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# 1 Fe-bearing phases in modern lacustrine microbialites from 2 Mexico

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## ABSTRACT

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Transition metal ions impurities in microbialites have been previously suggested as paleoenvironmental and/or paleobiological proxies. However, how metals are incorporated into microbialites remains poorly known. Here, in order to assess the distribution and speciation of Fe in modern microbialites, we conducted bulk x-ray diffraction, infrared spectroscopy, x-ray absorption near-edge structure (XANES) spectroscopy, electron microscopy and x-ray microscopy analyses on samples collected from shallow depths in five alkaline lakes in Mexico: Lake Alchichica, Lake La Preciosa, Lake Atexcac, Lake La Alberca de Los Espinos and Lake Pátzcuaro. A range of Fe contents were measured in these microbialites, from low (~0.12 wt.%) to relatively high (~2.2 wt.%). Fe was distributed heterogeneously in microbialites, mostly localized as hotspots or sometimes arranged as discrete laminae. Fe was mostly trivalent in all microbialites and was incorporated into diverse authigenic phases, the proportion of which varied among microbialites. Authigenic phases included Fe-bearing Mg-phyllsilicates such as kerolite and/or stevensite, i.e.  $(\text{Mg,Fe(II),Fe(III)})_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$  and Fe-Mg layered double hydroxides (LDH), i.e. pyroaurite  $[\text{Mg(II)}_6\text{Fe(III)}_2(\text{CO}_3)(\text{OH})_{16} \cdot 4\text{H}_2\text{O}]$  and/or iowaite  $[\text{Mg(II)}_6\text{Fe(III)}_2\text{Cl}_2(\text{OH})_{16} \cdot 4\text{H}_2\text{O}]$ , together with Fe-(oxyhydr)oxides. Carbonate phases were negligible carriers of Fe in all lakes. Iowaite/pyroaurite phases, which have often been found as low temperature alteration products in serpentinites, were surprisingly observed in Lake Alchichica, whereas Fe-bearing kerolite/stevensite was present in Lake La Preciosa, Lake Atexcac, Lake La Alberca de Los Espinos and Lake Pátzcuaro. Fe present in these shallow water microbialites may be originated from groundwater seepage derived from adjacent Fe-rich volcanic rocks. We suggest that the occurrence of iowaite/pyroaurite vs authigenic Fe-bearing kerolite/stevensite depends on the orthosilicic acid concentration in the lakes.

54 Pyroaurite/iowaite may form and stay preserved in Lake Alchichica because of the low  
55  $[H_4SiO_4]$  as well as high alkalinity,  $[Mg^{2+}]$ ,  $[CO_3^{2-}]$ ,  $[Cl^-]$  and pH ( $\sim 9$ ) prevailing in this lake,  
56 while in other lakes, where  $[H_4SiO_4]$  is higher (above  $\sim 0.4$  mM), Fe-bearing kerolite or  
57 smectite phases are formed. Overall, the message carried by the Fe-bearing mineral phases in  
58 these modern microbialites is multifold: Fe-bearing phases within microbialites may contain  
59 some information on environmental conditions (e.g.,  $[H_4SiO_4]$ ) as well as on geochemical  
60 processes implicated during their formation (e.g., seepage of anoxic Fe-bearing groundwater).  
61 Considering the reactivity of pyroaurite/iowaite and kerolite/stevensite and their possible  
62 transformation into diverse mineral phases upon microbial activity, burial and diagenesis, a  
63 careful appraisal of Fe speciation using a similar combination of bulk and microscopy  
64 analyses is required in order to better assess the origin of Fe in ancient microbialites.

65

66

## 1. INTRODUCTION

67

68 Microbialites are organo-sedimentary rocks formed in close association with  
69 microorganisms (Burne and Moore, 1987). These rocks have been repeatedly suggested to  
70 record information on the environmental conditions under which they formed (e.g., Chagas et  
71 al., 2016). Part of this information can be retrieved through the analysis of their chemical  
72 composition, including their trace and/or transition element content (Petrash et al., 2016). For  
73 example, some modern microbialites have been shown to retain shale-normalized rare earth  
74 element ( $REE_{SN}$ ) patterns similar to those of seawater, suggesting that ancient microbialites  
75 may be used to infer past chemical variations of seawater (Webb and Kamber, 2000).  
76 Alternatively, the trace element and transition metal content in microbialites may be impacted  
77 by some biological fractionation processes and provide information on past microbial  
78 activities (Kamber and Webb, 2007). The trace element chemical patterns may also be

79 modified secondarily by diagenetic processes, as shown for some ca 1.88 Ga old stromatolites  
80 from the Gunflint Formation (Petrash et al., 2016).

81 The Fe chemistry in microbialites has been specifically investigated as a potential  
82 source of paleoenvironmental information. For example, Von Blanckenburg et al. (2008)  
83 suggested that most of Fe found in some modern and ancient marine microbialites occurred in  
84 hydrogenous carbonates, rather than Fe and Mn-hydroxides. If this were true, the Fe isotope  
85 composition of ancient microbialites could be used to record ancient seawater Fe chemistry.  
86 Alternatively, Fe can be actively processed and transformed by diverse microorganisms,  
87 serving as an electron donor or acceptor for various microbial metabolisms and/or as a co-  
88 factor for several enzymes (e.g., Weber et al., 2006; Cornelis, 2014). For example, Planavsky  
89 et al. (2009) interpreted the Fe isotope composition of 1.89 Ga old microbialites as the result  
90 of microbially-mediated Fe precipitation involving Fe-oxidizing bacteria. Overall, there is a  
91 need to better understand how Fe becomes sequestered within microbialites.

92 Modern microbialites may form differently from ancient microbialites, especially from  
93 the Archean. Therefore, great care should be taken when applying interpretations from the  
94 modern to the past (e.g., Bosak et al., 2013). Yet the study of metal chemistry in modern  
95 microbialites may serve as a model case to better assess the complex processes involved in Fe  
96 sequestration within microbialites and the diversity of primary Fe-bearing mineral phases that  
97 may form. Fe was sometimes abundant in ancient microbialites, especially when ferruginous  
98 conditions were prevailing in aqueous environments (e.g., Von Blanckenburg et al., 2008). In  
99 contrast, low Fe contents are expected in the authigenic phases composing modern  
100 microbialites, which usually form in well oxygenated and alkaline water, because of the low  
101 solubility of Fe under these conditions (Schwertmann, 1991). Nevertheless, some modern  
102 shallow-water microbialites from the alkaline Mexican Lakes Alchichica, Atexcac and La  
103 Preciosa have been recently reported to contain relatively high amounts of Fe, i.e. >0.44 wt.%

104 of Fe<sub>2</sub>O<sub>3</sub> (Kaźmierczak et al., 2011; Zeyen et al., 2015). In order to understand the origin of  
105 this enrichment in Fe and determine whether this is due to authigenesis or detrital input, we  
106 characterized the speciation of Fe in Lake Alchichica and Atexcac microbialites as well as in  
107 microbialites from three other distinct alkaline lakes located in the trans Mexican volcanic  
108 belt. For this purpose, we combined bulk x-ray diffraction, Fourier-transform infrared  
109 spectroscopy and x-ray absorption near-edge structure (XANES) spectroscopy analyses,  
110 coupled with scanning and transmission electron microscopies as well as x-ray microscopy  
111 analyses. Overall, this enabled us to develop a consistent assessment of the Fe-bearing  
112 mineral phases composing these diverse modern microbialites, and thereby infer some of the  
113 geochemical processes that give rise to Fe enrichments in microbialites.

114

## 115 **2. MATERIALS AND METHODS**

116

### 117 **2.1. Samples**

#### 118 **2.1.1 Microbialite samples**

119 Field campaigns were conducted in June 2007, January 2012 and May 2014. Seven  
120 samples of modern microbialites were collected in five lakes: Alchichica, La Preciosa,  
121 Atexcac, La Alberca de Los Espinos and Pátzcuaro, all located within the trans Mexican  
122 volcanic belt (TMVB), a continental volcanic arc with an East-West orientation (Ferrari et al.,  
123 2012). Lake Pátzcuaro is older than 30,000 years and is a lava-dammed basin (Israde-  
124 Alcántara et al., 2005). The other lakes are maar lakes formed by phreato-magmatic  
125 explosions during the Pleistocene (Armienta et al., 2008; Siebe et al., 2014). Atexcac, La  
126 Preciosa and Alchichica maars are composed of tuff rings (Carrasco-Núñez et al., 2007). La  
127 Alberta de Los Espinos maar is a tuff cone (Siebe et al., 2014). Table 1 summarizes the main  
128 physical and geochemical parameters of these lakes.

129 Lake Alchichica harbored a high density of microbialites forming meter-scale  
130 bioherms all around the lake (Fig. SI-1a and d). The carbonate mineralogy and microbial  
131 diversity of Lake Alchichica microbialites have been extensively studied (Kaźmierczak et al.,  
132 2011; Couradeau et al., 2011; Couradeau et al., 2013; G erard et al., 2013; Sagha i et al., 2015;  
133 Sagha i et al., 2016). Many microbialites were white in cross-section, but some had a darker,  
134 orange to brown color as reported by Kaźmierczak et al. (2011). These orange-brown  
135 microbialites were located on the West shore of the lake (Fig. SI-1a). There, the crater rim  
136 was particularly steep due to the outcrop of a basaltic scoria cone (Fig. SI-1b). In the present  
137 study, we investigated Fe speciation in one sample of a brown, living (i.e. underwater and  
138 covered by a biofilm) microbialite sampled in May 2014 on the West shore of Lake  
139 Alchichica (AL2014-15) (Fig. SI-1c), and two white, living microbialites from the North  
140 shore, collected in June 2007 at a depth of about 0.1 and 4 meters and named AL13 and  
141 AL66, respectively (Fig. SI-1e).

142 Microbialites from Lake La Preciosa and Lake Atexcac were described by Zeyen et al.  
143 (2015). Fossil (i.e. dry and not covered by a biofilm) microbialites formed steep bioherms on  
144 the North shore of Lake La Preciosa (Fig. SI-1f). A grey fossil microbialite (Preciosa05-2012)  
145 was analyzed in the present study (Fig. SI-1g). Microbialites from Lake Atexcac formed a  
146 steep wall superimposed on the crater walls (Fig. SI-1h). Here, a living microbialite showing  
147 a grey to orange color inside (ATX-2C1-2012) was sampled on the northern wall of the lake  
148 (Fig. SI-1i). Lake La Alberca de Los Espinos harbored decimeter-sized living microbialites  
149 restricted to a small area close to the West shore of the lake. Here, the studied sample  
150 contained some black small columns and orange pustules (AlbEsp2014-01) (Fig. SI-1j and k).  
151 Finally, living microbialites were collected on the north-eastern shore of Lake P atzcuaro.  
152 Here, we studied a decimeter-sized brownish living laminated stromatolite (Patz2014-02),  
153 encrusting a basaltic rock (Fig. SI-1l and m). To our knowledge, microbialites from Lake

154 Pátzcuaro and Lake La Alberca de Los Espinos have not been reported before.

155

### 156 **2.1.2. Synthetic model compounds**

157 *Syntheses of nanocrystalline Fe(II):talc and Fe(III):talc*

158 Talc model compounds containing Fe(II) or Fe(III), partially substituted for Mg,  
159 referred to as nano-Fe(II):talc and nano-Fe(III):talc respectively, were synthesized using the  
160 protocol described by Juillot et al. (2006), with the stoichiometry  $\text{Fe}_{0.05}\text{Mg}_{2.95}\text{Si}_4\text{O}_{10}(\text{OH})_2$ ,  
161 close to that measured by electron microprobe in Atexcac microbialites (Zeyen et al., 2015).  
162 For this purpose, a solution of 200 ml of sodium metasilicate  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$  (0.1 M) was  
163 prepared. Then, for the synthesis of nano-Fe(III):talc, a mixture of  $\text{Fe}(\text{III})\text{Cl}_3 \cdot 6\text{H}_2\text{O}$  (0.01 M)  
164 and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  (0.29 M) was homogenized. Fifty milliliters of the Fe/Mg mixture were  
165 added to 200 ml of the sodium meta-silicate solution. After this step, the pH of the solution  
166 was 11.4. The pH was adjusted to around 10.9 using HCl (1M) and the solution was  
167 homogenized for 30 minutes. Precipitates were centrifuged at 9000 g for 10 minutes and  
168 washed four times with milli-Q water before being transferred into 8 glass serum bottles  
169 sealed with a butyl rubber stopper and an aluminum cap (0.5 g of hydrated precipitate per  
170 flask), each containing 100 ml of water. Flasks were placed in an oven for 7 days at 80°C.  
171 Finally, the solutions were centrifuged at 9000 g for 10 minutes and washed four times with  
172 milli-Q water. Precipitates were dried in the desiccator overnight. For the synthesis of nano-  
173 Fe(II):talc, the same protocol as above was followed except that the synthesis was carried out  
174 in an anaerobic glove box using  $\text{O}_2$ -free milli-Q water, and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  was used as a Fe(II)  
175 source. For this synthesis, the precipitate obtained before the aging period at 80°C was also  
176 washed and dried, and is designed hereafter as nano-Fe(II):talc-gel. In addition, in order to  
177 mimic oxidation of the structural Fe(II) in talc, a sample of nano-Fe(II):talc-gel dry powder  
178 was oxidized in an excess of 1 ml of 3%  $\text{H}_2\text{O}_2$  for about 5 hours before being rinsed with

179 milli-Q water and air dried. The resulting sample was referred to as nano-Fe(II):talc-gel H<sub>2</sub>O<sub>2</sub>  
180 oxidized.

181

### 182 *Synthesis of Fe(III):hydrotalcite*

183 Hydrotalcite containing Fe(III) as impurity, referred to as Fe(III):hydrotalcite, was  
184 synthesized with the following stoichiometry: Mg<sub>0.75</sub>Al<sub>0.24</sub>Fe(III)<sub>0.01</sub>OH<sub>2</sub>(CO<sub>3</sub>)<sub>0.125</sub>. For this  
185 purpose, a 100 mL solution containing MgCl<sub>2</sub>·6H<sub>2</sub>O (0.06 M), Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18H<sub>2</sub>O (0.01 M)  
186 and Fe(III)Cl<sub>3</sub>·6H<sub>2</sub>O (0.0008 M) was titrated with a mixture of NaOH (1.6 M) and Na<sub>2</sub>CO<sub>3</sub>  
187 (0.1 M) to pH 10. The solution was stirred for one hour. The precipitate was then centrifuged  
188 four times at 9000 g for 10 minutes and rinsed with milli-Q water. Finally, the precipitate was  
189 placed in a desiccator overnight. The purity of the synthesized phases was checked by FTIR  
190 and/or XRD (Fig. SI-2).

191

## 192 **2.2 Methods**

193 A quantity of about 10 g for each microbialite sample was finely ground in an agate  
194 mortar and aliquots of the same powdered sample were used for the different bulk analyses.

195

### 196 **2.2.1. Bulk chemical analyses of microbialites**

197

198 Bulk chemical compositions of microbialite samples were determined by the *Service*  
199 *d'Analyse des Roches et Minéraux* (SARM, Centre de Recherches Pétrographiques et  
200 Géochimiques, Nancy, France). About 2 g of ground powders were used for these analyses.  
201 Major element analyses were performed using an ICP-AES ICap 6500 (Thermo Fischer) after  
202 alkali fusion of rock samples with LiBO<sub>2</sub> followed by dissolution in HNO<sub>3</sub>. The uncertainties  
203 of the major element measurements were between 1% and 25% depending on their

204 concentrations (Table 2).

205

### 206 **2.2.2. Bulk mineralogical analyses of microbialites**

207

#### 208 *X-ray diffraction (XRD)*

209 The bulk mineralogical composition of microbialites was determined by XRD. About  
210 1 g of each microbialite powder was deposited on an aluminum sample holder. XRD  
211 measurements were performed using a Panalytical X'Pert diffractometer equipped with a  
212 cobalt anode (Co-K $\alpha$ ). Data were recorded at 40 kV and 40 mA in continuous-scan mode  
213 between 5 and 90° (2 $\theta$ ) with a step of 0.008°/s and a total counting time of ~3 h per scan.  
214 XRD data were analyzed using the PANalytical X'Pert Highscore software for background  
215 subtraction, peak finding, and matching with XRD patterns of reference compounds from the  
216 International Crystal Structure Database (ICSD, Fachinformationszentrum Karlsruhe,  
217 Germany; US Institute of Standards and Technology, USA).

218

#### 219 *Fourier transform infrared (FTIR) spectroscopy*

220 For FTIR spectroscopy analyses, 2.5 mg of microbialite powder and 300 mg of  
221 potassium bromide (KBr) were mixed and ground in an agate mortar. A KBr pellet was  
222 prepared for each microbialite sample using a vacuum press under 8 tons for 1 minute. Pellets  
223 were placed overnight in an oven (95°C) to remove the adsorbed water and were pressed a  
224 second time. Transmission spectra were recorded as 210 replicate scans between 400 and  
225 4000 cm<sup>-1</sup> with 1 cm<sup>-1</sup> resolution, using a Nicolet 6700 FTIR spectrometer.

226

### 227 **2.2.3. Analyses of bulk Fe speciation by x-ray absorption near-edge structure (XANES)** 228 **spectroscopy**

229

230 X-ray absorption near-edge structure (XANES) data of 7 microbialite samples (AL66,  
231 AL13, AL2014-15, Preciosa05-2012, ATX-2C1-2012, AbEsp2014-01 and Patz2014-02) were  
232 collected at the Fe K-edge in the fluorescence detection mode on beamline BM23 at the ESRF  
233 (Grenoble, France) using a Si(111) double crystal monochromator and a 13 elements Ge array  
234 detector. Duplicate data were recorded for sample AL66 on beamline BM30B FAME at the  
235 ESRF (Grenoble, France) using a Si(220) double crystal monochromator with sagittal  
236 focusing of the second crystal, and a 30 elements Ge array detector. Sample pellets were  
237 prepared using 130-230 mg of powder for all samples but the AL2014-15 sample, for which 5  
238 mg of powder were mixed with 50 mg of cellulose. In addition, XANES spectra were  
239 collected for 3 model compounds: Fe(III):hydrotalcite, nano-Fe(II):talc and nano-Fe(III):talc.  
240 This was achieved in transmission detection mode at the BM23 beamline on pellets prepared  
241 by mixing 20-30 mg sample with 40-30 mg cellulose. Analyses were conducted at a  
242 temperature of ~10 K. Energy was calibrated by setting to 7112 eV the first inflection point of  
243 the Fe K-edge XANES spectrum of a reference Fe(0) foil, recorded simultaneously with the  
244 samples. For each microbialite sample and model compound, 2–8 scans were recorded,  
245 depending on the Fe concentration. XANES spectra were acquired from a range of 7000–  
246 7575 eV. The background Fe fluorescence signal arising from the excitation of the beamline  
247 components by diffuse scattering (e.g. sample chamber inner walls and Fe impurities in Be  
248 windows) was collected by measuring a XANES spectrum on a pure cellulose pellet. All data  
249 were averaged and normalized using the ATHENA software (Ravel and Newville, 2005).

250 Fe K-edge XANES spectra of the microbialite samples were analyzed using a linear  
251 combination least-squares fitting (LC-LSF) procedure that was performed with a custom-built  
252 software based on a Levenberg–Marquardt least-squares minimization algorithm (Hohmann  
253 et al., 2011; Stetten et al. 2017). A large set of already available Fe K-edge XANES spectra of

254 natural and synthetic model compounds was already available for this fitting procedure. This  
255 dataset included a large variety of synthetic Fe compounds such as Fe(III) (oxyhydr)oxides,  
256 e.g. goethite ( $\alpha$ -FeOOH) and 6-line ferrihydrite (Maillot et al., 2011; Hohmann et al.,  
257 2011) and siderite ( $\text{FeCO}_3$ ) (Dublet et al., 2014), and 2) natural phyllosilicates (Cosmidis et  
258 al., 2014; Othmane et al., 2013), such as serpentine from New Idria Mining District (CA,  
259 USA) (Dublet et al., 2012; Noël et al., 2014) and illite from Le Puy-en-Velay, France, i.e.,  
260  $\text{Na}_{0.01}\text{K}_{0.64}\text{Ca}_{0.06}(\text{Al}_{1.19}\text{Fe(III)}_{0.36}\text{Mg}_{0.43}\text{Ti}_{0.04}\text{Mn}_{0.01})(\text{Si}_{3.53}\text{Al}_{0.47})\text{O}_{10}(\text{OH})_2$  (Ildefonse et al.,  
261 1998). This latter model compound, referred to as Fe(III):illite hereafter, was used as a proxy  
262 for structural Fe(III) in a dioctahedral 2:1 phyllosilicate. The background Fe signal from the  
263 beamline was systematically included as an additional component in the XANES LC-LSF  
264 procedure and accounted for 1 to 28% of the measured signal (Table SI-1), depending on Fe  
265 concentration and the amount of analysed microbialite sample. The quality of the LCF fits  
266 was estimated by a reduced chi-square parameter  $\chi^2_{\text{R}} = n / (n-p) \sum [\mu_{\text{exp}} - \mu_{\text{calc}}]^2$  where  $n$  is  
267 the number of independent parameters corresponding to the energy range divided by the  
268 natural width of the Fe K levels reported by Krause and Oliver (1979). The uncertainty on the  
269 fitting components was estimated by  $3 \times \sqrt{\text{VAR}(p) \chi_{\text{R}}^2}$ , where  $\text{VAR}(p)$  is the variance of  
270 parameter  $p$  returned by the Levenberg–Marquardt routine for the lowest  $\chi^2_{\text{R}}$  value (Stetten et  
271 al., 2017).

272

#### 273 **2.2.4. Microscopy analyses of microbialites**

274

##### 275 *Sample preparation for microscopy analyses*

276 Some microbialite samples (ATX-2C1-2012, Preciosa05-2012 and AlbEsp2014-01)  
277 were sawed to obtain ~5 mm thick sections and polished down to a ¼ of micron of surface  
278 roughness with diamond polishing compounds. Then, they were rinsed in an ultrasonic

279 cleaning bath with pure ethanol. Finally, polished sections were dried overnight in a  
280 desiccator. Samples were mounted on 2.5 cm wide aluminum stubs using double-sided carbon  
281 tape. Alchichica and Pátzcuaro microbialite samples (AL13, AL66, AL2014-15 and Patz-  
282 2014-02) were dehydrated in a gradual series of ethanol baths (30%, 50%, 70%, 90% and  
283 100%), and progressively impregnated with hard grade LR-white resin (Polysciences, Inc.).  
284 The samples were incubated for 18 h at 4-6°C in 1:2 (1:1 for AL13 and AL66 samples) and  
285 then in 2:1 mixture of LR-white/ethanol, and finally in pure LR-white resin. After 3 h at room  
286 temperature, samples were embedded in pure LRwhite resin for 1 h at 40°C and then for 24 h  
287 at 60°C. After polymerization, transverses sections were cut with a diamond wire to obtain ~2  
288 mm thick sections and polished until 1/4 µm of surface roughness. All samples were carbon-  
289 coated, except AlbEst2014-01, which was platinum-coated.

290

#### 291 *Scanning electron microscopy (SEM)*

292 Scanning electron microscopy analyses were performed using a Zeiss ultra 55 field  
293 emission gun (FEG) SEM. Backscattered electron (BSE) images were acquired using an angle  
294 selective backscattered (AsB) detector at an accelerating voltage of 15 kV and a working  
295 distance of ~7.5 mm. The elemental composition of mineral phases was determined by energy  
296 dispersive x-ray spectrometry (EDXS) using an EDS QUANTAX detector. EDXS data were  
297 analyzed using the ESPRIT software package (Bruker).

298

#### 299 *Micro x-ray fluorescence (µXRF) mapping*

300 X-ray fluorescence images were collected on AL13 and AL66 microbialite samples at  
301 the Stanford synchrotron radiation lightsource (SSRL) using beam line 2–3. The incident  
302 energy was set to 11 keV using a Si (111) double crystal monochromator with the storage ring  
303 Stanford Positron Electron Accelerating Ring (SPEAR) containing 500 mA in top-off mode at

304 3.0 GeV. The fluorescence lines of the elements of interest, as well as the intensity of the total  
305 scattered X-rays, were monitored using a Si drift Vortex detector (SII NanoTechnology USA  
306 Inc.) equipped with Xspress3 pulse processing electronics (Quantum Detectors). The raw  
307 spectra were binned at the time of collection into regions of interest representing the peak  
308 areas of the fluorescence emission. The entire fluorescence spectrum was also collected at  
309 each data point. The microfocused beam of 2x2 $\mu$ m was provided by a Pt-coated Kirkpatrick-  
310 Baez mirror pair (Xradia Inc.). The incident and transmitted x-ray intensities were measured  
311 with nitrogen-filled ion chambers. Samples were mounted at 45° to the incident x-ray beam  
312 and were spatially rastered in the microbeam using a Newport VP-25XA-XYZ stage. Beam  
313 exposure was 50 ms per pixel. Image data was processed using the MicroAnalysis Toolkit  
314 (Webb, 2011). The fluorescence regions of interest were corrected for any variations in the  
315 incident beam intensity, and placed on the same absolute magnitude scale for each individual  
316 element (Fe, Ca) for comparison between samples.

317

#### 318 *Focused ion beam (FIB) sectioning*

319 Four ultrathin electron-transparent foils were cut from polished sections AL13, AL66,  
320 AL2014-15 and ATX-2C1-2012 by focused ion beam milling using a FEI Strata Dual-beam  
321 235 instrument operating at 30 kV and 5 nA following the FIB lift-out method as described by  
322 Benzerara et al. (2005). Before milling, a platinum strap was deposited onto the region of  
323 interest of the sample. After *in situ* transfer to a copper grid, the foil was thinned down to  
324 around 100 nm with a Ga<sup>+</sup> beam current of about 100 pA and at glancing angle.

325

#### 326 *Transmission electron microscopy (TEM)*

327 FIB foils were analyzed by a JEOL 2100F transmission electron microscope (TEM)  
328 operating at 200 kV. This microscope is equipped with a FEG, an ultra-high resolution pole

329 piece, a Gatan energy filter GIF 2001, a JEOL detector with an ultrathin windowing detection  
330 of light elements, and a scanning TEM (STEM) device, which allows Z-contrast imaging in  
331 high angle annular dark field (HAADF) mode. Elemental mapping was acquired by EDXS in  
332 the STEM mode, using the JEOL software Analysis Station. Selected area electron diffraction  
333 (SAED) patterns were recorded to identify mineral phases and assess their crystallinity.  
334 SAED patterns were processed using the Image J software in order to measure *d*-spacings.  
335 The Crystallmaker software was used to index diffraction patterns.

336

### 337 *Scanning transmission x-ray microscopy (STXM)*

338 FIB foils extracted from Alchichica (AL13 and AL66) and Atexcac (ATX-2C1-2012)  
339 microbialite samples were analyzed by STXM at the C K-edge and the Fe L<sub>2,3</sub>-edges.  
340 Analyses were performed on beamline 11.0.2.2 at the Advanced Light Source (Berkeley,  
341 USA), using a 25 nm zone plate. Energy calibration was achieved using the well-resolved 3p  
342 Rydberg peak of gaseous CO<sub>2</sub> at 294.96 eV. Data included image stacks, from which XANES  
343 spectra and maps were retrieved. The aXis2000 software (Hitchcock, 2012) was used for data  
344 processing. More details on the principles of STXM can be found in Bourdelle et al. (2013).

345

346

## 3. RESULTS

347

### 348 **3.1. Bulk chemical composition of Mexican microbialites**

349 Microbialites from the different lakes showed diverse Fe contents (Table 2). Fe  
350 content in the microbialites from Preciosa05-2012 (Lake La Preciosa), AlbEsp2014-01 (Lake  
351 La Alberca de Los Espinos), ATX-2C1-2012 (Lake Atexcac), and Patz2014-02 (Lake  
352 Pátzcuaro) ranged between  $0.31 \pm 0.02$  wt.% and  $0.62 \pm 0.03$  wt.%. In Lake Alchichica, the  
353 white microbialites from the North shore (AL13) had a low Fe content of  $0.12 \pm 0.01$  wt.%,  
354 whereas the brown microbialites from the West shore (AL2014-15) contained a much higher

355 Fe content of  $2.24 \pm 0.04$  wt.%.

356 While Al and K contents correlated positively together (Fig. SI-3a), no correlation was  
357 detected between the Fe content and the Al, K or Ti contents of microbialites (Fig. SI-3b-c-d).  
358 For example, sample AL2014-15 had the highest Fe content but a Ti content below the  
359 detection limit (Table 2, Fig. SI-3d). This suggested that Fe was predominantly carried by  
360 non-detrital phases

361

### 362 **3.2. Fe bulk speciation in Mexican microbialites**

363 In order to obtain further insight on the identity of the mineral phases hosting Fe,  
364 XANES spectroscopy measurements were conducted at the Fe K-edge. These analyses were  
365 complemented by XRD and FTIR analyses for mineral identification. Altogether, these  
366 analyses showed that Fe-speciation in Alchichica microbialites (AL13, AL66 and AL2014-  
367 15) clearly differed from that in the other lakes.

368

#### 369 **3.2.1. Speciation of Fe in microbialites from Lake Alchichica**

370 Our best LC-LSF results for the Fe K-edge XANES spectra of all the Alchichica  
371 microbialites (AL2014-15, AL66 and AL13) were obtained by including a significant to  
372 major Fe(III):hydrotalcite component in the fits (Figs. 1 and SI-4; Tables 3 and SI-1), up to  
373 100% in the AL66 spectrum. This component was interpreted here as a proxy for Fe(III)-  
374 bearing layered double hydroxide (LDH), i.e., an anionic clay, with the general stoichiometry  
375  $[M(II)_{1-x}M(III)_x(OH)_2][A^{n-}_{x/n}] \cdot mH_2O$ , where M(II) (e.g., Mg(II)) and M(III) (e.g., Fe(III)) are  
376 di- and tri-valent cations in the octahedral sites within the hydroxide layers and  $A^{n-}$  (e.g., Cl  
377 or  $CO_3^{2-}$ ) is an exchangeable interlayer anion (Mills et al., 2012). Goethite and ferrihydrite  
378 fitting components were also found in the AL2014-15 spectrum, while nano-Fe(II):talc was  
379 needed to fit the AL13 spectrum. The nano-Fe(II):talc component was considered as a proxy

380 for Fe(II) in a trioctahedral 2:1 phyllosilicate structure. These XANES results indicated that  
381 AL2014-15 and AL66 microbialites contained Fe as Fe(III) only, whereas around 30% of Fe  
382 in AL13 microbialite was in the form of Fe(II).

383 FTIR and XRD analyses showed that AL13 and AL66 microbialites were mainly  
384 composed of hydromagnesite ( $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ) with lower amounts of aragonite  
385 ( $\text{CaCO}_3$ ), whereas AL2014-15 was mostly composed of aragonite with lower amounts of  
386 hydromagnesite (Figs. 2 and 3). In agreement with XANES analyses, the weak peaks at 7.59  
387 Å ( $13.4^\circ 2\Theta$ ) and 3.79 Å ( $27.3^\circ 2\Theta$ ) in the XRD pattern of the Fe-rich AL2014-15 sample  
388 (2.23 wt.%; Table 3) were consistent with the (003) and (006) Bragg reflections of LDH,  
389 respectively (Fig. 2). Accordingly, a peak at  $1384 \text{ cm}^{-1}$  was also detected in the same sample  
390 by FTIR spectroscopy (Fig. 3a) and could be interpreted as the carbonate asymmetric  
391 stretching mode ( $\nu_3\text{CO}_3$ ) in LDH (Ross et Kodama, 1967; Braithwaite et al., 1994; Frost and  
392 Erickson, 2004), indicating the presence of a  $\text{CO}_3$ -containing LDH phase. This peak has been  
393 also detected in aragonite by Jones and Jackson (1993), although we did not observe it in the  
394 aragonite sample from Molina, Aragon, Spain in the RRUFF database (RRUFF ID: R040078;  
395 data not shown). The  $\nu_3\text{CO}_3$  FTIR peak at  $1384\text{-}1385 \text{ cm}^{-1}$  possibly indicative of LDH (e.g.,  
396 pyroaurite and/or iowaite) was also detected in the Fe-poor AL13 and AL66 sample as a faint  
397 shoulder of an intense band attributed to hydromagnesite (Fig. 3c). LDH was not detected by  
398 XRD in these samples (Fig. 2), which could be explained by the very low Fe contents in these  
399 samples (e.g. 0.13 wt.% in AL13; Table 2). No peak at  $\sim 3680 \text{ cm}^{-1}$ , indicative of  $\text{Mg}_3\text{-OH}$   
400 stretching bands, characteristic of Mg in octahedral coordination such as in kerolite (Tosca et  
401 al., 2011), was observed for sample AL13. Moreover, such a phase was not detected by XRD  
402 in this sample, suggesting that if present, it was only in minute amount. The (101) Bragg  
403 reflection at 4.18 Å (e.g.,  $24.7^\circ 2\Theta$ ) of goethite (Schwertmann and Cornell, 2000) was not  
404 detected by XRD in AL2014-15, possibly because of overlap with the aragonite and

405 hydromagnesite patterns. Ferrihydrite could not be detected by XRD possibly owing to its  
406 nanocrystalline structure (Table 2).

407

### 408 **3.2.2. Speciation of Fe in microbialites from Lakes La Preciosa, Atexcac, La Alberca de** 409 **Los Espinos and Pátzcuaro**

410 The Fe K-edge XANES spectra of microbialites from La Preciosa, Atexcac, La  
411 Alberca de Los Espinos and Pátzcuaro were all best fitted with a combination of Fe:clay  
412 components, namely nano-Fe(II): and/or nano-Fe(III):talc and Fe(III):illite (Figs. 4 and SI-4;  
413 Tables 3 and SI-1). Linear fits with other model compounds, such as 1:1 phyllosilicate model  
414 compound (e.g., serpentine), provided lower quality fits. The nano-Fe(II):talc fitting  
415 component was considered as a proxy for Fe(II) substituting for Mg(II) in the octahedral layer  
416 of a trioctahedral 2:1 phyllosilicate, which was confirmed by a shell-by-shell analysis of this  
417 model compound (Materials and methods SI-1; Fig. SI-5; Table SI-2). Besides, the local  
418 structure around Fe in the synthetic nano-Fe(III):talc fitting component was close to that in  
419 the nano-Fe(II):talc-gel oxidized by H<sub>2</sub>O<sub>2</sub> and considered as a proxy for the poorly ordered  
420 oxidation byproduct of nano-Fe(II):talc (Figs. SI-5 and SI-6). The Fe K-edge EXAFS spectra  
421 of these Fe(III)-bearing talc model compounds significantly differed from those of  
422 ferrihydrite and illite (Fig. SI-6), indicating different local structures around Fe(III) in these  
423 three compounds (Table SI-2). Moreover, these three compounds could also be well  
424 distinguished by XANES as shown in Figs. 1 and 4. Fe(III):illite was considered as a proxy  
425 for Fe(III) in the octahedral layer of a dioctahedral 2:1 phyllosilicate in the LC-LSF XANES  
426 analysis of the microbialite samples. A large fraction of Fe (69-73%) was present in a  
427 nanocrystalline trioctahedral 2:1 phyllosilicate in the Preciosa05-2012 and ATX-2C1-2012  
428 samples with 22-26% of total Fe as Fe(II). The nanocrystalline trioctahedral 2:1 phyllosilicate

429 fraction was slightly lower in the AlbEsp201-01 (57%) and Patz2014-02 (67%) samples as  
430 well as the Fe(II) to total Fe proportion (9-10% of total Fe) (Tables 3 and SI-1).

431 Bulk XRD analyses showed that the major mineral phases composing these  
432 microbialites were: aragonite and calcite in La Preciosa; aragonite, calcite and  
433 hydromagnesite in Atexcac; calcite and monohydrocalcite in La Alberca de Los Espinos;  
434 calcite, monohydrocalcite and aragonite in Pátzcuaro (Fig. 5). In addition, broad peaks at 4.5  
435 Å ( $22.8^\circ 2\Theta$ ), 2.5 Å ( $42.3^\circ 2\Theta$ ) and 1.5 Å ( $72.1^\circ 2\Theta$ ) were detected in XRD patterns of  
436 Preciosa05-2012, ATX-2C1-2012 and Patz2014-02. These peaks may correspond to *d*-  
437 spacings at 4.55, 2.48 and 1.52 Å corresponding to two dimensional *hk* diffraction bands  
438 (respectively (02-11), (13-20) and (06-33)) characteristic of poorly ordered layer silicate such  
439 as hydrated talc (kerolite) or trioctahedral smectite phases (stevensite) (Brindley et al., 1955;  
440 Brindley et al., 1977) and/or dioctahedral Fe-smectite such as nontronite (Decarreau et al.,  
441 2008). Moreover, faint shoulders at  $\sim 11\text{Å}$  ( $9.3^\circ 2\Theta$ ) and  $\sim 10\text{Å}$  ( $10^\circ 2\Theta$ ) in the XRD patterns  
442 of the Preciosa05-2012 and Patz2014-02 samples, could correspond to basal reflections of  
443 poorly ordered smectite and talc phases, respectively (Fig. 5). The near absence of the (001)  
444 reflection could be consistent with a strong phase disorder and/or with the presence of  
445 nanophases(s). Some kerolite/stevensite/nontronite was also present in AlbEsp2014-01 as  
446 shown by a faint peak at 4.5 Å ( $22.8^\circ 2\Theta$ ) (Inset Fig. 5). In contrast, XRD patterns were not  
447 suggestive of 1:1 silicates (e.g., serpentine). For example, the (001) peak of lizardite (RRUFF  
448 ID: R060006) or antigorite (RRUFF ID: R070228) at 7.27 Å was not observed. Consistently,  
449 FTIR spectra of all four microbialites showed one peak at 1020-1026  $\text{cm}^{-1}$  (Fig. 6a),  
450 interpreted as Si-O stretching in tetrahedral vibration in a 2:1 layered configuration of  
451 tetrahedral silicate layers and octahedral  $\text{MgO}_6$  layers. This is consistent, but not exclusively,  
452 with the presence of a kerolite and/or stevensite phase. However, this large band at 1020-1026  
453  $\text{cm}^{-1}$  is not observed in 1:1 layered configuration silicates such as serpentines, which are

454 mainly characterized by 2 bands around 990 et 1080  $\text{cm}^{-1}$  (Yariv and Heller-Kallai, 1975).  
455 FTIR spectra of all four microbialites also showed one peak at 3679-3681  $\text{cm}^{-1}$ , interpreted as  
456 a  $\text{Mg}_3\text{-OH}$  stretching band, characteristic of Mg in octahedral coordination, consistent but not  
457 exclusively with kerolite/stevensite (Fig. 6b; Tosca et al., 2011). Additional bands at 3624 and  
458 3647  $\text{cm}^{-1}$  in the Pátzcuaro microbialite may result from a splitting of the hydroxyl stretching  
459 in kerolite due to the substitution of Mg by Fe (Fig. 6b; Wilkins and Ito, 1967). Again, these  
460 bands are significantly different from those observed in 1:1 layered configuration silicates  
461 such as serpentines, which appear at 3652, 3669, 3688 and 3703  $\text{cm}^{-1}$  for lizardite (Trittschack  
462 et al., 2012) or 3644 and 3689  $\text{cm}^{-1}$  in chrysotile (Bishop et al., 2002). Last but not least, the  
463  $\nu_3\text{CO}_3$  band at 1384-1385  $\text{cm}^{-1}$  was detected in La Preciosa, Atexcac, La Alberca de Los  
464 Espinos and Pátzcuaro (Fig. 6 a-c). While this band may be due to LDH and/or aragonite in  
465 ATX-2C1-2012, Preciosa05-2012, and Patz2014-02, it was likely associated with LDH in  
466 AlbEsp2014-02 since no other band characteristics of aragonite was observed in this sample.

467

### 468 **3.3. Microscopy analyses of Fe-bearing phases**

469 Fe-rich areas were observed by microscopy in all the samples except the La Preciosa  
470 microbialite. Light and scanning electron microscopies as well as  $\mu\text{-XRF}$  analyses showed  
471 that Fe distribution in microbialites was discrete, with the existence of Fe-hotspots (Figs. 7  
472 and 8). In AL2014-15, Fe was contained in numerous thin laminae, measuring less than 10  
473  $\mu\text{m}$  in thickness as well as patches of  $\sim 100 \mu\text{m}$  in width (Fig. 7 a-b). Fe-rich phases  
474 sometimes appeared extinct under cross polars as observed for AL2014-15 suggesting the  
475 presence of a poorly crystalline phase. In AL13, Fe hotspots appeared as laminae and patches  
476 beneath an aragonite layer located at the surface of microbialites (Fig. 7 c-d). In ATX-2C1-  
477 2012 and Patz2014-02, Fe phases were distributed as  $\sim 50\text{-}200 \mu\text{m}$  thick laminae (Fig. 7 e-f-g-  
478 h).

479

### 480 3.3.1. Fe-bearing phases in Alchichica microbialites

481           Synchrotron-based  $\mu$ -XRF maps showed that Fe in AL66 was concentrated in discrete  
482 laminae, beneath an aragonite layer located at the surface of microbialites (Fig. 8 a-b). The  
483 same Fe-rich areas were analyzed at a higher spatial resolution by SEM-EDXS. These Fe  
484 laminae showed a smooth texture and were sandwiched between a surface layer of aragonite  
485 and an inner mass of hydromagnesite (Fig. 8). One FIB foil was cut across a Fe-rich lamina  
486 (Fig. 8c) and analyzed by TEM. At the nanoscale, one phase with a fibrous texture appeared  
487 to bear Fe together with Mg and Cl and almost no Al (Fig. 9 a-b-e area#1). The selected area  
488 electron diffraction (SAED) pattern of this phase showed diffuse spots with  $d$ -spacings at  
489 2.65, 2.43 and 1.55 Å corresponding to the (101), (0-11) and (-1-10) lattice planes,  
490 respectively, viewed along the [1-1-1] zone axis of a LDH phase (Fig. 9c). In accordance with  
491 bulk XAS analyses, this phase was interpreted as a Mg-, Fe-, and Cl-rich LDH phase, i.e.  
492 iowaite ( $\text{Mg}_6\text{Fe(III)}_2(\text{OH})_{16}\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ ). Iowaite was overlain by crystalline micritic aragonite  
493 as attested by EDXS and SAED analyses (Figs. 9 a-b-d-e area#2 and SI-7).

494           Similar as in AL66, Fe-rich areas in AL13 also appeared between a surface aragonite  
495 layer and an inner mass of hydromagnesite forming the bulk of the microbialite (Fig. 10).  
496 Some Fe-rich laminae were also detected within the aragonite layer and a FIB foil was cut  
497 across one of them (Fig. 10c). The Fe-rich lamina sampled in the FIB foil measured  $\sim 1 \mu\text{m}$  in  
498 width. It was smooth and darker than the surrounding aragonite by STEM-HAADF (Fig. 11).  
499 This lamina was mostly composed of Mg, Cl and Fe, similarly to iowaite in AL66 with minor  
500 amounts of Si and Al. However, the rings in the SAED pattern were much more diffuse so  
501 that  $d$ -spacings could not be determined (Fig. 11d). Fe in this phase was mostly in the form of  
502 Fe(III) as shown by the prominent peak at 710.3 eV in the XANES spectrum measured by  
503 STXM at the Fe  $L_{2,3}$ -edges (Fig. 11g). This agreed with bulk XAS measurements. Finally, this

504 Fe-rich lamina contained organic matter as attested by STXM analyses at the C K-edge (Fig.  
505 11 h-i). Indeed, XANES spectra measured on the lamina showed peaks at 1) 284.9 eV,  
506 interpreted as carbon  $1s \rightarrow \pi^*$  electronic transitions in aromatic and/or olefinic groups (C=C);  
507 2) 286.6 eV, interpreted as carbon  $1s \rightarrow \pi^*$  electronic transitions in ketone/phenol group  
508 (C=O); 3) 287.3 eV, interpreted as carbon  $1s \rightarrow \sigma^*$  transitions in aliphatic groups and 4) 288.5  
509 eV, interpreted as carbon  $1s \rightarrow \pi^*$  transitions in carboxylic functional groups (Fig. 11i,  
510 Benzerara et al., 2004; Bernard et al., 2010). An additional peak at 290.3 eV was interpreted  
511 as carbonate C (Benzerara et al., 2004), suggesting that in addition to iowaite, there was also a  
512  $\text{CO}_3$ -containing LDH phase, i.e. pyroaurite ( $\text{Mg}_6\text{Fe(III)}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ ), in accordance  
513 with FTIR analyses.

514 AL2014-15 contained a much higher Fe content than AL13 and AL66. Consistently,  
515 large Fe-rich areas were observed by light microscopy and SEM (Figs. 7 a-b and 12). A FIB  
516 foil was cut within one of these areas, across two Mg- and Fe-rich, Si-poor objects with  
517 circular cross-sections surrounded by a Fe- and Si-rich mineral matrix (Fig. 12). TEM  
518 analyses showed three different mineral phases with different textures in the FIB foil (Fig.  
519 13): 1) pyroaurite/iowaite, appearing smooth when observed by bright-field TEM and STEM-  
520 HAADF and forming bands measuring 200 nm to 1  $\mu\text{m}$  in width and filling partially the  
521 objects. This phase was composed of Mg, Cl and Fe and showed a SAED pattern consistent  
522 with pyroaurite/iowaite observed along the [1-1-1] zone axis (Fig. 13a-b-c area#1-d). 2) The  
523 second mineral phase was fibrous and corresponded to the matrix surrounding the objects  
524 (Fig. 13 a-b-f-g). This phase was composed of Fe with Si and Mg as shown by EDXS  
525 analyses with a Fe proportion ( $X_{\text{Fe}} = \text{Fe}/(\text{Mg} + \text{Fe})$ ) close to 0.7 (Fig. 13 c area#2). Its SAED  
526 pattern showed diffuse rings at  $\sim 3.15$ ,  $\sim 2.55$  and  $\sim 1.50$  Å (Fig. 13 a-e), consistent with  
527 phyllosilicates such as the silico-ferric precipitates synthesized at 150°C by Decarreau et al.  
528 (1987). The  $d$ -spacings at 2.55 and 1.50 Å were also compatible with the (110) and (300)

529 planes of ferrihydrite, that may contain high amount of Si (Schwertmann and Cornell, 2000).  
530 3) Aragonite appeared as well crystalline micrometer-sized grains in bright-field TEM (Fig.  
531 13 f-h).

532

### 533 **3.3.2. Fe-bearing phases in Atexcac, La Alberca de Los Espinos and Pátzcuaro** 534 **microbialites**

535 Although Fe contents in ATX-2C1-2012, Patz2014-02 and AlbEsp2014-01 were  
536 relatively low, some Fe-containing areas could be detected by SEM-EDXS (Fig. 14). In all of  
537 them, Fe was systematically associated with Si and Mg (Fig. 14), consistently with bulk XAS,  
538 FTIR and XRD analyses that showed Fe incorporation in a talc-like phase. The presence of Fe  
539 in a talc-like phase in ATX-2C1-2012 microbialite sample was also supported by previous  
540 electron microprobe analyses showing (Mg+Fe)/Si ratio equal to  $0.82 \pm 0.06$  (Zeyen et al.,  
541 2015). Moreover, most of the occurrences that we observed were Al-poor except for  
542 Patz2014-02 (Fig. 14 d-e-f). FIB foils were cut within two distinct Fe-rich areas in ATX-2C1-  
543 2012: one was analyzed by Zeyen et al. (2015); one has been characterized by TEM and  
544 STXM in the present study (Figs. 15 and 16). This FIB foil contained two mineral phases: 1)  
545 aragonite which appeared as aggregated crystalline grains measuring few hundreds of  
546 nanometers, with a high diffraction contrast in bright field TEM, and a bright contrast in  
547 STEM-HAADF; 2) the Fe-rich phase with a smooth texture and a darker contrast in STEM-  
548 HAADF (Fig. 15 c-d). SAED patterns acquired on the Fe-rich phase showed very diffuse  
549 rings attesting that it was poorly crystalline (Fig. 15e). In agreement with SEM observations,  
550 STEM-EDXS analyses indicated that this Fe-rich phase contained mostly Si and Mg (Fig.  
551 15h). Some Al was also detected here in contrast with SEM analyses and previous TEM  
552 analyses on Fe- and Mg-rich silicates reported by Zeyen et al. (2015). XANES spectroscopy  
553 at the Fe L<sub>2,3</sub>-edges indicated that Fe was mostly in the form of Fe(III) in this phase (Fig. 16  
554 a-b). Again, this Fe- and Si-rich phase was associated with organic matter. XANES spectrum

555 at the C K-edge showed the same peaks as observed in the AL13 iowaite/pyroaurite lamina,  
556 indicative of aromatic and/or olefinic, ketone/phenol, aliphatic and carboxylic C-functional  
557 groups (Fig. 16c). Similarly, a peak located at 290.4 eV was observed and could be  
558 interpreted as carbonate C and/or metal-carboxylic C complexes (Chan et al., 2009).

559

560

## 4. DISCUSSION

561

### 4.1. Origins of the Fe content in Mexican microbialites: authigenesis vs detrital input

563 The Fe content of Mexican microbialites varied between 0.12 wt.% in AL13 and 2.24  
564 wt.% in AL2014-15. Depending on the lakes, Fe was found in a variety of mineral phases as  
565 summarized in Table 4, including pyroaurite/iowaite, Fe-bearing kerolite/stevensite, a  
566 dioctahedral 2:1 phyllosilicate, possibly illite and/or a smectite phase such as nontronite,  
567 ferrihydrite and possibly goethite, as inferred by a combination of XANES, XRD, FTIR and  
568 electron microscopy. As a comparison, carbonates (specifically analyzed by leaching  
569 experiments) within modern marine microbialites from the Heron Reef Formation (Australia)  
570 contained lower Fe concentrations, less than 0.005 wt.% (Von Blanckenbourg et al., 2008).  
571 The chemically sorted carbonate fraction composing Archaean stromatolites studied by Von  
572 Blanckenbourg et al. (2008) from the Strelley Pool Formation (Pilbara craton, Australia), the  
573 Mushandike Formation (Masvingo Greenstone Belt, Zimbabwe craton), the Gamohaam,  
574 Kogelbeen and the Boomplaas formations (KAAPVAAL craton, South Africa) had Fe  
575 concentrations ranging from 0.02 to 1.51 wt.%. Proterozoic stromatolites from the 1.89 Ga  
576 Gunflint and Biwabik Fe formations (Animikie basin) studied by Planavsky et al. (2009) had  
577 Fe contents varying between 0.02 and 14.11 wt.%, with Fe possibly comprised within  
578 hematite, magnetite, siderite and/or ankerite as inferred by XRD and standard petrographic  
579 techniques. All of them were interpreted as microbially-mediated authigenic phases. Overall,

580 Fe contents of the modern Mexican microbialites appeared relatively high, considering that  
581 they formed at shallow depth in oxic and alkaline water. Carbonate phases were a negligible  
582 carrier of Fe in Mexican microbialites. Instead, Fe was found in discrete laminae between  
583 distinct carbonate phases, such as hydromagnesite and aragonite. This suggests that Mexican  
584 microbialites formed by alternating periods when Fe-poor carbonates formed and periods  
585 when Fe-rich phases formed. Moreover, in Alchichica microbialites, Fe-rich laminae outlined  
586 some transition between hydromagnesite and aragonite laminae. Such an association is  
587 difficult to explain based on the hypothesis made by Kaźmierczak et al. (2011), who proposed  
588 that hydromagnesite forms secondarily as a replacement of aragonite. In contrast, the  
589 Holocene hydromagnesite deposits at Atlin (British Columbia, Canada) are mainly composed  
590 of hydromagnesite and magnesite, while aragonite is only observed in crack fills suggesting a  
591 primary origin for hydromagnesite formed by both abiotic and biotic processes (Stamatakis et  
592 al. 2007). In the Kozani Basin, an ancient lacustrine system in Greece, Stamatakis (1995)  
593 showed that  $p\text{CO}_2$  was the key parameter explaining the precipitation of hydromagnesite  
594 versus huntite, aragonite and brucite. Similarly, the aragonite-pyroaurite/iowaite-  
595 hydromagnesite association in Lake Alchichica may result from some significant  
596 hydrochemical variations, which occurred at a certain time in the lake from conditions  
597 conducive to hydromagnesite precipitation to conditions favoring aragonite formation through  
598 an episode of pyroaurite/iowaite precipitation. Regardless, we note that the environmental  
599 message carried by Fe in these microbialites relates to the origin and the fate of  
600 oxyhydroxides, silicates and layered double hydroxides and not the carbonate phases (i.e.  
601 aragonite, hydromagnesite, calcite or monohydrocalcite).

602         Some of the Fe-bearing phases may be detrital. In AL13, Preciosa05-2012, ATX-2C1-  
603 2012, AlbEsp2014-02 and Patz2014-02, XANES spectra included the contribution of a Fe-  
604 bearing dioctahedral 2:1 phyllosilicate. While the XANES spectrum of illite was used a

605 reference endmember for the fitting procedure, no illite was detected by XRD. Instead, this  
606 Fe-bearing dioctahedral 2:1 phyllosilicate might be nontronite, consistent with XRD data  
607 measured on Preciosa05-2012 and Patz2014-02 samples (Decarreau et al., 2008). Moreover,  
608 the occurrence within microbialites of nontronite, a common alteration product of basalt,  
609 would be consistent with the alteration of the surrounding mafic catchment/bedrock (Velde,  
610 2003). Alternatively, the broad XRD peaks at 4.5, 2.5 and 1.5 Å may relate to Mg-kerolite  
611 and/or stevensite only and not Fe-bearing phases. Microscopy analyses showed some  
612 occurrences of mineral phases containing Mg, Fe, Si and Al in ATX-2C1-2012 and Patz2014-  
613 02, which could be nontronite. Nevertheless, it should be noticed that a Mg-, Fe- and Si-rich  
614 phase with a very similar texture and no Al was also found in ATX-2C1-2012 (Zeyen et al.,  
615 2015), suggesting that if a dioctahedral 2:1 phyllosilicate such as nontronite phase may  
616 contain some of the Fe, an Al-free phyllosilicate also accommodates some of the Fe.  
617 Whatever the identity of the Fe-carrying dioctahedral 2:1 phyllosilicate, several observations  
618 suggest that a significant amount of Fe was carried by non-detrital phases in Mexican  
619 microbialites. First, no correlation was observed between Fe and the Al, K and Ti bulk  
620 contents of the microbialites, as this would be expected from a major detrital input. Moreover,  
621 Fe-bearing phases observed by microscopy frequently displayed textures indicative of *in situ*  
622 precipitation such as Fe-bearing phases templating objects with circular cross-sections,  
623 possibly biogenic structures. Thus, authigenesis scenarios are provided hereafter for the  
624 formation of Fe-bearing kerolite/stevensite-like and pyroaurite/iowaite phases, two of the  
625 main Fe-bearing phases detected in the microbialites.

626

#### 627 **4.2. Fe-bearing layered double hydroxides in Alchichica microbialites**

628 In Alchichica microbialites, part and sometimes most of Fe was borne by layered  
629 double hydroxides (LDH), sometimes referred to as hydrotalcite (Hall and Stamatakis, 2000),

630 a mineral supergroup comprising more than 40 naturally-occurring mineral species with a  
631 layered double hydroxide structure (Mills et al., 2012). LDH structure consists of positively  
632 charged brucite-type layers ( $\text{Mg}(\text{OH})_2$ ) separated by intercalated, charge balancing anions  
633 (Schutz and Biloen, 1987). Chemical compositions of LDH widely vary (Allada et al., 2006)  
634 in terms of their divalent cation content (e.g., Mn(II), Mg(II), Ni(II)), their trivalent cation  
635 content (e.g., Al(III), Fe(III), Cr(III)) and the interlayer anions (e.g.,  $\text{CO}_3^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ).  
636 Here, XANES, FTIR, STXM and TEM analyses showed that the LDH phase in Alchichica  
637 microbialites contained chloride and carbonates as interlayer anions, Mg as a divalent cation  
638 and Fe(III) as a trivalent cation. Therefore, this phase belongs to the iowaite  
639 ( $\text{Mg}_6\text{Fe(III)}_2(\text{OH})_{16}\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ ) – pyroaurite ( $\text{Mg}_6\text{Fe(III)}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ ) group.

640 A carbonate-bearing LDH phase was also detected by FTIR in microbialites from La  
641 Preciosa, Atexcac, La Alberca de Los Espinos and Pátzcuaro. However, XAS and electron  
642 microscopy analyses suggested that this phase was not a significant carrier of Fe in these  
643 microbialites, either because this phase was hydrotalcite *sensu stricto*, i.e. it contained Al(III)  
644 instead of Fe(III) as a trivalent cation and/or because iowaite/pyroaurite was rare compared to  
645 other Fe-phases.

646 Iowaite was first described in Precambrian serpentinites (Kohls and Roda, 1967).  
647 Nonetheless, this alteration phase postdates the formation and its age is not known. Iowaite  
648 and pyroaurite are rare minerals but they have been found in abundance in ultramafic deposits  
649 (e.g., Kohls and Rodda, 1967; Frost and Erickson, 2004; Bach et al., 2004; Turvey et al.,  
650 2017). For example, pyroaurite has been detected as one of the weathering byproducts of  
651 serpentinite following infiltration of alkaline ( $\text{pH} > 8$ ) groundwater rich in  $\text{Mg}^{2+}$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$   
652 and  $\text{Cl}^-$  (Taylor et al., 1991; Milodowski et al., 2009; Stamatakis and Mitsis, 2013). Pyroaurite  
653 is supposed to be late-stage alteration phase forming under oxidizing conditions (Bach et al.,  
654 2004). However, based on laboratory experiments, McCollom et al. (2016) suggested that

655 iowaite may precipitate under reducing conditions in some cases. Interestingly, the same  
656 mineral assemblage as that observed in Alchichica microbialites, i.e. pyroaurite and/or iowaite  
657 together with hydromagnesite, has been classically detected in carbonation products of the  
658 ultramafic tailings of the Clinton Creek asbestos mine (Yukon, Canada), the Mount Keith  
659 nickel mines (Western Australia) and the Woodsreef tailings (New South Wales, Australia)  
660 (Wilson et al., 2014; Power et al., 2014, McCutcheon et al., 2016; Turvey et al., 2017).  
661 Moreover, hydrotalcite, manasseite ( $\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$ ) and pyroaurite were  
662 observed in close association with hydromagnesite in heavily sheared serpentinized rocks in  
663 Nain Ophiolites (Iran) (Eslami et al., 2015). These authors argued that these Mg- and Fe-rich  
664 carbonates were formed by the percolation of Mg-rich meteoric water through serpentinites.  
665 Similarly, pyroaurite in association with hydromagnesite have also been observed as  
666 secondary alteration byproducts of serpentinites in the ophiolites from the Geraneia  
667 Mountains (Greece) due to groundwater circulation of alkaline fluids with a high Mg/Ca ratio  
668 (Stamatakis and Mitsis, 2013). Last, LDH (including iowaite) have been highlighted in a  
669 context of active serpentinization in hyperalkaline springs in Oman (Chavagnac et al., 2013).  
670 Nevertheless, the geodynamic environment in Alchichica is very different, indicating that the  
671 paragenesis hydromagnesite/pyroaurite-iowaite can be found in other environments than  
672 ultramafic massifs. Indeed, no ultramafic deposit has ever been reported in Alchichica or  
673 within the broader Serdan-Oriental Basin, where deposits are invariably basaltic, andesitic or  
674 rhyolitic (e.g., Siebe et al., 1995; Zimmer et al., 2010; López-Rojas and Carrasco-Nunez,  
675 2015). On the West shore of Lake Alchichica, where we observed the largest LDH contents in  
676 microbialites, the nearby basaltic scoria cone is the most likely Fe-rich source explaining the  
677 local high enrichment of microbialites in Fe. The high alkalinity of Lake Alchichica, possibly  
678 due to microbial activity, together with its low concentration in dissolved  $\text{H}_4\text{SiO}_4$ , possibly  
679 due to diatom activity, may explain why overall Lake Alchichica hydrochemistry looks

680 similar to that of fluids in weathered ultramafic settings and therefore why precipitating  
681 mineral phases are similar to those found in these environments.

682 In the context of basalt alteration, LDH phases can also form, but in this case the  
683 trivalent cation is generally Al(III). The mineral phase hydrotalcite  
684 ( $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ ) was observed in several experiments altering basalt glass in  
685 seawater (Larsen et al., 1991; Thomassin and Touray, 1982; Crovisier et al., 1983a;  
686 Abdelouas et al., 1994). For example, basaltic glass experimentally altered at 50°C for 20  
687 days was shown to be covered by a layered alteration shell, comprising hydrotalcite between  
688 an inner serpentine-type phyllosilicate layer and a saponite layer (Crovisier et al., 1983a).  
689 However, it was reported that pyroaurite formed at a lower temperature of 25°C after 240  
690 days (Crovisier et al., 1983b). The authors suggested that hydrotalcite formed at 50°C,  
691 because at this temperature Fe was poorly mobile and stayed at the base of the alteration shell,  
692 while at 25°C, Fe was more mobile and could react with dissolved Mg to precipitate  
693 pyroaurite from the solution. The absence of Al in Alchichica LDH phases suggests that they  
694 were not formed at the contact of basalts before transport to the microbialites but more likely  
695 formed from a solution similar to that prevailing in experiments by Crovisier et al. (1983b).

696 Whatever the geodynamic context, several modes of pyroaurite/iowaite formation  
697 have been suggested: these phases can form through a solid-state transformation of Fe(II)-  
698 bearing brucite by oxidation of Fe(II) to Fe(III) accompanied by the  $\text{Cl}^-$  and  $\text{CO}_3^{2-}$   
699 incorporation between brucite layers (Heling and Schwarz, 1992). Alternatively, Grguric et al.  
700 (2001) proposed that iowaite and pyroaurite formed by transformation of magnetite by  
701 reaction with alkaline and Cl-rich brines in the Mount Keith nickel deposits. Similarly, Wang  
702 et al. (2013) showed the transformation of lepidocrocite and akaganeite into iowaite after their  
703 exposure to the salt aerosols of Lake Qinghai. Last, Hansen and Koch (1995) showed that  
704 pyroaurite can precipitate from solution following Fe(II) oxidation in Mg-rich, carbonate-

705 and/or Cl<sup>-</sup>-containing solutions at pH>8.5. Here, we have no definitive evidence allowing us  
706 to discriminate between these three possibilities for the formation of pyroaurite/iowaite in  
707 Lake Alchichica. Nonetheless, in some cases, we observed that iowaite/pyroaurite was  
708 contained in biomorphs and was associated with organic matter down to the nm-scale (Figs.  
709 11 and 13), suggesting that it may have precipitated from solution in contact with  
710 microorganisms. Metagenomic studies of Lake Alchichica microbialites did not evidence 16S  
711 rDNA gene sequences indicative of classically known Fe-cycling bacteria, i.e., dissimilatory  
712 Fe-reducing bacteria or Fe-oxidizing bacteria (Saghaï et al., 2015 and 2016). However, these  
713 studies have shown that microbialites are associated with a large proportion of photosynthetic  
714 microorganisms that need Fe as a nutrient. Interestingly, there were significant differences in  
715 the local diversity of photosynthetic eukaryotes associated with North vs West microbialites.  
716 While diatoms dominated the eukaryotic fraction of a microbialite sample from the seepage-  
717 influenced West shore of Lake Alchichica, they were marginal in North shore microbialites,  
718 where eukaryotes were scarce and dominated by green algae (Saghaï et al., 2015 and 2016).  
719 In our study, the microbialite sample from the West shore of Lake Alchichica showed a  
720 higher Si concentration ( $1.02 \pm 0.05$  wt.%) compared to the microbialite from the North shore  
721 ( $0.65 \pm 0.03$  wt.%) (Table 2) and was characterized by large areas of Si associated with Fe  
722 (Fig. 12). This Si likely came from the groundwater seepage, which has been shown to be  
723 more Si-rich (between 13 and 230 times higher) than the Lake Alchichica water (Table 1;,  
724 Armienta et al., 2008; Kaźmierczak et al., 2011; Sigala et al., 2017). Future studies  
725 documenting the relative contribution of hydrothermalism/underground water to the  
726 hydrological budget of the lake will be interesting to address this point. The existence of local  
727 seepage rich in H<sub>4</sub>SiO<sub>4</sub> on the West shore is also consistent with the local proliferation of  
728 diatoms. In turn, diatom abundance implies the increased in situ availability of Si in  
729 microbialites from frustule dissolution. Therefore, in addition to the local variation of water

730 chemistry, the differential composition of microbial communities could also explain, at a  
731 smaller scale, the different type of minerals observed within microbialites. Microbes could  
732 play an important role in the precipitation of Fe-bearing phases by influencing particular  
733 concentration of ions (such as Fe or Si). Furthermore, the patchy distribution of Fe in  
734 microbialites suggests that Fe-rich conditions might be locally and temporally limited.  
735 Finding living microbialites mineralizing under Fe-rich conditions would be useful in order to  
736 better understand the potential interactions existing between microorganisms and Fe, their  
737 involvement in Fe-rich phase formation and subsequent transformation.

738 Overall, we suggest the following scenario similar to that proposed by Taylor et al.  
739 (1991) for the formation of pyroaurite associated with the weathering of partially  
740 serpentinised harzburgite in Oman (Fig. 17): (1) basalts around Lake Alchichica, outcropping  
741 mostly on the West shore of the lake, were altered by the circulation of groundwater anoxic  
742 fluids. Fe(II) but little Al and Si were released into these fluids. (2) When these fluids came  
743 into contact with Lake Alchichica water, Fe(II) became oxidized in a  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$ ,  $\text{CO}_3^{2-}$  and  
744  $\text{O}_2$ -rich solution as well as at high pH (~9) and high alkalinity (~40 mM), favoring  
745 pyroaurite/iowaite precipitation. Alternatively, Fe(II) may oxidize and be sequestered as Fe-  
746 oxyhydroxides first before secondary transformation into pyroaurite/iowaite following  
747 prolonged contact with Lake Alchichica water. Noteworthy, Fe-oxyhydroxides phases such as  
748 ferrihydrite have a slightly higher solubility at pH=9 than at pH=7 (Stefánsson, 2007). In  
749 addition, the presence of organic molecules may also increase the apparent solubility of Fe by  
750 complexation (Kuma et al., 1996), making Fe available for pyroaurite precipitation. Overall,  
751 the high Fe content in the microbialites and the presence of iowaite/pyroaurite trace  
752 groundwater input to the formation of microbialites.

753

#### 754 **4.3. LDH vs silicates**

755 While iowaite/pyroaurite were major carriers of Fe in Alchichica microbialites, these  
756 phases were not observed in microbialites from other lakes. Poorly crystalline Fe-bearing talc-  
757 like phases were observed instead. An authigenic hydrated and poorly crystalline talc-like  
758 phase ( $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ ) similar to kerolite and/or stevensite was detected in Lake  
759 Atexcac by Zeyen et al. (2015). Lake Atexcac, Lake La Preciosa, Lake Patzcuaro and Lake  
760 La Alberca de Los Espinos were all shown to be supersaturated with regards to Mg-silicates  
761 (Zeyen et al., 2017), which supports the possibility that such a phase precipitates in these  
762 lakes. Moreover, it was shown by microscopy that this phase sometimes contains Fe in Lake  
763 Atexcac, in agreement with the possibility that Fe(II) substitutes for Mg(II) and Fe(III)  
764 substitutes for Mg(II) (with the loss of a proton) and/or Si in the structure of nanocrystalline  
765 2:1 trioctahedral phyllosilicates such as kerolite and/or stevensite (Forbes, 1969; Corona et  
766 al., 2015).

767 It is important to note that the majority of Fe was in the form of Fe(III) in all Mexican  
768 microbialites. Fe may have been incorporated as Fe(II) in kerolite and/or stevensite before  
769 later solid-state oxidation at the contact with oxic water. This is consistent with the fact that  
770 EXAFS results on our model compounds suggest that the nano-Fe(III):talc component  
771 identified in the XANES spectrum of the Preciosa05-2012, AlbEsp2014-01, ATX-2C1-2012  
772 and Patz2014-02 microbialite samples can be interpreted as a byproduct of the oxidation of a  
773 nano-Fe(II)-talc component (Fig. SI-5). In the present study, we extend the record of such Fe-  
774 bearing talc phases to Lake La Alberca de Los Espinos and Lake Pátzcuaro. Following what  
775 was observed in Lake Alchichica, we proposed that Fe-enrichments may also be due to  
776 seepage in these volcanic lakes bringing Fe(II)-rich fluids to oxic water.

777 The reason why Fe was incorporated into pyroaurite/iowaite in Lake Alchichica vs  
778 kerolite/stevensite in other lakes, despite similar total Fe contents, might be related to the  
779 differences in chemical conditions prevailing in these lakes. Although the formation of

780 pyroaurite/hydrotalcite may require relatively higher pH than a silicate phase (e.g., Besson et  
781 al., 1974; Miyata and Okada, 1977; Crovisier et al., 1983b), this may not be a major  
782 parameter here since all studied lakes had similar pH values 8.5-9 (Zeyen et al., 2017). In  
783 contrast,  $\text{H}_4\text{SiO}_4$  concentrations were much lower in Lake Alchichica ( $[\text{H}_4\text{SiO}_4]= 0.017 \text{ mM}$ ;  
784 Kaźmierczak et al., 2011) compared to the other lakes which showed orthosilicic acid  
785 concentrations higher than 0.37 mM and up to 1.0 mM in Lake Atexcac (Zeyen et al., 2015 &  
786 2017). Chavagnac et al. (2013) argued that the chemical composition of the solution,  
787 specifically its  $\text{H}_4\text{SiO}_4$  concentration, is of essential importance in controlling the type of clay  
788 (cationic or anionic) formed. These authors detected LDH, including iowaite, in a springwater  
789 with a low  $\text{H}_4\text{SiO}_4$  content ( $<10 \mu\text{M}$ ) and a high pH (12). Interestingly, previous experimental  
790 studies of basaltic glass alteration have shown that hydrotalcite can transform into an Al-  
791 bearing serpentine and/or a smectite-like Fe-Mg-rich phase following reaction of the  
792 hydrotalcite precursor with orthosilicic acid accumulating at an increasing concentration in  
793 the solution (Thomassin and Touray, 1982; Crovisier et al., 1983a; Abdelouas et al., 1994).  
794 This hydrotalcite to silicate transformation has been suggested to occur through  
795 dissolution/precipitation in the presence of dissolved orthosilicic acid (Besson et al. 1974).  
796 Overall, LDH may form and stay preserved in Lake Alchichica because of the low  $[\text{H}_4\text{SiO}_4]$   
797 prevailing in this lake, while in other lakes, Fe-bearing kerolite or smectite phases form from  
798 the transformation of a transient iowaite/pyroaurite phase or direct precipitation. Future  
799 synthesis experiments will be necessary to better constrain chemical parameters (e.g.,  
800  $[\text{H}_4\text{SiO}_4]$ , alkalinity) favoring silicates versus LDH-like phases within microbialites.

801

802

## 5. CONCLUSION

803

804 Microbialites from Mexican alkaline crater lakes sometimes contain high Fe contents.

805 A large part of Fe is in the form of Fe(III). Part of Fe is mineralized in authigenic phases, i.e.  
806 iowaite/pyroaurite in Lake Alchichica and Fe-bearing kerolite and/or stevensite in lakes La  
807 Preciosa, Atexcac, Pátzcuaro and La Alberca de Los Espinos. These Fe-bearing phases are  
808 distributed along discrete thin laminae as well as large Fe-rich areas within microbialites.

809 The concentration of orthosilicic acid in the lakes seems to be a major parameter  
810 controlling the nature of the Fe-bearing phases that form. To our knowledge, layered double  
811 hydroxide (LDH) phases such as iowaite/pyroaurite phases have never been reported before in  
812 ancient or modern microbialites. This might be due to 1) the specific chemical conditions  
813 required for their formation, e.g. high alkalinity,  $[\text{CO}_3^{2-}]$ , pH,  $[\text{Cl}^-]$  and  $[\text{Mg}^{2+}]$  combined with  
814 low  $[\text{H}_4\text{SiO}_4]$ ; 2) the difficulty in detecting and characterizing these phases, especially when  
815 there are in low abundance; 3) the reactivity of these phases to silica, leading to potentially  
816 poor preservation in the geological record; 4) the presence of specific microbial communities  
817 locally modifying ion concentrations and pH.

818 While the Fe-bearing phases in modern microbialites may carry some information on  
819 their formation conditions, their fate in the geological record remains unknown. In these  
820 Mexican lakes, the LDH phases appear to sometimes be finely associated with organic matter.  
821 How their formation and reactivity interfere with microbial communities populating the  
822 surface of these microbialites and to which extent these phases are implicated in the  
823 fossilization processes of microorganisms will deserve further attention. Furthermore, the  
824 precise range of geochemical conditions allowing pyroaurite-iowaite formation and the  
825 stability of LDH through geological time will need to be determine in the future. To our  
826 knowledge, no study exists on the fate and transformation of LDH over geological time. We  
827 postulate that aging not involving fluids may not modify drastically the mineralogy of these  
828 phases. However, late circulations of  $\text{H}_4\text{SiO}_4$ -rich fluids may transform LDH into  
829 phyllosilicates as shown by several studies (Crovisier, 1983a, Ford and Spark, 2000). If these

830 transformations keep textures intact, the present study offers textural examples of what should  
831 be looked for as remnants of LDH within ancient microbialites. In any case, the present study  
832 highlights the diversity of the mineral phases bearing Fe in modern environments. This calls  
833 for a careful reappraisal of the primary Fe-bearing phases in ancient microbialites so that  
834 meaningful paleoenvironmental interpretations can be retrieved from e.g. Fe isotope  
835 measurements.

836

837

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1150

## FIGURE CAPTIONS

1151

1152

### 1153 **Figure 1.**

1154 XANES spectra at the Fe K-edge of AL2014-15, AL66 and AL13 microbialites from Lake  
1155 Alchichica. (a) Spectra of references (goethite, ferrihydrite, hydrotalcite, illite and nano-  
1156 Fe(II):talc) are shown in colors. Spectra of the microbialites (black lines) are superimposed on  
1157 fits (red lines) obtained by LC-LSF analysis. (b) Proportion of the fitting components:  
1158 Fe(III):hydrotalcite as a proxy for pyroaurite/iowaite, goethite and ferrihydrite as proxies for  
1159 Fe (oxyhydr)oxides, nano-Fe(II): and nano-Fe(III):talc as proxies for nanocrystalline 2:1  
1160 trioctahedral phyllosilicates, Fe(III)-bearing illite as proxy for 2:1 dioctahedral phyllosilicates.

1161

### 1162 **Figure 2.**

1163 Powder X-ray diffraction patterns of Alchichica microbialite samples. (a) AL2014-15, AL66  
1164 and AL13 microbialite samples. Aragonite (A), hydromagnesite (H) and layered double  
1165 hydroxide (LDH) were detected. (b-c) Close-ups on the LDH peaks at 7.59 Å (13.4° 2 $\Theta$ ) and  
1166 3.79 Å (27.3° 2 $\Theta$ ) observed in the pattern of AL2014-15, outlined by red rectangles.

1167

### 1168 **Figure 3.**

1169 FTIR analyses of Alchichica microbialites. (a) FTIR spectra of AL2014-15, AL66 and AL13  
1170 between 400 and 1800 cm<sup>-1</sup>. Labels are as follows: aragonite (A), hydromagnesite (H) and  
1171 layered double hydroxide (LDH). (b) FTIR spectra from 3000 to 4000 cm<sup>-1</sup>. (c) Close-up of  
1172 the band at 1384.5 cm<sup>-1</sup> for AL66 and AL13, interpreted as a carbonate asymmetric stretching  
1173 mode ( $\nu_3\text{CO}_3$ ) in LDH or aragonite.

1174

### 1175 **Figure 4.**

1176 XANES spectra at the Fe K-edge of microbialites from La Preciosa, Atexcac, La Alberca de  
1177 Los Espinos and Pátzcuaro. (a). Spectra of the microbialites (black lines) are superimposed on  
1178 fits (red lines) obtained by LC-LSF analysis (b) Proportion of the fitting components: nano-  
1179 Fe(II):talc and nano-Fe(III):talc as proxies for nanocrystalline 2:1 trioctahedral phyllosilicate,  
1180 and Fe(III):illite as proxy for 2:1 dioctahedral phyllosilicate.

1181

1182 **Figure 5.**

1183 Powder X-ray diffraction patterns of microbialites from Lakes La Preciosa, Atexcac, La  
1184 Alberca de Los Espinos and Pátzcuaro. Aragonite (A), calcite (C), monohydrocalcite (MC),  
1185 hydromagnesite (H) and kerolite/stevensite (K/S) were detected.

1186

1187 **Figure 6.**

1188 FTIR spectra of microbialites from Lakes La Preciosa, Atexcac, La Alberca de Los Espinos  
1189 and Pátzcuaro. (a) Spectra from 400 to 1800  $\text{cm}^{-1}$  (b) Spectra from 3000 to 4000  $\text{cm}^{-1}$ . (c)  
1190 Close-up of the spectral area between 1372 and 1395  $\text{cm}^{-1}$ . The peak at 1384.5  $\text{cm}^{-1}$  indicated  
1191 by a dashed line was assigned to carbonate asymmetric stretching in LDH and/or aragonite.  
1192 Peak labels are as follows: aragonite (A); calcite (C); monohydrocalcite (MC);  
1193 hydromagnesite (H); layered double hydroxide (LDH) and kerolite/stevensite (K/S).

1194

1195 **Figure 7.**

1196 Light microscopy observations of Fe spatial distribution in the microbialites. (a-b) Plane- and  
1197 cross-polarized light photomicrographs of AL2014-15 sample showing dense masses and Fe-  
1198 rich fine discrete laminae (arrows). (c-d) Plane- and cross-polarized light photomicrographs  
1199 of AL13 showing layers of a brownish Fe-bearing phase between aragonite (A) and  
1200 hydromagnesite (H) as well within hydromagnesite (white dashed arrow). (e-f) Plane- and

1201 cross-polarized light photomicrographs of ATX-2C1-2012 showing a beige Fe-bearing phase  
1202 forming a ~20 to 100  $\mu\text{m}$  thick layer at the surface of the microbialite. This phase shows total  
1203 extinction under cross-polarized light. **(g-h)** Plane- and cross-polarized light  
1204 photomicrographs of Patz2014-02 showing brown Fe-bearing laminae measuring ~50 to 150  
1205  $\mu\text{m}$  in thickness (white arrow) and showing extinction under cross polars. A darker Fe-rich  
1206 area is also observed (white dashed arrow).

1207

1208 **Figure 8.**

1209 Analysis of Fe distribution in AL66 by correlative electron/x-ray microscopy. **(a)** SEM image  
1210 acquired in the BSE (backscattered electron) mode. Labels are as follows: aragonite (A) and  
1211 hydromagnesite (H). **(b)**  $\mu$ -XRF mapping of Fe (red) and Ca (green) in AL66 in the area  
1212 outlined by a dashed rectangle in (a). **(c)** SEM image in backscattered electron mode of the  
1213 area outlined by a rectangle in (b). Resin appears on the left. Aragonite (A) and  
1214 hydromagnesite (H) are separated by a Fe-rich phase showing a darker contrast compared to  
1215 aragonite due to the presence of lighter element(s). The red rectangle indicates the localization  
1216 of the FIB section cutting across a Fe-rich lamina. **(d)** Overlay of the Fe (red), Mg (blue) and  
1217 Ca (green) SEM-EDXS maps. The Fe-rich phase appears in pink (i.e. a combination of Fe and  
1218 Mg).

1219

1220 **Figure 9.**

1221 Transmission electron microscopy analyses of a FIB foil cut across aragonite and the Fe-rich  
1222 phase in AL66, outlined in Fig. 8c. **(a)** STEM-HAADF image of the FIB foil. **(b)** STEM-  
1223 EDXS map of Fe (red), Mg (blue) and Ca (green) of the same area. The Fe-rich phase appears  
1224 in pink (i.e. a combination of Fe and Mg). **(c)** Selected area electron diffraction (SAED)  
1225 pattern of the circled area #1 on Fig. 9b. Diffuse diffraction spots and arcs were indexed as

1226 lattice planes of LDH and aragonite (A), as indicated on the pattern. **(d)** SAED pattern of  
1227 aragonite (area #2 as indicated on Fig. 9b). Radial intensity profile is shown in Fig. SI-7. **(e)**  
1228 EDXS spectra of the circled areas noted (1) and (2) on Fig. 9b, corresponding to the Fe-rich  
1229 area (composed by Fe, Mg and Cl) and aragonite, respectively (Cu peaks were emitted by the  
1230 Cu grid to which the FIB foil was attached).

1231

1232 **Figure 10.**

1233 Analysis of Fe distribution in AL13 by correlative electron/x-ray microscopy. **(a)** SEM  
1234 backscattered electron image. **(b)**  $\mu$ -XRF mapping of the area outlined by a rectangle in Fig.  
1235 10a. Fe and Ca are shown in red and green, respectively. **(c)** SEM backscattered electron  
1236 image of the area outlined by a rectangle in Fig. 10b. The red rectangle indicates the  
1237 localization of the FIB section cutting across a Fe-rich lamina. **(d)** SEM-EDXS map of the  
1238 same area showing Fe, Mg and Ca in red, blue and green, respectively.

1239

1240 **Figure 11.**

1241 Transmission electron microscopy analyses of a FIB foil extracted from AL13 (see rectangle  
1242 in Fig. 10c). **(a-b)** STEM-HAADF images of the FIB foil. **(c)** STEM-EDXS mapping of the  
1243 area outlined by a dashed rectangle in Fig. 11a and showing two distinct mineral phases. Iron,  
1244 Ca and Mg are shown in red, green and blue, respectively. **(d)** EDXS spectrum of the area  
1245 outlined by a white circle in Fig. 11c. **(e)** SAED pattern of the same area circled in Fig. 11c.  
1246 **(f)** STXM Fe map of the FIB foil obtained by subtracting an image at 704 eV (below the Fe  
1247  $L_{2,3}$ -edges) from an image at 709.7 eV (above the Fe  $L_3$ -edge). **(g)** XANES spectrum at the  
1248 Fe  $L_{2,3}$ -edges extracted from the area outlined in Fig. 11f. **(h)** STXM map of two C-bearing  
1249 species observed in the area outlined by a dashed rectangle in Fig. 11a, and discriminated  
1250 based on their XANES spectra at the C K-edge. Aragonite appears in green, while LDH

1251 appears in red. (i) XANES spectrum at the C K-edge of the LDH, observed in red in Fig. 11h.

1252

1253 **Figure 12.**

1254 SEM analysis of the Fe distribution in AL2014-15. (a) SEM backscattered electron image.

1255 The red rectangle indicates the localization of the FIB section cutting across two circular

1256 objects. (b) SEM-EDXS map of the area outlined by a dashed rectangle in Fig. 12a. Fe, Ca

1257 and Mg are shown in red, green and blue, respectively. Aragonite (A) and hydromagnesite

1258 (H) are surrounding by large Fe- and Si-rich areas. (c) SEM-EDXS map of Si corresponding

1259 to the area outlined in Fig. 12a.

1260

1261 **Figure 13.**

1262 TEM analyses of a FIB foil extracted from AL2014-15 as outlined in Fig. 12a. (a) Bright-

1263 field TEM image showing an object with a circular cross-section. (b) STEM-HAADF image

1264 of the object showed in Fig. 13a. (c) EDXS spectra of areas #1 and # 2, outlined in Fig. 13b.

1265 (d) SAED pattern of area outlined in Fig. 13a corresponding to area #1: LDH viewed along

1266 the [1-1-1] zone axis. The  $d$ -spacings at 2.66 Å, 1.55 Å and 1.30 Å corresponded to LDH (-

1267 10-1), (-1-10) and (-20-2) lattice planes. (e) SAED pattern of area outlined in Fig. 13a

1268 corresponding to area #2: silico-ferric precipitate as synthesized by Decarreau et al. (1987)

1269 and/or ferrihydrite.  $D$ -spacings at 3.15, 2.36 and 1.49 Å are identified. (f) Bright-field TEM

1270 image of the second object with a circular cross-section. (g) Close-up of the fibrous layer

1271 surrounding the object structures as outlined by a dashed rectangle in Fig. 13f. (h) SAED

1272 pattern of area 3 circled in Fig. 13f: aragonite with  $d$ -spacings at 2.48, 1.87, 1.25, 1.12 Å.

1273

1274 **Figure 14.**

1275 SEM observations of Fe-bearing silicates in ATX-2C1-2012, AlbEsp2014-01 and Patz2014-

1276 02. **(a-b-c)** SEM backscattered electron images. **(d-e-f)** EDXS spectra of the areas outlined by  
1277 a circle in SEM images. Platinum (Pt) was used to sputter-coat AlbEsp2014-01.

1278

1279 **Figure 15.**

1280 SEM and TEM analyses of ATX-2C1-2012. **(a)** SEM backscattered electron image. **(b)** SEM-  
1281 EDXS map of the area outlined in **(a)**. Fe and Ca are shown in red and green, respectively. **(c)**  
1282 STEM-HAADF image of the FIB foil extracted from the area outlined by a red rectangle in  
1283 **(a)**. **(d)** Bright-field TEM image showing the smooth texture of the Fe-rich phase and the  
1284 micritic texture of aragonite. **(e)** SAED pattern of the Fe-rich phase, as outlined by a circle in  
1285 **(d)**. **(f)** STEM-HAADF close-up of the area outlined in **(d)**. **(g)** STEM-EDXS map of the  
1286 same area. Fe, Ca and Mg are shown in red, green and blue. **(h)** EDXS spectrum of the area  
1287 circled in **(d)** and corresponding to the Fe-rich phase.

1288

1289 **Figure 16.**

1290 STXM analyses of a FIB foil extracted from ATX-2C1-2012. **(a)** STXM Fe map obtained by  
1291 subtracting an image at 700 eV converted in optical density (below the Fe L<sub>2,3</sub>-edges) from an  
1292 OD-converted image taken at 710 eV. **(b)** XANES spectrum at the Fe L<sub>2,3</sub>-edges of the Fe-  
1293 rich area outlined by a white circle in **(a)**. **(c)** XANES spectrum at the C K-edge of the Fe-rich  
1294 area outlined by an orange circle in **(a)**.

1295

1296 **Figure 17.**

1297 Schematic diagram suggesting the origin of pyroaurite precipitation in Lake Alchichica. (1)  
1298 Basalt alteration by groundwater, releasing Fe(II) (2) Fast oxidation of Fe(II) at the contact  
1299 with lake water, rich in Cl<sup>-</sup>, Mg<sup>2+</sup>, and CO<sub>3</sub><sup>2-</sup> and showing a high pH resulting in  
1300 pyroaurite/iowaite precipitation (3).

**Table 1.**  
Summary of the main physical and geochemical parameters of the lakes

| Lakes                            | Predominant ions          | Conductivity (mS/cm) | pH  | Alk (mM) | Mg (mM) | Cl (mM) | H <sub>4</sub> SiO <sub>4</sub> (mM) | Ca (mM) | References                   |
|----------------------------------|---------------------------|----------------------|-----|----------|---------|---------|--------------------------------------|---------|------------------------------|
| Alchichica (North shore)         | Cl(+HCO <sub>3</sub> )-Na | 13.3                 | 8.8 | 30.9     | 17.8    | 87.3    | 0.015                                | 0.368   | Kázmierczak et al., 2011     |
| Alchichica (West shore)          | Bic(+Cl)-Na               | 2.1                  | 7.3 | 9.34     | 3.7     | 5.47    | 0.694                                | 1.670   | Kázmierczak et al., 2011     |
| La Preciosa (surface)            | Bic-Mg                    | 2.2                  | 8.6 | 14.4     | 8.23    | 9.31    | 0.50                                 | 0.349   | Armienta et al., 2008        |
| Atexcac (surface)                | Cl(+HCO <sub>3</sub> )-Na | 11.7                 | 8.2 | 28.3     | 23.1    | 96.6    | 0.95                                 | 1.070   | Kázmierczak et al., 2011     |
| Alberca de Los Espinos (surface) | Bic(+Cl)-Na               | 1.25                 | 8.7 | 7.64     | 2.55    | 4.77    | 0.87                                 | 0.920   | Our data; Zeyen et al., 2017 |
| Pátzcuaro (surface)              | Na-Bic                    | 0.98                 | 8.2 | 11.04    | 1.48    | 3.0     | 0.45                                 | 0.549   | Sigala et al., 2017          |

**Table 2.**

Bulk chemical composition of studied microbialites (in wt.%)

| Sample          | Fe          | Al          | K           | Ti          | Na          | P             | Mn            | Mg         | Si          | Ca         |
|-----------------|-------------|-------------|-------------|-------------|-------------|---------------|---------------|------------|-------------|------------|
| AL2014-15       | 2.24 ± 0.04 | 0.12 ± 0.02 | 0.07 ± 0.01 | < 0.01      | 0.46 ± 0.02 | 0.040 ± 0.004 | 0.010 ± 0.001 | 6.3 ± 0.1  | 1.02 ± 0.05 | 23.6 ± 0.5 |
| AL13            | 0.12 ± 0.01 | 0.22 ± 0.02 | 0.06 ± 0.01 | < 0.01      | 0.20 ± 0.03 | < 0.02        | < 0.0002      | 22.2 ± 0.4 | 0.65 ± 0.03 | 4.0 ± 0.1  |
| Preciosa05-2012 | 0.31 ± 0.02 | 0.63 ± 0.06 | 0.16 ± 0.02 | 0.03 ± 0.01 | 0.29 ± 0.04 | < 0.02        | 0.040 ± 0.004 | 7.0 ± 0.1  | 11.3 ± 0.1  | 19.0 ± 0.4 |
| ATX-2C1-2012    | 0.54 ± 0.03 | 0.29 ± 0.03 | 0.11 ± 0.01 | 0.02 ± 0.01 | 0.33 ± 0.05 | < 0.02        | 0.040 ± 0.004 | 12.8 ± 0.3 | 13.9 ± 0.1  | 9.1 ± 0.2  |
| AlbEsp2014-01   | 0.38 ± 0.02 | 0.06 ± 0.01 | 0.02 ± 0.01 | < 0.01      | 0.04 ± 0.01 | 0.27 ± 0.03   | 0.46 ± 0.02   | 3.5 ± 0.1  | 3.3 ± 0.2   | 28.7 ± 0.6 |
| Patz2014-02     | 0.62 ± 0.03 | 0.35 ± 0.04 | 0.04 ± 0.01 | 0.02 ± 0.01 | 0.09 ± 0.01 | 0.07 ± 0.01   | 0.120 ± 0.006 | 5.5 ± 0.1  | 6.99 ± 0.07 | 25.2 ± 0.5 |

**Table 3.**

Result of the best fits of the Fe K-edge XANES spectra of the microbialite samples, expressed as the relative proportion of the model compounds components. The quality of the LCF fits was estimated by a reduced chi-square parameter  $\chi^2_R = n / (n-p) \sum [\mu_{\text{exp}} - \mu_{\text{calc}}]^2$  where p is the number of fitting components and n is the number of independent parameters corresponding to the energy range divided by the natural width of the U LIII or Fe K levels reported by Krause and Oliver (1979). Figures between brackets indicate  $2\sigma$  confidence intervals ( $2 \times$  standard deviation).

| Sample          | goethite | 2L-ferrihydrate | Fe(III):hydrotalcite | nano-Fe(II):talc | nano-Fe(III):talc | Fe(III):illite | $\chi^2_R$ | Fe(III)/Fe <sub>tot</sub> |
|-----------------|----------|-----------------|----------------------|------------------|-------------------|----------------|------------|---------------------------|
| AL2014-15       | 47 (4)   | 24 (5)          | 29 (3)               | -                | -                 | -              | 0.0003     | 1.0                       |
| AL66            | -        | -               | 100 (1)              | -                | -                 | -              | 0.0047     | 1.0                       |
| AL13            | -        | -               | 43 (19)              | 33 (3)           | -                 | 24 (19)        | 0.0040     | 0.7                       |
| Preciosa05-2012 | -        | -               | -                    | 26 (3)           | 43(16)            | 31 (15)        | 0.0045     | 0.7                       |
| ATX-2C1-2012    | -        | -               | -                    | 22 (2)           | 51 (11)           | 27 (10)        | 0.0021     | 0.8                       |
| AlbEsp2014-01   | -        | -               | -                    | 9 (1)            | 48 (9)            | 43 (9)         | 0.0015     | 0.9                       |
| Patz2014-02     | -        | -               | -                    | 10(1)            | 47 (4)            | 43 (4)         | 0.0003     | 0.9                       |

1 **Table 4.**

2 Summary of the mineralogical composition of the microbialite samples analyzed in this study.

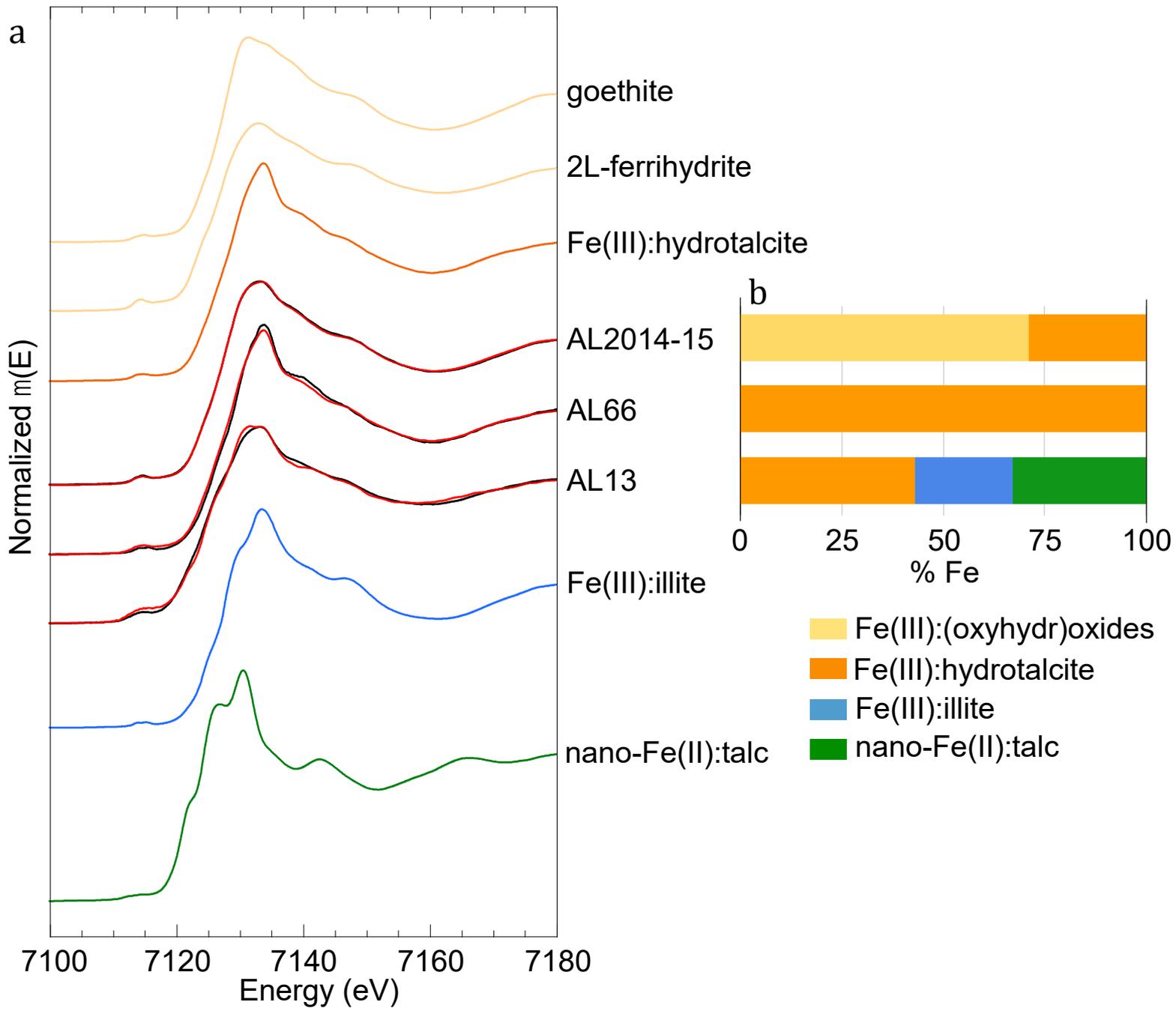
3 The identity of the Fe-bearing mineral phases is indicated.

4

| Sample          | Main minerals (DRX-FTIR)                                     | Authigenic Fe-bearing phase (XANES, DRX, FTIR, MEB, MET, SAED) |
|-----------------|--|--|
| AL2014-15       | aragonite– hydromagnesite – LDH                              | pyroaurite/iowaite – ferrihydrite – goethite                   |
| AL66            | hydromagnesite – aragonite                                   | pyroaurite/iowaite   |
| AL13            | hydromagnesite – aragonite                                   | pyroaurite/iowaite – dioctahedral 2:1 phyllosilicate           |
| Preciosa05-2012 | aragonite – kerolite/stevensite – calcite                    | kerolite/stevensite – dioctahedral 2:1 phyllosilicate          |
| ATX-2C1-2012    | kerolite/stevensite – aragonite – calcite – hydromagnesite   | kerolite/stevensite – dioctahedral 2:1 phyllosilicate          |
| AlbEsp2014-01   | calcite – monohydrocalcite – kerolite/stevensite             | kerolite/stevensite – dioctahedral 2:1 phyllosilicate          |
| Patz2014-02     | calcite – aragonite – monohydrocalcite – kerolite/stevensite | kerolite/stevensite – dioctahedral 2:1 phyllosilicate          |

5

Figure 1



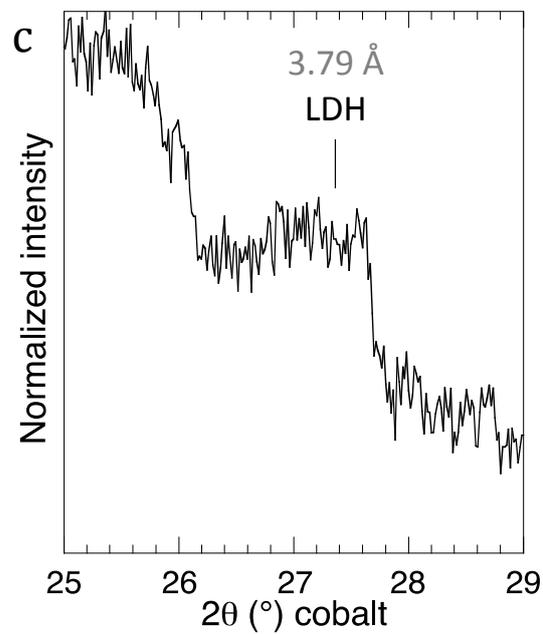
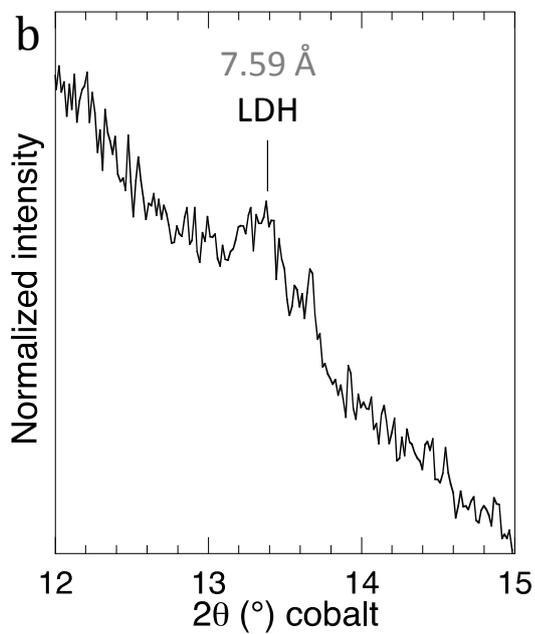
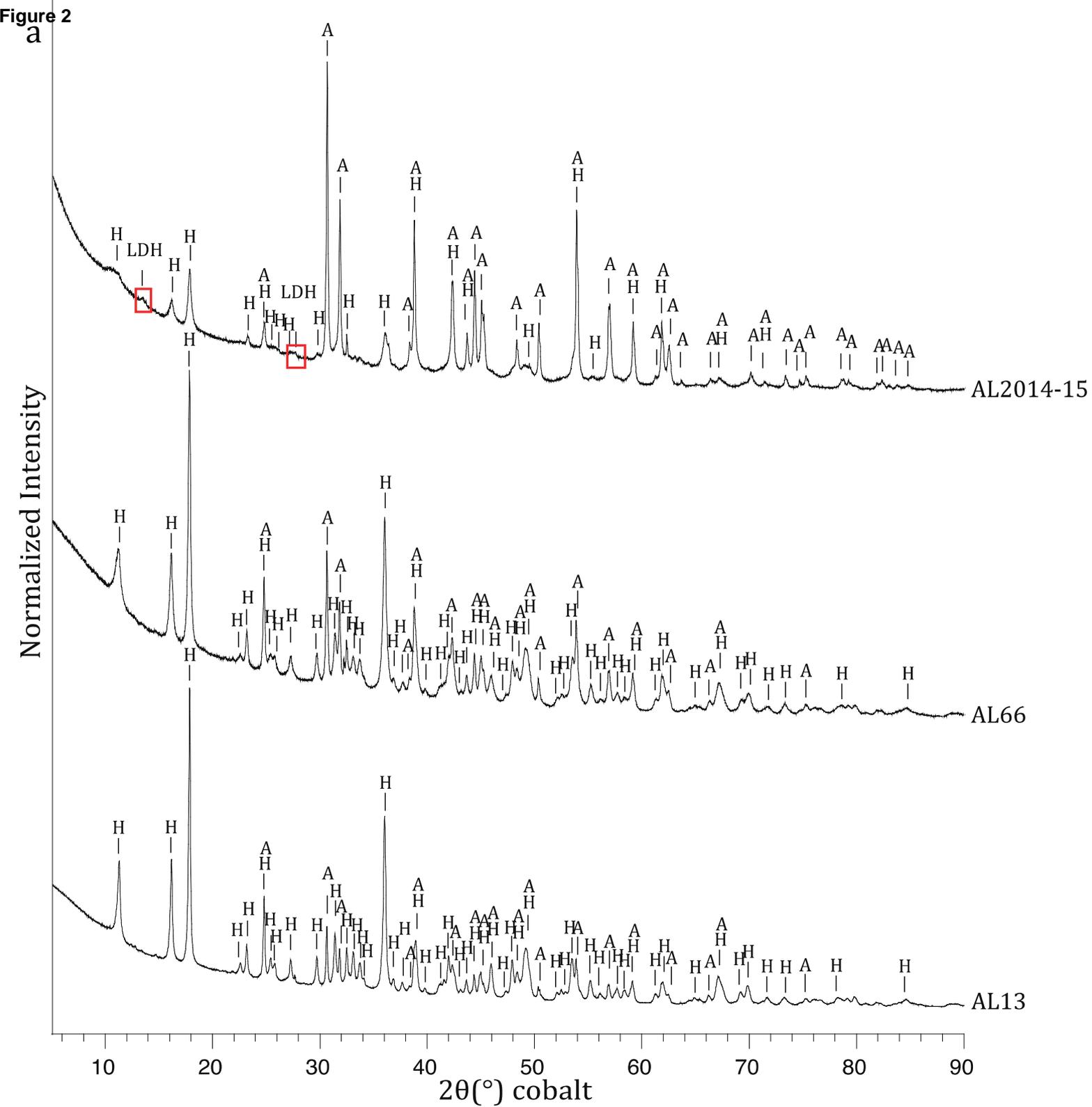


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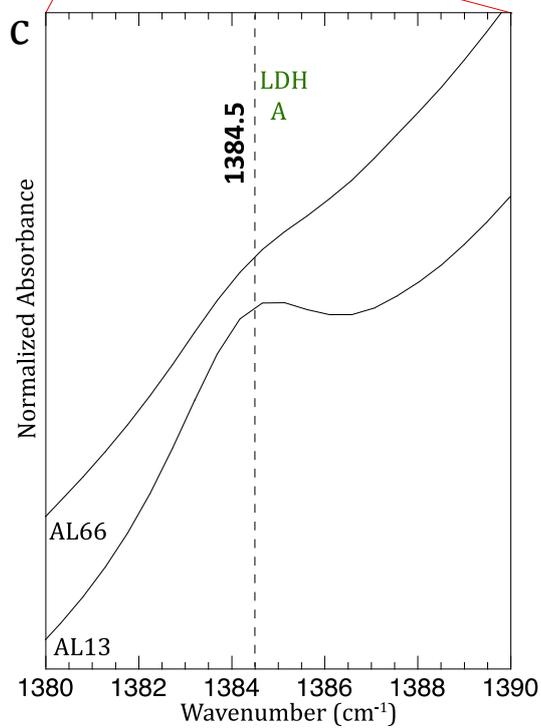
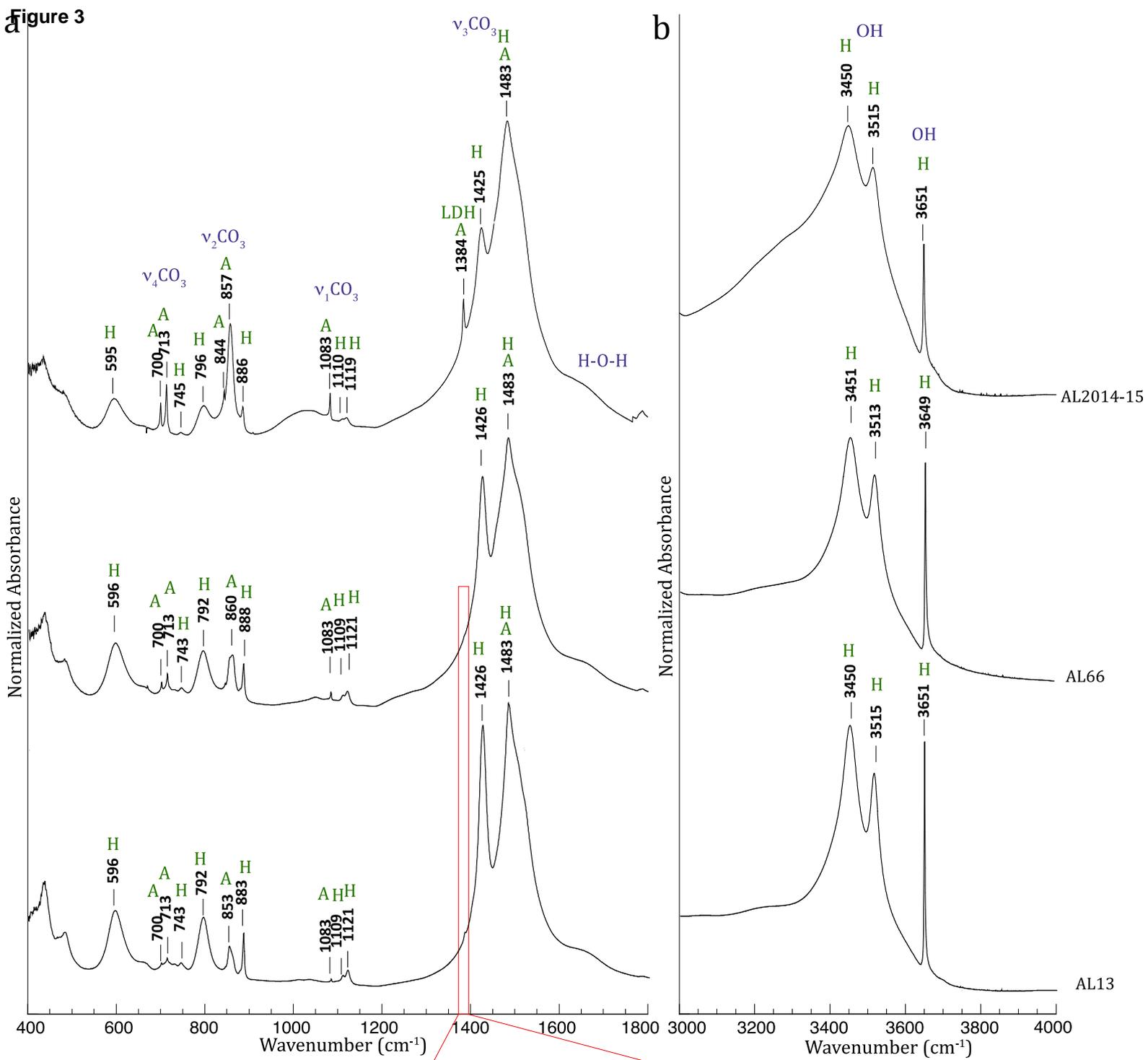


Figure 4

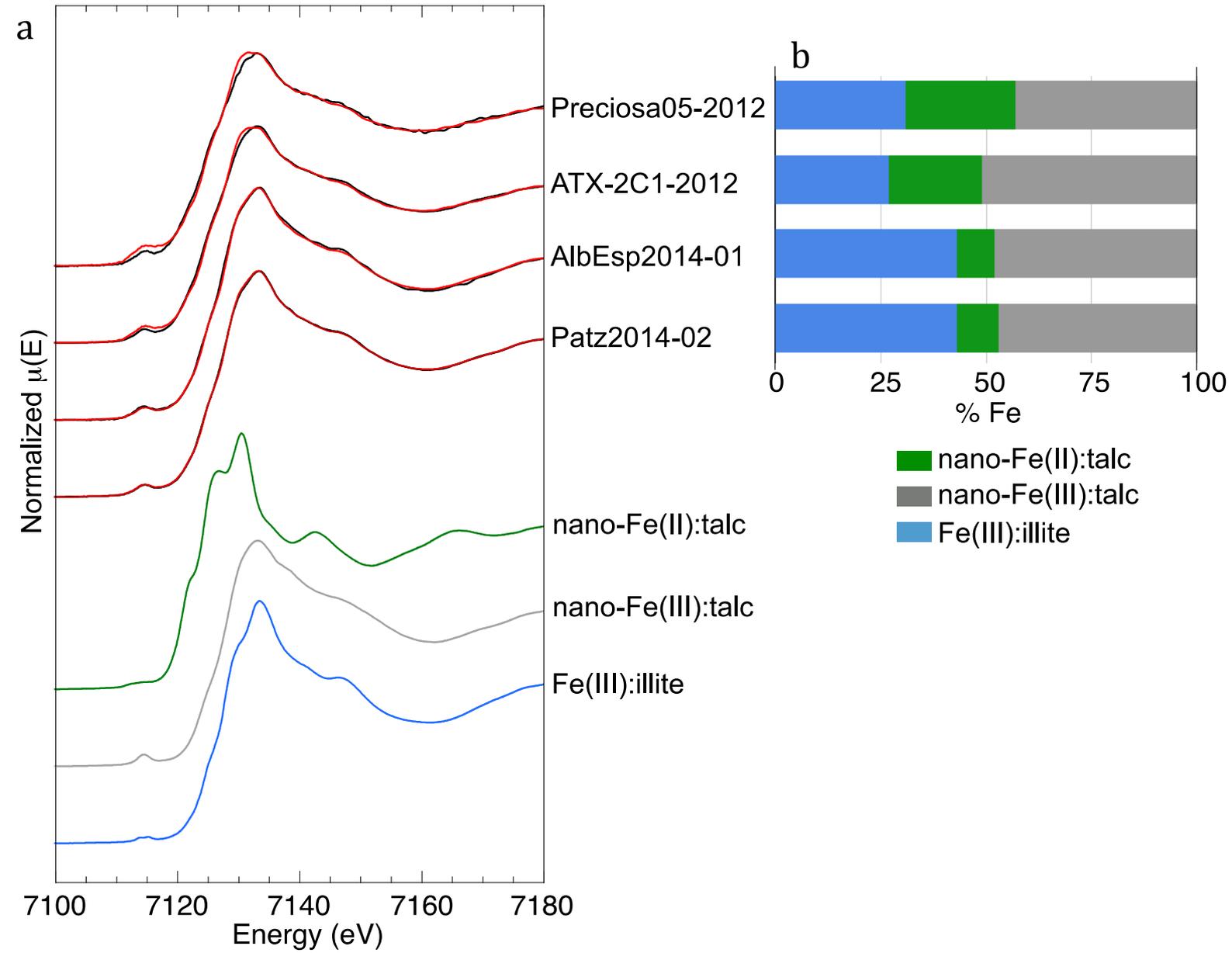


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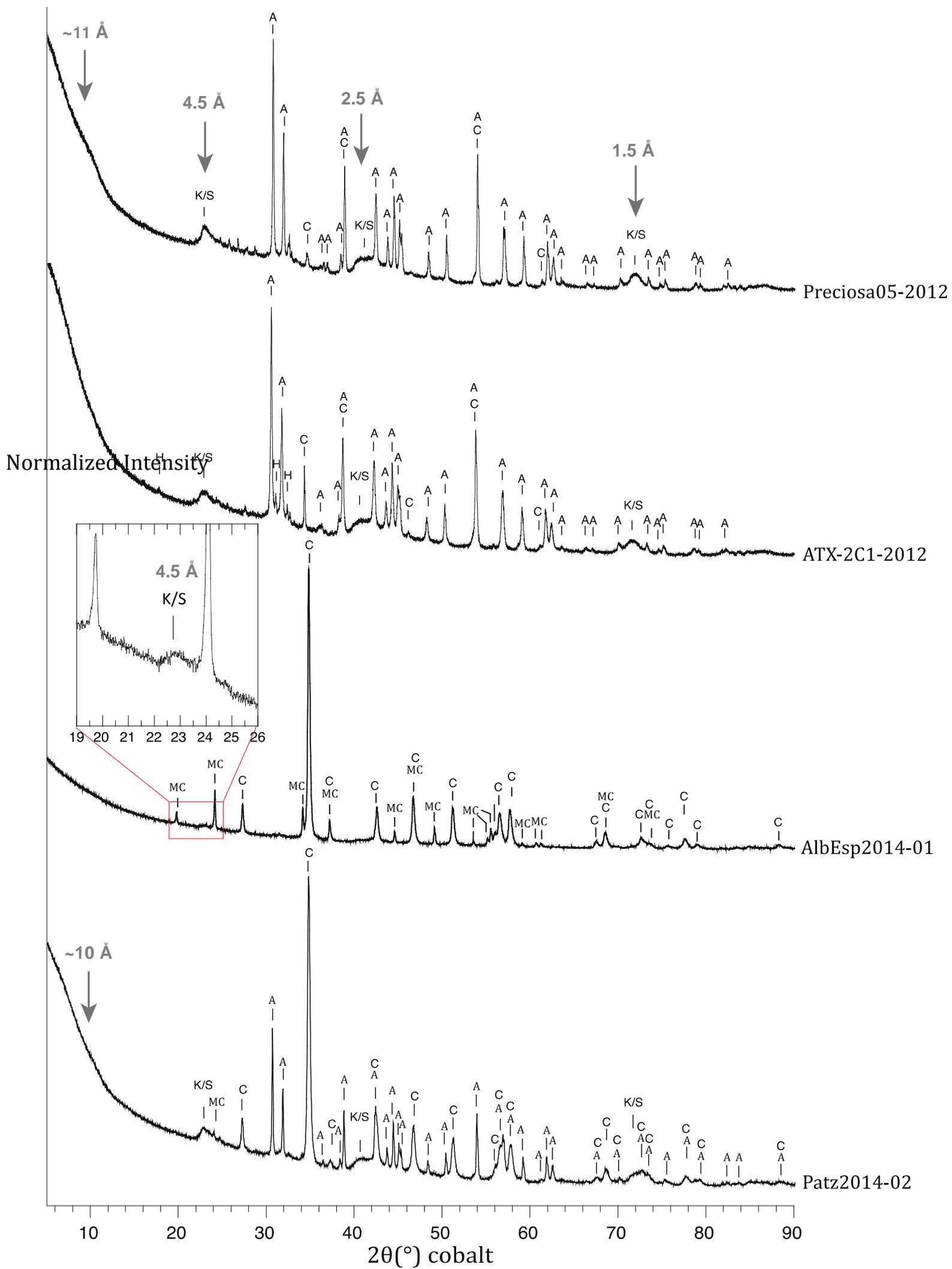


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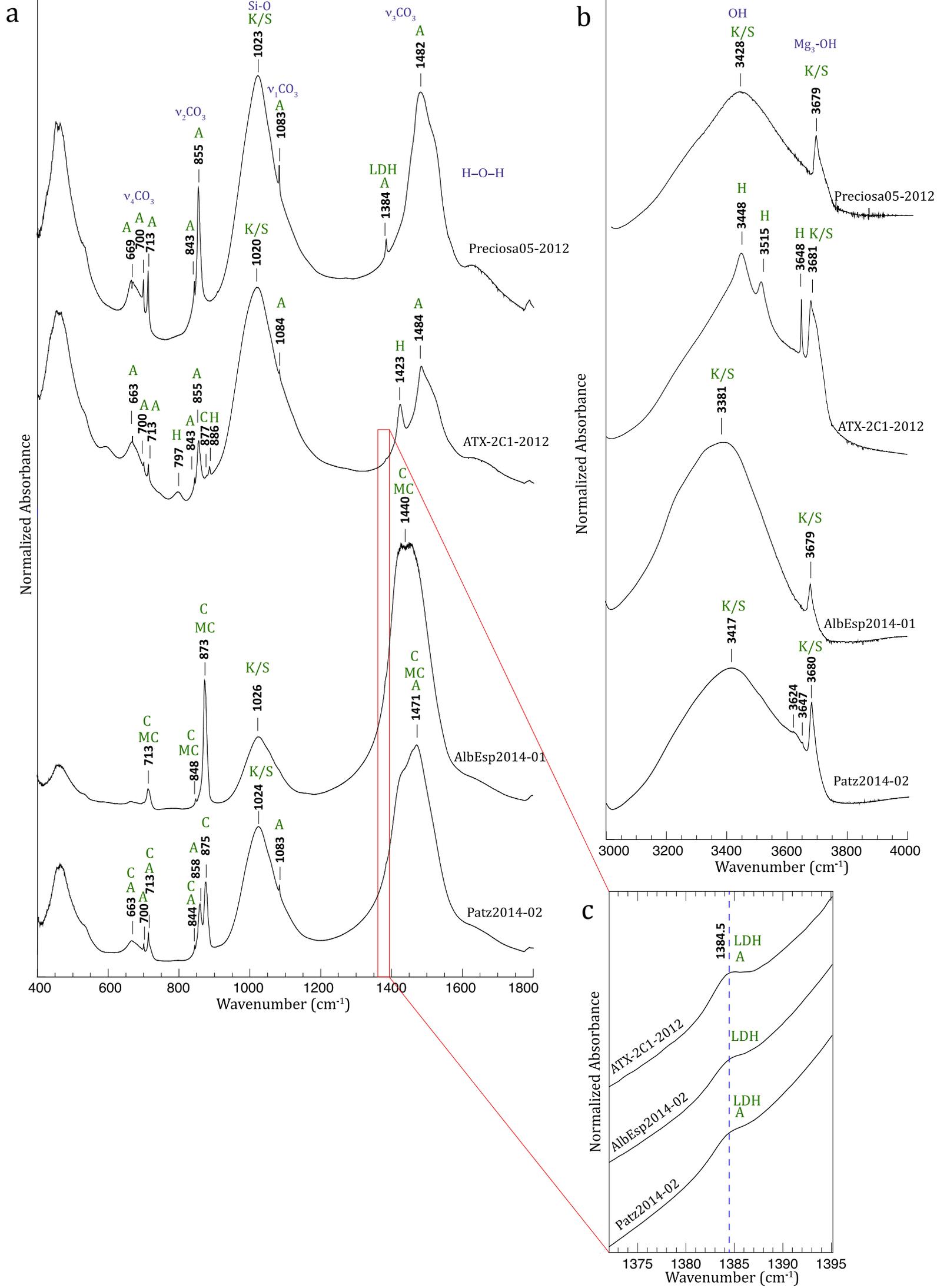


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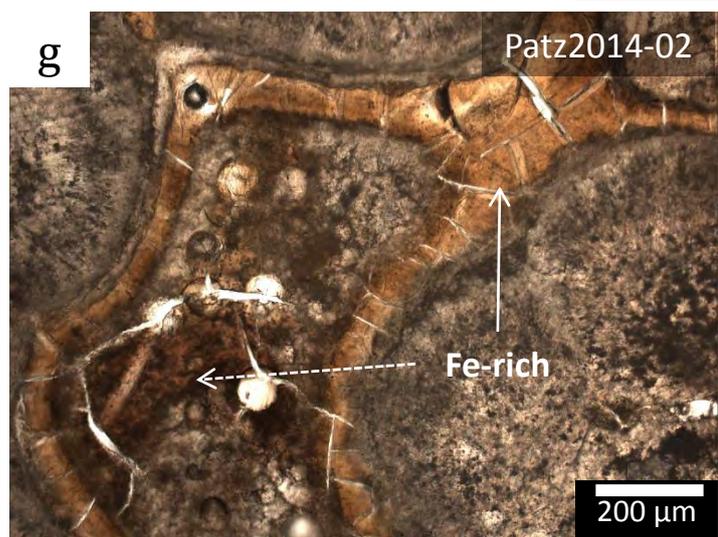
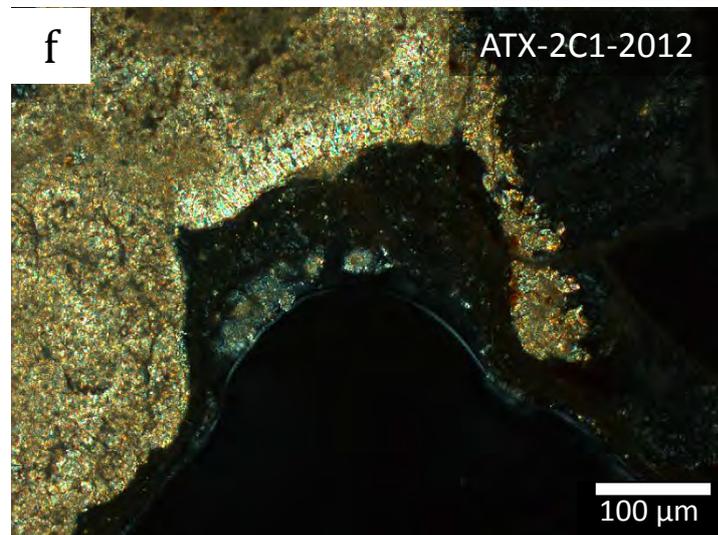
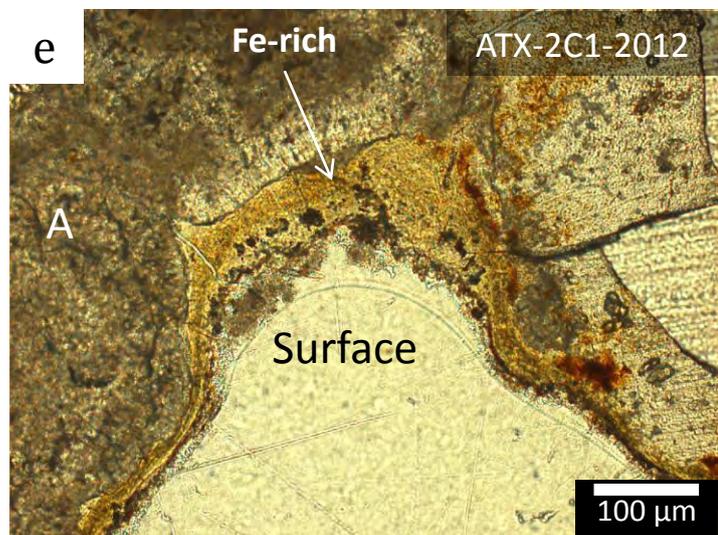
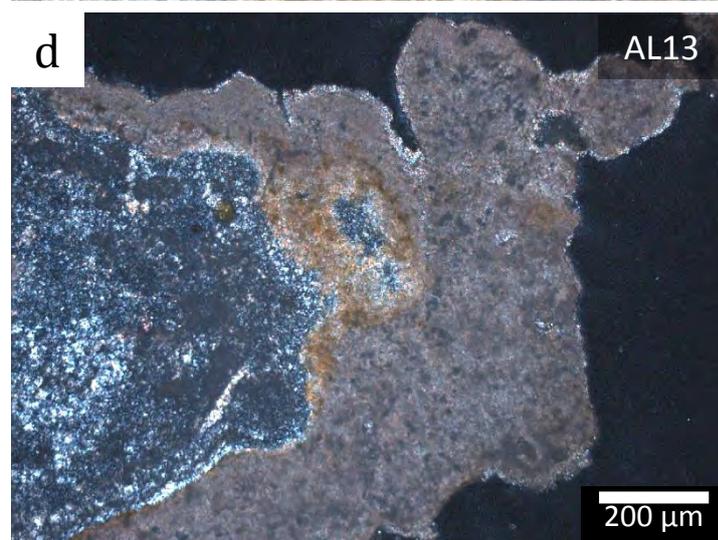
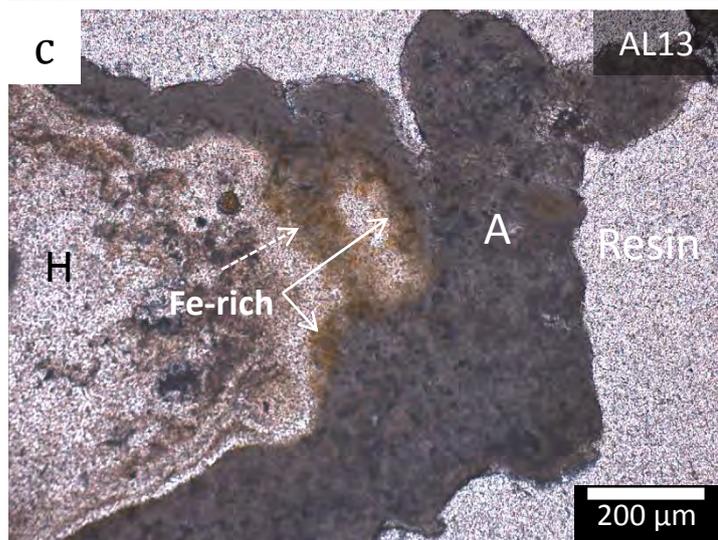
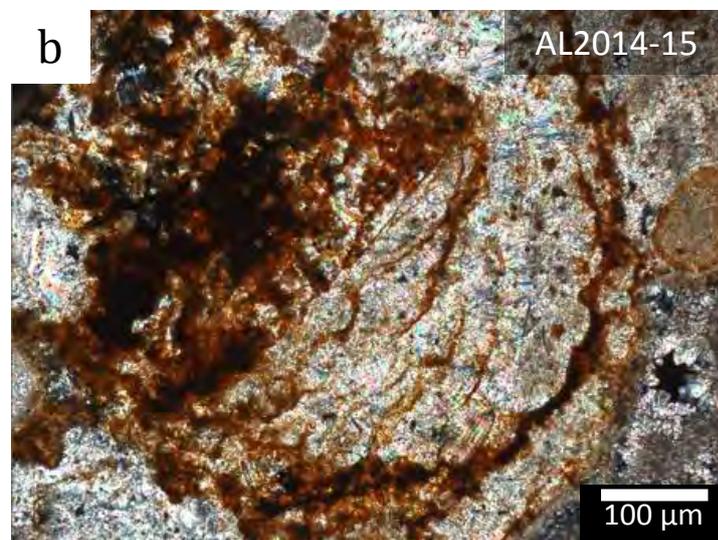
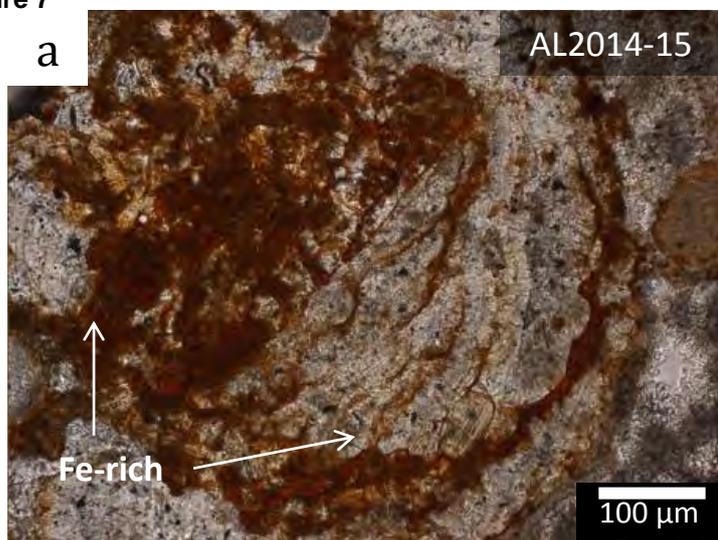


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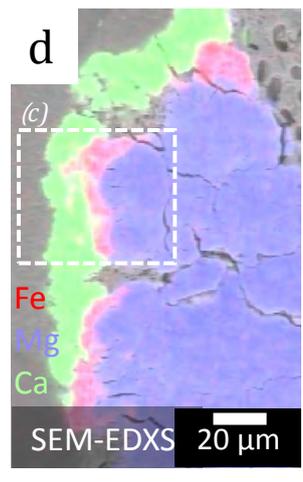
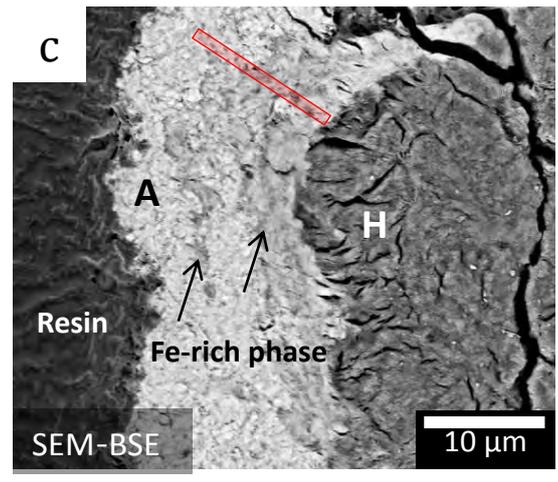
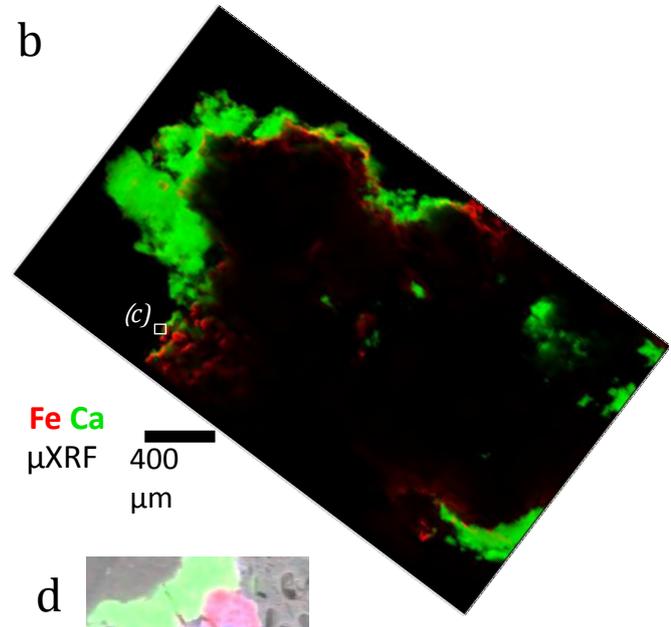
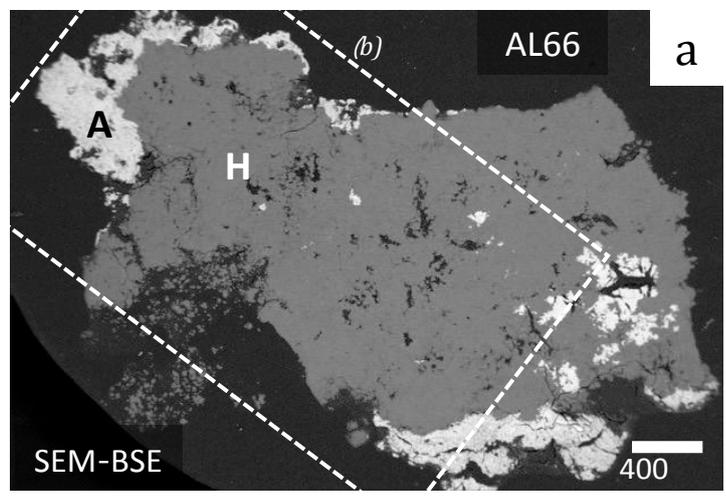


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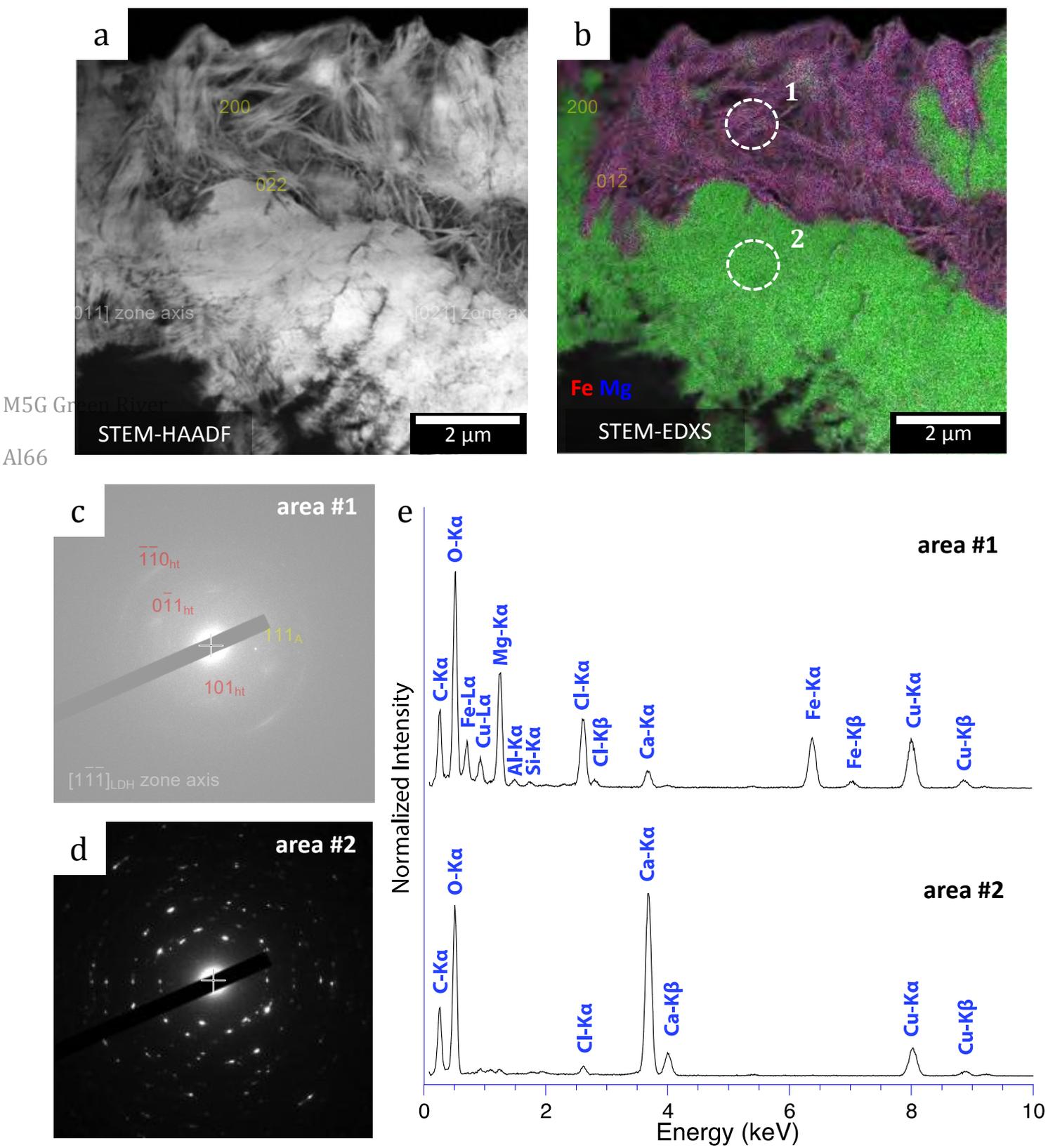


Figure 10

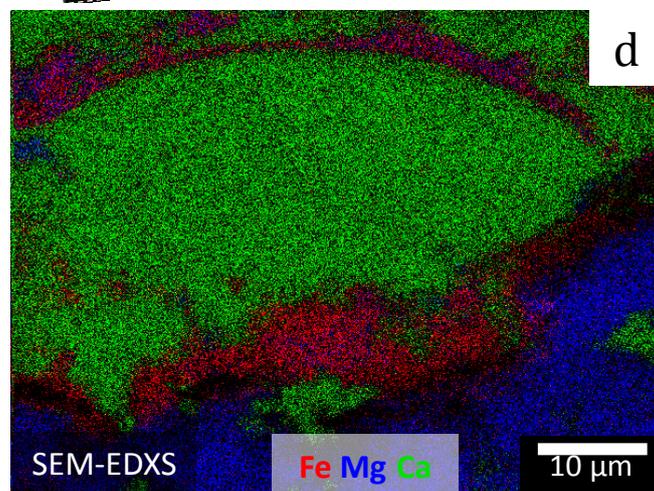
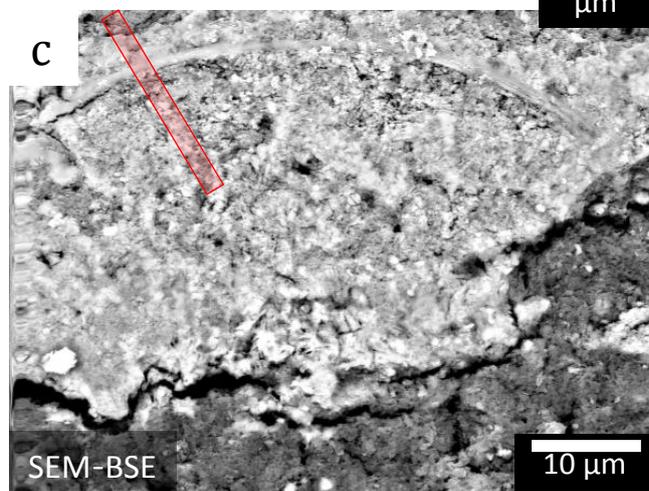
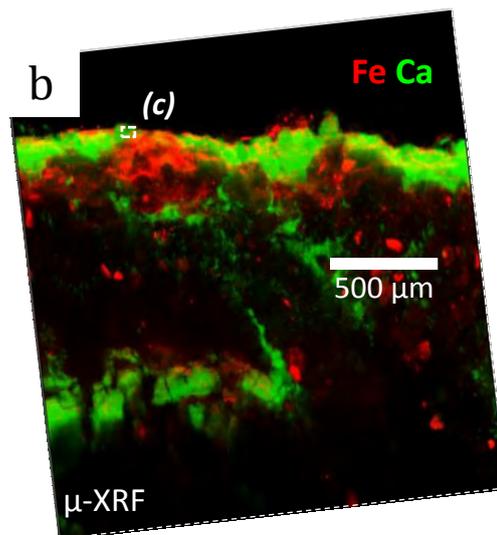
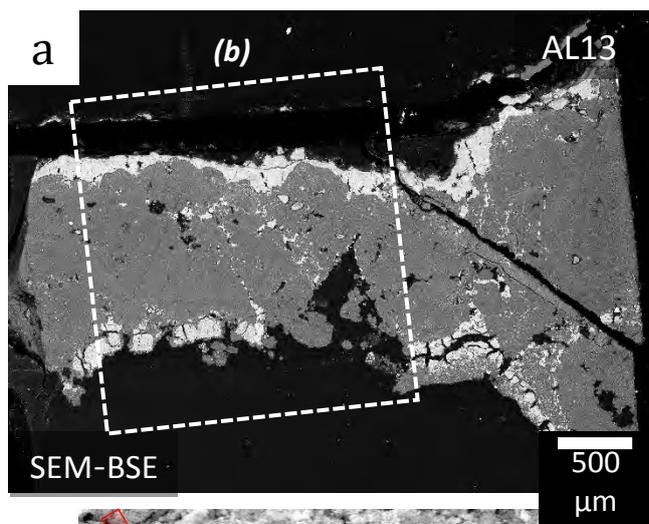


Figure 11

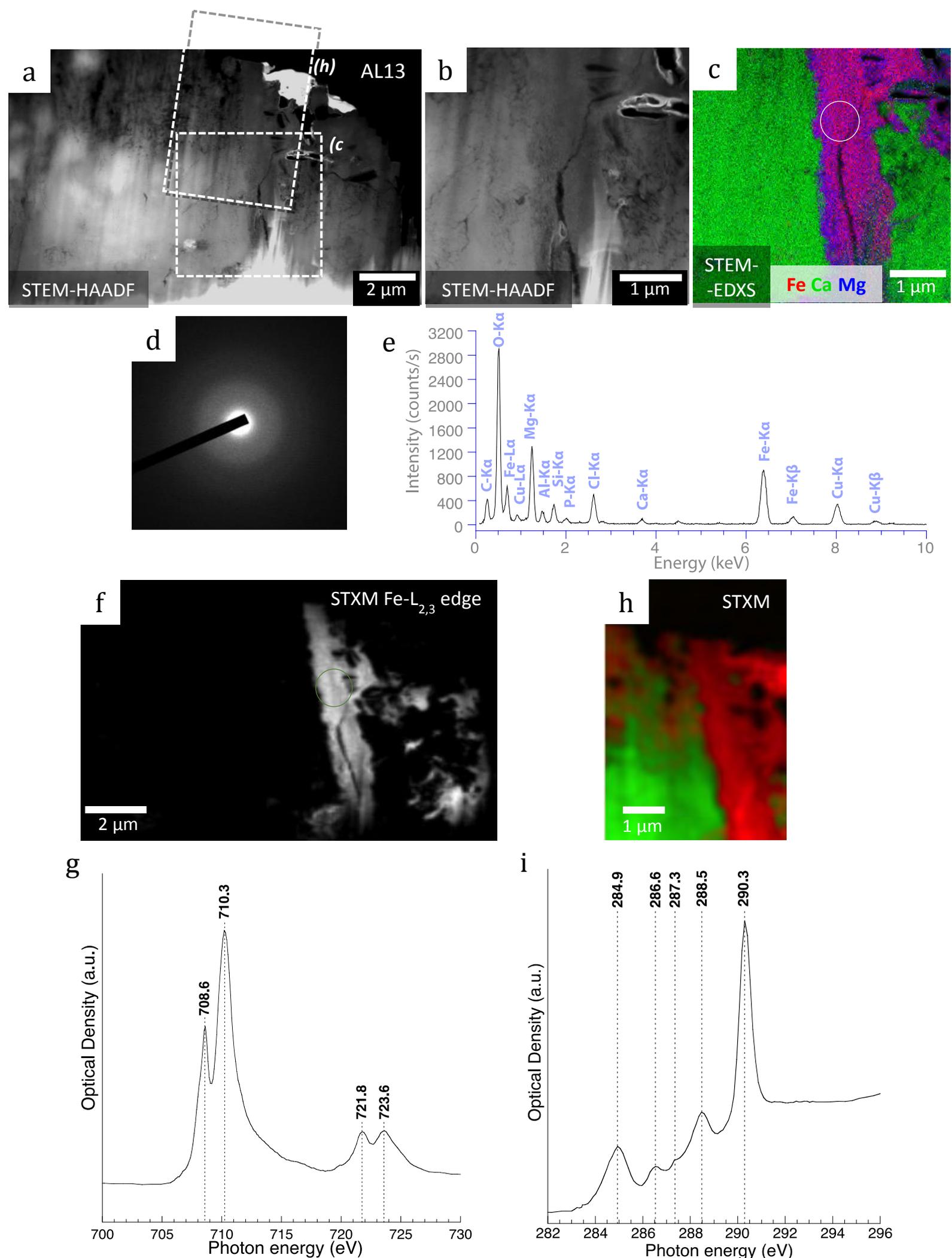


Figure 12

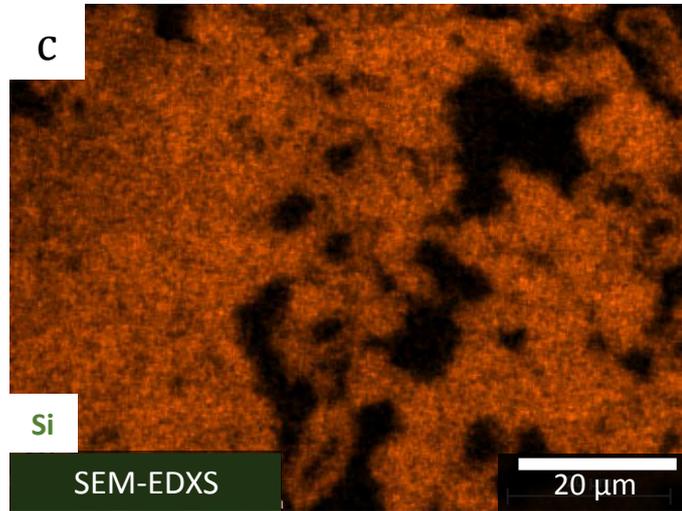
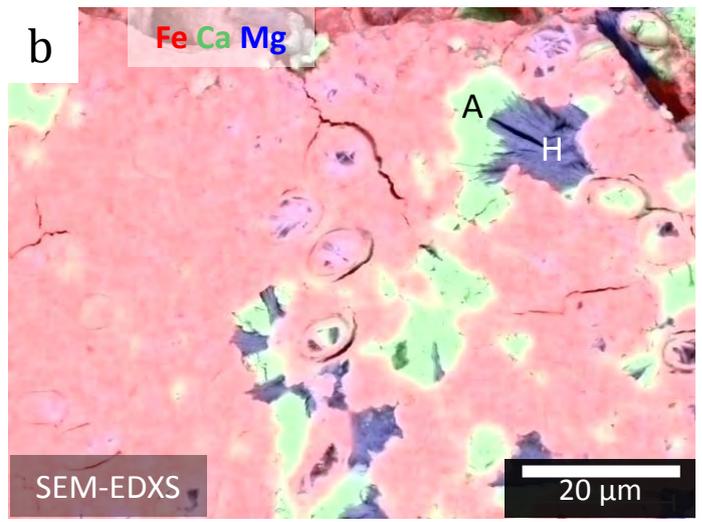
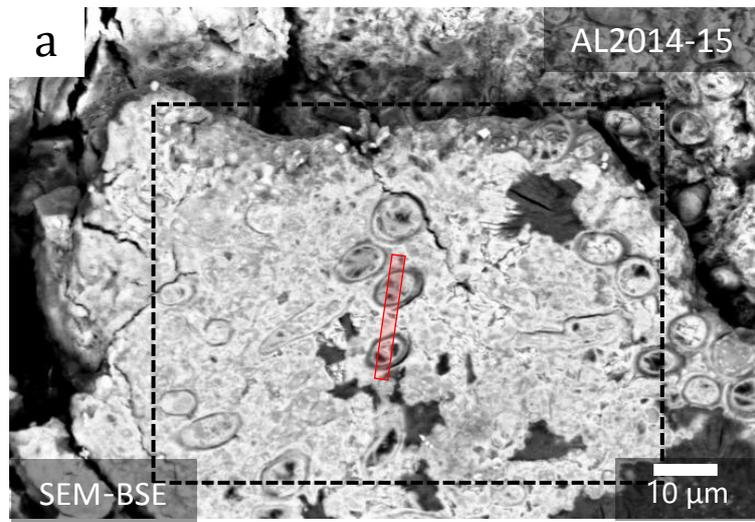


Figure 13

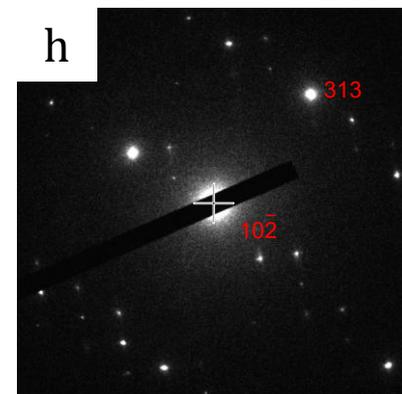
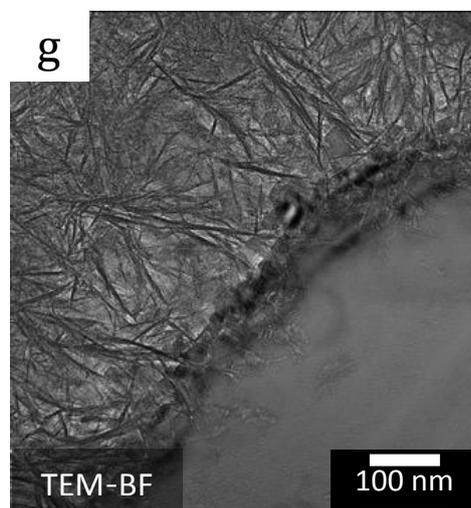
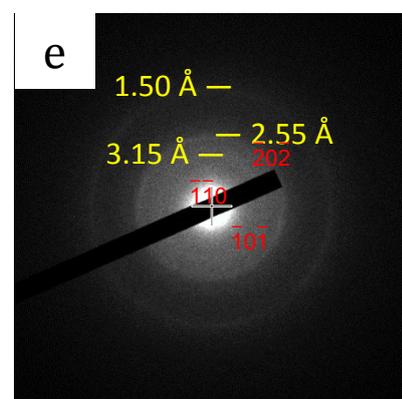
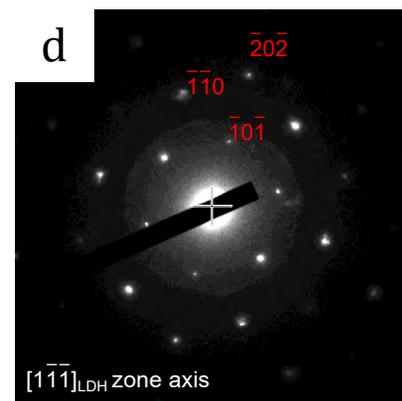
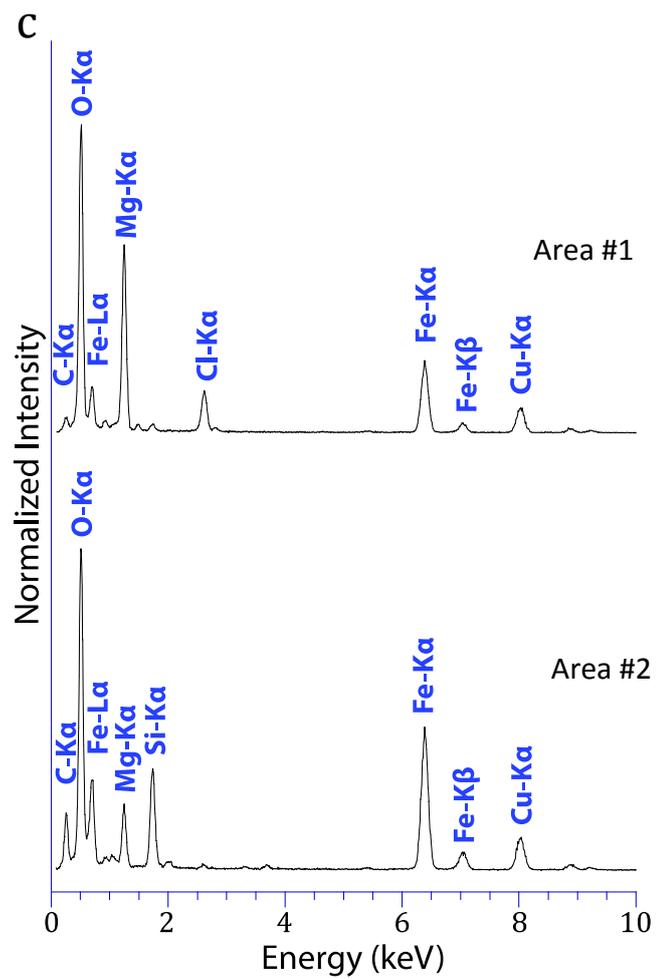
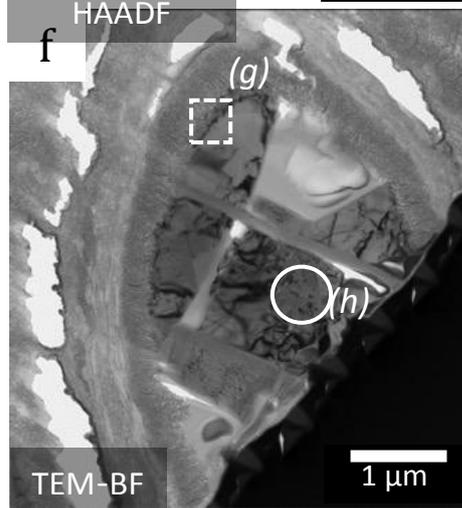
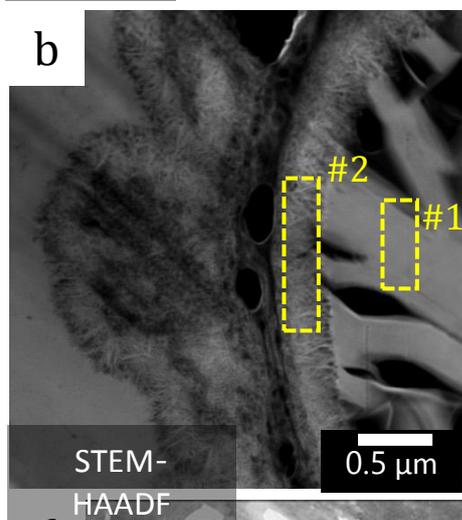
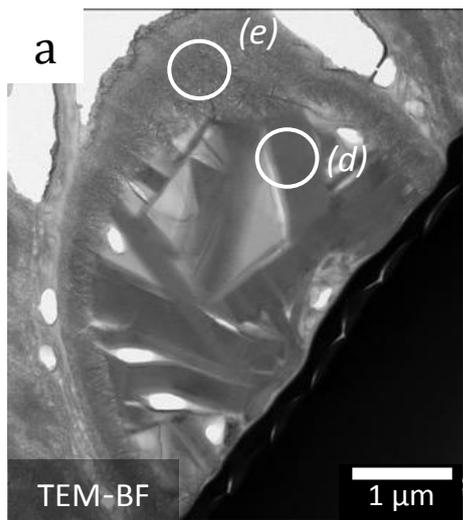


Figure 14

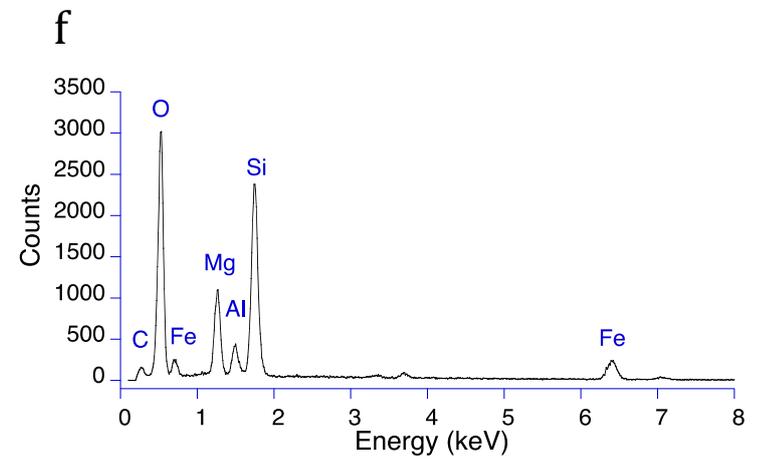
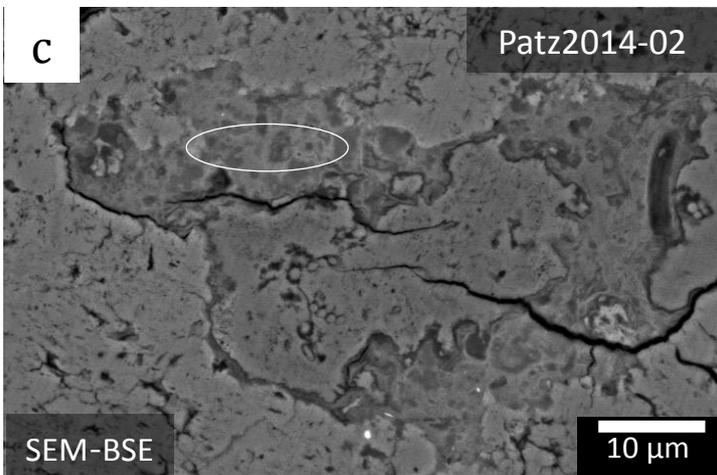
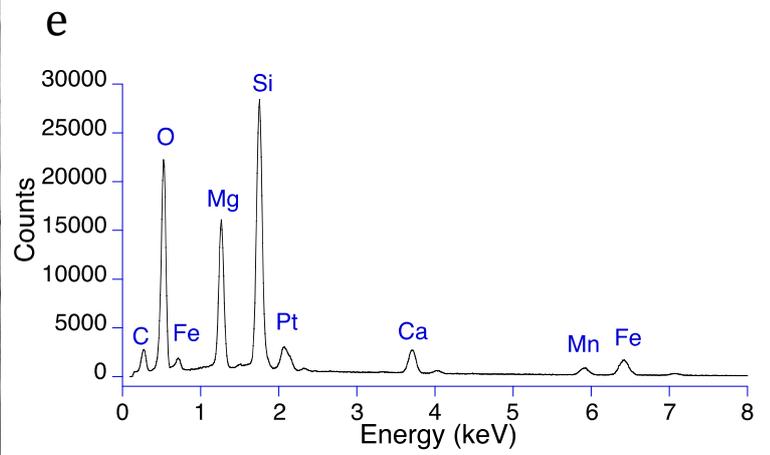
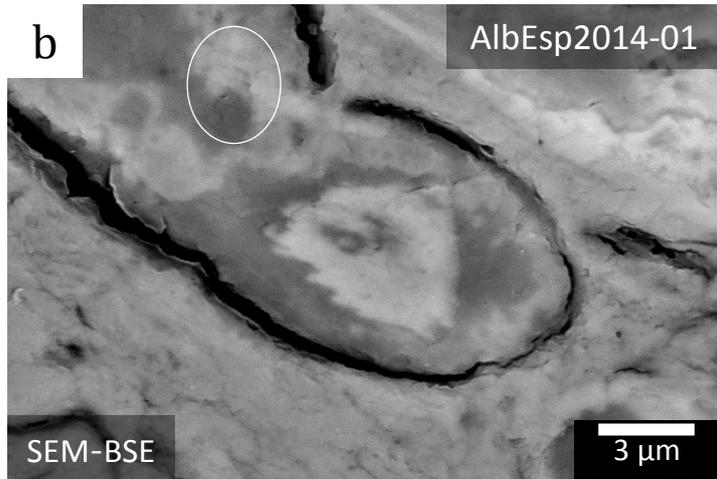
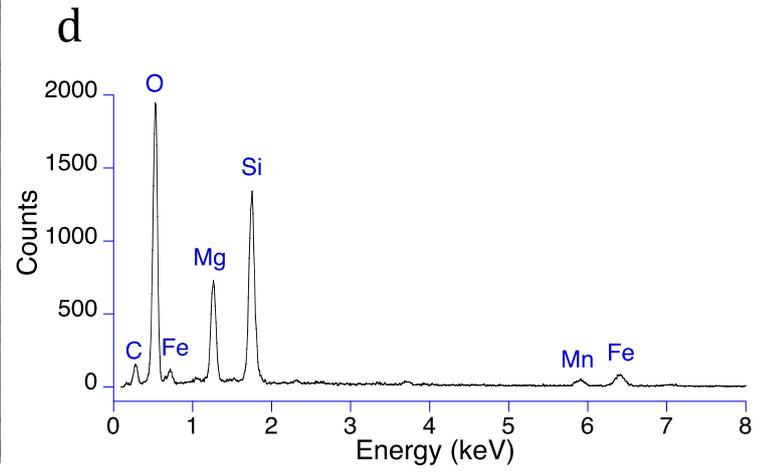
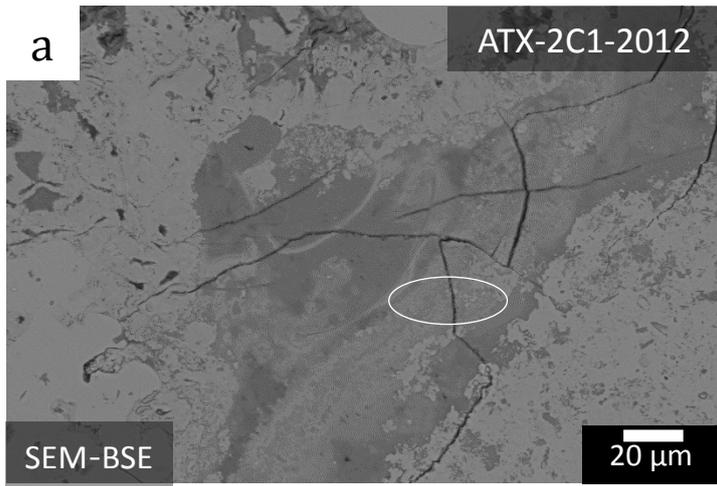


Figure 15

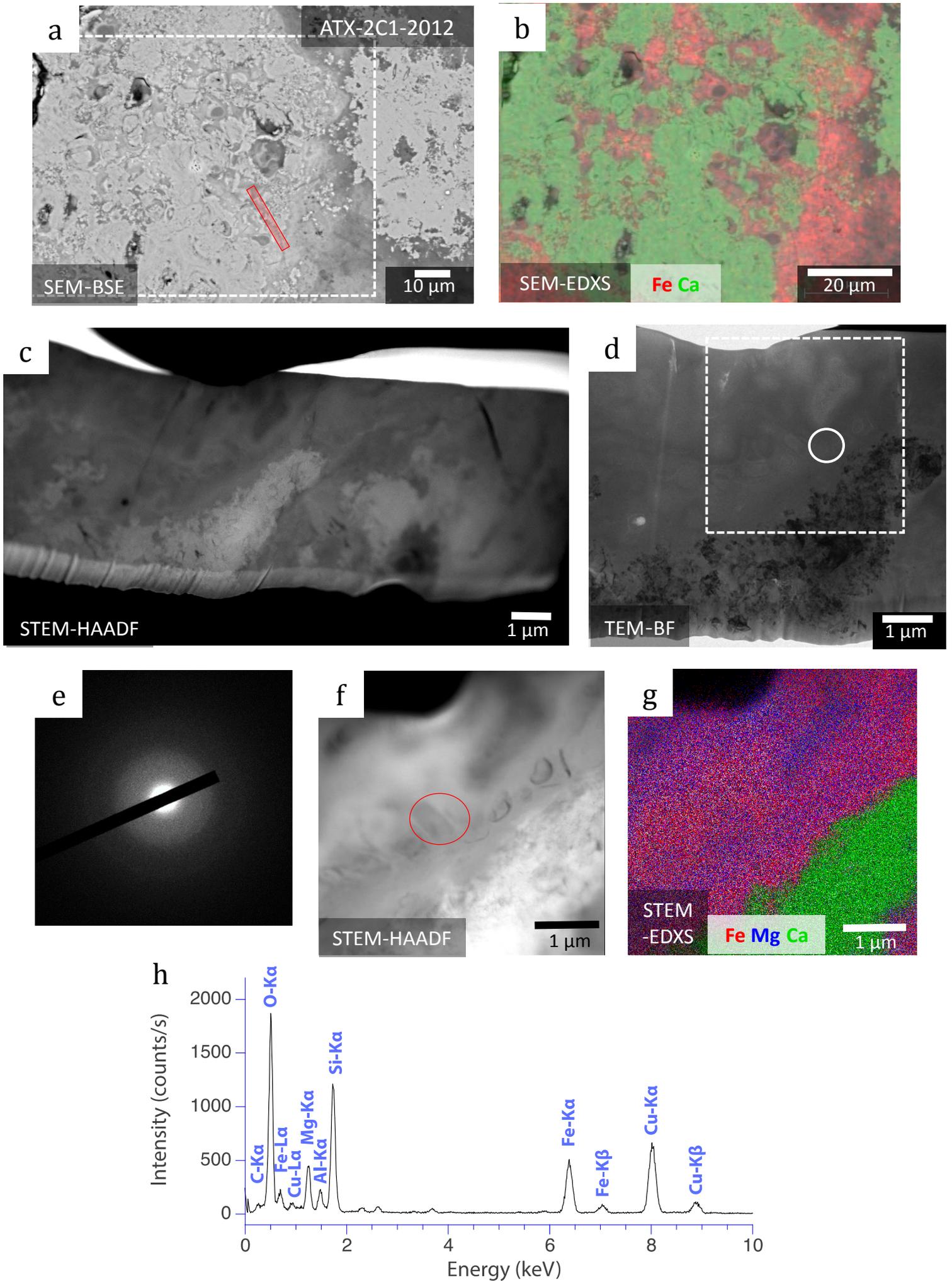
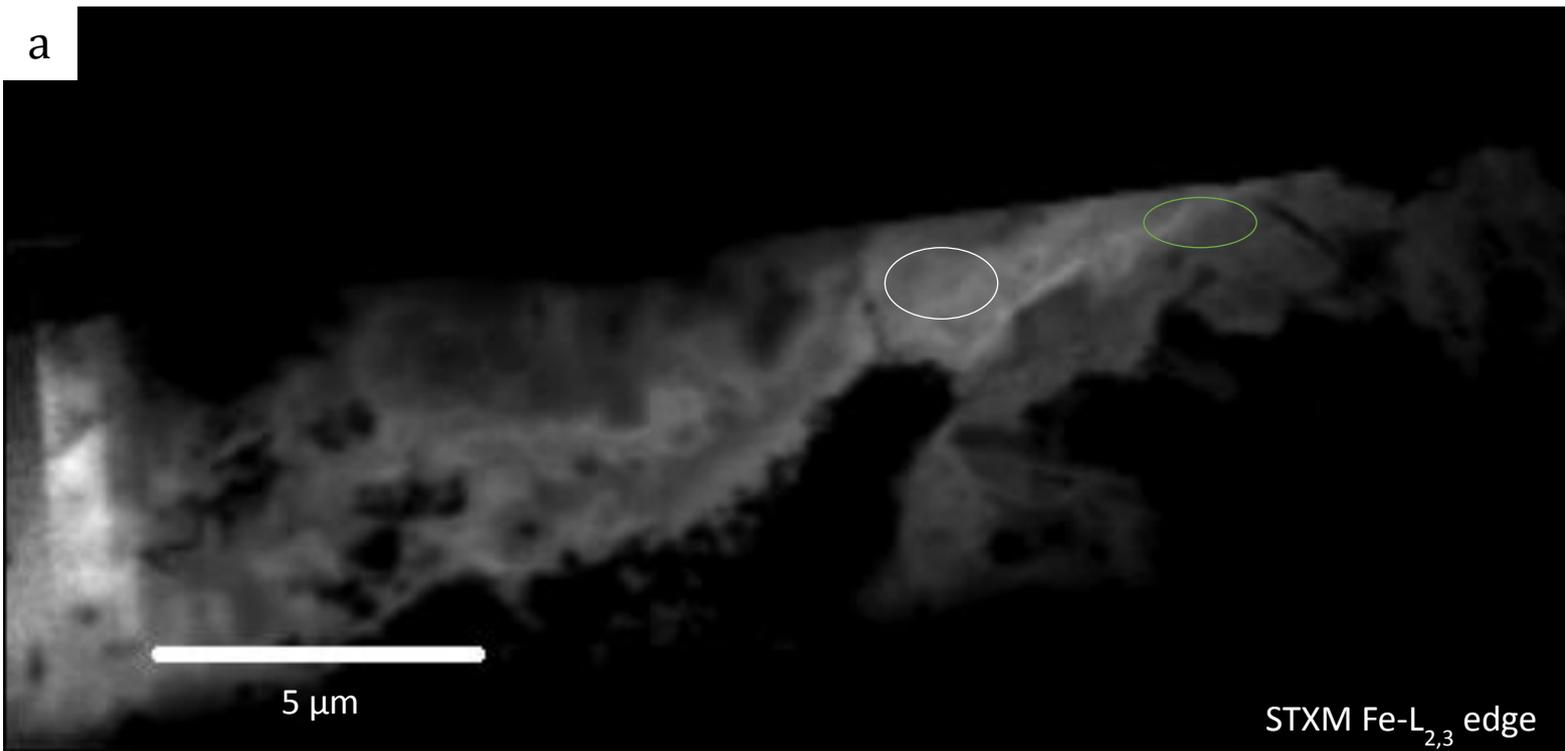
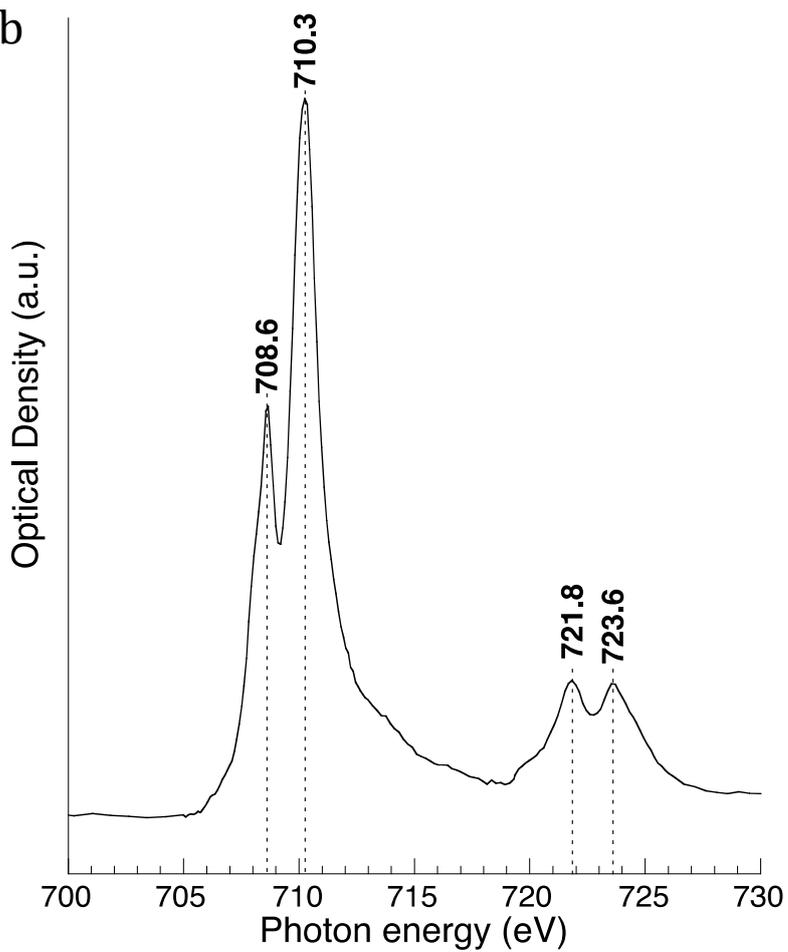


Figure 16

a



b



c

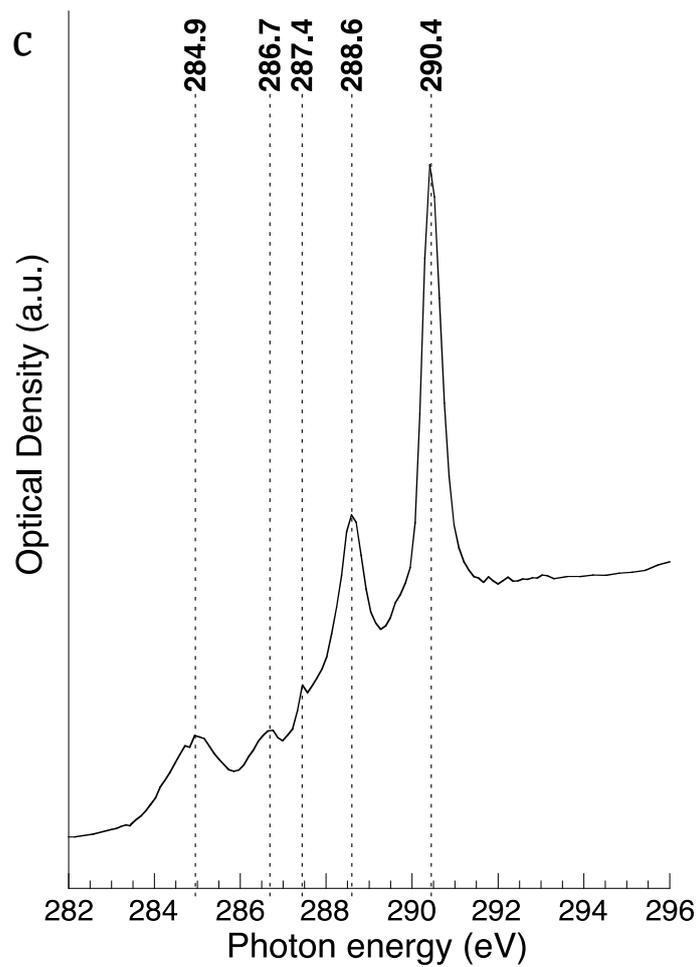
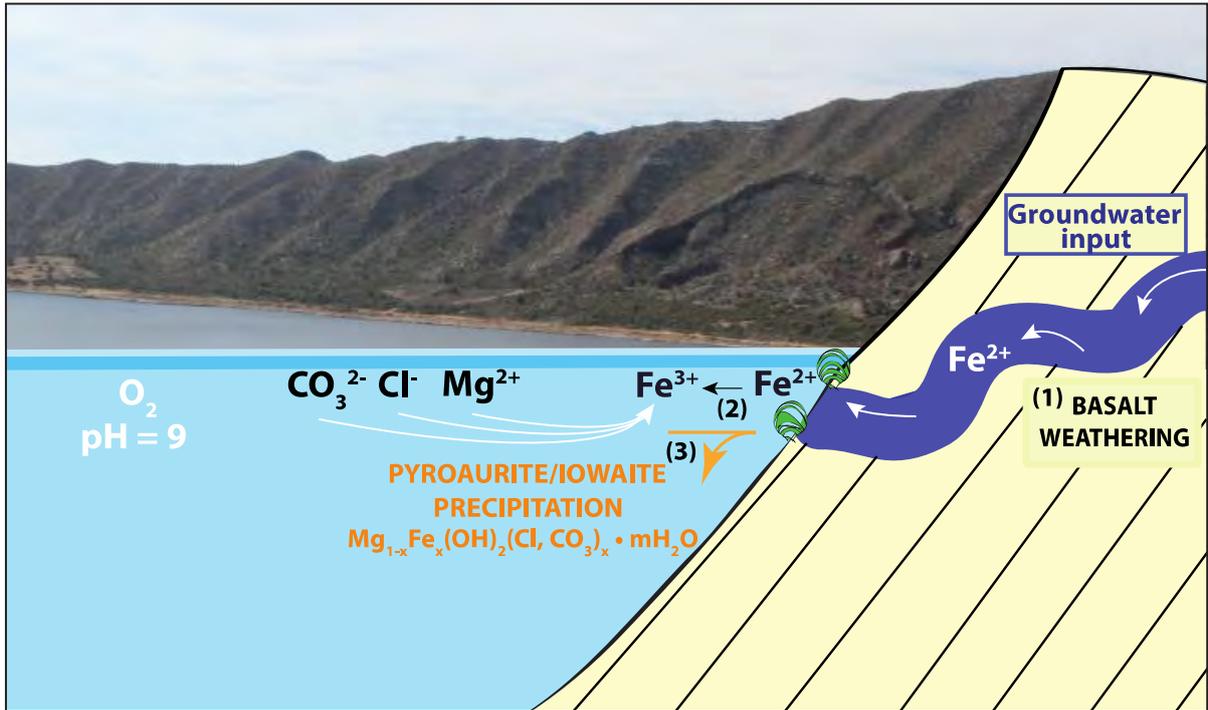


Figure 17



Revised Electronic Annex

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