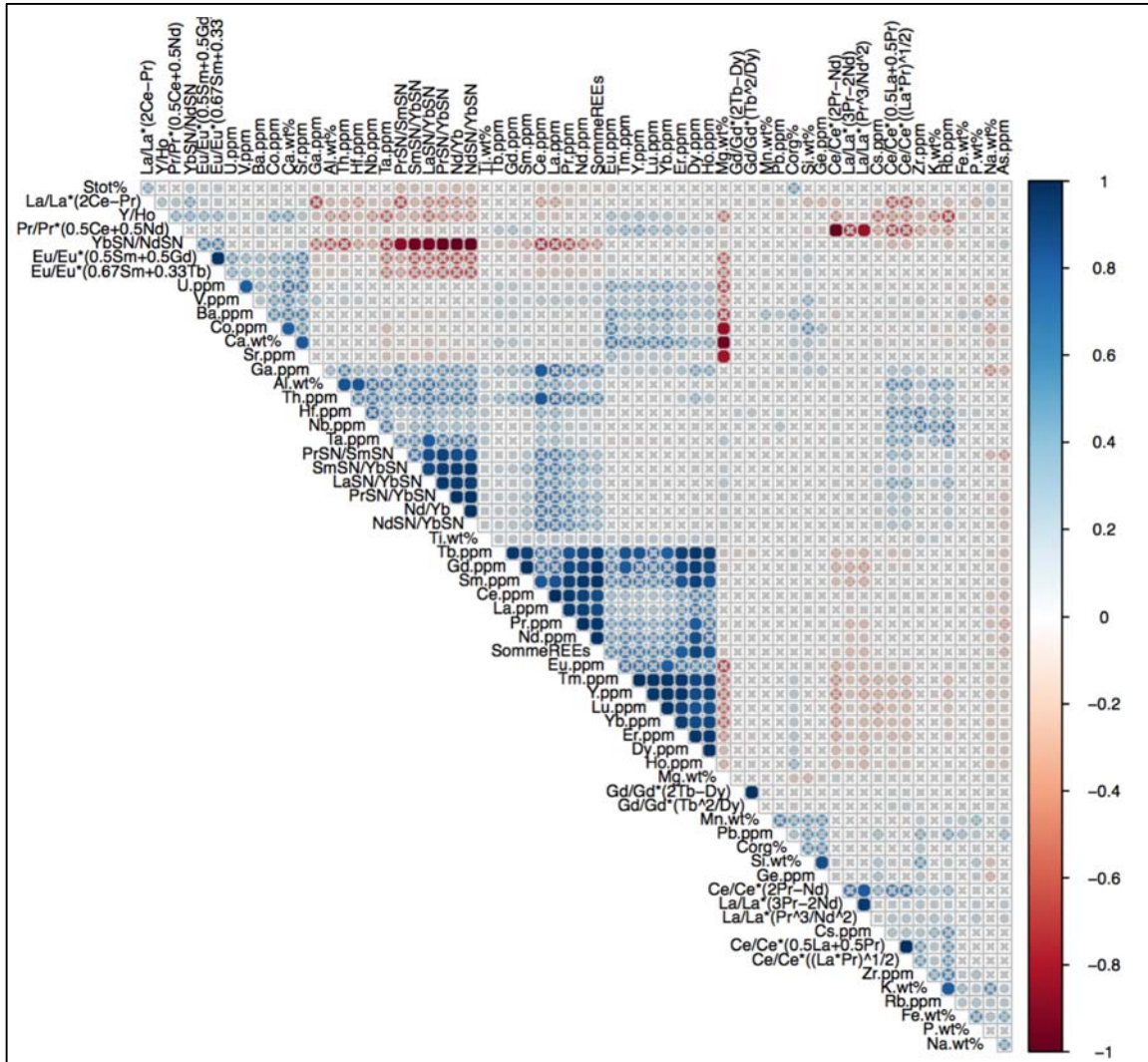


Figure SI-6. Correlation matrix of the chemical variables describing the authigenic-dominated microbialites

Spearman pairwise correlations of the 63 chemical variables (major, trace elements, REEs anomalies) describing the group of 18 authigenic-dominated microbialite samples. The Spearman's correlation coefficients (*i.e.*, r_s values) are ranging from -1 to +1 and are represented by both the circle color (*i.e.*, r_s values) and the circle size in the diagram. The statistical significance of each correlation was assessed and indicated by a p -value: correlations were considered as significant when the Spearman's correlation coefficient (r_s) followed the relationship: $|r_s| \geq 0.6$ and/or when the p -value (p) was lower than 2.56×10^{-5} (corresponding to an error lower than 5% per test). Non-significant correlations were marked by grey crosses in the Spearman diagram.

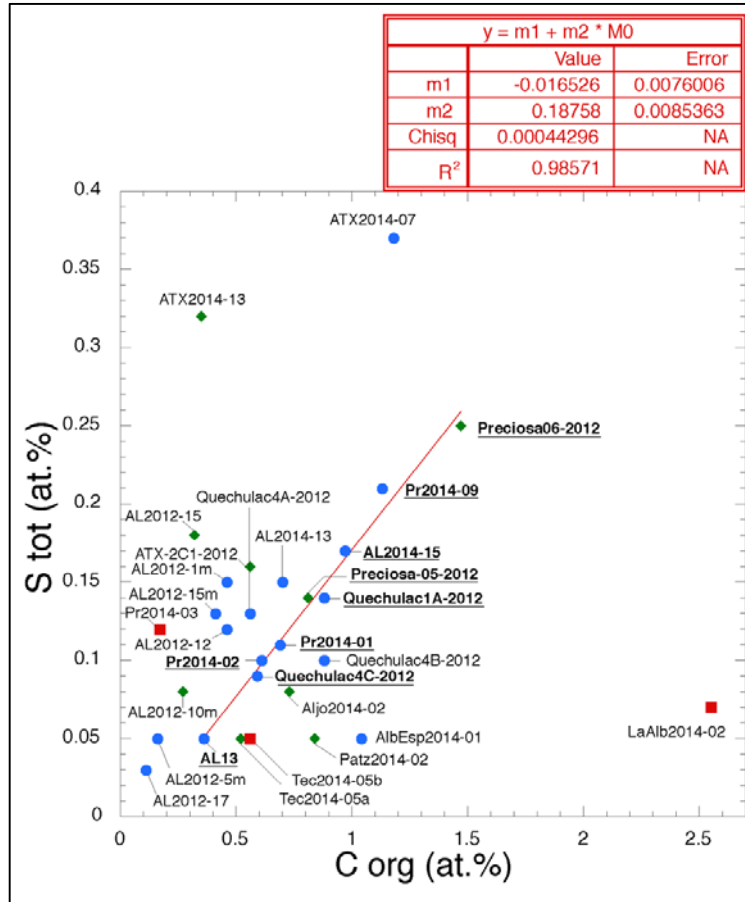
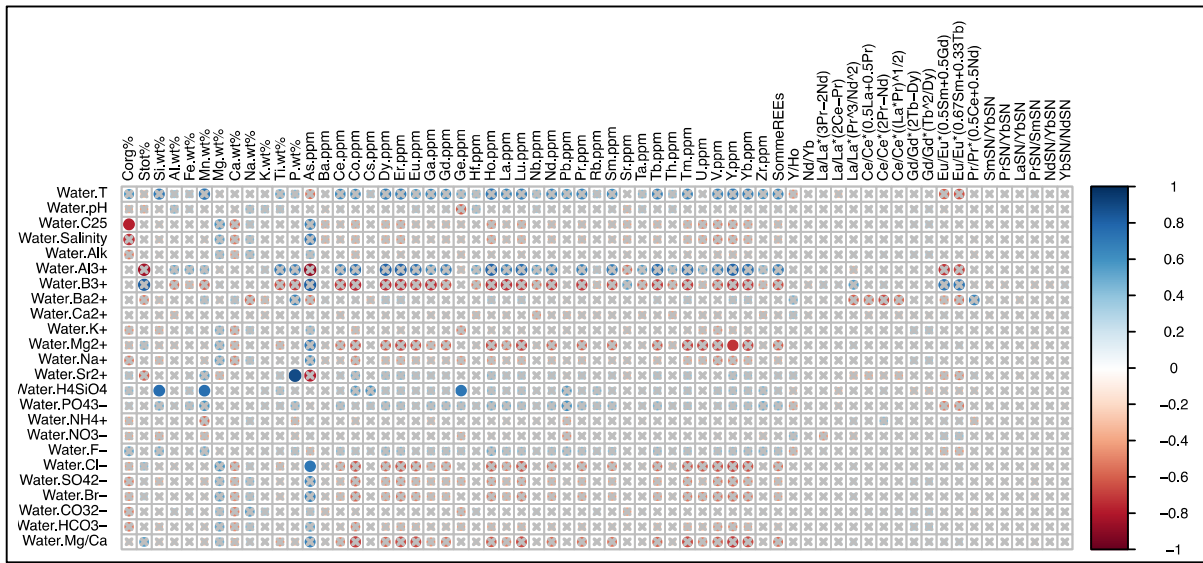


Figure SI-7. Organic carbon vs. total sulphur of all the studied microbialite samples (except 3 microbialite samples collected in 2007 for which total S was not measured). A strong positive correlation was observed for 9 samples (in bold and underlined). The regression coefficient (R^2) of the plot is 0.99. The correlation slope is 0.188 ± 0.009 . Blue dots stand for 18 microbialites poorly concentrated in Al (authigenic-dominated); red squares correspond to microbialites highly affected by detrital contamination; green diamonds stand for intermediately contaminated microbialites considered in this study as moderately affected by detrital input.



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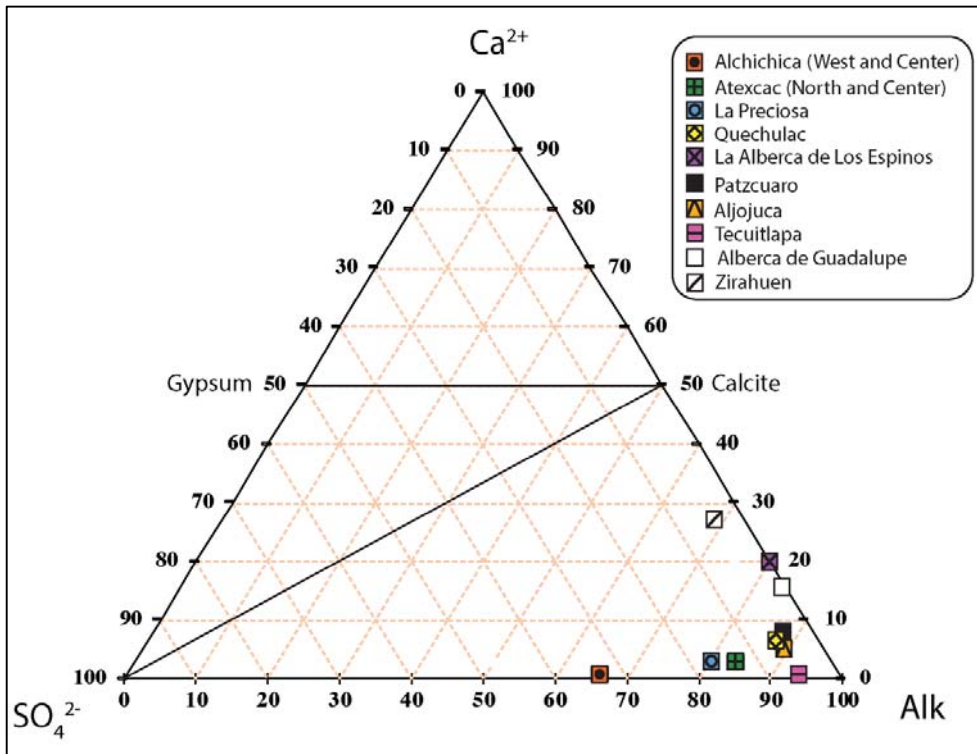


Figure SI-9. Distribution of Mexican lakes in the Spencer (Alk-SO₄-Ca) ternary diagram
 The aqueous concentrations are reported in meq.

II. TABLES

Aqueous sample	Location in the lake	Analyses
Preciosa2014_0m	North-East (close to the collected microbialites)	cations; Si-P-N ; anions ; alk; ⁸⁷ Sr/ ⁸⁶ Sr; REE+Y
Preciosa2012_0m	North (close to the collected microbialites)	cations; Si; anions ; alk
Quechulac2014_0m_N	North	cations; Si-P-N ; anions ; alk; REE+Y
Quechulac2012_0m_M	Center (close to the collected microbialites forming the island)	cations; Si; anions ; alk
ATX2014_0m_M	Center (Niskin bottle)	cations; Si-P-N ; anions ; alk; ⁸⁷ Sr/ ⁸⁶ Sr ; REE+Y
ATX2014_3m	Center (Niskin bottle)	cations; Si-P-N ; anions ; alk
ATX2014_10m	Center (Niskin bottle)	cations; Si-P-N ; anions ; alk
ATX2014_20m	Center (Niskin bottle)	cations; Si-P-N ; anions ; alk
ATX2014_30m	Center (Niskin bottle)	cations; Si-P-N ; anions ; alk
ATX2014_0m_N	North (close to the collected microbialites)	cations; Si-P-N ; anions
ATX2012_0m_N	North West (close to the collected microbialites)	cations; Si; anions ; alk
AL2014_0m_M	Center (Niskin bottle)	cations; Si-P-N ; anions ; alk; ⁸⁷ Sr/ ⁸⁶ Sr
AL2014_3m	Center (Niskin bottle)	cations; Si-P-N ; anions ; alk REE+Y
AL2014_10m	Center (Niskin bottle)	cations; Si-P-N ; anions ; alk
AL2014_25m	Center (Niskin bottle)	cations; Si-P-N ; anions ; alk
AL2014_40m	Center (Niskin bottle)	cations; Si-P-N ; anions ; alk
AL2014_55m	Center (Niskin bottle)	cations; Si-P-N ; anions ; alk
AL2014_0m_W	West (close to the collected microbialites)	cations; Si-P-N ; anions
AL2012_0m_M	Center (Niskin bottle)	cations; Si; anions ; alk
AL2012_3m	Center (Niskin bottle)	cations; Si; anions ; alk
AL2012_10m	Center (Niskin bottle)	cations; Si ; anions ; alk
AL2012_25m	Center (Niskin bottle)	cations; Si; anions ; alk
AL2012_40m	Center (Niskin bottle)	cations; Si; anions ; alk
AL2012_55m	Center (Niskin bottle)	cations; Si; anions ; alk
AL2012_0m_W	North West (close to the microbialites)	cations; Si; anions ; alk
Aljojuca2014_0m	North East (close to the microbialites)	cations; Si-P-N ; anions ; alk
Tecuitlapa2014_0m	North-East (close to the microbialites)	cations; Si-P-N ; anions ; alk
AlbEsp2014_0m	North (close to the microbialites)	cations; Si-P-N ; anions ; alk; ⁸⁷ Sr/ ⁸⁶ Sr; REE+Y
Alb2014_0m	South (close to the microbialites)	cations; Si-P-N ; anions ; alk
Patz2014_0m	North East (close to the microbialites)	cations; Si-P-N ; anions ; alk
Zirahuen2014_0m	Center	cations; Si-P-N ; anions ; alk; ⁸⁷ Sr/ ⁸⁶ Sr

Table SI-1. List of the aqueous samples, their location and performed analyses

Cation concentrations were determined by ICP-AES; H₄SiO₄ (noted Si), nitrogen compounds (noted N) and phosphate (noted P) concentrations were determined by continuous flow colorimetry; other anion concentrations were determined by ion chromatography; alkalinity (alk) was determined by titration; strontium isotope ratios (⁸⁷Sr/⁸⁶Sr) were measured using high performance ion chromatography and ICP-MS; trace element concentrations (REE+Y) were determined by ICP-MS. See the main text for more details about these analyses. The sampling location using a Niskin bottle at the center of Lake Alchichica was different in January 2012 and May 2014.

Aqueous sample	Temperature (°C)	C ₂₅ (mS/cm)	Salinity (g/l)
Preciosa2014_0m	19.0	2.30	1.35
Preciosa2012_0m	16.2	2.24	1.40
Quechulac2014_0m_N	22.5	0.86	0.45
Quechulac2012_0m_M	15.4	0.84	0.51
ATX2014_0m_M	20.2	11.65	7.39
ATX2014_3m	19.6	11.51	7.40
ATX2014_10m	19.4	11.55	7.46
ATX2014_20m	16.8	11.41	7.84
ATX2014_30m	15.7	11.37	8.03
ATX2014_0m_N	NM	NM	-
ATX2012_0m_N	15.8	12.31	8.73
AL2014_0m_M	19.5	12.76	8.29
AL2014_3m	19.2	12.48	8.15
AL2014_10m	18.1	12.61	8.46
AL2014_25m	15.9	12.38	8.76
AL2014_40m	15.3	12.56	9.03
AL2014_55m	15.1	12.51	9.04
AL2014_0m_W	NM	NM	-
AL2012_0m_M	15.1	13.45	9.78
AL2012_3m	15.1	13.46	9.78
AL2012_10m	15.0	13.47	9.82
AL2012_25m	14.9	NM	-
AL2012_40m	14.8	13.40	9.81
AL2012_55m	15.2	NM	-
AL2012_0m_W	15.1	13.45	9.78
Aljojuca2014_0m	20.6	1.27	0.70
Tecuitlapa2014_0m	23.4	4.94	2.74
AlbEsp2014_0m	23.0	1.25	0.65
Alb2014_0m	21.0	0.40	0.21
Patz2014_0m	28.5	1.09	0.50
Zirahuen2014_0m	22.2	0.14	0.08

Table SI-2. Determination of salinity

Salinity (S) determined using the equation described by Aminot and K erouel (2004) and using temperature (t) and specific conductance C₂₅:

$$S = a_0 + a_1.R_t^{0.5} + a_2.R_t + a_3.R_t^{1.5} + a_4.R_t^2 + a_5.R_t^{2.5} + \{(t - 15)/[1 + k(t-15)]\} \times (b_0 + b_1.R_t^{0.5} + b_2.R_t + b_3.R_t^{1.5} + b_4.R_t^2 + b_5.R_t^{2.5})$$

With $k=0.0162$; $a_0= 0.0080$; $a_1=-0.1692$; $a_2=25.3851$; $a_3=14.0941$; $a_4=-7.0261$; $a_5=2.7081$; $b_0=0.0005$; $b_1=-0.0056$; $b_2=-0.0066$; $b_3=-0.0375$; $b_4=0.0636$; $b_5=-0.0144$;

$$R_t = C_{25} / (42.914 \cdot r_t)$$

$r_t = c_0 + c_1t + c_2t^2 + c_3t^3 + c_4t^4$, with $c_0= 0.6766097$; $c_1=0.0200564$; $c_2=0.00011043$; $c_3=-6.9698E-07$; $c_4=1.0031E-09$

(NM): not measured. (-): calculation not possible.

Mineral Phase	Reaction	Log Ks	Reference(s)
Aragonite	$\text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}$	-8.34	Plummer and Busenberg, 1982
Calcite	$\text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}$	-8.48	Plummer and Busenberg, 1982
Mg-calcite	$\text{Mg}_{0.1}\text{Ca}_{0.9}\text{CO}_3 \rightleftharpoons 0.9\text{Ca}^{2+} + 0.1\text{Mg}^{2+} + \text{CO}_3^{2-}$	-8.30	obtained from Testemale et al., 2009
Monohydrocalcite (MHC)	$\text{CaCO}_3 \cdot \text{nH}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-} + \text{nH}_2\text{O}$	-7.65	Fukushi and Matsumiya, 2018
Vaterite	$\text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}$	-7.91	Plummer and Busenberg, 1982
Dolomite	$\text{CaMg}(\text{CO}_3)_2 \rightleftharpoons \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{CO}_3^{2-}$	-17.09	Ball and Nordstrom, 1991
Hydromagnesite	$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O} + 2\text{H}^+ \rightleftharpoons 5\text{Mg}^{2+} + 4\text{CO}_3^{2-} + 4\text{H}_2\text{O}$	-8.77	Robie and Hemingway, 1973
Amorphous Ca-carbonate (ACC)	$\text{CaCO}_3 \cdot \text{nH}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-} + \text{nH}_2\text{O}$	-6.40	Brechevic and Nielsen, 1989
Amorphous Mg-carbonate (AMC2)	$\text{MgCO}_3 \cdot \text{nH}_2\text{O} \rightleftharpoons \text{Mg}^{2+} + \text{CO}_3^{2-} + \text{nH}_2\text{O}$	-5.59	Fukushi and Matsumiya, 2018
Sepiolite (crystalline)	$\text{Mg}_2\text{Si}_3\text{O}_{7.5}(\text{OH}) \cdot 3\text{H}_2\text{O} + 4\text{H}^+ + 1/2\text{H}_2\text{O} \rightleftharpoons 2\text{Mg}^{2+} + 3\text{H}_4\text{SiO}_4(\text{aq})$	15.76	Stoessell, 1988
Sepiolite (amorphous)	$\text{Mg}_2\text{Si}_3\text{O}_{7.5}(\text{OH}) \cdot 3\text{H}_2\text{O} + 4\text{H}^+ + 1/2\text{H}_2\text{O} \rightleftharpoons 2\text{Mg}^{2+} + 3\text{H}_4\text{SiO}_4(\text{aq})$	18.78	Wollast et al., 1968
Kerolite	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot \text{H}_2\text{O} + 6\text{H}^+ + 3\text{H}_2\text{O} \rightleftharpoons 3\text{Mg}^{2+} + 4\text{H}_4\text{SiO}_4(\text{aq})$	25.79	Stoessell, 1988
Stevensite	$\text{Mg}_{2.9}\text{Ca}_{0.1}\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot \text{H}_2\text{O} + 6\text{H}^+ + 3\text{H}_2\text{O} \rightleftharpoons 2.9\text{Mg}^{2+} + 4\text{H}_4\text{SiO}_4(\text{aq}) + 0.1\text{Ca}^{2+}$	25.45	Chahi et al., 1997
Talc	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 + 6\text{H}^+ + 4\text{H}_2\text{O} \rightleftharpoons 3\text{Mg}^{2+} + 4\text{H}_4\text{SiO}_4(\text{aq})$	23.02	Jones and Galan, 1988
Amorphous silica	$\text{SiO}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{H}_4\text{SiO}_4(\text{aq})$	-2.71	Ball and Nordstrom, 1991
Hydroxyapatite	$\text{Ca}_5(\text{PO}_4)_3(\text{OH}) + 4\text{H}^+ \rightleftharpoons 5\text{Ca}^{2+} + 3\text{HPO}_4^{2-} + \text{H}_2\text{O}$	-44.33	NIST 46.7 (Shen et al.)

Table SI-3. Precipitation reactions of diverse phases and their associated solubility constants

Equations of precipitation for the main phases (Ca- and/or Mg-carbonates, silicates and hydroxyapatite) susceptible to form in Mexican lakes and thermodynamic solubility constants (*log Ks*) at 25 °C (see references) used in Visual MINTEQ for the calculations of saturation index (*SI*) and/or used to plot the solubility lines in the figs. 2 and 3 (main text).

Sites	Sampling Period	Aqueous sample	pH	Alk mM	Al ³⁺ mM	B ³⁺ mM	Ba ²⁺ mM
La Preciosa	May 2014	Preciosa2014_0m	8.75	14.22	< 0.0002	0.2439	0.0001
La Preciosa	Jan. 2012	Preciosa2012_0m	8.88	14.13	NM	NM	NM
Quechulac	May 2014	Quechulac2014_0m_N	8.92	6.55	0.0002	0.0463	0.0001
Quechulac	Jan. 2012	Quechulac2012_0m_M	8.80	6.68	NM	NM	NM
Atexcac	May 2014	ATX2014_0m_M	8.45	31.37	< 0.0002	5.8564	0.0001
Atexcac	May 2014	ATX2014_3m	8.55	31.80	< 0.0002	5.7283	0.0001
Atexcac	May 2014	ATX2014_10m	8.64	31.16	< 0.0002	5.7009	0.0001
Atexcac	May 2014	ATX2014_20m	8.62	30.98	< 0.0002	5.6845	0.0001
Atexcac	May 2014	ATX2014_30m	8.61	30.90	< 0.0002	5.6993	0.0001
Atexcac	May 2014	ATX2014_0m_N	8.45	31.37*	< 0.0002	5.7947	0.0001
Atexcac	Jan. 2012	ATX2012_0m_N	8.75	30.53	NM	NM	NM
Alchichica	May 2014	AL2014_0m_M	9.02	43.01	< 0.0002	3.6142	0.0001
Alchichica	May 2014	AL2014_3m	9.07	43.10	< 0.0002	3.6755	0.0001
Alchichica	May 2014	AL2014_10m	9.06	43.16	< 0.0002	3.6962	0.0001
Alchichica	May 2014	AL2014_25m	9.05	42.77	< 0.0002	3.6322	0.0001
Alchichica	May 2014	AL2014_40m	9.07	42.97	< 0.0002	3.6440	0.0001
Alchichica	May 2014	AL2014_55m	9.02	43.05	< 0.0002	3.6937	0.0001
Alchichica	May 2014	AL2014_0m_W	9.02	43.01**	< 0.0002	3.6571	0.0001
Alchichica	Jan. 2012	AL2012_0m_M	9.08	42.66	NM	NM	NM
Alchichica	Jan. 2012	AL2012_3m	9.10	42.99	NM	NM	NM
Alchichica	Jan. 2012	AL2012_10m	9.11	42.86	NM	NM	NM
Alchichica	Jan. 2012	AL2012_25m	9.11	42.88	NM	NM	NM
Alchichica	Jan. 2012	AL2012_40m	9.12	42.81	NM	NM	NM
Alchichica	Jan. 2012	AL2012_55m	9.06	42.94	NM	NM	NM
Alchichica	Jan. 2012	AL2012_0m_W	9.08	36.81	NM	NM	NM
Aljojuca	May 2014	Aljojuca2014_0m	9.14	13.17	0.0002	0.0379	0.0004
Tecuitlapa	May 2014	Tecuitlapa2014_0m	9.63	49.40	0.0003	0.0548	0.0001
La Alberca de los Espinos	May 2014	AlbEsp2014_0m	8.67	7.64	0.0002	0.0470	0.0007
Alberca de Guadalupe	May 2014	Alb2014_0m	9.32	4.28	0.0255	0.0131	0.0001
Pátzcuaro	May 2014	Patz2014_0m	8.94	10.62	0.0045	0.0275	0.0008
Zirahuén	May 2014	Zirahuen2014_0m	8.65	1.23	0.0007	0.0136	0.0002

Table SI-4. Physical and chemical parameters of the studied lakes

Concentrations of main cations and anions, dissolved silica (H₄SiO₄) and alkalinity (Alk) are in mmol/L. C₂₅ stands for specific conductance of water (conductivity normalized at 25°C). Asterisks (*) and (**) stand for alkalinity values measured from the middle of the corresponding lakes (ATX2014_0m_M and AL2014_0m_M, respectively) at the time of the sampling. NM stands for “not measured” and concerns some minor/trace elements in the 2012 samples. Detection limits are given for Al³⁺, Cu²⁺, Fe²⁺, Mn²⁺, Ni²⁺, Ti²⁺, Zn²⁺, H₄SiO₄, NH₄⁺, NO₃⁻, F⁻. Charge balances (Bal), calculated as 100*(Σcations - Σanions)/((Σcations + Σanions)/2), are in %. “_xm” refers to the depth at which samples were collected; “_M” means: sampled at the center of the lake; “_W” means: sampled on the western shore of the lake; “_N means”: sampled on the northern shore of the lake.

Aqueous Sample	Ca ²⁺ mM	Cu ²⁺ mM	Fe ²⁺ mM	K ⁺ mM	Mg ²⁺ mM	Mn ²⁺ mM	Na ⁺ mM	Ni ²⁺ mM	Sr ²⁺ mM
Preciosa2014_0m	0.25	< 0.00002	< 0.00002	0.38	8.33	< 0.0000004	7.72	< 0.0001	0.0004
Preciosa2012_0m	0.61	NM	NM	0.40	8.12	NM	9.00	NM	NM
Quechulac2014_0m_N	0.22	< 0.00002	< 0.00002	0.18	2.33	< 0.0000004	3.32	< 0.0001	0.0004
Quechulac2012_0m_M	0.45	NM	NM	0.20	2.37	NM	3.40	NM	NM
ATX2014_0m_M	0.52	< 0.00002	0.0006	2.32	22.82	< 0.0000004	79.31	< 0.0001	0.0014
ATX2014_3m	0.50	< 0.00002	0.0006	2.25	22.19	< 0.0000004	77.86	< 0.0001	0.0014
ATX2014_10m	0.47	< 0.00002	0.0005	2.35	22.01	< 0.0000004	77.74	< 0.0001	0.0014
ATX2014_20m	0.35	< 0.00002	< 0.00002	2.15	21.95	< 0.0000004	77.02	< 0.0001	0.0009
ATX2014_30m	0.28	< 0.00002	< 0.00002	2.35	21.96	0.0001	77.21	< 0.0001	0.0007
ATX2014_0m_N	0.47	< 0.00002	< 0.00002	2.36	21.04	< 0.0000004	82.17	< 0.0001	0.0014
ATX2012_0m_N	0.62	NM	NM	2.93	24.39	NM	80.67	NM	NM
AL2014_0m_M	0.19	< 0.00002	< 0.00002	5.47	17.18	< 0.0000004	102.88	< 0.0001	0.0003
AL2014_3m	0.19	< 0.00002	< 0.00002	5.70	17.45	< 0.0000004	101.97	< 0.0001	0.0003
AL2014_10m	0.19	< 0.00002	< 0.00002	5.67	17.84	< 0.0000004	103.17	< 0.0001	0.0003
AL2014_25m	0.19	< 0.00002	< 0.00002	5.52	17.41	< 0.0000004	102.25	< 0.0001	0.0003
AL2014_40m	0.18	< 0.00002	< 0.00002	5.69	17.37	< 0.0000004	102.48	< 0.0001	0.0003
AL2014_55m	0.18	< 0.00002	< 0.00002	5.91	18.07	0.0001	101.15	< 0.0001	0.0003
AL2014_0m_W	0.23	< 0.00002	< 0.00002	5.82	17.83	< 0.0000004	100.66	< 0.0001	0.0004
AL2012_0m_M	0.46	NM	NM	5.94	18.34	NM	105.73	NM	NM
AL2012_3m	0.47	NM	NM	5.83	18.51	NM	106.76	NM	NM
AL2012_10m	0.41	NM	NM	5.63	18.34	NM	105.21	NM	NM
AL2012_25m	0.43	NM	NM	5.66	18.46	NM	104.46	NM	NM
AL2012_40m	0.42	NM	NM	5.89	18.61	NM	106.31	NM	NM
AL2012_55m	0.46	NM	NM	5.81	18.68	NM	106.25	NM	NM
AL2012_0m_W	0.90	NM	NM	4.73	15.97	NM	85.89	NM	NM
Aljojuca2014_0m	0.43	< 0.00002	< 0.00002	0.68	2.90	< 0.0000004	8.13	< 0.0001	0.0051
Tecuitlapa2014_0m	0.17	< 0.00002	< 0.00002	3.06	0.51	< 0.0000004	51.29	< 0.0001	0.0006
AlbEsp2014_0m	0.92	< 0.00002	0.0002	0.68	2.55	< 0.0000004	5.04	< 0.0001	0.0061
Alb2014_0m	0.40	< 0.00002	0.0018	0.38	0.91	< 0.0000004	1.36	< 0.0001	0.0030
Patz2014_0m	0.43	0.0001	0.0011	1.18	1.28	< 0.0000004	7.72	< 0.0001	0.0043
Zirahuen2014_0m	0.24	< 0.00002	0.0001	0.11	0.24	< 0.0000004	0.35	< 0.0001	0.0012

Table SI-4. Continued

Aqueous Sample	Ti ²⁺ mM	Zn ²⁺ mM	H ₄ SiO ₄ mM	PO ₄ ³⁻ mM	NH ₄ ⁺ mM	NO ₂ ⁻ mM	NO ₃ ⁻ mM	F ⁻ mM	Cl ⁻ mM
Preciosa2014_0m	< 0.0000006	0.0001	0.5626	0.0007	0.0009	0.0001	< 0.0001	0.1838	9.62
Preciosa2012_0m	NM	NM	0.5750	NM	NM	NM	0.020	0.0454	9.36
Quechulac2014_0m_N	< 0.0000006	< 0.000009	0.2268	0.0005	0.0019	0.0005	0.0048	0.0285	2.48
Quechulac2012_0m_M	NM	NM	0.2080	NM	NM	NM	0.008	0.0262	2.09
ATX2014_0m_M	< 0.0000006	0.0001	1.1233	0.0008	0.0011	0.0002	0.0005	0.6817	109.57
ATX2014_3m	< 0.0000006	0.0001	1.1264	0.0007	0.0008	0.0002	0.0005	0.6970	109.35
ATX2014_10m	< 0.0000006	0.0001	1.1292	0.0007	< 0.0005	0.0002	0.0005	0.6874	110.70
ATX2014_20m	< 0.0000006	0.0001	1.0940	0.0006	< 0.0005	0.0017	0.0027	0.6517	110.42
ATX2014_30m	< 0.0000006	0.0001	1.0795	0.0006	< 0.0005	0.0002	0.0097	0.5703	112.05
ATX2014_0m_N	< 0.0000006	0.0001	1.1222	0.0006	0.0010	0.0002	0.0004	0.7424	110.65
ATX2012_0m_N	NM	NM	1.0368	NM	NM	NM	< 0.0001	0.0068	107.36
AL2014_0m_M	< 0.0000006	< 0.000009	0.0013	0.0012	0.0034	0.0006	0.0008	0.2653	87.48
AL2014_3m	< 0.0000006	< 0.000009	0.0011	0.0011	0.0011	0.0005	0.0003	0.3340	87.05
AL2014_10m	< 0.0000006	< 0.000009	< 0.001	0.0009	0.0014	0.0005	< 0.0001	0.4965	87.24
AL2014_25m	< 0.0000006	< 0.000009	0.0016	0.0009	0.0009	0.0064	0.0024	0.8601	87.56
AL2014_40m	< 0.0000006	0.0002	0.0132	0.0012	< 0.0005	0.0120	0.0029	0.6940	89.11
AL2014_55m	< 0.0000006	0.0001	0.0300	0.0019	< 0.0005	0.0083	0.0002	0.5933	87.83
AL2014_0m_W	< 0.0000006	0.0001	0.0254	0.0008	0.0013	0.0008	< 0.0001	0.6422	85.84
AL2012_0m_M	NM	NM	0.0046	NM	NM	NM	0.045	< 0.0003	94.51
AL2012_3m	NM	NM	< 0.001	NM	NM	NM	0.000	< 0.0003	94.48
AL2012_10m	NM	NM	< 0.001	NM	NM	NM	0.054	< 0.0003	99.44
AL2012_25m	NM	NM	0.0044	NM	NM	NM	0.074	< 0.0003	94.90
AL2012_40m	NM	NM	0.0037	NM	NM	NM	0.060	0.0959	94.72
AL2012_55m	NM	NM	< 0.001	NM	NM	NM	0.068	< 0.0003	100.87
AL2012_0m_W	NM	NM	0.2863	NM	NM	NM	0.043	< 0.0003	74.47
Aljojuca2014_0m	< 0.0000006	< 0.000009	0.1572	0.0012	0.0007	0.0004	0.0003	0.7109	1.49
Tecuitlapa2014_0m	< 0.0000006	0.0001	0.6174	0.0033	0.0448	0.0102	0.0012	0.8568	6.12
AlbEsp2014_0m	< 0.0000006	< 0.000009	0.8770	0.0055	0.0009	0.0003	< 0.0001	0.4838	4.77
Alb2014_0m	< 0.0000006	< 0.000009	1.7737	0.0009	< 0.0005	0.0001	< 0.0001	0.0296	0.17
Patz2014_0m	0.0001	< 0.000009	0.3660	0.0006	< 0.0005	0.0001	< 0.0001	0.6493	1.49
Zirahuen2014_0m	< 0.0000006	< 0.000009	0.0099	0.0004	0.0008	0.0003	0.0003	0.0045	0.17

Table SI-4. Continued

Aqueous Sample	SO ₄ ²⁻ mM	Br ⁻ mM	CO ₃ ²⁻ mM	HCO ₃ ⁻ mM	Σ Cations mM	Σ Anions mM	Bal %	Mg/Ca
Preciosa2014_0m	1.475	0.0139	0.36	13.50	25.99	27.00	-3.8	33.6
Preciosa2012_0m	1.296	0.013	0.48	13.17	26.86	26.15	2.6	13.3
Quechulac2014_0m_N	0.197	0.0026	0.24	6.07	8.76	9.46	-7.7	10.4
Quechulac2012_0m_M	0.182	0.003	0.19	6.30	9.24	9.17	0.7	5.3
ATX2014_0m_M	2.453	0.1318	0.41	30.54	145.88	146.65	-0.5	44.2
ATX2014_3m	2.423	0.1334	0.52	30.75	142.69	146.83	-2.9	44.4
ATX2014_10m	2.449	0.1308	0.62	29.91	142.15	147.58	-3.7	46.5
ATX2014_20m	2.431	0.1306	0.59	29.79	140.82	147.05	-4.3	63.5
ATX2014_30m	2.440	0.1326	0.58	29.74	141.16	148.54	-5.1	77.1
ATX2014_0m_N	2.547	0.1340	0.41	30.54	144.93	147.99	-2.1	45.2
ATX2012_0m_N	2.063	0.166	0.78	28.98	133.62	142.19	-6.2	39.3
AL2014_0m_M	10.837	0.1148	1.96	39.09	153.93	152.55	0.9	90.0
AL2014_3m	9.661	0.1151	2.18	38.74	153.99	149.92	2.7	90.8
AL2014_10m	12.692	0.1138	2.14	38.89	155.99	156.41	-0.3	93.5
AL2014_25m	10.153	0.1112	2.07	38.62	153.86	151.62	1.5	93.0
AL2014_40m	10.639	0.1101	2.17	38.63	154.21	154.18	0	96.7
AL2014_55m	10.929	0.1131	1.96	39.13	154.64	153.45	0.8	98.3
AL2014_0m_W	10.842	0.1141	1.96	39.09	153.56	151.29	1.5	78.6
AL2012_0m_M	10.178	0.104	2.22	38.23	149.28	157.67	-5.5	40.0
AL2012_3m	10.105	0.111	2.32	38.35	150.55	157.79	-4.7	39.1
AL2012_10m	10.174	0.117	2.33	38.20	148.34	162.81	-9.3	45.0
AL2012_25m	10.212	0.108	2.35	38.18	147.90	158.38	-6.8	42.7
AL2012_40m	10.194	0.114	2.39	38.02	150.27	158.19	-5.1	44.3
AL2012_55m	10.964	0.144	2.13	38.69	150.33	165.96	-9.9	40.5
AL2012_0m_W	8.196	0.092	1.91	32.99	124.35	127.81	-2.7	17.8
Aljojuca2014_0m	0.403	0.0020	0.77	11.64	15.60	16.19	-3.7	6.8
Tecuitlapa2014_0m	1.596	0.0221	7.16	35.08	55.93	59.61	-6.4	3.0
AlbEsp2014_0m	0.003	0.0050	0.16	7.31	12.83	12.92	-0.7	2.8
Alb2014_0m	0.010	0.0004	0.36	3.56	4.50	4.50	0	2.3
Patz2014_0m	0.268	0.0010	0.41	9.80	12.43	13.29	-6.7	3.0
Zirahuen2014_0m	0.038	< 0.0004	0.03	1.18	1.48	1.49	-0.7	1.0

Table SI-4. Continued

Aqueous Sample	pH	Alk	CO ₃ ²⁻ (1)	HCO ₃ ⁻ (1)	NH ₃	H ₂ BO ₃ ⁻	H ₃ SiO ₄ ⁻	H ₃ PO ₄	HPO ₄ ²⁻	PO ₄ ³⁻	HF	OH ⁻	H ⁺	Σ	CO ₃ ²⁻ (2)	HCO ₃ ⁻ (2)
Preciosa2014_0m	8.75	14.22	0.36	13.50	1.33E-04	0.06	0.04	1.12E-12	3.25E-04	1.56E-07	2.97E-07	0.004	2.10E-06	0.10	0.36	13.40
Quechulac2014_0m_N	8.92	6.55	0.24	6.07	5.06E-04	0.02	0.02	6.09E-13	2.97E-04	1.70E-07	4.02E-08	0.008	1.34E-06	0.05	0.24	6.02
ATX2014_0m-M	8.45	31.37	0.41	30.54	8.65E-05	0.94	0.05	2.88E-12	3.26E-04	1.37E-07	1.69E-06	0.003	4.66E-06	0.99	0.40	29.58
ATX2014_0m_N	8.45	31.37*	0.41	30.54	7.42E-05	0.93	0.05	2.24E-12	2.53E-04	1.06E-07	1.88E-06	0.003	4.65E-06	0.98	0.40	29.58
AL2014_0m_M	9.02	43.01	1.96	39.09	7.69E-04	1.41	0.00	3.63E-13	5.75E-04	8.91E-07	1.94E-07	0.009	1.26E-06	1.42	1.89	37.80
AL2014_0m_W	9.02	43.01**	1.96	39.09	2.91E-04	1.43	0.00	2.40E-13	3.79E-04	5.87E-07	4.67E-07	0.009	1.26E-06	1.44	1.89	37.78
Aljojuca2014_0m	9.14	13.17	0.77	11.64	2.17E-04	0.02	0.02	4.66E-13	6.98E-04	7.15E-07	5.70E-07	0.011	8.26E-07	0.05	0.77	11.59
Tecuitlapa2014_0m	9.63	49.40	7.16	35.08	2.83E-02	0.04	0.26	1.25E-13	2.47E-03	1.25E-05	2.26E-07	0.047	2.90E-07	0.37	7.11	34.81
AlbEsp2014_0m	8.67	7.64	0.16	7.31	1.52E-04	0.01	0.06	1.78E-11	2.93E-03	1.03E-06	1.19E-06	0.005	2.42E-06	0.08	0.16	7.24
Alb2014_0m	9.32	4.28	0.36	3.56	4.52E-14	0.01	0.37	1.86E-13	5.15E-04	6.19E-07	1.76E-08	0.017	5.18E-07	0.40	0.32	3.23
Patz2014_0m	8.94	10.62	0.41	9.80	3.59E-14	0.01	0.05	7.87E-13	4.28E-04	3.08E-07	1.00E-06	0.013	1.30E-06	0.08	0.41	9.73
Zirahuen2014_0m	8.65	1.23	0.03	1.18	1.32E-04	0.00	0.00	2.81E-12	3.12E-04	7.10E-08	1.36E-08	0.004	2.35E-06	0.01	0.03	1.17

Table SI-5. Calculations of [HCO₃⁻] and [CO₃²⁻] by two different methods

(1) from alkalinity, pH and (HCO₃⁻; CO₃²⁻) pKa. (2) based on the exact formula of alkalinity (Dickson, 1981) including aqueous species (*i.e.*, NH₃, H₂BO₃⁻, H₃SiO₄⁻, H₃PO₄, HPO₄²⁻, PO₄³⁻, HF, OH⁻ and H⁺). Overall, both methods provide the same results. Asterisks (*) and (**) indicate that in these cases, alkalinity value was taken from another sample, collected in the center of the corresponding lakes (ATX2014_0m_M and AL2014_0m_M, respectively) at the same date.

Lake	Zirahuén	Alberca de Guadalupe	Quechulac (center)	Quechulac (North)	La Alberca de Los Espinos	La Preciosa (North)	La Preciosa (North-East)	Pátzcuaro	Aljojuca	Tecuitlapa	Atexcac (North)	Atexcac (center)	Alchichica (West)	Alchichica (center)	Alchichica (center)
Sampling Time	May 2014	May 2014	Jan. 2012	May 2014	May 2014	Jan. 2012	May 2014	May 2014	May 2014	May 2014	Jan. 2012	May 2014	Jan. 2012	Jan. 2012	May 2014
Sample Symbol	●Z	●Alb	◆Q	●Q	●AE	◆LP	●LP	●P	●Alj	●T	◆ATX-N	●ATX-M	◆AL-W	◆AL-M	●AL-M
<i>Phase</i>															
Aragonite <i>CaCO₃</i>	- 0.06	1.11	0.79	0.66	1.11	1.13	0.67	1.17	1.26	1.22	1.06	0.80	1.51	1.23	0.85
Calcite <i>CaCO₃</i>	0.09	1.26	0.94	0.81	1.25	1.28	0.82	1.31	1.41	1.36	1.21	0.95	1.66	1.38	1.00
Mg-calcite <i>Mg_{0.5}Ca_{0.5}CO₃</i>	- 0.04	1.20	1.03	0.79	1.16	1.39	0.92	1.11	1.41	1.28	1.38	1.03	1.81	1.57	1.13
Monohydrocalcite <i>CaCO₃·nH₂O</i>	-0.73	0.45	0.16	- 0.01	0.44	0.49	0.02	0.46	0.60	0.54	0.43	0.14	0.88	0.60	0.20
Vaterite <i>CaCO₃</i>	- 0.49	0.68	0.35	0.24	0.68	0.69	0.24	0.75	0.83	0.79	0.62	0.37	1.07	0.79	0.42
Dolomite <i>CaMg(CO₃)₂</i>	0.28	3.01	2.63	2.78	3.08	3.72	3.25	3.32	3.79	3.50	4.04	3.61	4.61	4.41	4.07
Hydromagnesite <i>Mg₃(CO₃)₄(OH)₂·4H₂O</i>	- 11.50	- 3.53	-4.75	- 2.99	- 4.03	-1.10	- 1.28	- 2.76	- 1.04	- 2.08	0.38	- 0.66	1.28	1.60	1.87
Sepiolite <i>Mg₃Si₄O₁₀(OH)₂·nH₂O</i>	-3.87	6.16	1.93	2.90	3.80	4.39	4.08	3.27	3.05	4.07	5.18	4.36	4.22	-1.11	- 2.79
Amorph. Sepiolite <i>Mg₃Si₄O₁₀(OH)₂·nH₂O</i>	- 6.70	3.41	-0.43	0.05	0.91	1.98	1.47	0.02	0.33	1.16	2.80	1.67	1.89	-3.45	- 5.44
Kerolite <i>Mg₃Si₄O₁₀(OH)₂·nH₂O</i>	- 5.16	8.93	3.60	4.30	5.29	6.99	6.22	4.17	4.82	5.84	8.08	6.37	7.01	-0.09	- 2.80
Talc <i>Mg₃Si₄O₁₀(OH)₂</i>	- 2.35	11.76	6.51	7.11	8.09	9.89	9.08	6.88	7.65	8.63	11.00	9.21	9.93	2.83	0.05
Stevensite <i>Ca_{0.1}Mg_{2.9}Si₄O₁₀(OH)₂·nH₂O</i>	- 4.78	9.29	4.01	4.57	5.62	7.34	6.49	4.40	5.13	6.14	8.41	6.62	7.37	0.23	- 2.58
Amorph. Silica <i>SiO₂</i>	- 2.26	- 0.08	-0.88	- 0.93	- 0.33	-0.45	- 0.48	- 0.79	- 1.09	- 0.68	-0.17	- 0.17	-0.75	-2.54	- 3.14
Hydroxyapatite <i>Ca₅(PO₄)₃(OH)</i>	3.34	6.75	/	2.94	7.95	/	1.63	4.41	5.46	3.70	/	0.53	/	/	0.59

Table SI-6. Saturation indices of the 2012 and 2014 surface water solutions

Saturation indices of the surface water solutions of the lakes sampled in May 2014 and January 2012 for various Ca- and/or Mg-carbonates, silicates and hydroxyapatite. Saturation indices were calculated using the Visual MINTEQ software. Positive values (in bold characters) indicate that solutions are supersaturated. Saturation indices with respect to hydroxyapatite were not calculated for the 2012 surface water (/) because [PO₄³⁻] was not analyzed for those samples.

Lake	Microbialite Sample	Type	Location on the lake	Detrital contamination	Main Mineralogy
Alchichica	AL13 (*)	Living	North	LDC	H – A – LDH
	AL66 (*)	Living	North	/	H – A – LDH
	AL69-2m	Living	North	LDD	H – A
	AL60-6m	Living	North	IDC	H – A – An
	AL54-11m	Living	North	IDC	H – A
	AL2012-1m	Living	North	LDC	H – A
	AL2012-5m	Living	North	LDC	H – A
	AL2012-10m (*)	Living	North	IDC	H – A – LDH – I
	AL2012-15m	Living	North	LDC	H – A
	AL2012-12 (*)	Living	North-West	LDC	H – A
	AL2012-15 (*)	Non-living	North-West	IDC	A – C
	AL2012-17	Non-living	North-West	LDC	A – LDH
	AL2014-12	Living	North-West	/	H – A
	AL2014-13 (*)	Living	North-West	LDC	A – H – K/S
	AL2014-15 (*)	Living	North-West	LDC	A – H – LDH
	AL2014-26	Living	North-West	/	A – H – LDH
Atexcac	ATX-2C1-2012 (*)	Living	North	IDC	K/S – A – C – H
	ATX2014-02 (*)	Non-living	North	/	A – K/S
	ATX2014-07	Living	North	LDC	A – K/S – C
	ATX2014-13 (*)	Living	South	IDC	A – K/S – D – C – An
La Preciosa	Preciosa-05-2012 (*)	Non-living	North	IDC	A – K/S – C – An
	Preciosa-06-2012	Living	North	IDC	A – K/S – C – An
	Pr2014-01	Non-living	East	LDC	A – K/S – C
	Pr2014-02	Non-living	East	LDC	A – K/S – D – C
	Pr2014-03	Non-living	East	HDC	MgC – An – D – A – K/S
	Pr2014-05	Non-living	East	/	A – K/S
	Pr2014-06	Non-living	East	/	A – K/S
	Pr2014-08	Living	East	/	A – K/S
	Pr2014-09 (*)	Living	East	LDC	A – K/S
Quechulac	Quechulac-1A-2012 (*)	Living	Center	LDC	A – K/S
	Quechulac-4A-2012	Non-living (external part)	Center	LDC	A – C
	Quechulac-4B-2012	Non-living (intermediate part)	Center	LDC	A – C
	Quechulac-4C-2012	Non-living (internal part)	Center	LDC	A – C
Tecuitlapa	Tec2014-05a	Non-living (external white part)	East	IDC	MHC – MgC – A – Ab
	Tec2014-05b	Non-living (intermediate green part)	East	HDC	MHC – Ab – A – K/S
	Tec2014-06 (*)	Living	East	/	MgC – MHC – A – K/S
La Alberca de Los Espinos	AlbEsp2014-01 (*)	Living	West	LDC	MgC – MHC – K/S
Pátzcuaro	Patz2014-01	Non-living	North-East	/	MgC
	Patz2014-02 (*)	Living	North-East	IDC	MgC – A – MHC – K/S
Aljojuca	Aljo2014-01	Non-living	North	/	MgC – MHC – A – Ab
	Aljo2014-02 (*)	Living	North	IDC	MHC – MgC – A – Ab
Alberca de Guadalupe	Alb2014-02 (*)	Living	South	HDC	Ab – MgC – K/S

Table SI-7. Mineralogical composition of the studied microbialites

Mineralogical composition of living and non-living microbialites hosted by the studied Mexican lakes as determined by XRD and FTIR and/or observed by optical and scanning electron microscopy. Mineralogical differences exist in a given lake between non-living *vs* living microbialites and/or microbialites at different locations in the lake. Mineral phases are listed in order of abundance. (C: calcite; MgC: magnesian calcite; MHC: monohydrocalcite; A: aragonite; D: dolomite; H: hydromagnesite; K/S: kerolite and/or stevensite; LDH: layered double hydroxide; Ab: albite; An: anorthite; Q: quartz; I: illite). Asterisk (*) stands for samples observed by SEM and/or optical microscopy. The bulk chemistry of samples in bold was analyzed (32 samples in total). The extent of detrital contamination was assessed based on bulk chemistry. HDC: samples highly affected by detrital contamination; IDC: samples intermediately affected by detrital contamination and LDC: samples the least affected by detrital contamination (*i.e.*, authigenic-dominated samples).

Microbialite Sample	Aragonite wt.%	Mg-Calcite wt.%	Monohydrocalcite wt.%	Hydromagnesite wt.%	Talc wt.%	Fe-Talc wt.%
AL13	12	/	/	88	/	/
AL69-2m	22	/	/	78	/	/
AL2012-1m	23	/	/	77	/	/
AL2012-5m	18	/	/	82	/	/
AL2012-15m	44	/	/	56	/	/
AL2012-12	23	/	/	77	/	/
AL2012-17	98	/	/	2	/	/
AL2014-13	91	/	/	9	/	/
AL2014-15	74	/	/	26	/	/
ATX2014-07	67	/	/	/	32	1
Pr2014-01	70	/	/	/	29	1
Pr2014-02	62	/	/	/	38	1
Pr2014-09	75	/	/	/	24	1
Quechulac-1A-2012	96	/	/	/	4	/
Quechulac-4A-2012	100	/	/	/	/	/
Quechulac-4B-2012	99	/	/	/	/	1
Quechulac-4C-2012	97	/	/	/	/	3
AlbEsp2014-01	/	61	27	/	12	/

Table SI-8. Proportions of the mineral phases in the authigenic-dominated microbialites

Approximate mass proportions of the mineral phases composing Al-poor microbialite samples, based on bulk chemical composition, XRD and FTIR analyses, and optical and scanning electron microscopies.

Microbialite Sample	Corg (at.%)	S total (at.%)	Si (wt.%)	Al (wt.%)	Fe (wt.%)	Mn (wt.%)	Mg (wt.%)	Ca (wt.%)	Na (wt.%)	K (wt.%)	Ti (wt.%)	P (wt.%)
AL13	0.36 ±0.05	0.05 ±0.01	0.65 ±0.03	0.21 ±0.02	0.12 ±0.01	< 0.0002	22.23 ±0.44	4.0 ±0.1	0.20 ±0.02	0.06 ±0.01	< 0.01	< 0.02
AL69-2m	0.36 ±0.05	NM	0.2 ±0.02	0.08 ±0.01	0.078 ±0.004	0.005 ±0.001	19.71 ±0.39	7.1 ±0.1	0.22 ±0.02	0.04 ±0.01	< 0.01	< 0.02
AL60-6m	0.28 ±0.04	NM	2.56 ±0.08	0.83 ±0.08	0.39 ±0.01	0.017 ±0.002	17.33 ±0.35	8.5 ±0.2	0.50 ±0.02	0.18 ±0.02	0.04 ±0.01	0.022 ±0.005
AL54-11m	0.29 ±0.04	NM	2.46 ±0.07	0.29 ±0.03	0.15 ±0.01	0.011 ±0.001	20.85 ±0.42	3.9 ±0.1	0.24 ±0.02	0.07 ±0.01	0.020 ±0.005	0.022 ±0.005
AL2012-1m	0.46 ±0.07	0.15 ±0.02	0.54 ±0.03	0.14 ±0.02	0.090 ±0.004	0.007 ±0.002	19.04 ±0.38	7.5 ±0.1	0.23 ±0.02	0.05 ±0.01	< 0.01	0.017 ±0.004
AL2012-5m	0.16 ±0.02	0.05 ±0.01	0.75 ±0.04	0.11 ±0.02	0.049 ±0.005	0.004 ±0.001	21.02 ±0.42	5.8 ±0.1	0.15 ±0.01	0.03 ±0.01	< 0.01	0.022 ±0.005
AL2012-10m	0.27 ±0.04	0.08 ±0.02	3.83 ±0.08	1.01 ±0.1	0.17 ±0.01	0.014 ±0.001	17.22 ±0.34	8.5 ±0.2	0.48 ±0.02	0.21 ±0.02	0.014 ±0.003	0.017 ±0.004
AL2012-15m	0.41 ±0.06	0.13 ±0.02	0.45 ±0.02	0.09 ±0.01	0.1 ±0.005	0.009 ±0.001	14.59 ±0.29	14.9 ±0.3	0.32 ±0.03	0.04 ±0.01	< 0.01	< 0.02
AL2012-12	0.46 ±0.07	0.12 ±0.02	0.26 ±0.03	0.06 ±0.01	0.2 ±0.01	0.007 ±0.002	18.79 ±0.38	7.5 ±0.2	0.21 ±0.02	0.03 ±0.01	< 0.01	0.017 ±0.004
AL2012-15	0.32 ±0.05	0.18 ±0.02	1.86 ±0.09	0.26 ±0.03	1.68 ±0.03	0.018 ±0.002	1.11 ±0.06	32.6 ±0.7	0.79 ±0.02	0.17 ±0.02	0.018 ±0.004	0.048 ±0.005
AL2012-17	0.11 ±0.02	0.03 ±0.01	1.02 ±0.05	0.09 ±0.01	2.49 ±0.05	0.012 ±0.001	0.52 ±0.03	35.1 ±0.7	0.27 ±0.03	0.05 ±0.01	< 0.01	0.092 ±0.009
AL2014-13	0.70 ±0.07	0.15 ±0.02	0.73 ±0.04	0.15 ±0.02	0.15 ±0.01	0.005 ±0.001	2.38 ±0.07	32.5 ±0.6	0.44 ±0.02	0.06 ±0.01	< 0.01	0.017 ±0.004
AL2014-15	0.97 ±0.1	0.17 ±0.02	1.02 ±0.05	0.12 ±0.02	2.24 ±0.04	0.015 ±0.001	6.34 ±0.13	23.6 ±0.5	0.46 ±0.02	0.07 ±0.01	< 0.01	0.04 ±0.01
ATX-2C1-2012	0.56 ±0.08	0.16 ±0.02	13.87 ±0.14	0.29 ±0.03	0.54 ±0.02	0.036 ±0.004	12.76 ±0.26	9.1 ±0.2	0.33 ±0.03	0.11 ±0.01	0.019 ±0.005	< 0.02
ATX2014-07	1.18 ±0.12	0.37 ±0.02	7.4 ±0.07	0.05 ±0.01	0.12 ±0.01	0.033 ±0.003	5.28 ±0.11	22.3 ±0.4	0.54 ±0.02	0.07 ±0.01	< 0.01	0.048 ±0.005
ATX2014-13	0.35 ±0.05	0.32 ±0.02	2.58 ±0.08	0.58 ±0.06	0.67 ±0.01	0.018 ±0.002	0.57 ±0.03	34.9 ±0.7	0.5 ±0.02	0.13 ±0.01	0.035 ±0.009	0.017 ±0.004
Preciosa-05-2012	0.81 ±0.08	0.14 ±0.02	11.34 ±0.11	0.63 ±0.06	0.31 ±0.01	0.037 ±0.004	7.03 ±0.14	19.0 ±0.4	0.29 ±0.03	0.16 ±0.02	0.031 ±0.008	< 0.02
Preciosa-06-2012	1.47 ±0.15	0.25 ±0.01	5.35 ±0.05	0.49 ±0.07	0.26 ±0.01	0.033 ±0.003	3.16 ±0.06	26.4 ±0.5	0.26 ±0.03	0.12 ±0.01	0.031 ±0.008	< 0.02
Pr2014-01	0.69 ±0.1	0.11 ±0.02	7.25 ±0.07	0.22 ±0.02	0.13 ±0.01	0.032 ±0.003	5.2 ±0.1	25.2 ±0.5	0.12 ±0.01	0.06 ±0.01	< 0.01	0.017 ±0.004
Pr2014-02	0.61 ±0.09	0.1 ±0.02	8.98 ±0.09	0.19 ±0.02	0.088 ±0.004	0.02 ±0.002	6.85 ±0.14	22.9 ±0.5	0.11 ±0.01	0.05 ±0.01	< 0.01	0.017 ±0.004
Pr2014-03	0.17 ±0.03	0.12 ±0.02	15.29 ±0.15	3.73 ±0.19	1.28 ±0.03	0.06 ±0.006	7.2 ±0.1	13.5 ±0.3	1.10 ±0.03	0.55 ±0.03	0.15 ±0.01	0.048 ±0.005
Pr2014-09	1.13 ±0.11	0.21 ±0.02	5.23 ±0.05	0.06 ±0.01	0.082 ±0.004	0.044 ±0.004	4.14 ±0.08	26.6 ±0.5	0.10 ±0.01	0.02 ±0.01	< 0.01	< 0.02
Quechulac-1A-2012	0.88 ±0.09	0.14 ±0.02	1.01 ±0.05	0.08 ±0.01	0.03 ±0.01	0.005 ±0.001	0.65 ±0.01	35.3 ±0.7	0.10 ±0.01	0.02 ±0.01	< 0.01	< 0.02
Quechulac-4A-2012	0.56 ±0.08	0.13 ±0.02	1.21 ±0.06	0.06 ±0.01	0.03 ±0.01	0.005 ±0.001	0.90 ±0.02	35.4 ±0.7	0.13 ±0.01	0.02 ±0.01	< 0.01	< 0.02
Quechulac-4B-2012	0.88 ±0.09	0.1 ±0.02	1.51 ±0.08	0.27 ±0.03	0.12 ±0.01	0.007 ±0.002	0.79 ±0.02	34.4 ±0.7	0.14 ±0.01	0.06 ±0.01	0.015 ±0.004	0.031 ±0.008
Quechulac-4C-2012	0.59 ±0.09	0.09 ±0.01	1.13 ±0.06	0.08 ±0.01	0.02 ±0.01	0.004 ±0.001	0.79 ±0.02	35.9 ±0.7	0.10 ±0.01	0.03 ±0.01	< 0.01	< 0.02
Tec2014-05a	0.52 ±0.08	0.05 ±0.01	4.28 ±0.09	0.59 ±0.06	0.29 ±0.01	0.017 ±0.002	2.51 ±0.08	29.0 ±0.6	0.28 ±0.03	0.13 ±0.01	0.034 ±0.009	0.044 ±0.004
Tec2014-05b	0.56 ±0.08	0.05 ±0.01	16.9 ±0.17	3.57 ±0.18	2.11 ±0.04	0.053 ±0.005	6.8 ±0.1	12.4 ±0.2	1.2 ±0.1	0.56 ±0.03	0.24 ±0.02	0.070 ±0.007
AlbEsp2014-01	1.04 ±0.1	0.05 ±0.01	3.33 ±0.1	0.06 ±0.01	0.38 ±0.01	0.464 ±0.009	3.54 ±0.07	28.7 ±0.6	0.04 ±0.01	0.02 ±0.01	< 0.01	0.27 ±0.02
Patz2014-02	0.84 ±0.08	0.05 ±0.01	6.98 ±0.07	0.35 ±0.04	0.62 ±0.02	0.121 ±0.006	5.5 ±0.1	25.2 ±0.5	0.09 ±0.01	0.04 ±0.01	0.019 ±0.005	0.074 ±0.007
Aljo2014-02	0.73 ±0.07	0.08 ±0.02	3.6 ±0.04	1.15 ±0.06	0.54 ±0.02	0.023 ±0.002	0.60 ±0.03	30.7 ±0.6	0.42 ±0.04	0.20 ±0.02	0.054 ±0.013	0.12 ±0.01
LaAlb2014-02	2.55 ±0.13	0.07 ±0.01	14.53 ±0.15	3.46 ±0.17	2.23 ±0.04	0.218 ±0.011	3.94 ±0.08	12.9 ±0.3	1.06 ±0.11	0.63 ±0.03	0.27 ±0.02	0.092 ±0.008

Table SI-9. Bulk chemical compositions of the studied microbialites (major elements)

Microbialite sample	As ppm	Ba ppm	Be ppm	Bi ppm	Cd ppm	Co ppm	Cr ppm	Cs ppm	Cu ppm	Ga ppm	Ge ppm	Hf ppm	In ppm	Mo ppm	Nb ppm
AL13	2.40	73.45	< 0.40	< 0.10	< 0.12	0.44	2.96	0.10	< 5.00	0.52	< 0.15	0.11	< 0.07	< 0.50	0.25
AL69-2m	2.88	99.50	< 0.40	< 0.10	< 0.12	0.30	< 2.00	< 0.10	< 5.00	0.23	< 0.15	0.05	< 0.07	< 0.50	0.16
AL60-6m	6.67	167.30	< 0.40	< 0.10	< 0.12	1.32	7.68	0.31	< 5.00	1.78	0.14	0.32	< 0.07	< 0.50	0.82
AL54-11m	3.11	68.67	< 0.40	< 0.10	< 0.12	0.55	< 2.00	0.10	< 5.00	0.85	0.12	0.24	< 0.07	< 0.50	0.38
AL2012-1m	2.37	121.70	< 0.40	< 0.10	< 0.12	0.76	< 2.00	< 0.10	< 5.00	0.35	< 0.15	0.08	< 0.07	< 0.50	0.16
AL2012-5m	1.66	82.41	< 0.40	< 0.10	< 0.12	1.10	< 2.00	< 0.10	< 5.00	0.25	< 0.15	0.10	< 0.07	< 0.50	0.15
AL2012-10m	6.58	236.90	< 0.40	< 0.10	< 0.12	0.62	< 2.00	0.15	< 5.00	2.13	0.18	0.35	< 0.07	< 0.50	1.41
AL2012-15m	5.97	262.70	< 0.40	< 0.10	< 0.12	0.83	< 2.00	< 0.10	< 5.00	< 0.20	< 0.15	0.07	< 0.07	< 0.50	0.17
AL2012-12	7.39	166.20	< 0.40	< 0.10	< 0.12	0.70	< 2.00	< 0.10	< 5.00	< 0.20	< 0.15	0.03	< 0.07	< 0.50	0.10
AL2012-15	27.60	886.60	< 0.40	0.10	< 0.12	3.83	< 2.00	0.14	5.38	0.53	< 0.15	0.20	< 0.07	< 0.50	0.43
AL2012-17	25.39	1120.00	< 0.40	< 0.10	< 0.12	2.80	< 2.00	< 0.10	< 5.00	< 0.20	< 0.15	0.09	< 0.07	< 0.50	0.14
AL2014-13	4.06	612.30	< 0.40	< 0.10	< 0.12	1.06	< 2.00	< 0.10	< 5.00	0.27	< 0.15	0.08	< 0.07	< 0.50	0.19
AL2014-15	56.81	739.40	< 0.40	< 0.10	< 0.12	0.88	< 2.00	< 0.10	< 5.00	0.26	< 0.15	0.13	< 0.07	< 0.50	0.28
ATX-2C1-2012	24.51	191.20	< 0.40	< 0.10	0.17	1.84	< 2.00	3.87	5.55	0.83	4.07	0.21	< 0.07	1.12	0.42
ATX2014-07	4.04	286.90	< 0.40	< 0.10	< 0.12	1.26	< 2.00	1.53	< 5.00	< 0.20	8.20	0.04	< 0.07	< 0.50	0.13
ATX2014-13	5.44	657.00	< 0.40	< 0.10	< 0.12	2.58	5.20	0.56	< 5.00	1.23	1.09	0.30	< 0.07	< 0.50	0.59
Preciosa-05-2012	7.90	268.50	< 0.40	< 0.10	< 0.12	3.01	< 2.00	0.21	7.65	1.61	0.67	0.31	< 0.07	< 0.50	0.85
Preciosa-06-2012	4.42	442.30	< 0.40	< 0.10	< 0.12	2.52	< 2.00	0.15	< 5.00	1.32	0.73	0.24	< 0.07	< 0.50	0.62
Pr2014-01	3.46	359.90	< 0.40	< 0.10	0.17	1.42	< 2.00	0.10	5.07	0.46	1.11	0.13	< 0.07	< 0.50	0.29
Pr2014-02	4.12	366.30	< 0.40	< 0.10	0.18	1.23	< 2.00	0.10	8.12	0.44	0.91	0.10	< 0.07	< 0.50	0.24
Pr2014-03	2.24	316.80	0.92	< 0.10	0.13	5.93	20.71	0.91	12.87	9.02	0.84	1.87	< 0.07	< 0.50	3.57
Pr2014-09	4.26	432.50	< 0.40	< 0.10	< 0.12	1.33	< 2.00	< 0.10	< 5.00	0.31	0.89	0.07	< 0.07	< 0.50	0.19
Quechulac-1A-2012	< 1.50	407.90	< 0.40	< 0.10	< 0.12	1.85	< 2.00	< 0.10	< 5.00	0.24	< 0.15	0.05	< 0.07	< 0.50	0.11
Quechulac-4A-2012	< 1.50	366.30	< 0.40	< 0.10	< 0.12	1.82	< 2.00	< 0.10	< 5.00	0.26	0.17	0.05	< 0.07	< 0.50	0.12
Quechulac-4B-2012	< 1.50	378.60	< 0.40	< 0.10	< 0.12	1.81	< 2.00	< 0.10	< 5.00	0.74	0.24	0.16	< 0.07	< 0.50	0.35
Quechulac-4C-2012	< 1.50	358.90	< 0.40	< 0.10	< 0.12	1.67	< 2.00	< 0.10	10.40	0.37	0.20	0.07	< 0.07	< 0.50	0.15
Tec2014-05a	< 1.50	207.90	< 0.40	< 0.10	< 0.12	2.51	9.28	0.15	6.55	1.42	0.18	0.31	< 0.07	< 0.50	0.65
Tec2014-05b	< 1.50	363.30	0.55	< 0.10	0.13	11.64	76.99	0.58	12.34	8.10	0.64	1.92	< 0.07	< 0.50	3.42
AlbEsp2014-01	< 1.50	620.20	< 0.40	< 0.10	< 0.12	2.14	< 2.00	< 0.10	< 5.00	0.97	1.38	0.06	< 0.07	< 0.50	0.12
Patz2014-02	< 1.50	660.30	< 0.40	< 0.10	< 0.12	4.15	4.89	< 0.10	13.67	1.88	< 0.15	0.25	< 0.07	< 0.50	0.95
Aljo2014-02	< 1.50	231.20	< 0.40	< 0.10	< 0.12	3.09	6.78	0.17	11.12	2.39	0.18	0.46	< 0.07	< 0.50	0.60
LaAlb2014-02	< 1.50	351.80	0.59	< 0.10	< 0.12	10.14	180.30	0.44	10.31	7.41	0.72	1.60	< 0.07	1.68	4.84

Table SI-10. Bulk chemical compositions of the studied microbialites (minor and trace elements excluding REE+Y)

Microbialite sample	Ni ppm	Pb ppm	Rb ppm	Sc ppm	Sb ppm	Sn ppm	Sr ppm	Ta ppm	Th ppm	U ppm	V ppm	W ppm	Zn ppm	Zr ppm
AL13	< 5.00	1.05	1.73	< 1.00	< 0.20	< 0.45	359.05	0.02	0.15	0.11	3.07	< 0.10	7.55	4.18
AL69-2m	< 5.00	0.65	1.00	< 1.00	< 0.20	< 0.45	628.30	0.03	0.06	0.04	1.15	< 0.10	< 7.00	2.05
AL60-6m	< 5.00	1.70	5.80	< 1.00	< 0.20	< 0.45	719.20	0.08	0.46	0.20	7.16	0.12	< 7.00	10.75
AL54-11m	< 5.00	0.72	1.88	< 1.00	< 0.20	< 0.45	311.40	0.03	0.19	0.15	4.36	< 0.10	< 7.00	11.49
AL2012-1m	< 5.00	< 0.60	1.25	< 1.00	< 0.20	< 0.45	694.80	0.01	0.10	0.09	1.75	< 0.10	< 7.00	3.22
AL2012-5m	< 5.00	< 0.60	0.85	< 1.00	< 0.20	< 0.45	538.60	0.01	0.08	0.10	2.39	< 0.10	< 7.00	4.10
AL2012-10m	< 5.00	2.02	5.52	< 1.00	< 0.20	< 0.45	739.60	0.14	0.86	0.60	4.92	< 0.10	14.35	12.02
AL2012-15m	< 5.00	1.14	0.80	< 1.00	< 0.20	< 0.45	1484.00	< 0.01	0.08	0.09	1.59	< 0.10	< 7.00	2.69
AL2012-12	< 5.00	0.78	0.70	< 1.00	< 0.20	< 0.45	735.10	< 0.01	0.07	0.11	1.10	< 0.10	< 7.00	1.28
AL2012-15	< 5.00	1.76	3.71	< 1.00	< 0.20	0.63	3232.00	0.02	0.21	1.48	8.39	< 0.10	11.52	9.47
AL2012-17	< 5.00	1.06	0.93	< 1.00	< 0.20	< 0.45	3441.00	< 0.01	< 0.06	1.25	3.05	< 0.10	< 7.00	3.75
AL2014-13	< 5.00	0.96	1.56	< 1.00	< 0.20	< 0.45	4133.00	0.02	0.13	1.07	2.36	< 0.10	< 7.00	3.59
AL2014-15	< 5.00	2.17	1.87	< 1.00	< 0.20	< 0.45	2448.00	0.01	0.13	0.62	4.84	< 0.10	< 7.00	6.54
ATX-2C1-2012	7.03	2.78	5.48	< 1.00	1.34	< 0.45	837.50	0.03	0.23	0.25	13.67	< 0.10	28.02	13.59
ATX2014-07	< 5.00	1.22	2.12	< 1.00	0.31	< 0.45	2624.00	< 0.01	< 0.06	0.05	2.23	< 0.10	< 7.00	4.70
ATX2014-13	< 5.00	1.61	4.68	< 1.00	0.23	< 0.45	4217.00	0.05	0.35	0.43	9.28	< 0.10	< 7.00	12.68
Preciosa-05-2012	6.61	2.75	6.28	< 1.00	1.99	< 0.45	1470.00	0.08	0.70	0.62	12.18	< 0.10	14.31	12.57
Preciosa-06-2012	7.82	4.71	4.14	< 1.00	0.42	< 0.45	2237.00	0.05	0.42	0.59	11.53	< 0.10	14.17	12.49
Pr2014-01	< 5.00	23.78	2.50	< 1.00	1.55	< 0.45	2162.00	0.02	0.17	0.37	3.73	< 0.10	13.88	5.33
Pr2014-02	< 5.00	28.83	2.70	< 1.00	2.94	< 0.45	2628.00	0.02	0.16	0.54	5.82	< 0.10	< 7.00	4.33
Pr2014-03	< 5.00	6.93	22.68	4.61	0.71	0.76	1153.00	0.37	3.15	0.90	27.85	< 0.10	29.54	68.83
Pr2014-09	< 5.00	8.07	0.91	< 1.00	0.36	< 0.45	2616.00	< 0.01	< 0.06	0.43	4.33	< 0.10	< 7.00	5.54
Quechulac-1A-2012	< 5.00	< 0.60	0.50	< 1.00	< 0.20	< 0.45	2724.00	< 0.01	0.07	2.73	12.13	< 0.10	< 7.00	2.65
Quechulac-4A-2012	< 5.00	< 0.60	0.50	< 1.00	< 0.20	< 0.45	2795.00	< 0.01	0.08	2.77	7.59	< 0.10	< 7.00	2.78
Quechulac-4B-2012	< 5.00	0.89	1.80	< 1.00	< 0.20	< 0.45	2589.00	0.03	0.22	2.55	10.47	< 0.10	11.08	6.54
Quechulac-4C-2012	< 5.00	0.95	0.63	< 1.00	< 0.20	< 0.45	2694.00	< 0.01	0.08	2.88	12.50	< 0.10	13.02	2.97
Tec2014-05a	< 5.00	1.64	4.01	< 1.00	< 0.20	< 0.45	914.00	0.05	0.50	1.84	51.40	< 0.10	< 7.00	15.56
Tec2014-05b	34.34	4.53	17.71	7.03	0.26	0.81	971.30	0.24	1.88	3.27	117.80	< 0.10	33.62	84.99
AlbEsp2014-01	< 5.00	2.99	0.70	< 1.00	< 0.20	< 0.45	1312.00	< 0.01	0.08	0.05	2.24	< 0.10	< 7.00	2.79
Patz2014-02	< 5.00	1.41	2.43	1.47	< 0.20	< 0.45	3297.00	0.03	0.33	1.76	63.08	< 0.10	12.65	13.41
Aljo2014-02	< 5.00	6.07	4.72	1.82	< 0.20	< 0.45	1092.00	0.05	0.53	1.57	18.31	< 0.10	14.55	17.89
LaAlb2014-02	85.65	20.25	16.96	6.11	0.30	0.69	813.30	0.37	1.24	0.57	56.55	0.82	35.32	67.88

Table SI-10. Continued

Microbialite sample	La ppm	Ce ppm	Pr ppm	Nd ppm	Sm ppm	Eu ppm	Gd ppm	Tb ppm	Dy ppm	Y ppm	Ho ppm	Er ppm	Tm ppm	Yb ppm	Lu ppm	ΣREE ppm
AL13	0.51	1.03	0.14	0.54	0.13	0.04	0.11	0.02	0.10	0.60	0.02	0.06	0.01	0.06	0.01	3.37
AL69-2m	0.26	0.47	0.07	0.29	0.07	0.02	0.06	0.01	0.07	0.44	0.01	0.04	0.01	0.04	0.01	1.87
AL60-6m	1.64	3.15	0.44	1.65	0.36	0.10	0.31	0.04	0.25	1.51	0.05	0.13	0.02	0.14	0.02	9.81
AL54-11m	0.63	1.21	0.17	0.62	0.14	0.04	0.12	0.02	0.10	0.64	0.02	0.06	0.01	0.06	0.01	3.84
AL2012-1m	0.32	0.65	0.09	0.33	0.08	0.03	0.07	0.01	0.07	0.46	0.02	0.04	0.01	0.05	0.01	2.22
AL2012-5m	0.27	0.52	0.06	0.29	0.06	0.02	0.05	0.01	0.04	0.30	0.01	0.02	0.00	0.03	0.01	1.70
AL2012-10m	2.31	4.37	0.48	1.65	0.31	0.11	0.25	0.03	0.17	0.91	0.03	0.08	0.01	0.07	0.01	10.78
AL2012-15m	0.32	0.48	0.09	0.39	0.11	0.05	0.10	0.02	0.10	0.68	0.02	0.06	0.01	0.06	0.01	2.49
AL2012-12	0.21	0.39	0.06	0.30	0.07	0.03	0.07	0.01	0.07	0.53	0.02	0.05	0.01	0.06	0.01	1.89
AL2012-15	0.74	1.39	0.19	0.74	0.18	0.12	0.16	0.03	0.15	1.12	0.03	0.09	0.02	0.11	0.02	5.09
AL2012-17	0.22	0.37	0.05	0.19	0.06	0.10	0.06	0.01	0.05	0.58	0.01	0.04	0.01	0.06	0.01	1.83
AL2014-13	0.44	0.83	0.12	0.50	0.12	0.05	0.12	0.02	0.11	0.78	0.03	0.07	0.01	0.07	0.01	3.28
AL2014-15	0.43	0.76	0.12	0.51	0.12	0.06	0.12	0.02	0.11	0.82	0.03	0.08	0.01	0.09	0.01	3.27
ATX-2C1-2012	0.85	1.58	0.21	0.87	0.21	0.06	0.19	0.03	0.16	1.14	0.03	0.09	0.02	0.10	0.02	5.54
ATX2014-07	0.13	0.24	0.04	0.16	0.04	0.02	0.04	0.01	0.05	0.36	0.01	0.03	0.01	0.03	0.01	1.18
ATX2014-13	1.42	2.86	0.40	1.67	0.37	0.12	0.35	0.05	0.34	2.26	0.07	0.21	0.03	0.21	0.03	10.39
Preciosa-05-2012	1.87	3.70	0.44	1.62	0.33	0.09	0.29	0.04	0.26	1.65	0.05	0.15	0.03	0.17	0.03	10.71
Preciosa-06-2012	1.40	2.81	0.34	1.37	0.29	0.11	0.26	0.04	0.26	1.79	0.06	0.16	0.03	0.18	0.03	9.12
Pr2014-01	0.55	1.09	0.13	0.53	0.11	0.04	0.09	0.01	0.08	0.49	0.02	0.05	0.01	0.05	0.01	3.26
Pr2014-02	0.50	0.98	0.12	0.46	0.09	0.04	0.07	0.01	0.08	0.44	0.02	0.05	0.01	0.05	0.01	2.91
Pr2014-03	9.64	19.17	2.35	9.05	1.89	0.47	1.59	0.23	1.41	7.99	0.29	0.77	0.11	0.80	0.12	55.88
Pr2014-09	0.14	0.28	0.04	0.17	0.05	0.03	0.06	0.01	0.08	0.68	0.02	0.05	0.01	0.07	0.01	1.69
Quechulac-1A-2012	0.35	0.66	0.11	0.44	0.11	0.06	0.10	0.02	0.10	0.96	0.02	0.07	0.01	0.07	0.01	3.09
Quechulac-4A-2012	0.41	0.75	0.15	0.63	0.15	0.07	0.14	0.02	0.14	1.12	0.03	0.09	0.01	0.09	0.01	3.80
Quechulac-4B-2012	0.90	1.79	0.24	0.97	0.21	0.09	0.18	0.03	0.16	1.21	0.04	0.10	0.02	0.11	0.02	6.04
Quechulac-4C-2012	0.37	0.75	0.11	0.49	0.11	0.06	0.10	0.02	0.11	0.95	0.02	0.07	0.01	0.08	0.01	3.24
Tec2014-05-a	2.43	5.66	0.72	3.05	0.68	0.18	0.65	0.11	0.75	6.00	0.17	0.52	0.08	0.57	0.09	21.65
Tec2014-05-b	10.70	21.78	2.72	10.87	2.22	0.65	1.89	0.28	1.65	9.87	0.35	0.94	0.14	0.95	0.15	65.15
AlbEsp2014-01	1.65	1.76	0.52	2.20	0.46	0.14	0.44	0.07	0.48	3.75	0.11	0.28	0.04	0.27	0.04	12.22
Patz2014-02	4.15	7.77	1.33	5.88	1.43	0.39	1.55	0.26	1.80	15.69	0.44	1.26	0.18	1.21	0.19	43.53
Aljo2014-02	2.69	5.39	0.75	3.10	0.67	0.20	0.60	0.09	0.56	3.68	0.12	0.32	0.05	0.33	0.05	18.59
LaAlb2014-02	7.90	15.36	2.01	8.13	1.75	0.52	1.56	0.23	1.41	8.51	0.30	0.79	0.11	0.73	0.12	49.44

Table SI-11. Bulk chemical composition of the studied microbialites: REE (+Y)
ΣREE stands for the sum of the REE +Y

Aqueous Sample	Altitude (m)	SI-CO ₂ (g)	pCO ₂ (g)/pCO ₂ atm
Preciosa2014_0m	2330	-2.99	3.4
Quechulac2014_0m_N	2330	-3.44	1.2
ATX2014_0m-M	2360	-2.41	12.8
AL2014_0m_M	2320	-2.95	3.7
Aljojuca2014_0m	2379	-3.42	1.3
Tecuitlapa2014_0m	2380	-3.54	1.0
AlbEsp2014_0m	1985	-3.10	2.5
Alb2014_0m	2066	-4.12	0.2
Patz2014_0m	2044	-3.21	1.9
Zirahuen2014_0m	2082	-3.81	0.5

Table SI-12. Determination of the pCO₂(g)/pCO₂atm ratio of the 2014 surface water lakes

SI-CO₂ (g) corresponds to the saturation index of the lake water solutions with respect to CO₂ gas, SI=log(pCO₂). It was calculated using the software PHREEQC 3 (Parkhurst and Appelo, 2013) and the thermodynamic database “thermoddem.dat” (Blanc et al., 2012). pCO₂atm is based on the global atmospheric pCO₂ recorded in May 2014 at 1.01325 bar = 401.78 ppm (from NOAA database) and calculated at the pressure corresponding to the elevation of each sites. Determination of the pCO₂(g)/pCO₂(atm) of the studied lakes

III. TEXTS

Text SI-1. REE+Y calculations and correlations between variables

In order to characterize the REE+Y patterns of microbialites, we calculated different shale normalized (SN) indices (Table SI-1-1 below). Ce anomalies were expressed in 3 different manners: $Ce/Ce^*=(Ce/(0.5La+0.5Pr))_{SN}$ (Bau and Dulski, 1996), $Ce/Ce^*=(Ce/(2Pr-Nd))_{SN}$ (Bolhar and Van Kranendonk, 2007) and $Ce/Ce^*=(Ce/((La \times Pr)^{1/2}))_{SN}$ (Barrat et al., 2000). La/La* anomalies were also defined in 3 different ways: $(La/(3Pr-2Nd))_{SN}$ (Bau and Dulski, 1996), $(La/(2Ce-Pr))_{SN}$ (Bolhar and Van Kranendonk, 2007) and $(La/(Pr^3/Nd^2))_{SN}$ (Bolhar and Van Kranendonk, 2007). Gd/Gd* anomalies were defined in 2 different ways: $(Gd/(2Tb-Dy))_{SN}$ (Bau and Dulski, 1996) and $(Gd/(Tb^2/Dy))_{SN}$ (Bolhar and Van Kranendonk, 2007). Eu/Eu* anomalies were defined as $(Eu/(0.5Sm+0.5Gd))_{SN}$ (Johannesson et al., 2014) and $(Eu/(0.67Sm+0.33Tb))_{SN}$ (Kamber and Webb, 2001). Pr/Pr* anomaly was expressed as $(Pr/(0.5Ce+0.5Nd))_{SN}$ (Bau and Dulski, 1996). Additionally, we calculated $(Pr/Yb)_{SN}$ (Bolhar and Van Kranendonk, 2007; Corkeron et al., 2012), $(La/Yb)_{SN}$ (Barrat et al., 2000), $(Nd/Yb)_{SN}$ (Webb and Kamber, 2000) and $(Pr/Sm)_{SN}$ (Bolhar and Van Kranendonk, 2007) to describe the LREE (light rare earth elements) enrichment of microbialites. We calculated the $(Sm/Yb)_{SN}$ ratio to describe the MREE (middle rare earth elements) enrichment of microbialites (Bolhar and Van Kranendonk, 2007). We calculated the $(Yb/Nd)_{SN}$ ratio to describe the HREE (heavy rare earth elements) enrichment of microbialites. In addition, we calculated the non-normalized Nd/Yb ratio, used by Webb and Kamber (2000) to compare this ratio with that of seawater (between 2.69 and 3.22 in South Pacific) (Zhang and Nozaki, 1996). Finally, the Y/Ho ratio was determined and compared with that of chondrites (*i.e.*, 26-28; Kamber and Webb, 2001).

Several anomalies (*i.e.*, Eu/Eu*, Gd/Gd*, Ce/Ce*, La/La*) used to describe REE+Y patterns have varying expressions in the literature. We observed that most of the varying expressions of a given anomaly were highly correlated between each other (Fig. SI-6). However, one of the expression for the La/La* anomaly $(La/(2Ce-Pr))_{SN}$ was not correlated with the other two ($r_s=-0.06$ with the expression $(La/(3Pr-2Nd))_{SN}$ and -0.13 with the expression $(La/(Pr^3/Nd^2))_{SN}$). As expected, the four variables describing an enrichment in LREE (light rare earth elements), *i.e.*, $(La/Yb)_{SN}$, $(Pr/Yb)_{SN}$, $(Nd/Yb)_{SN}$ and $(Pr/Sm)_{SN}$ shale normalized ratios, were

positively correlated ($r_s \geq 0.88$). These four variables were correlated with $(\text{Sm}/\text{Yb})_{\text{SN}}$ ($r_s \geq 0.78$) describing the MREE (middle rare earth elements) enrichment of microbialites and negatively correlated with $(\text{Yb}/\text{Nd})_{\text{SN}}$ ($r_s \geq -0.89$), which measures the HREE (heavy rare earth elements) enrichment of microbialites. The Ce/Ce* anomaly $(\text{Ce}/(2\text{Pr}-\text{Nd}))_{\text{SN}}$ was positively correlated with the La/La* anomaly $(\text{La}/((\text{Pr}^3/\text{Nd}^2)))_{\text{SN}}$ ($r_s = 0.84$) and negatively correlated with the Pr/Pr* anomaly $(\text{Pr}/(0.5\text{Ce}+0.5\text{Nd}))_{\text{SN}}$ ($r_s = -1$) (Fig. SI-6).

Microbialite sample	La/La* (3Pr-2Nd)	La/La* (2Ce-Pr)	La/La* (Pr ³ /Nd ²)	Ce/Ce* (0.5La+0.5Pr)	Ce/Ce* (2Pr-Nd)	Ce/Ce* (La*Pr) ^{1/2}	Gd/Gd* (2Tb-Dy)	Gd/Gd* (Tb ² /Dy)	Eu/Eu* (0.5Sm+0.5Gd)	Eu/Eu* (0.675Sm+0.33Tb)	Pr/Pr* (0.5Ce+0.5Nd)
AL13	1.03	1.15	1.01	0.94	0.95	0.94	1.08	1.07	1.55	1.56	1.02
AL69-2m	1.05	1.67	1.02	0.82	0.84	0.82	0.81	0.81	1.47	1.37	1.08
AL60-6m	0.86	1.33	0.86	0.89	0.83	0.89	0.96	0.95	1.61	1.61	1.09
AL54-11m	0.90	1.26	0.90	0.90	0.86	0.91	1.05	1.05	1.50	1.51	1.07
AL2012-1m	0.98	1.14	0.97	0.94	0.94	0.95	1.30	1.26	2.26	2.35	1.03
AL2012-5m	1.75	1.08	1.43	0.97	1.22	0.97	1.15	1.15	1.88	1.95	0.92
AL2012-10m	0.98	1.00	0.97	1.00	0.99	1.00	1.08	1.07	2.06	2.14	1.00
AL2012-15m	1.02	4.51	0.97	0.66	0.67	0.67	1.20	1.18	2.26	2.30	1.17
AL2012-12	1.71	1.84	1.25	0.80	0.98	0.81	0.84	0.84	2.35	2.19	1.01
AL2012-15	1.05	1.26	1.03	0.90	0.92	0.90	0.89	0.89	3.87	3.73	1.04
AL2012-17	1.08	1.38	1.07	0.86	0.90	0.86	1.81	1.66	9.03	10.04	1.05
AL2014-13	1.12	1.43	1.06	0.86	0.91	0.87	1.17	1.17	1.93	2.03	1.04
AL2014-15	1.39	1.61	1.21	0.83	0.95	0.83	0.99	0.99	2.52	2.50	1.02
ATX-2C1-2012	1.19	1.27	1.14	0.90	0.97	0.90	0.96	0.96	1.64	1.66	1.01
ATX2014-07	1.79	1.57	1.37	0.83	1.05	0.83	1.06	1.04	2.68	2.67	0.98
ATX2014-13	1.15	1.24	1.07	0.91	0.97	0.92	1.16	1.14	1.74	1.77	1.01
Preciosa-05-2012	1.01	1.02	1.01	0.99	0.99	0.99	1.00	1.00	1.60	1.60	1.00
Preciosa-06-2012	1.14	1.04	1.11	0.98	1.04	0.98	1.02	1.02	2.18	2.16	0.98
Pr2014-01	1.15	1.05	1.13	0.97	1.04	0.97	1.08	1.08	2.08	2.08	0.98
Pr2014-02	1.11	1.05	1.09	0.98	1.03	0.98	0.97	0.96	2.43	2.32	0.99
Pr2014-03	1.02	1.07	1.02	0.97	0.98	0.97	1.05	1.05	1.45	1.45	1.01
Pr2014-09	1.11	1.41	1.03	0.87	0.91	0.88	1.16	1.06	2.62	2.51	1.04
Quechulac-1A-2012	1.03	1.79	0.97	0.81	0.82	0.82	0.89	0.89	3.19	3.09	1.08
Quechulac-4A-2012	0.96	3.47	0.87	0.72	0.71	0.74	0.97	0.96	2.43	2.36	1.14
Quechulac-4B-2012	1.10	1.17	1.06	0.93	0.97	0.94	0.97	0.97	2.32	2.30	1.01
Quechulac-4C-2012	1.28	1.35	1.10	0.89	0.98	0.90	1.17	1.13	3.02	2.97	1.01
Tec2014-05a	1.13	0.94	1.04	1.03	1.08	1.04	1.13	1.09	1.44	1.42	0.97
Tec2014-05b	1.08	1.07	1.06	0.97	1.01	0.97	1.00	1.00	1.68	1.68	1.00
AlbEsp2014-01	1.02	-3.22	0.95	0.45	0.46	0.46	1.02	1.01	1.69	1.65	1.30
Patz2014-02	1.18	2.08	1.02	0.78	0.84	0.80	1.09	1.05	1.38	1.37	1.07
Aljo2014-02	1.09	1.25	1.04	0.91	0.95	0.91	1.07	1.07	1.64	1.65	1.02
LaAlb2014-02	1.13	1.18	1.09	0.93	0.98	0.93	1.04	1.04	1.66	1.67	1.01

Table SI-1-1.

REE anomalies. The detailed expression of each anomaly is reported. For example, La/La* is defined as La/(3Pr-2Nd). SN stands for the shale-normalized data (normalization against the Post-Archean Australian Shale) after Pourmand et al. (2012).

Microbialite sample	Y/Ho	Nd/Yb	(Sm/Yb) _{SN}	(Pr/Yb) _{SN}	(La/Yb) _{SN}	(Pr/Sm) _{SN}	(Nd/Yb) _{SN}	(Yb/Nd) _{SN}
AL13	28.42	8.60	0.90	0.64	0.55	0.71	0.69	1.44
AL69-2m	34.15	7.30	0.75	0.53	0.45	0.71	0.59	1.70
AL60-6m	31.44	11.61	1.12	0.93	0.78	0.83	0.94	1.07
AL54-11m	30.33	9.66	0.97	0.77	0.66	0.79	0.78	1.28
AL2012-1m	30.40	6.92	0.70	0.53	0.45	0.75	0.56	1.79
AL2012-5m	33.33	8.50	0.77	0.56	0.53	0.72	0.69	1.46
AL2012-10m	36.56	23.21	1.90	1.99	2.20	1.05	1.87	0.53
AL2012-15m	37.56	6.48	0.82	0.46	0.36	0.57	0.52	1.91
AL2012-12	33.31	5.09	0.56	0.32	0.25	0.58	0.41	2.44
AL2012-15	36.10	6.51	0.70	0.49	0.44	0.70	0.53	1.90
AL2012-17	58.00	3.00	0.42	0.23	0.23	0.56	0.24	4.13
AL2014-13	31.08	7.08	0.76	0.51	0.42	0.67	0.57	1.75
AL2014-15	31.54	5.95	0.64	0.40	0.34	0.63	0.48	2.08
ATX-2C1-2012	35.59	8.65	0.90	0.63	0.57	0.70	0.70	1.43
ATX2014-07	32.73	4.76	0.55	0.31	0.26	0.55	0.38	2.60
ATX2014-13	30.93	7.79	0.76	0.55	0.45	0.72	0.63	1.59
Preciosa-05-2012	31.69	9.42	0.83	0.75	0.74	0.90	0.76	1.32
Preciosa-06-2012	31.46	7.76	0.71	0.57	0.54	0.81	0.63	1.60
Pr2014-01	27.11	10.33	0.94	0.77	0.73	0.82	0.83	1.20
Pr2014-02	29.33	10.29	0.90	0.78	0.75	0.86	0.83	1.20
Pr2014-03	27.64	11.32	1.03	0.87	0.82	0.84	0.91	1.09
Pr2014-09	35.74	2.62	0.35	0.18	0.14	0.52	0.21	4.73
Quechulac-1A-2012	39.88	6.23	0.65	0.44	0.34	0.68	0.50	1.99
Quechulac-4A-2012	37.47	6.98	0.72	0.48	0.31	0.66	0.56	1.78
Quechulac-4B-2012	34.60	9.03	0.86	0.66	0.57	0.77	0.73	1.37
Quechulac-4C-2012	39.42	5.94	0.58	0.40	0.30	0.69	0.48	2.09
Tec2014-05a	34.90	5.37	0.53	0.37	0.29	0.71	0.43	2.31
Tec2014-05b	28.52	11.45	1.02	0.85	0.76	0.83	0.92	1.08
AlbEsp2014-01	34.68	8.29	0.76	0.58	0.42	0.76	0.67	1.50
Patz2014-02	36.07	4.86	0.52	0.33	0.23	0.63	0.39	2.55
Aljo2014-02	31.48	9.52	0.89	0.68	0.56	0.76	0.77	1.30
LaAlb2014-02	28.36	11.11	1.05	0.81	0.73	0.78	0.90	1.12

Table SI-1-1. Continued.

Text SI-2. Geochemical signatures of detrital contamination in microbialites

It is of first importance to identify the chemical signatures of detrital contamination and defining thresholds below which such contamination is not affecting the chemical signature of the authigenic fraction of microbialites. This is crucial if one intends to use the mineralogy and chemistry of microbialites as reliable proxies for their formation environments. Modern and past lacustrine microbialites have often been mentioned to be affected by important detrital contamination, which obscures the message conveyed by their REE+Y composition (Solari et al., 2010; Álvaro et al., 2010; Sarg et al., 2013; Gallois et al., 2018). Previous studies have followed different strategies to limit issues due to contamination by terrigenous detritus: 1) analysis of the REE+Y composition of the carbonate fraction only, after its dissolution and/or 2) checking the low bulk content of samples in some specific chemical elements tracing detrital contamination (*e.g.*, Sc, Th, Hf, Zr) (Webb and Kamber, 2000; Frimmel, 2009; Kamber et al., 2014). Here, we followed the second strategy.

Several samples of Mexican microbialites were clearly affected by detrital contamination. This contamination was assessed based on PCA analyses of the bulk chemical composition of the microbialites, especially their content in Al as well as in elements strongly correlated with Al: Ga, Nb, Ta, K, Rb, Hf and Zr (Fig. 8 in the Main text). All these elements have been used before as tracers of the contribution of detrital particles (Weaver, 1967; Gertsch et al., 2011; Bassetti et al., 2016). They are all lithophile, except Ga, which is chalcophile but can replace Al or Fe in amphibole, feldspar, mica and clay minerals (Salminen et al., 2005). Nb, Ta, Hf and Zr are high field strength elements (HFSE), *i.e.*, they have high cationic charges and small ionic radii and are immobile during alteration (Babechuk et al., 2015). K and Rb are large ion lithophile elements (LILE) with a low cationic charge and a large ionic radius, and are considered as mobile during weathering processes because of their high hydration energies.

Three microbialites (LaAlb2014-02, Pr2014-03 and Tec2014-05b) were identified as highly affected by input of detrital particles with a content in Al, Ga, Nb, Ta, K, Rb, Hf and Zr significantly higher than that of all other samples. Eleven microbialites, clustered in an “intermediate” group as moderately affected by detrital contamination. Last, 18 samples clustered as a group of authigenic-dominated microbialites (Fig. 8 in the Main text). Consistently, all three microbialite samples identified as strongly affected by detrital inputs contained plagioclase grains and LaAlb2014-02 also contained quartz and pyroxene as shown by XRD analyses (Fig. SI-3d)

and SEM-EDXS (data not shown). In contrast, no detrital phase was detected by SEM, XRD and FTIR in the group of authigenic-dominated microbialite samples. Microbialites clustering in the authigenic-dominated microbialite group showed concentrations in $Al \leq 0.27$ wt.%, $Ga \leq 0.97$ ppm, $Nb \leq 0.35$ ppm, $Ta \leq 0.027$ ppm, $K \leq 0.07$ wt.%, $Rb \leq 2.70$ ppm, $Hf \leq 0.157$ ppm and $Zr \leq 6.54$ ppm.

Interestingly, the 3 samples strongly affected by detrital contamination showed different contents in the different elements tracing detritism (Fig. 8b in the Main Text). This suggests that they were affected by different sources of contamination. The LaAlb2014-02 microbialite had relatively higher Nb and Ta contents, while Pr2014-03 had higher K and Rb contents and Tec2014-05b had higher Hf and Zr contents. Nb and Ta are highly incompatible elements and may reach high concentrations in evolved rocks (Dostal and Chatterjee, 2000). As shown by the XRD pattern of LaAlb2014-02, feldspar is one of the main minerals observed in this sample and could be associated with Nb and Ta as also described by Larsen (2002). Since K and Rb are easily lost during weathering processes (Nath et al., 2000), the relatively higher concentration of these elements in Pr2014-03 may indicate that this microbialite was contaminated by detrital particles, which have experienced a low intensity of weathering. Last, Zr and Hf are mostly concentrated in heavy minerals and in the coarse (silt-sand) fraction of fine-grained siliciclastic sediments, while Rb is mainly in the fine-grained fraction (Condie, 1991; Fralick and Kronberg, 1997; Dypvik and Harris, 2001). How different detrital contaminations can be traced by these elements remain however to be further understood.

Text SI-3. REE+Y patterns of microbialites depending on their level of contamination by detrital particles

As mentioned in the main text, the Σ REE content of microbialites was positively correlated with their Al content (Fig. SI-3-1), and there were clear correlations between the Al content of microbialites and several REE anomalies, in particular in Eu, Ce, Pr, La and/or Gd, their Y/Ho ratio and the HREE to LREE enrichment $[(Yb/Nd)_{SN}]$. Three categories of microbialites were discriminated based on their content of detritism-indicative elements: authigenic-dominated microbialites, microbialites intermediately affected by detrital contamination and microbialites highly affected by detrital contamination. Here, we detail their respective REE+Y signatures.

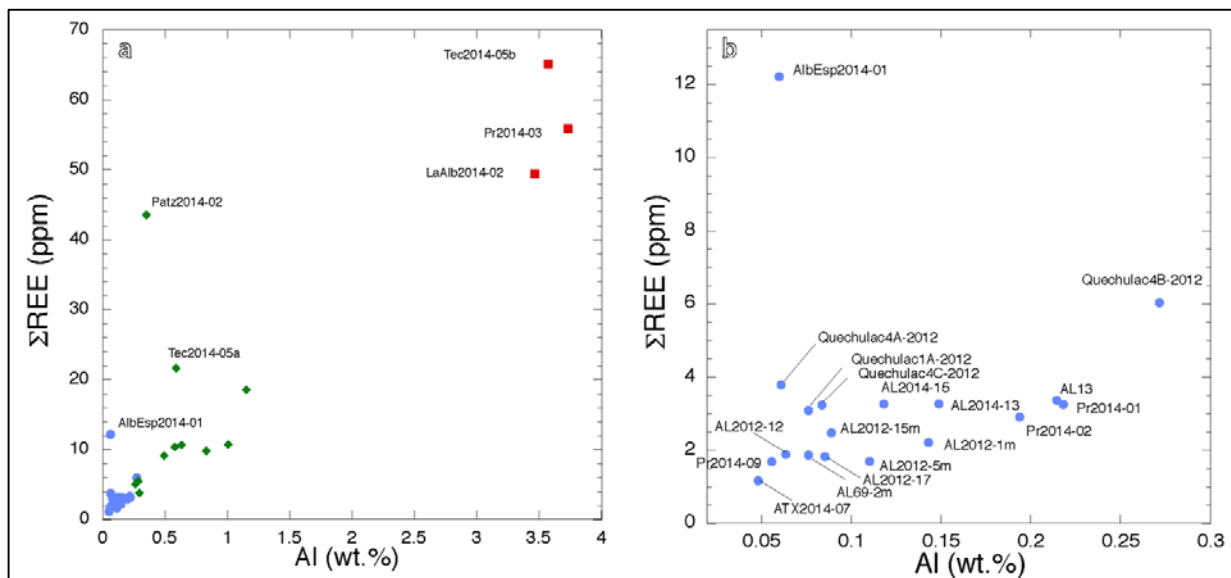


Figure SI-3-1.

Aluminum content versus sum of REEs(+Y) of the studied microbialites. **(a)** All the samples showing a positive correlation ($r_s=0.81$). **(b)** Only the authigenic-dominated samples are plotted, showing no significant positive correlation ($r_s=0.39$). Blue dots stand for 18 microbialites poorly concentrated in Al (authigenic-dominated); red squares correspond to microbialites highly affected by detrital contamination; green diamonds stand for intermediately contaminated microbialites considered in this study as moderately affected by detrital input.

A PCA was performed on the group of authigenic-dominated microbialites considering the set of 20 variables describing REE+Y patterns of microbialites (Fig. SI-3-2).

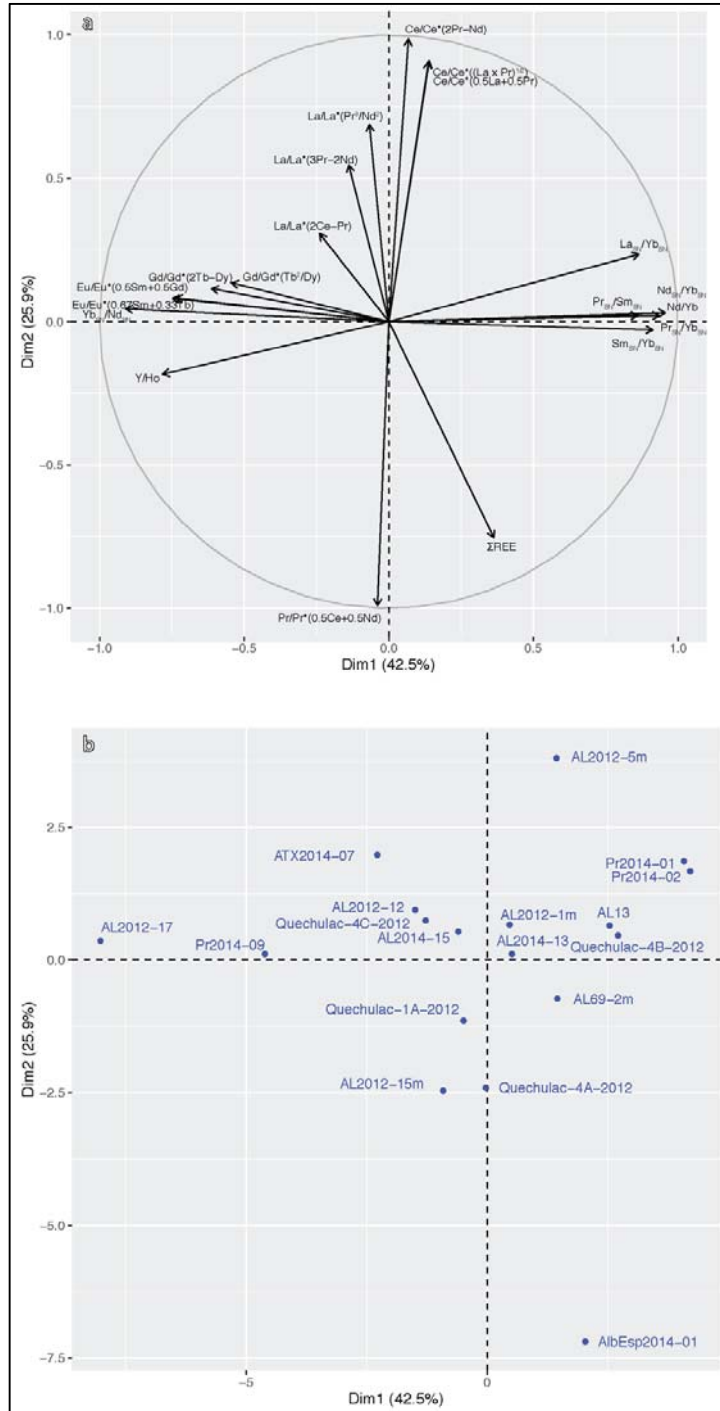


Figure SI-3-2.

PCA performed on the group of the 18 authigenic-dominated microbialite samples. (a) PCA variables factor map representing the 20 variables describing the REE+Y patterns of microbialites. Eu/Eu^* anomalies, Y/Ho and variables describing the enrichment in LREE ($(La/Yb)_{SN}$, $(Pr/Sm)_{SN}$, $(Pr/Yb)_{SN}$, $(Nd/Yb)_{SN}$), MREE ($(Sm/Yb)_{SN}$) and HREE ($(Yb/Nd)_{SN}$), contributed significantly to axis 1 (explaining 42.5% of the total variability). The Pr/Pr^* anomalies, ΣREE , all the Ce/Ce^*

anomalies, and the 2 expressions of La/La* anomalies significantly contributed to axis 2 (explaining 25.9% of the total variability). **(b)** PCA plot with samples plotted in two dimensions using their projections onto the first two principal components. The AL2012-17, Pr2014-09, Pr2014-01 and Pr2014-02 microbialite samples contributed significantly to axis 1. The AlbEsp2014-01, Quechulac-4A-2012, AL2012-15m and AL2012-5m microbialite samples contributed significantly to axis 2.

For microbialites highly affected by detrital contamination ($Al \geq 3.46$ wt.%, *e.g.*, Tec2014-05b, Pr2014-03 and LaAlb2014-02 samples), there was no HREE to LREE enrichment, as expected (Fig. SI-3-3a). For microbialites intermediately affected by detrital contamination, the AL2012-10m microbialite stood out of the relationship and showed a pronounced LREE enrichment with a $(Yb/Nd)_{SN}$ ratio of 0.53 (Fig. SI-3-3a and Table SI-11). For authigenic-dominated microbialites, HREE to LREE enrichment (*i.e.*, $(Yb/Nd)_{SN}$) ranged between 1.20 for Pr2014-01 and Pr2014-02 up to 4.73 for Pr2014-09 (Fig. SI-3-3b).

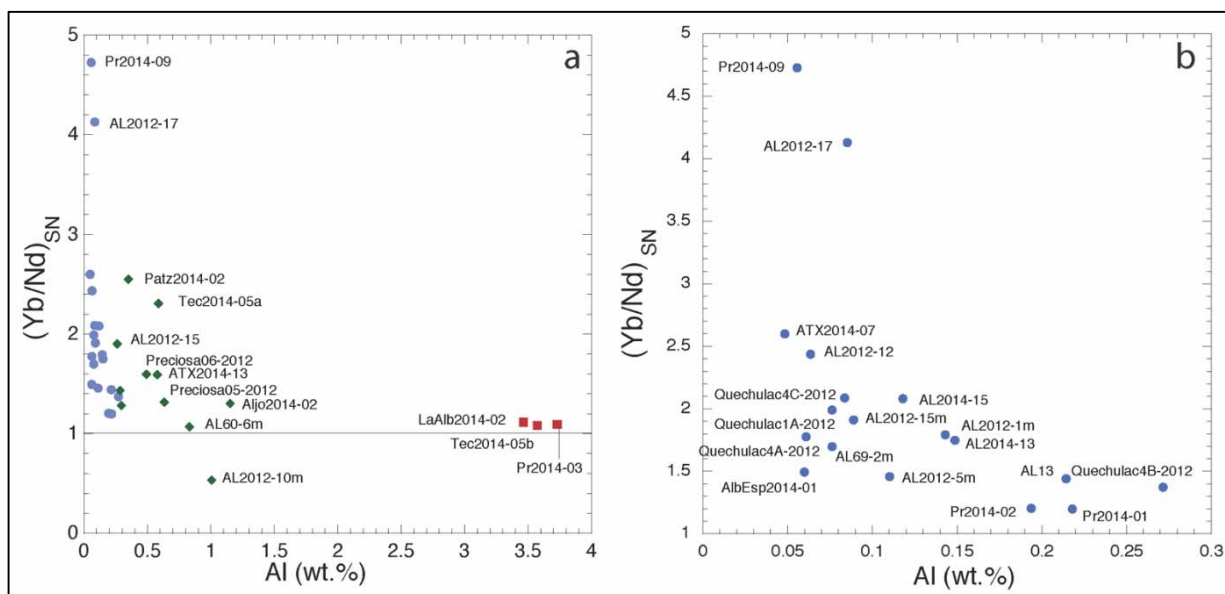


Figure SI-3-3.

Shale-normalized $(Yb/Nd)_{SN}$ ratio of microbialites indicating an enrichment in HREE, *versus* Al content. Samples with high detrital contamination: red squares; "intermediately" contaminated samples: green diamonds; authigenic-dominated samples: blue circles. **(a)** All samples. Microbialites strongly affected by detrital contamination (red squares) show a $(Yb/Nd)_{SN}$ close to 1 and a variability in HREE enrichment significantly lower compared to both intermediately contaminated samples ($p=0.0056$) and samples the least affected by detrital contamination ($p=0.0019$). **(b)** Close-up on the group of authigenic-dominated samples showing a negative correlation of $(Yb/Nd)_{SN}$ with the microbialite Al content ($r_s=-0.68$).

Microbialites systematically showed positive Eu anomalies. When the microbialites were Al-rich, their Eu anomaly were close to 1.6, while Eu/Eu^* were more variable for the other samples, reaching 9.03 for AL2012-17, an authigenic-dominated microbialite (Fig. SI-3-4a). In addition, considering specifically the group of authigenic-dominated microbialites, Eu/Eu^* was positively correlated ($r_s=0.61$) with their Ca content (Fig. SI-3-4b). As a result, microbialites from Lake Quechulac, AL2014-13, AL2014-15, Pr2014-09, Pr2014-01, Pr2014-02, which were composed of aragonite as the main carbonate phase showed the highest Eu/Eu^* values. In contrast, Mg-rich microbialites dominated by hydromagnesite (*i.e.*, microbialite samples AL2012-12, AL2012-1m and AL13) showed lower Eu/Eu^* values (Fig. SI-3-4b). AL2012-17 sample departed from this trend with a very high Eu/Eu^* compared to the other samples rich in aragonite (Fig. SI-3-4b). Moreover, for these microbialites, we observed a particularly clear positive correlation between Eu/Eu^* (with $\text{Eu}^*=0.5\text{Sm}+0.5\text{Gd}$) and the HREE enrichment of microbialites ($r_s=0.69$) (Fig. SI-3-4c).

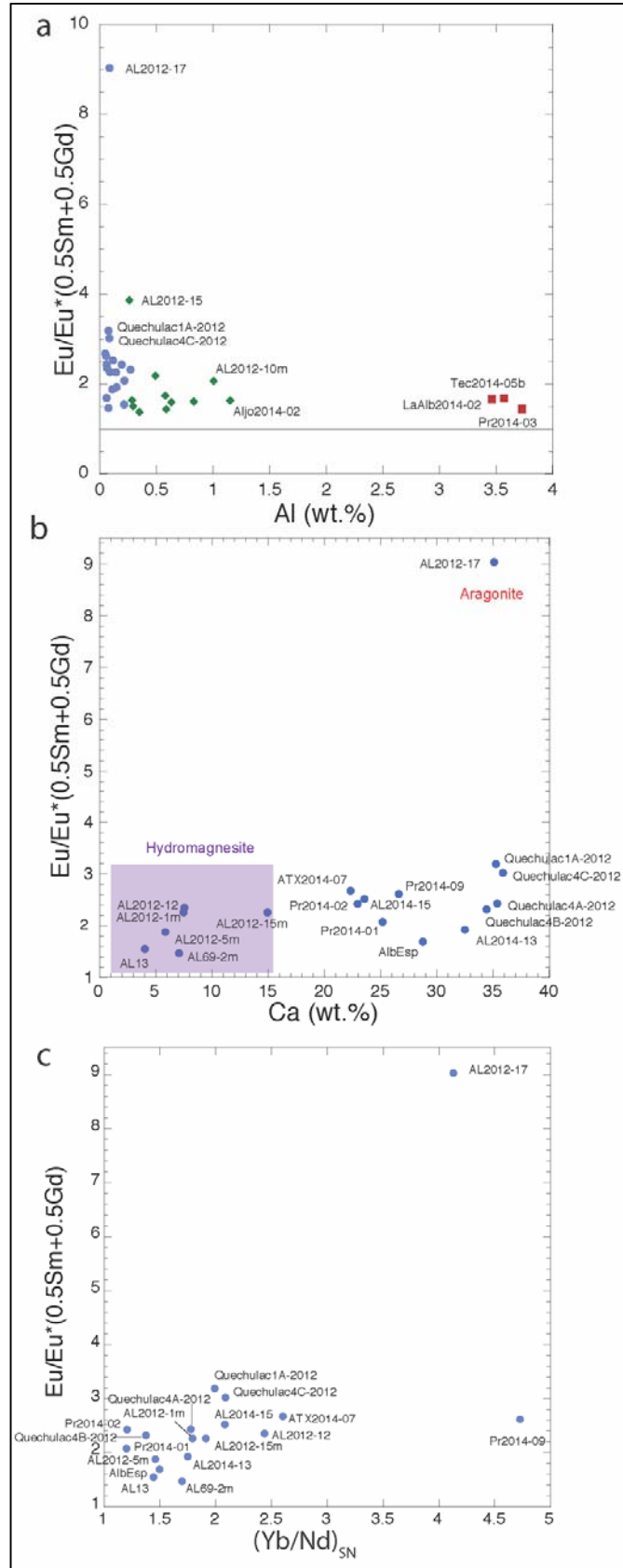


Figure SI-3-4.

Scatter plots of Europium anomaly *versus* other chemical parameters. Samples with high detrital contamination: red squares; "intermediately" contaminated samples: green diamonds; authigenic-dominated samples: blue circles. **(a)** Eu/Eu^* *versus* Al for all microbialites. Microbialites the least affected by detrital contamination exhibited a broader variability of the (positive) Eu anomaly compared to both intermediately contaminated samples ($p=0.026$) and samples strongly affected by detrital contamination ($p=0.037$). **(b)** Eu/Eu^* *versus* Ca for the authigenic-dominated samples. There is a linear relationship between the Ca content of the microbialites and the Eu anomaly except for AL2012-17. **(c)** Eu/Eu^* *versus* $(\text{Yb}/\text{Nd})_{\text{SN}}$ (HREE enrichment) for the authigenic-dominated samples. Eu anomaly is positively correlated with $(\text{Yb}/\text{Nd})_{\text{SN}}$ ($r_s=0.69$).

Microbialites intermediately and strongly affected by detrital contamination showed constant Pr/Pr^* values close to 1 except the "intermediate" samples AL60-6m, AL54-11m and Patz2014-02, which showed Pr/Pr^* of 1.06-1.09 (Fig. SI-3-5a). By contrast, authigenic-dominated microbialites exhibited variable Pr anomalies (considering Pr/Pr^* as $(\text{Pr}/(0.5\text{Ce}+0.5\text{Nd}))_{\text{SN}}$), higher than 1 for most of them, up to 1.30 for AlbEsp2014-01 and lower than 1 in several other cases (*e.g.*, 0.92 for AL2012-5m).

Most microbialites exhibited Ce anomalies (expressed as $\text{Ce}/\text{Ce}^*=(\text{Ce}/(0.5\text{La}+0.5\text{Pr}))_{\text{SN}}$) lower than 1 (negative anomalies), except the "intermediate" samples Tec2014-05a and AL2012-10m (1.03 and 1.00 respectively), (Fig. SI-3-5b). As already mentioned, the lower the Al content, the higher the Ce depletion, with Ce/Ce^* as low as 0.45 for AlbEsp2014-01 (Table SI-11 and Fig. SI-3-5b). Most of the authigenic-dominated microbialites showed La anomalies (considering La/La^* as $(\text{La}/(3\text{Pr}-2\text{Nd}))_{\text{SN}}$) higher than 1 (Fig. SI-3-5c). For example, positive La anomalies were remarkably high for the ATX2014-07, AL2012-5m and AL2012-12 microbialites, with values reaching 1.79, 1.75 and 1.71, respectively. Authigenic-dominated microbialites showed variable Gd anomalies (considering the anomaly $\text{Gd}/\text{Gd}^*=(\text{Gd}/(2\text{Tb}-\text{Dy}))_{\text{SN}}$) between 0.81 (AL69-2m) and 1.81 (AL2012-17), while microbialites highly affected by detrital contamination showed Gd/Gd^* anomalies close to 1 (Fig. SI-3-5d).

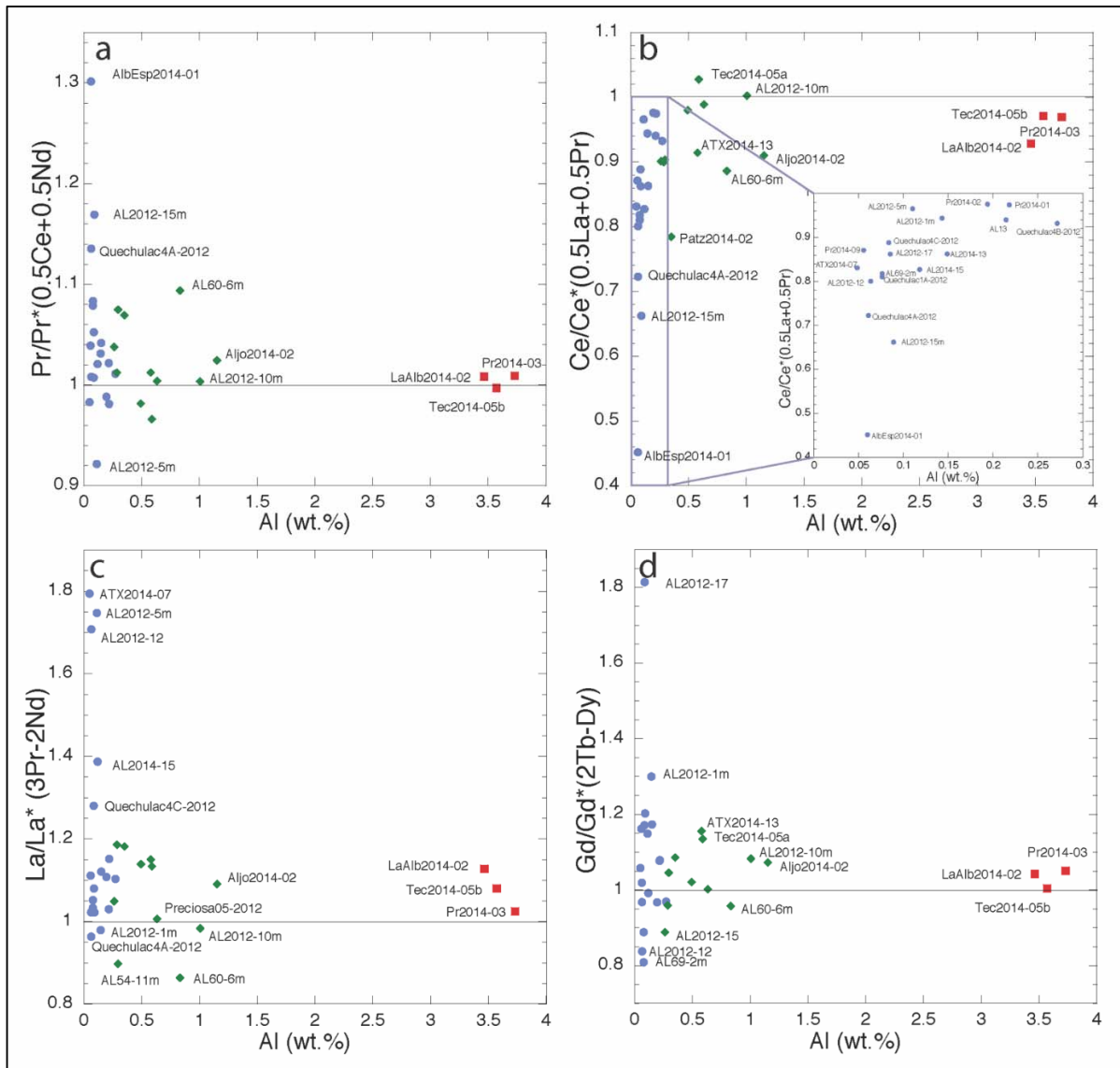


Figure SI-3-5.

Scatter plots of Pr, Ce, La and Gd REE anomalies versus the Al content of microbialites. Authigenic-dominated microbialites (Al-poor) show more variable Pr, Ce, La and Gd anomalies. **(a)** Al versus Pr/Pr*: broader variability of the anomaly within authigenic-dominated microbialites compared to samples strongly affected by detrital contamination ($p=0.038$); **(b)** Al versus Ce/Ce* and close-up showing a positive correlation between both parameters for the authigenic-dominated microbialites ($r_s=0.66$); **(c)** Al versus La/La* **(d)** Al versus Gd/Gd*. Samples with strong detrital contamination: red squares; intermediately contaminated samples: green diamonds; Authigenic-dominated samples: blue dots. Authigenic-dominated microbialites exhibited a broader variability of the La and Gd anomalies compared to intermediate samples ($p=0.021$ and $p=0.0073$, respectively).

Finally, the Y/Ho ratio of microbialites also depended on the Al content of microbialites. Al-rich microbialites showed a chondritic Y/Ho ratio (26-28), while Al-poor microbialites had a more variable Y/Ho. In the latter case, the Y/Ho ranged from 27.1 (Pr2014-01) up to 58.0 (AL2012-17) (Table SI-11 and Fig. SI-3-6a). Again, considering authigenic-dominated microbialites, there was a negative correlation ($r_s=-0.53$) between Y/Ho and their Al content (Fig. SI-3-6b). In addition, similarly to the Eu/Eu* anomaly, Y/Ho was positively correlated with the Ca content of the authigenic-dominated microbialites ($r_s=0.58$) (Fig. SI-3-6c).

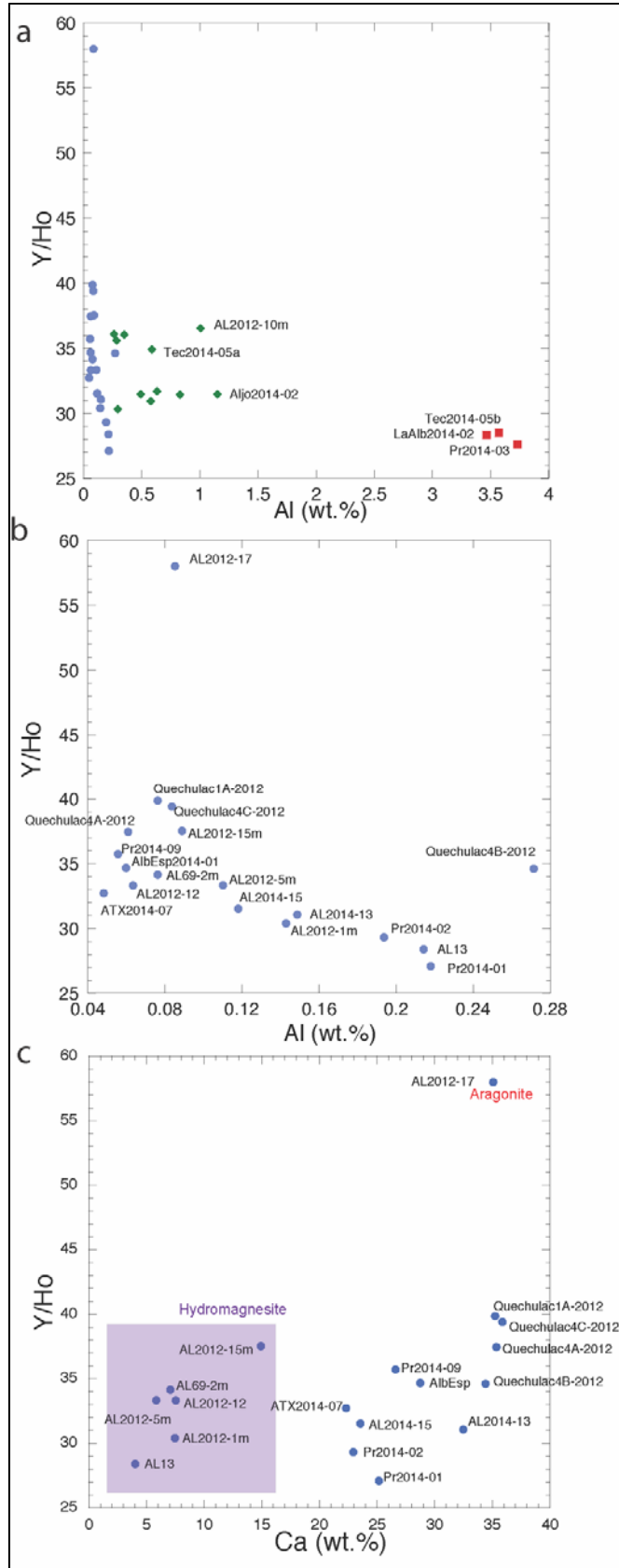


Figure SI-3-6.

Scatter plots of the Y/Ho ratio versus the Al and Ca contents of microbialites. **(a)** Al *versus* Y/Ho for all microbialites: authigenic-dominated microbialites exhibited a broader variability of the (positive) Y/Ho anomaly compared to both intermediately contaminated samples ($p=0.0076$) and samples strongly affected by detrital contamination ($p=0.028$); **(b)** Close-up on the samples poorly affected by detrital contamination showing a non-significant negative correlation between Al content and Y/Ho ratio ($r_s = -0.53$). **(c)** Ca *versus* Y/Ho. Samples with high detrital contamination: red squares; Intermediately contaminated samples: green diamonds; Authigenic-dominated samples: blue dots.

Overall, microbialites highly affected by detritism showed a flat REE+Y pattern, grasped by, *e.g.*, a shale normalized Yb/Nd ratio close to 1. This is consistent with the results by Álvaro et al. (2010) who showed that lacustrine stromatolites from the Ediacaran Ouarzazate Supergroup (Anti-atlas, Morocco) had a flat REE+Y pattern with the lack of distinct REE anomalies and mentioned a potentially strong contamination of the stromatolites by andesites and andesitic/rhyolitic tuffs. The flat REE+Y patterns of these Ediacaran lacustrine stromatolites were associated with high REE+Y contents (between 26.0 and 30.6 ppm) and concentrations in Al, Ga, Nb, Ta, K, Rb, Hf and Zr higher than those measured in the Mexican microbialites. A similar flat REE+Y pattern with a lack of pronounced anomalies were described for a mixed carbonate-siliciclastic microbialite sample from the Upper Jurassic Pagny-sur-Meuse formation (France) (Olivier and Boyet, 2006).

One question is whether the authigenic-dominated microbialites are not affected by detrital contamination at all. There are contrasted views in the literature about how to assess whether detrital contamination affects REE signatures. For example, Zhao and Zheng (2017) suggested that marine carbonate samples with a Th content lower than 0.6 ppm had seawater-like REE+Y patterns, indicating a poor contribution by silicate contamination. In contrast, they observed that samples with $[Th] > 1.0$ ppm showed higher REE+Y concentrations and shale-like REE+Y patterns. Consistently, Th correlated in our study with the 8 elements that we used as tracers of detritism and is therefore likely a good indicator of detritism (Fig. 8 in the main text). Mexican authigenic-dominated microbialites showed Th contents systematically lower than 0.22 ppm, *i.e.*, fitting with Zhao and Zheng's definition of poorly affected by contamination. In contrast, Li et al. (2019) suggested that a Zr content above 0.5 ppm in ooids was indicative of siliciclastic contamination as also attested by flat shale-normalized REE+Y patterns. Moreover, Webb and Kamber (2000)

suggested that very low contents in Th (<0.062 ppm), Hf (<0.007 ppm) and Sc (<0.429 ppm) in Heron microbialites were indicative of the absence of contamination by terrigenous detritus. In the latter case, these are not thresholds though. In our study, all the studied microbialite samples showed Zr contents higher than the one indicated by Li et al (2019), ranging between 1.28 ppm and 84.99 ppm but this was not associated with flat REE+Y patterns. Moreover, only three samples (AL2012-17, Pr2014-09 and ATX-2C1-2012) had Th concentrations below the values suggested by Webb and Kamber (2000) and all had Hf contents above 0.007 ppm. We cannot discuss Sc values since the detection limit of the ICP-MS measurements in our study (1 ppm) was above the value indicated by Webb and Kamber (2000).

No positive correlation was detected between the total REE+Y and Al contents of Mexican microbialites with an Al content lower than 0.27 wt.% ($r_s=0.39$; Fig. SI-3-1). Their total REE+Y content was lower than 3.8 ppm, excluding AlbEsp 2014-01 and Quechulac4B-2012 which had a total REE+Y content superior to some of the “intermediate” microbialite samples moderately affected by detrital contamination. Moreover, these samples showed a higher variability of the Gd, La, Eu and Pr anomalies, Y/Ho ratio and the HREE enrichment (see figures above). This suggests that the detrital contamination has a limited influence on their REE+Y patterns. Similarly, Li et al., (2019) noted that the variability of REE anomalies in marine and lacustrine ooids (Great Bahama Bank and the Great Salt Lake) poorly affected by siliciclastic contamination was higher than in ooids affected by detritism.

The lack of negative correlation between some elements tracing detritism (Zr, Sc, Th, Hf) and Y/Ho has been used by several studies as another indicator of poorly contaminated carbonates (Webb and Kamber, 2000; Bolhar and Van Kranendonk, 2007; Zhao and Zheng 2017). Here, considering the group of authigenic-dominated microbialites, we did not observe significant negative correlations between Y/Ho and Zr, Th, Hf, Ga, Al, and K ($r_s<0.58$). However, we observed a significant negative correlation between Y/Ho and Rb ($r_s=-0.74$) and between Y/Ho and Ta ($r_s=-0.66$). In addition, we observed that the Ce anomaly in authigenic-dominated microbialites was positively correlated with some of the chemical elements tracing detrital contamination (Al [$r_s=0.66$], Hf [$r_s=0.65$], Rb [$r_s=0.61$] and Nb [$r_s=0.60$]) (Fig. SI-6). The Ce content of microbialites was positively correlated with their Al content for all samples ($r_s=0.9$). Last, we observed a significant negative correlation between Al content and (Yb/Nd)_{SN} ($r_s=0.68$;

Fig. SI-3-3). Overall, Rb, Ta and Ce contents, Ce anomaly and $(Yb/Nd)_{SN}$ might be the parameters the most sensitive to detrital contamination in the present study.

Text SI-4. Discussion about the potential origins of REE signatures of Mexican authigenic-dominated microbialites

As mentioned in the main manuscript, REE+Y patterns of Mexican authigenic-dominated microbialites showed (i) a relatively higher proportion of HREE, (ii) relatively high (positive or negative) anomalies in Eu, Ce, La, Gd and Pr and (iii) a high Y/Ho ratio (Text SI-3). By measuring the REE+Y composition of some lake solutions (Table SI-4-1), we could retrieve solid/solution fractionation patterns for these lakes (Fig. SI-4-1).

Aqueous Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu
AL2014_3m	<3E-07	<3E-07	<2E-07	9.50E-07	<1.3E-06	1.31E-06	2.55E-06	2.56E-07	1.23E-06	1.40E-06	3.62E-07	<9E-07	2.98E-07	1.51E-06	2.96E-07
Quechulac2014_0m_N	3.35E-06	3.97E-06	6.73E-07	2.94E-06	1.39E-06	6.47E-07	<1.5E-06	2.01E-07	1.10E-06	1.48E-05	2.56E-07	1.28E-06	2.30E-07	9.05E-07	2.14E-07
AlbEsp2014_0m	1.21E-06	< 3E-07	8.33E-07	9.85E-07	1.33E-06	3.80E-06	1.97E-06	3.62E-07	9.61E-07	1.40E-05	3.15E-07	1.51E-06	<2E-07	1.17E-06	2.30E-07
ATX2014_0m	1.88E-06	2.08E-06	5.32E-07	3.08E-06	2.29E-06	1.02E-06	3.08E-06	4.98E-07	2.62E-06	1.32E-05	5.67E-07	1.30E-06	4.63E-07	1.93E-06	3.38E-07
Preciosa2014_0m	5.42E-07	6.86E-07	<2E-07	<7E-07	<1.3E-06	4.42E-07	<1.5E-06	<1.5E-07	8.01E-07	4.30E-06	<2E-07	<9E-07	2.24E-07	7.59E-07	1.39E-07

Table SI-4-1.

REE+Y concentrations (ppm) of some of the aqueous solutions.

Cerium is sensitive to changes in the redox conditions of water because oxidized Ce is tetravalent, less soluble and more easily absorbed onto particles (De Baar et al., 1988; Bolhar and Van Kranendonk, 2007). Negative Ce anomalies (also expressed as $Pr/Pr^*_{SN} > 1$) are therefore commonly interpreted as indicative of oxygenated conditions at the time of the deposition (De Baar et al., 1988; Kamber and Webb, 2001). Most of the Mexican authigenic-dominated microbialites showed negative Ce anomalies. The solid/solution fractionation patterns show a high Ce fractionation to the solid (Fig. SI-4-1), which might be well explained by incorporation of detrital particles, even in authigenic-dominated samples (Text SI-3). This suggests that in the absence of detrital contamination, one may expect even stronger negative anomalies. Overall, such negative anomalies are consistent with the oxidized conditions observed at shallow depth in the lakes. However, AL2012-5m showed a marked positive Ce anomaly (Text SI-3). This anomaly could be a record of a poorly oxygenated environment at this depth during microbialite formation. Such an anomaly may record periods of water mixing of the lake in December/January

(corresponding to the sampling period of this sample, *i.e.*, January 2012), when anoxic water from the bottom of Lake Alchichica mixes with top water, resulting in lower oxygen fugacity (Macek et al., 2009). Alternatively, this anomaly may record the input of poorly oxygenated groundwater fluids at or close to the formation site of this sample. No positive Ce anomaly (*i.e.*, indicative of anoxic water conditions) was observed for the Fe-rich microbialites, although they potentially formed with the input of anoxic groundwaters. Biological activity surely impacts the redox state of the pore solution at the lithified biofilm/biofilm interface possibly explaining the lack of Ce-positive anomaly for most of the samples.

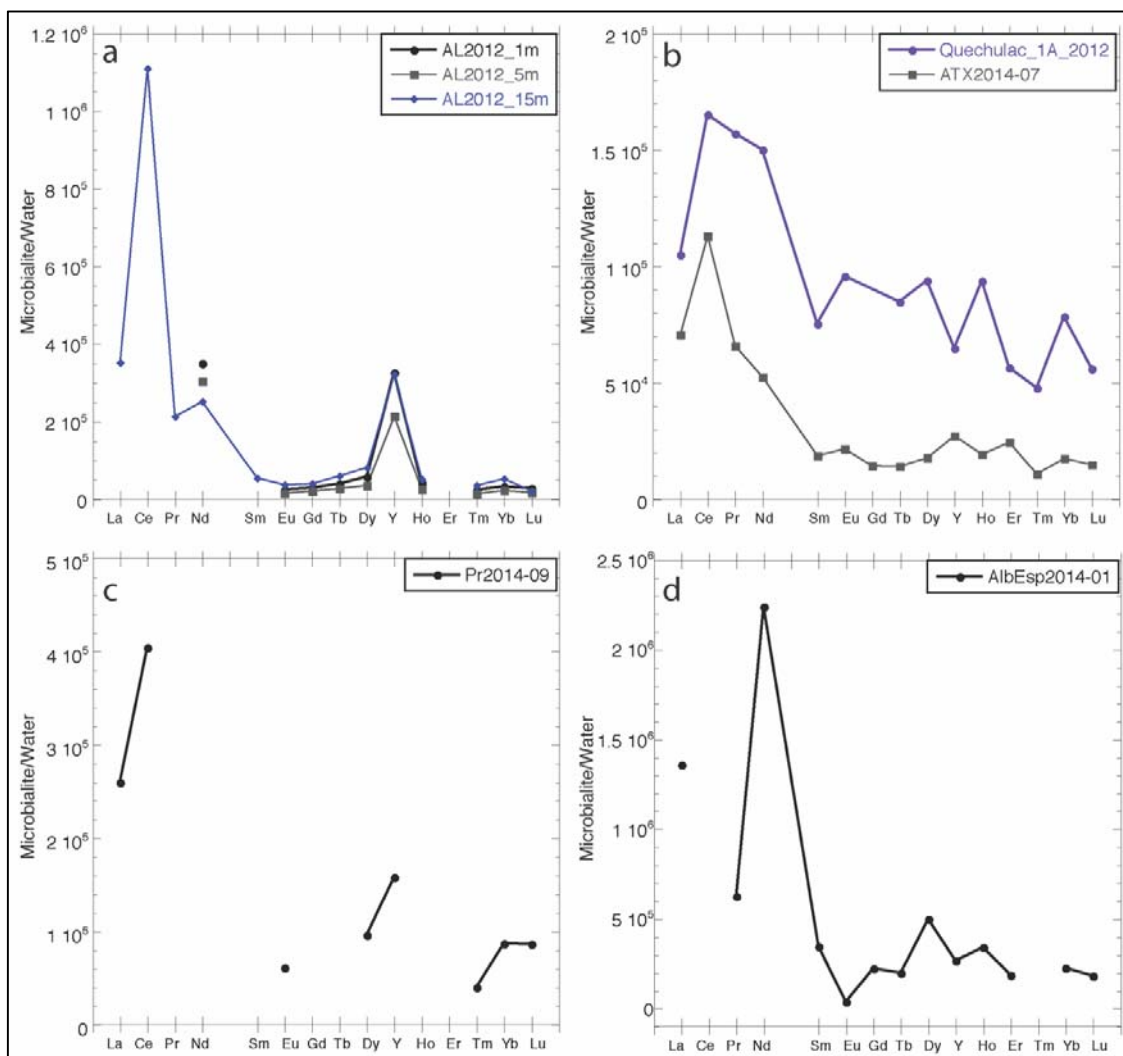


Figure SI-4-1.

REE microbialite/solution fractionation patterns calculated from the analyses of the authigenic-dominated microbialites. The patterns are not flat suggesting fractionation during the incorporation of these elements into the microbialites.

All studied microbialites showed a positive Eu anomaly. Moreover, no strong Eu enrichment of the solid could be seen compared to the solution (Fig. SI-4-1), *i.e.*, water also showed this positive Eu anomaly. The marine positive Eu anomaly is classically interpreted as related to an input of hydrothermal fluids, which have leached basalts under hot and acidic conditions at mid-oceanic ridges (Derry and Jacobsen, 1990; Danielson et al., 1992; Bolhar and Van Kranendonk, 2007). The outflow of underground fluids has been shown to occur at/or close to the location of microbialite formation (Kaźmierczak et al., 2011; Zeyen et al., 2019). In agreement, Lim et al. (2009) and Warden et al. (2019) emphasized the importance of groundwater flow for the formation of microbialites. Other lakes populated by microbialites such as Lake Van, Mono Lake, Lake Walyungup and Great Salt Lake are impacted by groundwater discharge (Kempe et al., 1991; Bischoff et al., 1993; Coshell et al., 1998; Bouton et al., 2016). Moreover, we note that Eu anomalies [Eu/Eu*, Eu* as (0.5Sm+0.5Gd)] were positively correlated with Ca ($r_s=0.61$), Sr ($r_s=0.69$), U ($r_s=0.59$) and to a lesser extent Ba ($r_s=0.48$) in authigenic-dominated microbialites. Since these elements are preferentially enriched in aragonite (Thompson and Livingston, 1970; Dietzel et al., 2004), this suggests that positive Eu anomalies may be mostly carried by aragonite rather than hydromagnesite or Mg-silicate. Interestingly, the non-living microbialite AL2012-17 combined the highest Eu anomaly (9.03), the highest Gd anomaly (1.81) and the highest Y/Ho ratio (58.00) with the highest Fe concentration (2.49 wt.%) among the studied microbialites. Since Fe enrichment within shallow microbialites might originate from groundwater seepage derived from adjacent Fe-rich volcanic rocks (Zeyen et al., 2019), Eu and Gd positive anomalies and high Y/Ho ratio within microbialites might together be good indicators of seepage of anoxic Fe-bearing groundwater into the lakes.

Last, authigenic-dominated microbialites were enriched in HREE relatively to LREE. Yet, LREE are expected to be scavenged preferentially by the solids because HREE form stronger aqueous complexes with carbonate ions (De Baar et al., 1988, Smrzka et al., 2019). Interestingly, Takahashi et al. (2007) observed a preferential incorporation of HREE *versus* LREE in some biofilms and Takahashi et al. (2005) showed that Tm, Yb and Lu can be particularly highly complexed and concentrated by carboxylate and phosphate groups at the surface of bacterial cells. Similarly, Johannesson et al. (2014) observed a fractionation between Cuatro Ciénegas microbialites and ambient continental water with preference for HREE. Such processes may therefore help understanding the HREE enrichment in Mexican microbialites. However, when

assessing the solid/solution fractionation of REE in Mexican lakes, we did not observe a preferential HREE incorporation but a general stronger incorporation of LREE *versus* HREE with some specific strong fractionations of some elements depending on the lakes (Fig. SI-4-1). This suggests that the overall microbialite patterns are controlled by that of the solution. The Y/Ho anomaly was correlated with the Ca content of the microbialites ($r_s=0.58$) and therefore microbialite samples composed of aragonite showed the highest Y/Ho (from 37.5 to 58.0), while microbialites mainly composed of hydromagnesite showed lower Y/Ho values (from 28.4 to 37.6). The transition metal Y and the lanthanide Ho are often referred to as geochemical twins because they generally show little fractionation upon metamorphic or weathering processes, due to their closely similar chemical properties and nearly identical ionic radii (Leggett, 2017). However, Y strongly fractionates from Ho upon calcite or aragonite precipitation, especially in highly alkaline solutions with a faster uptake of Ho by the solid phase (Qu et al., 2009). From this observation, it could be postulated that massive Ca-carbonate precipitation in Mexican lakes may have resulted in a high increase of the Y/Ho ratio of the epilimnion where microbialites form. Microbialites rich in Ca may form under these conditions, while Mg-rich microbialites may form under conditions where such massive precipitation did not occur. Alternatively, we observed almost systematically a strong Y fractionation between microbialites and the solution, which was not observed for Ho. The molecular mechanisms responsible for this fractionation remain to be understood.

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