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# *A search for life in Palaeoproterozoic marine sediments using Zn isotopes and geochemistry*

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## **Abstract**

Sediments from the 2.1- to 1.9-billion-year-old Francevillian Group in southeastern Gabon include centimeter-sized pyritized structures suggestive of colonial organisms (El Albani et al., 2010), some of which may have been motile (El Albani et al., 2019). However, these interpretations were largely based on morphological and geochemical characteristics that lack metabolic clues and/or can be explained by abiotic processes. To move this work forwards, we describe other centimeter-sized specimens, loosely referred to as lenticular forms (LF), from the same area and apply a more holistic approach including morphology, mineralogy, and geochemistry. The objects are 0.2–4 cm in diameter, and most of them are endowed with a regular brim that scales proportionally to external diameter reminiscent of biological order, hence rendering the LF putative biogenic traces. The LF are perfectly delineated in every direction and deflect the sedimentary layers on which they rest. X-ray microtomography further demonstrates that the LF are syn-depositional features and not

40 concretions, while lead isotope systematics indicate that the geochemical imprint of diagenesis is  
41 inconsequential. Low sulfur content is largely concentrated in the organic matrix, and scarcity of  
42 pyrite and its persistence as micron-sized crystals show that the role of sulfate reduction is minor.  
43 Most interestingly, the fillings of the LF cavities show large and correlated excesses of organic carbon  
44 and zinc, with the latter being distinctly enriched in its light isotopes. The geochemical anomalies of  
45 the fillings relative to the host rock, notably those associated with Zn, clearly were buried with the  
46 LF, and further imply biogenicity. In this regard, a ten-fold increase in LF size towards the top of the  
47 black shale series might be related to increasing Zn (nutrient) availability. Although we cannot  
48 conclude with any certainty what these remnant organisms were, their features all taken together  
49 are evocative of very large agglutinate protists that grazed on bacterial biomass either in the water  
50 column or as benthic mats.

51

## 52 **1. Introduction**

53 The composition of the Archean and Paleoproterozoic biosphere remains uncertain largely due to  
54 the scarcity of an unequivocal Precambrian palaeobiological record. The recovery of benthic  
55 microfossils – the physical remains of microorganisms that grew attached to ancient sediments –  
56 has provided relevant guidance for understanding the trajectory of biological evolution (Butterfield,  
57 2007; Knoll, 2014), but ultimately their interpretation is based primarily on subjective morphological  
58 features. The difficulties associated with such determinations are well-identified and repeatedly  
59 reviewed (see a recent account with references in Neveu et al., 2018). In short, abiotic processes  
60 can almost always explain features reminiscent of microfossils. Moreover, demonstrating the  
61 biological nature of putative fossil remains in ancient terrestrial rocks is a formidable challenge due  
62 to post-depositional alteration via burial, lithification, and secondary fluid flow through porous and  
63 fractured rocks (Neveu et al., 2018).

64

65 Spectroscopy and geochemistry offer another approach. Vibrational, infrared, and Raman  
66 spectroscopy, for example, allows the molecular compounds present in organic material and the  
67 thermal maturity of a fossil to be determined (Hickman-Lewis et al., 2016; Olcott Marshall and  
68 Marshall, 2015). Carbon isotope analysis (Rosing, 1999; Tashiro et al., 2017) of carbonaceous  
69 remains adds a strong component to help determine the biogenic character, or not, of a given relic.  
70 But both techniques are sensitive to metamorphic alteration and to date have been more efficient  
71 at characterizing unambiguous fossils and less at providing incontrovertible proof of the nature of  
72 enigmatic biological traces (Marshall et al., 2005; Sforza et al., 2014), particularly in carbon-rich  
73 materials. Trace elemental geochemistry as a tool suitable for the quest of biogenicity has also been  
74 applied. Using microbeam particle-induced X-ray emission ( $\mu$ PIXE), Hickman-Lewis et al. (2020)  
75 demonstrated association of transition metals and metalloids with carbonaceous materials in 3.33  
76 Ga-old cherts from the Barberton greenstone belt and suggested that patterns in elemental  
77 abundance might help constrain the metabolic networks present in fossilized ecosystems. Gangidine  
78 et al. (2021) analyzed hot-spring deposits from the mid-Paleozoic Drummond Basin, Australia, but  
79 the elements for which they identified excesses associated with putative fossils would normally  
80 qualify as terrigenous for modern oceanographers. Sforza et al. (2022) recently showed associations  
81 of nickel with putative porphyrins in Proterozoic microfossils. Sedimentological evidence for a

82 biological role of this highly toxic and poorly chelated element in organic-rich material still remains  
83 ambiguous as nickel isotope analysis suggests that isotope fractionation may be an effect of the  
84 weathering environment (Porter et al., 2014). Other micro-nutrients, notably cobalt, copper, iron,  
85 manganese, and molybdenum are all essential for biological activity, yet most of these elements are  
86 redox-sensitive and, thus, their concentrations and isotopic signatures, whenever more than one  
87 isotope is present, are readily overprinted by the decay of organic matter and diagenesis (Wacey,  
88 2009).

89

90 Apart from iron, zinc is the most abundant trace element in modern plankton (Twining and Baines,  
91 2013) and, therefore, is particularly useful as a potentially strong biosignature. Further,  $Zn^{2+}$  is non-  
92 toxic, redox-*insensitive*, and of all the transition elements, it shows the highest affinity for a large  
93 spectrum of ligands of biological interest. This makes Zn a versatile element in thousands of proteins  
94 of biological interest, in particular as a co-factor of carbonic anhydrase, alkaline phosphatase, zinc  
95 fingers, and other biological components (Weber et al., 2018). Zinc is known to be protective against  
96 oxidative and saline stress as well as increasing membrane stability in plants (Tufail et al., 2018).  
97 Importantly, unlike carbon and nitrogen, Zn has the potential for preserving both chemical and  
98 isotopic memories of biological precursors of cyanobacteria, algae, and other aquatic  
99 photoautotrophs. Preferential uptake of light Zn isotopes by organic material has been clearly  
100 considered by earlier Zn isotope work on modern carbonates (Pichat et al., 2003) and on the water  
101 column (Weber et al., 2018), but has not so far been explicitly considered as a useful biogenicity  
102 indicator. This is the purpose of the present work, which makes a strong case in favor of Zn  
103 abundances and isotopic compositions as a new biosignature.

104

105 Contrary to complex and potentially misleading morphological criteria, with well-known cases being  
106 the ALH84001 Martian meteorite (Neveu et al., 2018), ‘cyanobacterial filaments’ in the 3465 Ma  
107 Apex Chert in the Pilbara Craton, Western Australia (Brasier et al., 2002), and the purported  
108 stromatolites from the 3.7 Ga old Isua supracrustal belt, southwest Greenland (Allwood et al., 2018),  
109 well-resolved spectroscopic and geochemical measurements are repeatable by any observer or  
110 analyst with a reproducible outcome. Here we will focus primarily on the geochemical approach and  
111 test whether, among other geochemical tracers, Zn and its isotopes may help track ancient life on  
112 early Earth and other planets.

113

114 Specifically we address the issue of biogenicity in deep-time sedimentary rocks by using a particular  
115 group of putative biological traces found in sediments from the Francevillian series deposited in the  
116 2.1 to 1.9 Gy interval, previously described in a series of publications (El Albani et al., 2010; El Albani  
117 et al., 2014; El Albani et al., 2019) and referred to here as lenticular forms (LF). The decisive  
118 advantages of the Gabon putative life forms over those from the Late Proterozoic and the Cambrian,  
119 such as the Burgess Shale (Butterfield et al., 2007; Gaines et al., 2019; Powell, 2003), is their very  
120 mild degree of diagenesis; their huge enrichment in organic carbon (up to 10% ) and bitumen, and  
121 their deposition in an oxygen-poor, clay-rich environment that offers a higher degree of  
122 preservation potential. We combine macroscopic and tomographic morphological evidence with a

123 broad coverage of major and trace element and isotopic evidence, with emphasis on Zn, to address  
124 hotly debated questions that generally accompany ancient putative traces of life:

125

- 126 a) Could biological-like morphology be an artefact of early or late diagenesis or even be  
127 concretions?  
128 b) What is the chemical imprint of diagenesis and in particular the role of sulfate reduction?  
129 c) If the enigmatic investigated traces are of biogenic origin, which order do they represent,  
130 typically prokaryotes vs eukaryotes, multicellular colonial vs metazoan organisms?

131

132 In addition to the issue of biogenicity, the present work is relevant to two other broad questions  
133 pertinent to early life reconstruction. First, could the emergence of eukaryotes, largely believed to  
134 have taken place at the onset of the Mesoproterozoic ~1.6 Gy ago, instead have arisen much earlier  
135 (Javaux and Lepot, 2018; Knoll, 2014)? Second, what is the relevance of the putative Gabon life  
136 forms to the ~2.1 Ga old Lomagundi event, a period characterized by the burial of organic matter  
137 and increased atmospheric oxygenation (Melezhik et al., 2013; Canfield et al., 2013; Mänd et al.,  
138 2020).

## 139 **2. Geological and sedimentary setting**

140 The Francevillian basin consists of 35,000 km<sup>2</sup> of unmetamorphosed sedimentary rocks that were  
141 deposited on the margin of the Birimian (Eburnean) craton during the Paleoproterozoic Eon in an  
142 epicontinental setting in what is now the Republic of Gabon, western equatorial Africa (Bonhomme  
143 et al., 1982; Bros et al., 1992; Reynaud et al., 2018) (Fig. 1). The sediment package is between 1000  
144 and 2500 m thick and is subdivided into four lithostratigraphic units, FA to FD, which rest  
145 unconformably on Archean basement rocks. The FA unit mainly consists of fluvial and deltaic  
146 sandstones. At the top, it contains uranium enrichments and hosts the well-known Oklo natural  
147 nuclear reactors (Gauthier-Lafaye et al., 1989). These reactors are heat sources that trigger the  
148 convection of interstitial fluids. The FB unit consists of marine sediments deposited mainly below  
149 the storm wave base. It has been recognized as the source of massive petroleum generation which  
150 played a major role in the formation of the uranium-rich deposits that triggered the Oklo natural  
151 nuclear reactors (Mossman, 2001). Because of its diverse lithological composition, the FB unit is  
152 further divided into the FB1 (a, b, and c) and FB2 (a and b) subunits. The FB1a and FB1b subunits  
153 consist of interlayered shales, sandstones, and conglomerates, fining upwards to predominantly  
154 shales at the top. The FB1c subunit consists of shales, but also contains a thin iron formation overlain  
155 by black shales and a thick interval rich in manganese. The FB2a subunit consists of sandstone beds  
156 deposited in channels near the fair-weather wave base. These are sharply overlain by the FB2b  
157 subunit including finely-laminated black shales (Fig. 2) interbedded with thin siltstone layers  
158 deposited by waning storm surges. All of the specimens presented here were collected from the  
159 FB2b black shales (Fig. 2). In the quarry that was investigated, the FB2b black shales are 5 m thick.  
160 The overlying FC unit is dominated by dolomites and stromatolitic cherts, indicating shallow-water  
161 conditions. The FD unit corresponds to black shales deposited during a transgressive phase. A large  
162 portion of the Francevillian series was deposited during the Lomagundi-Jatuli Event carbon isotope  
163 excursion dated in the Transfennoscandian Greenstone Belt at ca. 2.22-2.06 Ga (Canfield et al.,  
164 2013; Martin et al., 2013) but, on a global scale, they may be basin-specific or diachronous and could

165 locally extend to younger ages (Martin et al., 2015). The preservation of randomly ordered smectite-  
166 rich illite/smectite mixed layer minerals (R0-type) demonstrates unusually slow mineral  
167 transformation and only a moderate degree of diagenesis, which is remarkable considering the  
168 Paleoproterozoic age of the sedimentary succession (Gauthier-Lafaye et al., 1996). It also has no  
169 indication of hydrothermal influence (Gauthier-Lafaye et al., 1996).

170 Previous publications assessed that the Francevillian black shales were deposited from an  
171 oxygenated water column in a quiet, low-energy marine environment (Canfield et al., 2013; El Albani  
172 et al., 2010). They are interbedded with thin sandstone layers lacking specimens. They are  
173 distributed without significant overlap on the black-shale bedding planes. Fine laminae, prevailing  
174 in the enclosing shales, surround the lenticular form (LF) specimens investigated here with a  
175 selection illustrated in Fig. 3 and Fig. S1. This indicates that the structures were in place before burial  
176 compaction as illustrated in Fig. 4. Most specimens are filled with fine-grained sediments, yet some  
177 are only represented as impressions. Both molds and impressions are commonly preserved in three  
178 dimensions.

179

### 180 **3. Materials and Methods**

181 About 300 LF specimens with exquisitely preserved morphologies were collected from the FB2b  
182 subunit at the Moulendé Quarry within a ~5m thick black-shale layer dominated by silts and clays  
183 (El Albani et al., 2010; El Albani et al., 2019). They were photographed at the University of Poitiers  
184 using a Nikon Europe D610 digital single-lens reflex camera equipped with a Nikon AF-S 24-120 mm  
185 f/4G ED VR lens. The textural contrasts between a given LF specimen's filling and its host rock were  
186 investigated on polished slab sections with a ZEISS Discovery V8 stereoscope coupled with an Axio  
187 Cam ERc 5s microscope camera.

188

189 Described as one of the largest Paleoproterozoic accumulations of organic matter in the world and  
190 based on their high total organic carbon (TOC) at current high maturity (Mossman, 2001), the FB  
191 black shales are widely regarded as the source rocks of the remarkably large oil field of Franceville.  
192 Liquid hydrocarbon, the remnants of which have since solidified, was generated through the "oil  
193 window" (<100°C) (Mossman et al., 2005). Such low temperatures make Raman geothermometers  
194 unsuitable to assess the intensity of metamorphism. Beyssac et al.'s (2002; 2003) thermometer is  
195 best calibrated above 300°C, while the peak-width thermometer of Kouketsu et al. (2014) is  
196 unreliable below 150°C and has an uncertainty of ±50°C. In addition, the Raman spectra of organic  
197 carbon depends not only on the maximum temperature but also on the nature of organic precursor  
198 (Quirico et al., 2009). In particular, Phanerozoic organic material cannot be used as reference for  
199 establishing temperatures on early sediments. Raman spectra were therefore not obtained.

200

#### 201 *3.1 Synchrotron radiation induced X-ray fluorescence (SR-XRF) analysis*

202 Polished slab sections of representative samples were chosen for scanning X-ray fluorescence  
203 analysis. The SR-XRF measurements were performed on several areas within the studied samples at  
204 the Nanoscopium hard X-ray nanoprobe beamline (Somogyi et al., 2015) at Synchrotron Soleil,  
205 France. The monochromatic X-ray beam of 18 keV energy was focused on the sample area by a  
206 Kirckpatrick-Baez nano-focusing mirror. Micrometer resolution for elemental maps of mm<sup>2</sup>-sized

207 sample areas was obtained by implementing the fast continuous scanning (FLYSCAN) technique. Full  
208 XRF spectra were collected for each pixel of the scans by two Si-drift detectors (VITUS H50, KETEK  
209 GmbH) in order to increase the solid angle of detection. The XRF sum-spectra of the measured  
210 regions were fitted by the PyMCA software (Solé et al., 2007) to identify the elements detectable in  
211 the samples. The spatial distribution of the identified elements, S, K, Ca, Ba, Mn, Fe, Ni, Cu, Zn, Ga,  
212 Ge, As, Se, Pb, Sr, and Zr, was reconstructed by a home-made Matlab code, which also corrects for  
213 spectral overlapping. Each elemental intensity map was then corrected for the variation of the  
214 incoming X-ray intensity and measurement dead-time and was normalized to 10 ms/pixel exposure  
215 time. The semi-quantification of the elemental distribution maps was obtained by a home-made  
216 Matlab code converting the measured intensity distributions into mass fractions by using calibration  
217 factors obtained by measuring a known sample in the same measurement conditions.

218

### 219 *3.2 X-ray microtomography*

220 Micro-computed tomography (microtomography or micro-CT) analyses were done at the University  
221 of Poitiers on an RX-solutions EasyTom XL Duo equipment, which has one micro- and one nanofocus  
222 (LaB6 filament) Hamamatsu X-ray source coupled to a Varian PaxScan 2520DX flat panel.  
223 Reconstructions were done with the XAct software (RX-solutions) using a classical filtered back  
224 projection algorithm and reduction of beam hardening artefact. Virtual sections, 3D rendering, and  
225 videos were done with Avizo Fire v.9.2 (FEI).

226

### 227 *3.3 X-ray diffraction*

228 Approximately the same quantity of whole-rock powder and clay mineral fraction (<2 µm) from 28  
229 samples (14 LF fillings and 14 samples of their host rock) were analyzed with a Bruker D8 ADVANCE  
230 diffractometer at the University of Poitiers using CuK $\alpha$  radiation operating at 40 kV and 40 mA. The  
231 <2 µm clay fraction was separated by dispersion of gently hand-crushed bulk samples in deionized  
232 water with an Elma S60 ultrasonic agitation device without any chemical pre-treatment. The  
233 dispersed particles were allowed to settle under gravity at a controlled room temperature of 20°C  
234 and centrifuged to separate the <2 µm clay fraction. Oriented slides were prepared by drying ~1 mL  
235 of suspension on glass slides at room temperature. Analysis of whole-rock powder samples was  
236 performed over an angular range of 2-65° 2 $\theta$  with a step size of 0.025° 2 $\theta$  per 3 s. Oriented slides of  
237 the <2 µm clay fraction were analyzed at a step size of 0.02° 2 $\theta$  per 3 s counting time and over 2 to  
238 30° 2 $\theta$  angular range after successive air drying (AD) and ethylene glycol (EG) saturation. Oriented  
239 samples were then prepared and analyzed in AD and EG states. Background stripping, indexing of  
240 peaks, and mineral identification were done using Bruker Eva software by comparing with  
241 International Centre for Diffraction Data (ICDD) files. The results were compared with reference data  
242 }. We fitted one experimental sample from each lithology (LF fillings and host rock) in AD and EG  
243 states. Instrumental and experimental factors, such as the divergence slit, goniometer radius, soller  
244 slits, sample length, and quartz reference intensity, which are specific to the Bruker D8 ADVANCE  
245 diffractometer, were introduced. Sigmastar and the mass adsorption coefficient for Cu radiation  
246 were set to 13 and 45 cm<sup>2</sup> g<sup>-1</sup>, respectively.

247

248 *3.4 Electron microscopy*

249 Samples were carbon coated and imaged with an FEI Quanta 200 scanning electron microscope  
250 (SEM) equipped with an energy-dispersive X-ray spectrometer (EDX) at the Universities of Poitiers  
251 and Lille. Mineral identification and documentation of textural relationships were acquired in back-  
252 scattered electron mode (BSE) operated at an accelerating voltage of 15 kV, 1 nA beam current, and  
253 a working distance of 10.5 mm.

254

255 *3.5 Whole-rock chemical analysis*

256 Major, trace, and rare-earth element abundances were determined on 14 LF fillings (specimens) and  
257 14 host rock samples (the host sediments) at Service d'Analyse des Roches et Minéraux (SARM) of  
258 the Centre de Recherches Pétrographiques et Géochimiques (CRPG), Nancy, France, following the  
259 technique described by Carignan et al. (2001).

260

261 *3.6 Carbon abundance and  $\delta^{13}\text{C}$  analysis*

262 Fourteen LF fillings and 14 host rock samples were powdered for the measurement of organic  
263 matter content. A FlashEA 1112 (ThermoFisher Scientific) CHNS analyser was used for flash dynamic  
264 combustion at 970°C under a constant helium flow. The Eager 300 software was used for data  
265 acquisition. A calibration curve was performed with aspartic acid and nicotinamide before each  
266 analysis. The measured carbon content includes both inorganic and organic carbon, but whole-rock  
267 geochemical data show that CaO contents are low. The analytical technique used for  $\delta^{13}\text{C}$  analysis  
268 was described by Mercuzot et al. (2021).

269

270 *3.7 Zinc and lead isotope analysis*

271 Lead and Zn were separated by anion-exchange column chromatography and their isotopic  
272 compositions measured by multiple-collector inductively coupled plasma mass spectrometry (MC-  
273 ICP-MS) at the Ecole Normale Supérieure de Lyon (ENS Lyon). Ultrapure water and distilled nitric  
274 acid ( $\text{HNO}_3$ ), hydrochloric acid (HCl), and hydrobromic acid (HBr) were used throughout.

275

276 About 100 mg of bulk sample was digested in a Savillex PFA beaker using 3 mL concentrated HCl and  
277 0.5 mL concentrated  $\text{HNO}_3$  at 100°C for 72 h. After evaporation to dryness, 2 mL concentrated HCl  
278 were added for a second round of digestion at 100°C for 24 h. The digested sample was evaporated  
279 to dryness and redissolved in 0.2 mL 2M HBr at 100°C for 2 h, evaporated to dryness, and redissolved  
280 in 1 mL 2M HBr for chromatographic separation of Pb and Zn on micro-columns filled with 0.5 mL  
281 new Biorad AG1-X8 (100-200 mesh). Samples were centrifuged prior to loading the supernatant  
282 onto the anion-exchange columns, which had been cleaned with 6M HCl and preconditioned with  
283 2M HBr. The sample matrix was discarded with 3 mL 2M HBr, while Pb was eluted with 3 mL 6M HCl  
284 and Zn was eluted with 3 mL 0.5M  $\text{HNO}_3$ . Zinc was purified a second time following the same elution  
285 protocol. The procedural blanks were <300 pg (Pb) and <30 ng (Zn).

286

287 The Pb isotope compositions were analyzed on a Nu Plasma 500 HR MC-ICP-MS at ENS Lyon using a  
288 DSN100 desolvation nebulizer system. Samples were dissolved in distilled 0.05M  $\text{HNO}_3$  with 5 ppb  
289 Tl and concentrations were adjusted to 30 ppb. Instrumental mass bias was corrected using Tl while



290 the accuracy of the measurements was adjusted by sample-standard bracketing relative to NIST  
291 SRM 981 (the Pb isotopic Standard Reference Material (SRM) 981 from the National Institute of  
292 Standards and Technology (NIST)) (Albarède et al., 2004). NIST 981 was measured systematically  
293 every second sample throughout each individual run session allowing for a final normalization to  
294 the double-spike values of Eisele et al. (2003). The repeated measurements of NIST SRM 981 yielded  
295 an external reproducibility < 100 ppm (0.01%) for <sup>204</sup>Pb-normalized ratios and < 50 ppm (0.005%)  
296 for <sup>207</sup>Pb/<sup>206</sup>Pb and <sup>208</sup>Pb/<sup>206</sup>Pb. Zinc isotope abundances also were analyzed on the Nu Plasma 500  
297 HR MC-ICP-MS at ENS Lyon but without desolvation. Instrumental mass bias was corrected using Cu  
298 NIST SRM 976 and sample-standard bracketing (Albarède et al., 2004). Zinc concentrations were  
299 adjusted to 200 ppb by dilution with 0.05M HNO<sub>3</sub>. The Zn isotopic compositions are reported in  
300 parts per 1000 relative to the Lyon JMC in-house standard in delta notation. Typical δ<sup>66</sup>Zn error bars  
301 are 0.05‰.

302

## 303 **4. Results**

### 304 *4.1 Sample morphology*

305 Visual observation (Figs. 3 and 4) and X-ray tomography reveal lenticular to circular shapes with  
306 radial symmetry (Fig. S1). Many specimens are rimmed by a mm-wide brim (Fig. 2 and Fig. 3), with  
307 a width proportional to the object size. The significance of samples with and without brims is  
308 unclear. Some specimens presented in Fig. 3 and Fig. S1 further show a radial pattern. Whether this  
309 pattern signals the presence of internal compartments in some individuals or a particular  
310 mechanical behavior of the LF will be discussed in a separate paper. Back-scattered electron and  
311 microtomography images of cross-sections demonstrate that the LF deflect the underlying  
312 sedimentary laminae (Fig. 4). Their diameters vary systematically with stratigraphic height (Fig. 5),  
313 ranging from 0.2 to 1 cm at the bottom of the black-shale layer and continue to increase  
314 systematically to >3 cm (almost 4 cm) at the top of the succession.

315

### 316 *4.2 Grain size and mineralogy*

317 Based on scanning electron microscopy-back-scattered electron imaging (SEM-BSE) coupled to  
318 energy-dispersive X-ray spectrometry (EDX), the LF show a stark contrast with its host sediments  
319 (Fig. 6). The LF have a fine-grained composition, with a sharp contact with the host sediments. The  
320 composition of the LF is typically enriched in clay minerals and organic carbon content. Metal  
321 sulfides and carbonate minerals are absent. The clay minerals are parallel to the bedding and aligned  
322 along the perimeter of the specimens. This relationship confirms pre-compactional formation of the  
323 LF, resulting in local rearrangement of sediment grains during compaction. In this regard,  
324 taphonomical preservation occurred during early burial by the decay of organic matter leading to  
325 the complexation of organic matter with hydrous fine-sized clay minerals uniformly filling the  
326 available space provided by the LF.

327

328 The bulk X-ray mineralogical data on both the fillings and the host black shales show the presence  
329 of quartz, micas, illite, chlorite, and other clay minerals (Fig. 6 and Fig. S2). The grain-size of the LF  
330 is clearly finer than that of the host rock (Fig. 6). Smectite is particularly abundant within the LF.

331 Very few detrital minerals (e.g., quartz, micas) are scattered within the LF, whereas a matrix of mixed  
332 organic material and clays is pervasive to the whole specimen.

333

### 334 4.3 Geochemistry

335 Figures 7a-d reveal important geochemical features of the LF and their host rock. First, Pb isotope  
336 compositions were measured on two different fractions of the 14 samples: (1) a clay fraction largely  
337 composed of the LF fillings, and (2) a fraction of the host sediment (Table S1). In  $^{207}\text{Pb}/^{206}\text{Pb}$ -  
338  $^{204}\text{Pb}/^{206}\text{Pb}$  space, all the data points define a linear array with a robust age of  $1890\pm 100$  Ma (2-  
339 sigma error) (Fig. 7a) consistent with literature data (Bonhomme et al., 1982; Bros et al., 1992;  
340 Gauthier-Lafaye et al., 1996). The absolute age is key to assessing whether the Pb-Pb age refers to  
341 a diachronous Lomagundi or a post-Lomagundi event (see Supplementary Information for details).  
342 Both the alignment itself and the age of the alignment confirm that if diagenesis had affected these  
343 samples, it could only have been *shortly after* sediment deposition of the Francevillian series.

344

345 Second, as summarized in Table 1 from the complete data set listed in Supplementary Tables- S1-S3  
346 and shown in Figs. 7a-d, the marked geochemical and isotopic contrasts between the LF and their  
347 host rock are statistically robust and significant. The LF are characterized by higher Lu/Hf ratios and  
348 have higher concentrations of organic C and Zn, but contain less Si, K, Zr, and Hf than their host rock.  
349 The Zn contents of the host rock are consistent with the range observed for other black shales  
350 worldwide over the last 2.7 Ga (Scott et al., 2013) with the consistency being linked to organic  
351 complexes playing an important role in controlling Zn solubility through time (Robbins et al., 2013).  
352 The Zn excess (*xs*) in the fillings (*fil*) can be calculated by subtracting a Zn component chemically  
353 similar to the host rock (*hr*) from the total concentration. With elemental Fe in organic material  
354 being negligible, this gives the simple relationship  $[\text{Zn}]_{xs} = [\text{Zn}]_{fil} - (\text{Zn}/\text{Fe})_{hr} \times [\text{Fe}]_{fil}$ , where brackets refer  
355 to concentrations. The average  $\text{Zn}_{xs}$  values in nine specimens is  $111\pm 44$  ppm. Consistent Zn excess  
356 values are obtained by replacing Fe with other lithogenic elements, such as Y, Zr, Al, or Ti (97-  
357 140 ppm).

358

359 Zinc is isotopically lighter and Pb more radiogenic in the LF with respect to their host rock. The  $\delta^{66}\text{Zn}$   
360 values of the LF host rock average  $0.36\pm 0.10\text{‰}$  (1 sigma) (Table S1), which is well within the  
361 lithogenic range (Moynier et al., 2017) but in stark contrast to the average  $\delta^{66}\text{Zn}$  of the LF fillings of  
362  $0.10\pm 0.10\text{‰}$ , which a *t*-test shows to be highly statistically significant ( $p=7\times 10^{-7}$ ) (Figs. 7b and d,  
363 Table S1).

364

365 The  $\delta^{13}\text{C}$  of a selection of carbon fractions (Table S4) shows no significant difference between the  
366 fillings and the host sediments. The average  $\delta^{13}\text{C}$  value ( $-34.5\pm 0.5\text{‰}$ ) is consistent with Canfield et  
367 al.'s (2013) data and falls well within the range of Proterozoic kerogen samples (Des Marais, 1997).

368

## 369 5. Discussion

### 370 5.1 Diagenesis

371 A preliminary issue about the present data set is whether the original geochemistry of the LF and  
372 their host rock material has been reset by metamorphism or diagenesis. Iconic Cambrian

373 Lagerstätten, such as the Burgess Shale and Siriuspasset fossil assemblages, were buried to  
374 temperatures of ~300°C, typical of greenschist facies (Butterfield et al., 2007; Gaines et al., 2019;  
375 Powell, 2003), which would have been detrimental to the preservation of a primary geochemical  
376 signal. By contrast, the Francevillian black shales still contain smectite-rich clays with randomly  
377 mixed layers, which attest to a very low diagenetic grade. Persisting smectite relicts within illite at  
378 the burial stage limit the temperature of diagenesis to <80°C (Velde and Vasseur, 1992). This  
379 observation is consistent with the maturation of the abundant organic material present in the FB  
380 within the oil formation window (<100°C).

381

382 The preservation of an isochronous relationship with the correct geological age indicates that the  
383 U-Th-Pb system was not reset by any event potentially taking place after early diagenesis. By  
384 extension it can therefore confidently be assumed that neither were Zn isotopes. Over nearly five  
385 decades, several authors have pointed out that Co fluxes to oceanic sediments have remained  
386 constant over the last 200 Ma (Dunlea et al., 2015; Krishnaswami, 1976; Zhou and Kyte, 1992).  
387 Thibon et al. (2019) demonstrated on cores from the pre-GOE Transvaal Supergroup, South Africa,  
388 that Co relative chronometry can be used to estimate sedimentation rates that are within 50% of  
389 the rates provided by zircon U-Pb chronology. In order to calculate the time interval  $\Delta t$  during which  
390 a series of sediments with thickness  $\Delta d$  (in meters), dry bulk density  $\rho_{\text{sed}}$  (in  $\text{g cm}^{-3}$ ), and Co  
391 concentration [Co] (in ppm) is deposited, they used the mass-conservation relationship:

392

$$\Delta t = \rho_{\text{sed}} [\text{Co}] \Delta d / Q_{\text{Co}}$$

393

394 where  $Q_{\text{Co}}$  is the modern cobalt deposition rate of  $3600 \mu\text{g cm}^{-2} \text{Ma}^{-1}$  (Thibon et al., 2019). With all  
395 due caution taken with respect to the uncertainties associated with this technique, this expression  
396 suggests that the ~5 m-thick layer of black shales hosting the LF specimens was deposited in about  
397 20,000 years ( $25 \text{ cm ka}^{-1}$ ). In the modern ocean, such rapid sedimentation rates are observed along  
398 passive margins and in the distal parts of the Bengal and Indus fans (Dutkiewicz et al., 2016)

399

#### 401 *5.2 The lenticular forms are neither secondary features nor concretions*

402 The LF are not syn-depositional or secondary features formed during burial. Morphology shows that  
403 the LF are pre-compaction features that cannot be confused with concretions for two reasons: (1)  
404 the brim width is proportional to the size of the specimen, which argues against control by diffusion;  
405 and (2) Fig. 4 shows that the silt laminae below the specimen are visibly deflected. The geochemical  
406 contrast between the LF and their host rock therefore predates compaction. The persistence of this  
407 contrast through diagenesis indicates that only the finest clay material could infiltrate what must  
408 have been the LF cavity.

409

410 Microtomography shows that the minerals of the brims are the same as those present in the host  
411 rock and the interior of the LF (Fig. 4b). The remarkably constant ratio of brim to external diameter  
412 of  $0.15 \pm 0.04$  (Fig. 5 inset) over a range of external diameters of 0.2 to 4 cm is consistent with a  
413 simple principle of comparative anatomy: for a given species and regardless of the size of  
414 individuals, the relative proportions between anatomic units tend to remain similar. If the brims

415 represented diffusion boundary layers, they would be scaled by external physical and chemical  
416 parameters, typically in the form of  $(Dt)^{1/2}$ , with  $t$  being the duration of the exchange and  
417 temperature-dependent  $D$  the diffusion coefficient of the elements moving in and out of the form.  
418 The brims would in this case be expected to have the same width in any given layer which is not  
419 what is observed.

420

421 The distinctly lenticular shape of these objects and the regular progression of their size over time  
422 are therefore better reconciled with a biological origin than a sedimentary phenomenon such as  
423 minute mud volcanoes or sedimentary nodules.

424

425 Finally, should diagenesis from fluid circulation have affected the geochemistry in general, and the  
426 Zn isotopes in particular, both the host rock and the LF would have been affected. Post-mortem  
427 infiltration of fine-grained sediment into the LF inner cavity should not be mistaken for diagenetic  
428 modification. Even in hand specimens, the LF appear as distinct bodies with sharp convex outlines  
429 in every dimension, so much so that individual LF are easily freed from their host rock (Fig. 3, Fig. 2  
430 and Fig. S1). As for most bona fide macroscopic fossils, such an effortless release of the LF indicates  
431 a strong rheological discontinuity and the lack of a diffusion rim. The fact that Zn and C  
432 concentrations and Zn isotopes in the interior of the forms are anomalous with respect to the host  
433 rock is evidence that the LF were buried with their geochemical anomaly already in place.

434

### 435 *5.3 Pyritization of the circular forms is an uncommon local feature associated with fractures*

436 Sedimentary pyrite is formed by either syngenetic precipitation of minute crystals when at least  
437 some layers of the water column are euxinic or during diagenetic sulfate reduction (Canfield et al.,  
438 1996; Shen et al., 2002).-The scatter of micron-sized pyrite crystals (illustrated by, for example, the  
439 Fe and S distribution in Fig. S3 does not support sulfate reduction except along some rare  
440 stratigraphic diastems which favor water flow. The bimodal grain size of pyrite crystals strongly  
441 argues against pyrite dissolution during diagenetic evolution. Disseminated tiny pyrite crystals (1-3  
442  $\mu\text{m}$ ) persist in the matrix next to larger crystals ( $>30 \mu\text{m}$ ). Because of their high surface energy, small  
443 crystals are much more soluble than large crystals. When diagenetic fluids percolate, small crystals  
444 dissolve and redeposit onto larger crystals, a mechanism known as Ostwald ripening. Most  $\delta^{34}\text{S}$   
445 values in both disseminated pyrite (about  $-25 \pm 5 \text{‰}$  (El Albani et al., 2014)) and large crystals ( $>30$   
446  $\mu\text{m}$ ) are consistent with the net burial of organic material (Planavsky et al., 2012). Much less  
447 frequent  $\delta^{34}\text{S}$  values  $> -20 \text{‰}$  may occur at the periphery of large pyrite crystals growing along  
448 fractures.

449

450 Mass balance also requires that the modal proportion of pyrite in the samples is very small: making  
451 the extreme assumption that all S in the sample is in the form of pyrite (i.e., no S in the matrix) and  
452 dividing the maximum S concentration in the sample (3000 ppm, Table S3) by the S concentration  
453 in pyrite ( $\sim 36 \text{ wt.}\%$ ), the maximum weight proportion of pyrite is 0.8%. This is in excellent agreement  
454 with the  $\sim 1\%$  pyrite micro-crystals detected by synchrotron-based scanning X-ray fluorescence  
455 microscopy (SR-XRF) imaging (Fig. S3 and Fig. S4). SR-XRF data indicate that the actual Zn  
456 concentration in pyrite is in the range of  $< 100 \text{ ppm}$ . Scarcity of pyrite has also been pointed out in

457 the Burgess Shale by Anderson et al. (2021). Even if an extreme value of 2000 ppm Zn in sedimentary  
458 pyrite (Large et al., 2014) is adopted, the calculated pyrite abundance would only account for 15  
459 ppm of the rock's Zn inventory, which is insufficient to explain the anomalously light  $\delta^{66}\text{Zn}$  values of  
460 the LF fillings (see below). The suggestion (Conway and John, 2014; Little et al., 2016) that diagenetic  
461 fluids cause loss of isotopically heavy Zn associated with the formation of modern sedimentary  
462 sulfides therefore is not applicable to the Francevillian black shales. Sulfate reduction to pyrite is  
463 *not* the process controlling the Zn budget or the Zn isotopic compositions of these samples.

464

465 The distinctive Zn anomalies cannot be explained by pyritization either. The large Zn excesses (~100  
466 ppm) observed in the fillings of the LF are not supported by the rare minute crystals of pyrite  
467 observed by SR-XRF (Fig. S3). The distribution maps of S, K, Ca, and Mn do not show any significant  
468 co-localization with Zn (see Fig. S5). It can therefore be concluded that Zn is not linked to S, K, Ca,  
469 or Mn-containing mineral phases whether in the LF or the host rocks. High-resolution Zn, Fe, and S  
470 concentration maps at a micron-scale resolution and ppm-range sensitivity across the specimens  
471 distinctly show that the Zn/Fe ratios in pyrite are about two orders of magnitude smaller than the  
472 ratios in the matrix. Pyrite crystals are definitely not Zn hot-spots. In addition, the spatial dispersion  
473 of Zn throughout the black shales shows that Zn excesses within the LF fillings are randomly  
474 distributed across the sample. They follow a Poisson distribution (Fig. 8), and, with rare exceptions,  
475 do not follow stratification or fractures.

476

#### 477 *5.4 The biological nature of the lenticular forms*

478 The singular behavior of Zn, an element particularly abundant in cellular interiors, is correlated with  
479 LF organic carbon. Figure 6c shows how C contents correlate with Zn contents after normalization  
480 to Al to account for variable clay abundances. The atomic C/P ratio in the interior of the LF objects  
481 is in general high, up to about 140 (average  $\sim 95 \pm 27$ , 1 sigma) and is consistent with the Redfield  
482 ratio of modern eukaryotes (Körtzinger et al., 2001). The average  $\delta^{13}\text{C}$  value of  $-34.5 \pm 0.5\%$  confirms  
483 the lack of major organic carbon oxidation.

484

485 With sulfate reduction being dismissed, the most parsimonious explanation for the Zn excesses  
486 observed in the fillings of the LF specimens is via an organic carrier. The Zn/Al ratio is up to a factor  
487 of 4.3 higher (2.3 on average) in the fillings relative to their host rock and correlates with C content  
488 (Fig. 7c). The proportion  $f_{xs}$  of organic-bound Zn in the fillings is also remarkably constant at  $61 \pm 8$   
489 wt.%. Such Zn excess values are well within the range of Zn concentrations measured in modern  
490 dry phytoplankton (Collier and Edmond, 1984).

491

492  $\delta^{66}\text{Zn}$  values of Archean and Proterozoic pyrite have been shown to be indistinguishable from the  
493 lithogenic range (Isson and Planavsky, 2018), which reflects that sulfide minerals do not  
494 fractionate Zn isotopes with respect to seawater (Fujii et al., 2014). By contrast, isotopically light  
495 Zn isotopes preferentially bind to sulfur-rich amino acid (notably cysteine) (Fujii et al., 2014;  
496 Moynier et al., 2017). By subtracting, as above, the host-rock component and taking the mass-  
497 balance condition  $\delta^{66}\text{Zn}_{xs} = [\delta^{66}\text{Zn}_{fil} - (1 - f_{xs}) \delta^{66}\text{Zn}_{hr}] / f_{xs}$  into account, the mean  $\delta^{66}\text{Zn}$  of the organic  
498 component of the LF fillings is estimated to be  $-0.08 \pm 0.20\%$ , a value about  $0.4\%$  lighter than the

499 value of lithogenic Zn, which for an element as relatively heavy as Zn is a substantial shift. Such a  
500 low value is consistent with the range of  $\delta^{66}\text{Zn}$  obtained from phytoplankton cultured in seawater  
501 (Köbberich and Vance, 2019; Samanta et al., 2018), and with Archean and Proterozoic kerogen  
502 (Isson et al., 2018). The systematically lighter  $\delta^{66}\text{Zn}$  values of the LF fillings with respect to their  
503 host rock therefore indicate that organic material in the LF fillings is not due to infiltration of liquid  
504 hydrocarbons but represent primary organic material.

505

506 A back-of-the-envelope calculation rooted in the concept of 'minimum Zn quota', which is the  
507 lowest amount of zinc per cell that allows for optimal growth (Outten and O'Halloran, 2001), drives  
508 home the point that significant phytoplankton biomass was incorporated into the LF. For example,  
509 assuming 100 ppm Zn excess in the LF (Table 1), which can be conservatively represented by a 0.1 x  
510 1.0 cm cylinder with a density of  $2.5 \text{ g cm}^{-3}$ , leads to  $3.33 \text{ }\mu\text{M Zn}$ . Based on the Zn content of a  
511 modern anoxygenic photoautotroph (Konhauser et al., 2018), where one cell has  $8.08 \times 10^{-18} \text{ mol}$   
512 Zn, then  $3.33 \text{ }\mu\text{M Zn}$  require  $4.1 \times 10^{11}$  cells. If the mass of the LF was 77.5 mg ( $0.031 \text{ cm}^3 \times 2.5 \text{ g cm}^{-3}$ ),  
513 then  $5.3 \times 10^9$  cells were required for each mg of LF. To put this number into context, humans  
514 have an estimated 37 trillion cells (Bianconi et al., 2013), which, based on a 70 kg person, is  
515 equivalent to  $5.3 \times 10^8 \text{ cells mg}^{-1}$ .

516

517 Zinc excesses, high C/P ratios, and low  $\delta^{66}\text{Zn}$  in the LF fillings therefore concur to show that the LF  
518 inherited abundant material of organic origin. Infiltration of fine clay mineral into the cavity was  
519 probably facilitated by post-mortem bloating of the LF. Zinc is a particularly widespread co-factor of  
520 a large number of proteins and a micronutrient of phytoplankton (Moore et al., 2013). Irrespective  
521 of whether the LF were prokaryotic or eukaryotic, the present observations validate Zn excesses and  
522 Zn isotopes as robust biosignatures consistent with morphological criteria.

523

524 The exact kind of life form that the LF represent will be addressed in detail in a separate manuscript,  
525 but we will allow ourselves some preliminary speculation here. The internal organic material may  
526 consist of cyanobacteria carrion harvested in the nepheloid layer. The presence of a brim therefore  
527 suggests that the LF were floating in the water column. This way of living is supported by their  
528 settling on different type of substrata. The LF could represent the remnants of prokaryote gigantism,  
529 in which case they would be the largest bacteria on record, more than an order of magnitude than  
530 the biggest extant species (e.g., up to  $750 \text{ }\mu\text{m}$  for *Thiomargarita namibiensis* (Schulz and Jørgensen,  
531 2001)). It is conceivable that the early appearance gigantism of the LF is in some way related to the  
532 underlying Oklo natural nuclear reactors that would have heated the deep interstitial waters and  
533 thereby triggered the convection of diagenetic fluids and favored extraction (leaching) of nutrients  
534 by interaction of seawater with the host rock.

535

536 More fittingly though, the LF could be eukaryotes, which are often suggested to have appeared 300  
537 My later in the early Mesoproterozoic (Knoll et al., 2006). A caveat is that the date of eukaryote  
538 emergence is contingent on the reliability of molecular clocks (Butterfield, 2015) and scant field  
539 observations. The LF could represent one of the earliest organisms hypothesized by some authors  
540 (Javaux and Lepot, 2018; Knoll, 2014), in this case a soft epibenthic eukaryote. A large variety of cm-

541 sized single-cell organisms using sediment grains to build a delicate agglutinated shell exist in the  
542 modern abyssal ocean (Gooday et al., 2017). Agglutination of silt material, which appeared multiple  
543 times in the evolutionary history of protists (Bowser et al., 2006), would explain the preservation of  
544 LF morphological details through fossilization. Given the multiple biological requirements for Zn, its  
545 concomitant increase in concentration and LF size up strata may simply reflect the greater Zn  
546 demand with increasing cell volume.

## 547 **6. Conclusions**

548 The geochemical features of ~2 Ga old objects in Francevillian sediments demonstrate their  
549 biogenicity under conditions that may be more typical of deep time on Earth and other planets than  
550 the extremely differentiated faunas from the Late Proterozoic and the Early Cambrian. We have  
551 reached the following conclusions:

- 552 a. Diagenetic changes were limited and largely without effect on the mineralogy of the  
553 Francevillian LF. Most non-volatile elements, including Pb and Zn and their isotope  
554 systematics, were left unchanged.
- 555 b. The LF are clearly not concretions or secondary features. The stark geochemical contrasts  
556 between the host rock and the LF fillings, notably those associated with Zn, were buried with  
557 the LF.
- 558 c. Pyritization, when present, is limited to rare fractures and does not affect the bulk of sulfur  
559 concentrated in the organic material and leaves the Zn budget largely unaffected.
- 560 d. The criteria used in this work are heavily biased towards geochemical observations and  
561 demonstrate the biogenic nature of the lenticular forms. These organisms probably  
562 represent clay-clad protists of exceptionally large size.

563e. The decision tree leading to infer the biogenicity of the Francevillian LF may be extended in deep  
564 time to other sedimentary features, while the approach itself of investigating biogenicity of  
565 fossilized remnants using Zn isotopes together with other isotopes (e.g., S and C) and organic  
566 tracers, may be extended to extraterrestrial samples.

567

568

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570 the manuscript. A.E.A, E.C.F, and J.N.G did the field work. J.N.G., C.F., J.N.G., and A.E.A. prepared  
571 the samples and performed XRD analyses and models. A.M. performed X-Ray microtomography.  
572 A.E.A. analyzed morphology, A.R. analyzed carbon and sulfur concentrations. A.C.P.W. analyzed  
573 carbon isotopes. A.L. analyzed Zn and Pb isotope compositions with assistance from J.B.T. A.S  
574 carried out the synchrotron experiments and processed the data.

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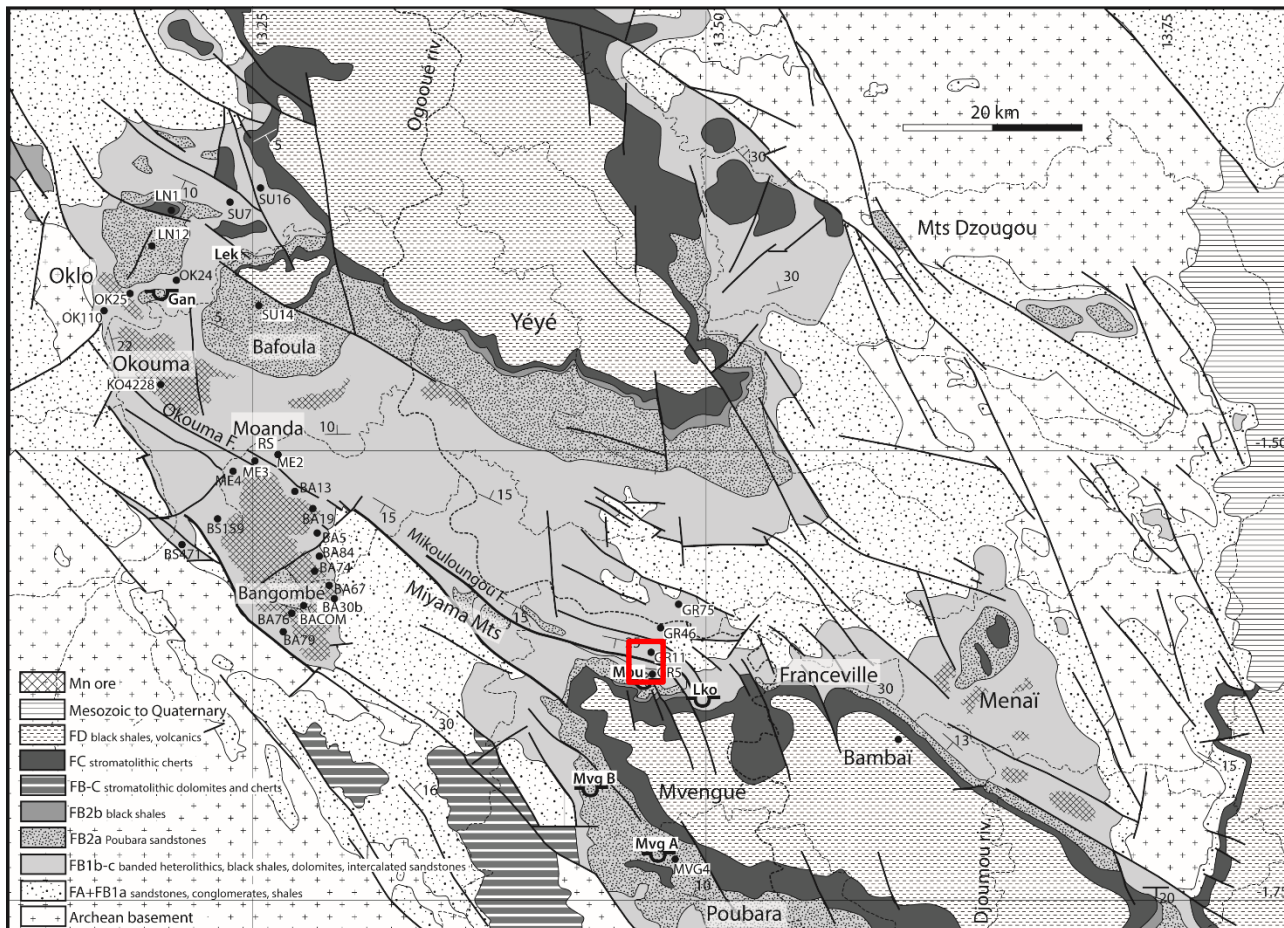
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797 **Figure 1.** Geological map of the Franceville Basin. The studied outcrops are located in the Moulende  
 798 quarry (red square). Structural framework and unit contours modified from Weber (1968) and  
 799 Gauthier-Lafaye (1986).

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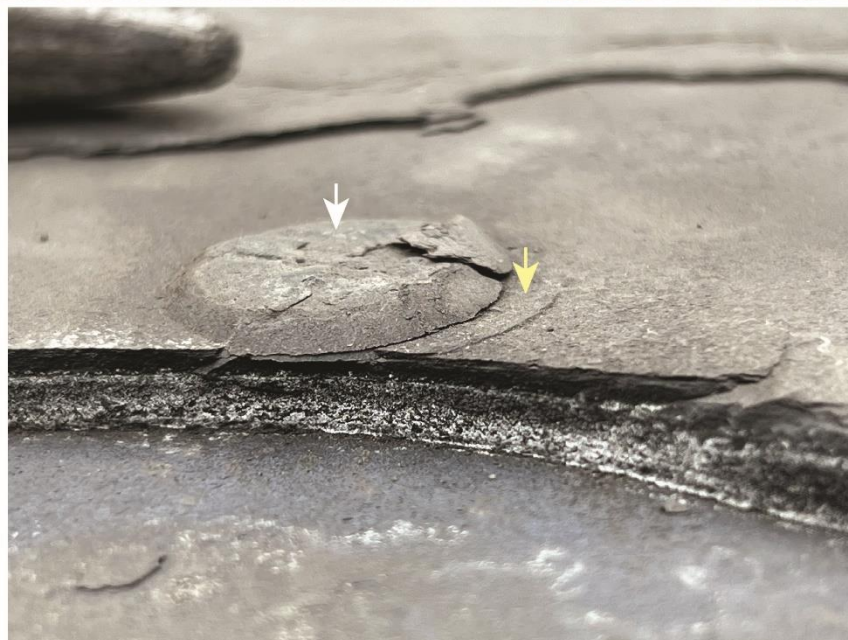
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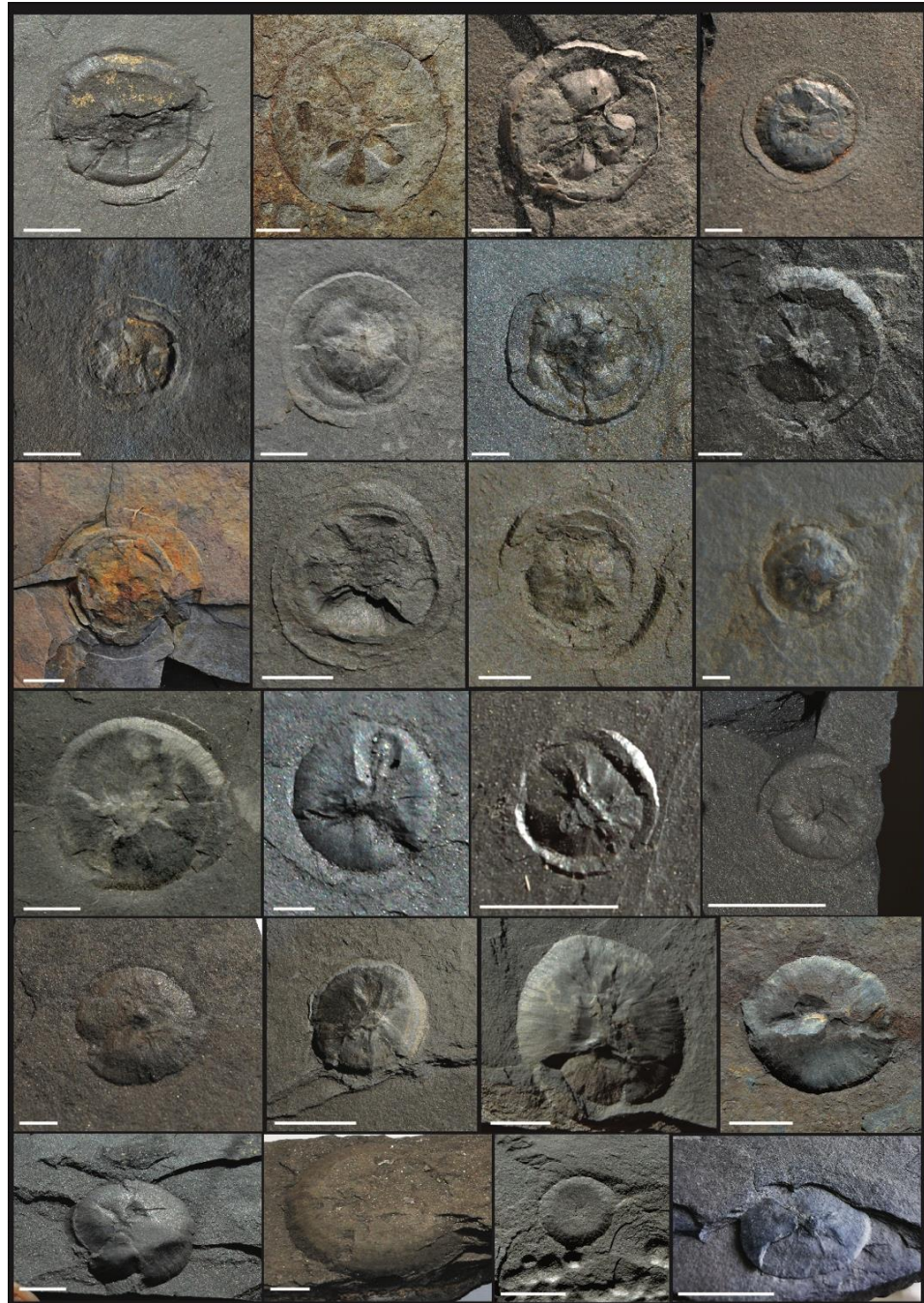


828 **Figure 2: (Top)** View of the outcrop: the 5 m-thick finely horizontally laminated black shales are  
829 interbedded with thin, silty sandstone layers hosting the LF (black arrow), which are homogeneously  
830 distributed throughout the section. **(Bottom)** The white arrow shows the body of an LF specimen,  
831 while the yellow arrow points to its brim.

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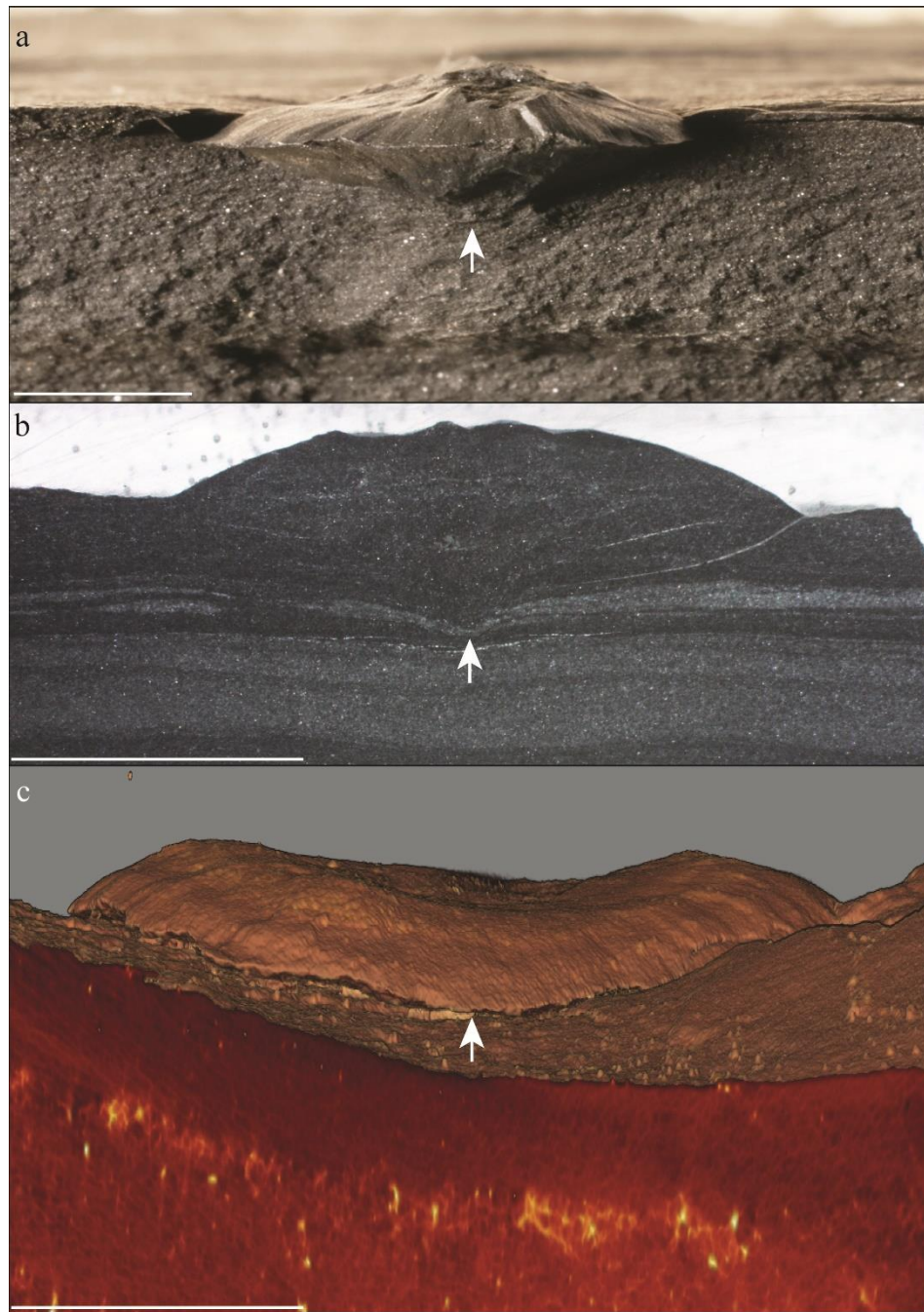


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835 **Figure 3.** Plate of 24 photographs of circular forms (LF) embedded in their black shale host rock  
 836 (from subunit FB2b) arranged in a (row × column) array. Scale bars represent 1 cm. The morphology  
 837 is lenticular, occasionally segmented by radial structures (e.g., 1 × 2, 1 × 3, 3 × 1, 4 × 1), and the outline  
 838 is circular. A brim is present in some of the specimens (e.g., 1 × 1, 1 × 2, 1 × 4, 2 × 2, 3 × 2). Other samples  
 839 miss the brim (e.g., 5 × 3, 5 × 4, 6 × 1, 6 × 3). This dichotomy may represent a contrast between the  
 840 bottom and the top of the organism or be a preservation artefact. The dome part is filled with  
 841 organic-rich clay.

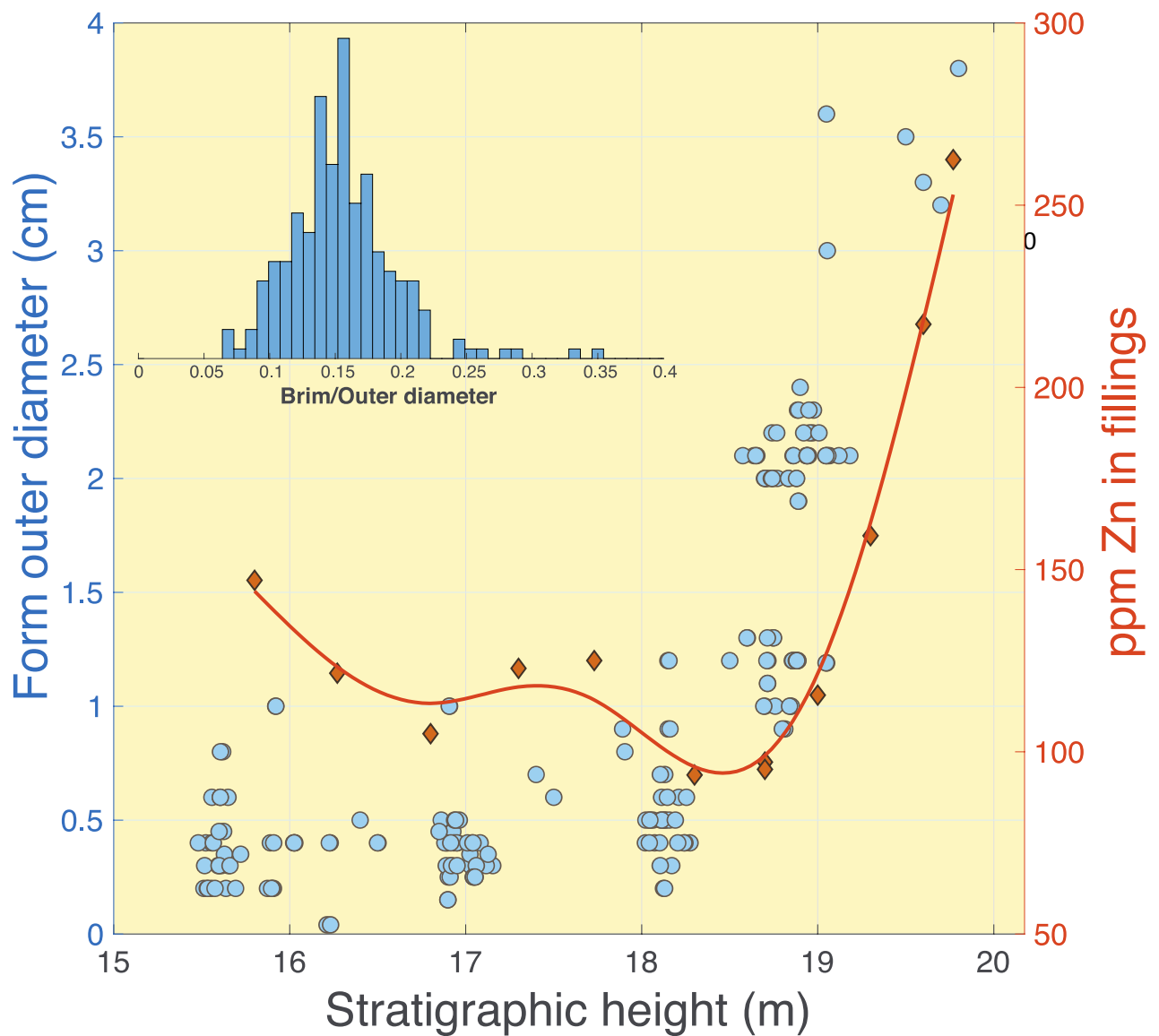


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**Figure 4. (a)** Biconvex LF specimen surrounded by its host rock. White arrows show the upper and lower apex, respectively. Scale bars are 1 cm. **(b,c)** Two cross-sections showing the relationship between an LF specimen and its underlying sediment. **(b)**: Reflected-light microscopic view. **(c)** Three-dimensional color X-ray microtomography. In both cases, the LF is clearly observed to deflect the underlying laminae (white arrows), which attests that the LF are syndepositional features and not secondary concretions. White scale bar is 1cm.

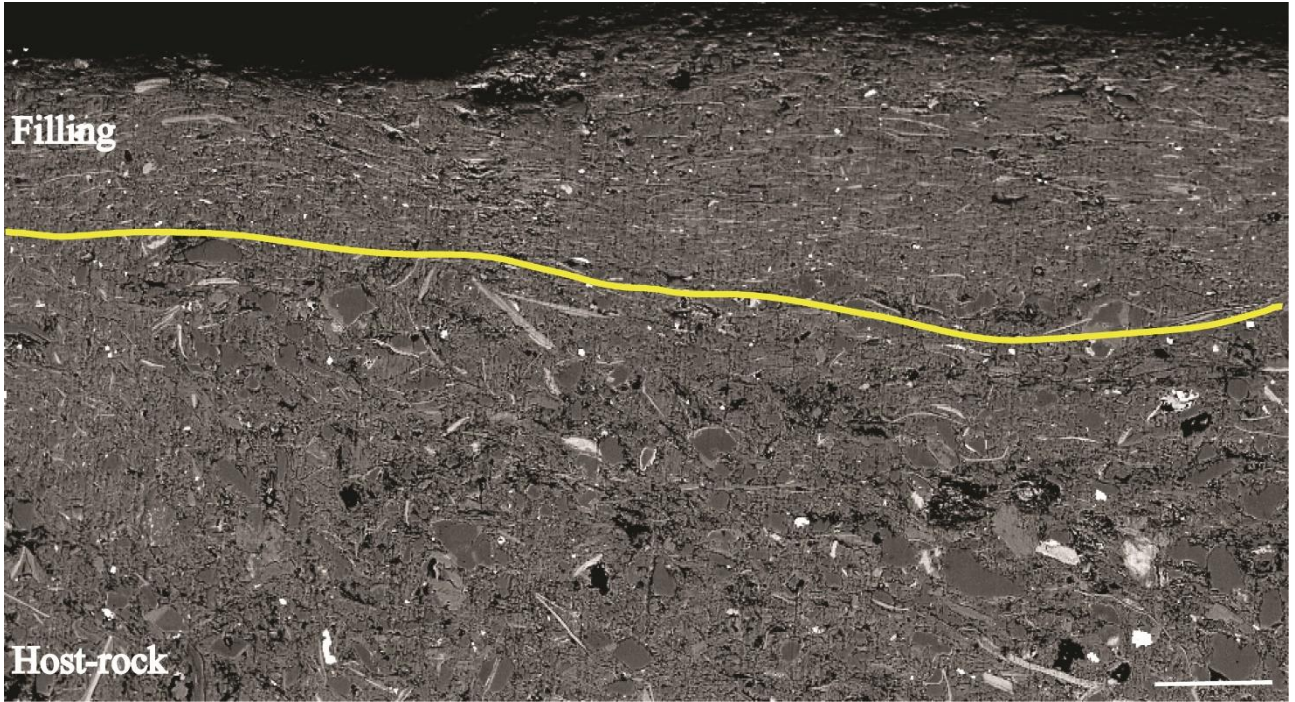
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896 **Figure 5.** Lenticular form diameters (in blue) and Zn contents of their fillings (in red) vs stratigraphic  
897 height. Jitter has been applied to the x-axis for better readability. The red curve is a fit of the filling  
898 data with a smoothing spline. The sharp increase of both parameters starting at 18.5 m indicates  
899 that a sudden increase in nutrient supply contributed to the ten-fold increase in organism size. Inset:  
900 Histogram of the brim/external diameter ratio, which shows that the geometric characteristics of  
901 the LF remain in constant proportion, a feature indicative of a biological origin.

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904 **Figure 6.** Scanning electron microscopy-back-scattered electron imaging (SEM-BSE) coupled to  
905 energy-dispersive X-ray spectrometry (EDX) showing contrast in textural and mineralogical  
906 compositions within the LF comparing to the host rock. The yellow line traces the contact between  
907 the LF specimen and its host rock. It shows very clearly to the naked eye that the grain size of quartz,  
908 micas, and chlorite are coarser and more randomly distributed in the host rock than in the LF  
909 specimen. White scale bar is 1 mm.

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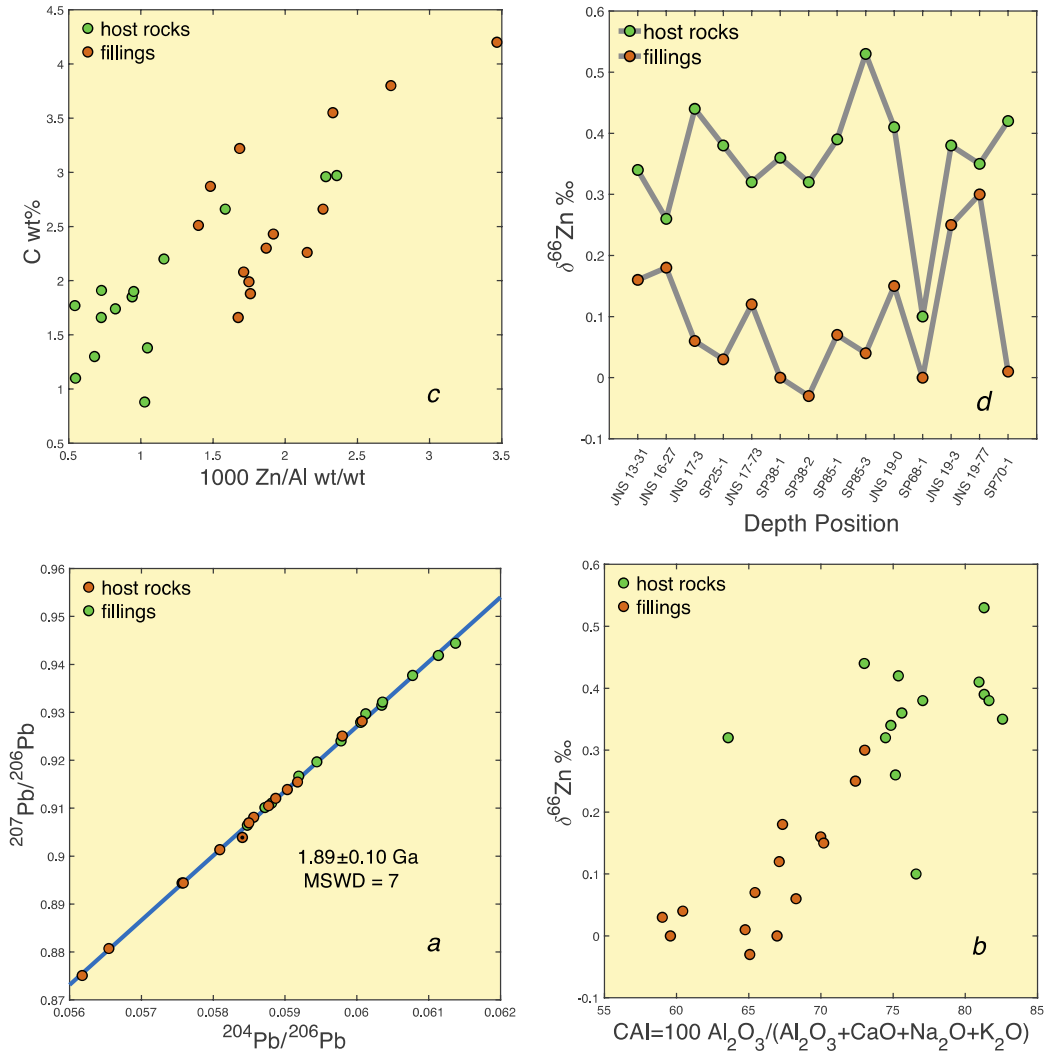
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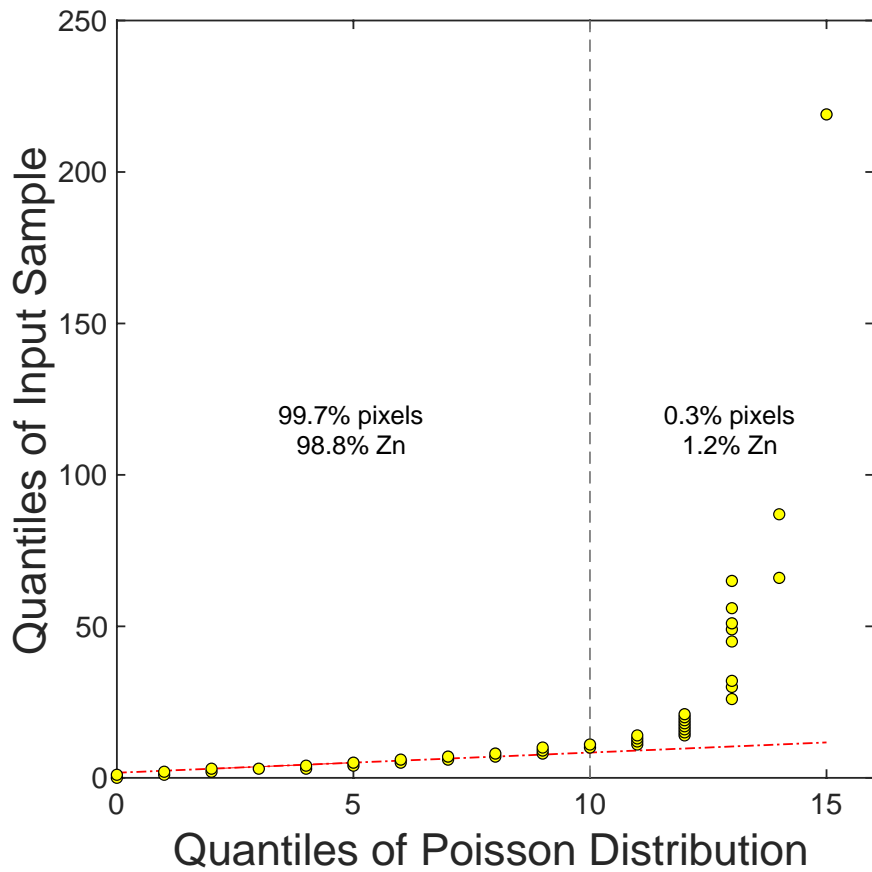


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919 **Figure 7.** Geochemistry of the host rock of the LF and their fillings. **(a)** The Pb-Pb linear array (inverse  
920 isochron) shows that if the U-Pb chronometer has been reset, it could only have been shortly after  
921 sedimentation. The sample with a dotted symbol has been left out of the calculations. The error bar  
922 includes correction for an MSWD value of 7 and is identical at the same confidence level to the  
923 errors calculated by Monte Carlo and bootstrapping. The age is indistinguishable from literature  
924 dates (Bonhomme et al., 1982; Bros et al., 1992). **(b)** Relationship between  $\delta^{66}\text{Zn}$  and the Chemical  
925 Index Alteration (CIA) (Nesbitt and Young, 1982). The host rock is dominated by residual material  
926 from thoroughly lixiviated soils, whereas the LF fillings contain large fractions of fine-grained  
927 material (clays) eroded from the continental surface. **(c)** Correlation between the organic carbon  
928 contents of the host rock and the fillings and Zn/Al ratios. The main Zn carrier is clearly associated  
929 with the organic component. **(d)** Comparison between the  $\delta^{66}\text{Zn}$  values of the host rock and the  
930 corresponding LF fillings. The  $\delta^{66}\text{Zn}$  values of the host rock fall within the lithogenic range  
931 ( $0.28 \pm 0.13\%$  (Moynier et al., 2017)), whereas the fillings are characterized by significantly lower  
932  $\delta^{66}\text{Zn}$  indicative of organic carbon sediments (Little et al., 2016). Typical error bars are 0.05‰.



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**Figure 8:** Quantile-quantile plot comparing, as an example, the observed frequency of the Zn intensity (counts per 10 ms per pixel) measured in the fillings by SR-XRF (shown in Fig. 7a) with the frequencies expected from a Poisson (random) distribution. The 1:1 straight-line (in stippled red) shows the perfect correspondence for low-counts pixels, which are the overwhelming majority. The array deviates from linearity at  $\sim 10$  cps. Only 0.3 % of the pixels are outliers ( $>10$  cp10ms) with respect to a Poisson distribution and they account for 1.2% of the total Zn concentration of the measured region. The bulk of the Zn inventory, and in particular Zn excesses, therefore should be associated with the carbon-rich background matrix and not with disseminated sulfide crystals. We found Poisson distributions with similar (Zn outlier)/(total Zn) ratios for all the measured regions.

960 **Table 1.** Mineralogical and geochemical contrasts between host rock and LF fillings. Parameter  $p$   
 961 measures the probability that the LF and their host rock belong to the same population (t-test). The  
 962 standard asterisk scale is \*\*\* for  $p < 0.001$ , \*\* for  $p < 0.01$ , and \* for  $p < 0.05$ .

Host rock	LF fillings	$p$
40% clay minerals	70% clay minerals	n/a
av. diameter of quartz grains 50 $\mu\text{m}$	av. diameter of quartz grains 25 $\mu\text{m}$	n/a
C=0.16 $\pm$ 0.05 mol/100g	C=0.22 $\pm$ 0.06 mol/100g	*
High Si, K, Zr, Hf High CAI	High Na, Ca, Er-Lu High Na/K, Lu/Hf	***
av. [Zn]=94 $\pm$ 40 ppm	av. [Zn]=175 $\pm$ 54 ppm	***
av. $\delta^{66}\text{Zn}$ =0.36 $\pm$ 0.10‰	av. $\delta^{66}\text{Zn}$ =0.10 $\pm$ 0.10‰	***
av. $^{206}\text{Pb}/^{204}\text{Pb}$ =16.70 $\pm$ 0.25	av. $^{206}\text{Pb}/^{204}\text{Pb}$ =17.14 $\pm$ 0.33	**

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Supplementary Table S1. Zn and Pb isotope compositions of the lenticular forms and their host rocks

	$\delta^{66}\text{Zn} \text{‰}^a$	$^{206}\text{Pb}/^{204}\text{Pb}$	$\pm 2s$	$^{207}\text{Pb}/^{204}\text{Pb}$	$\pm 2s$	$^{208}\text{Pb}/^{204}\text{Pb}$	$\pm 2s$
Host rocks							
JNS 13,31	0.34	16.8229	6	15.4712	8	40.9248	25
JNS 16,27	0.26	16.6325	7	15.4628	7	45.4806	24
JNS 17,3	0.44	17.0301	9	15.5003	9	47.9881	31
SP25-1	0.38	16.5712	6	15.4355	7	42.9549	22
JNS 17,73	0.32	16.6512	6	15.4529	7	45.2254	22
SP38-1	0.36	16.7282	9	15.4573	11	40.4249	37
SP38-2	0.32	16.3574	8	15.4062	11	39.1924	33
SP85-1	0.39	16.6520	5	15.4514	5	40.9423	14
SP85-3	0.53	16.2938	5	15.3882	7	41.0597	21
JNS 19,0	0.41	17.0031	8	15.4908	8	47.9608	26
SP68-1	0.10	16.8948	6	15.4873	7	41.2919	23
JNS 19,3	0.38	16.4538	10	15.4284	12	40.9575	41
JNS 19,77	0.35	17.1014	7	15.5010	10	45.0732	20
SP70-1	0.42	16.5680	6	15.4434	5	43.7276	17
Lenticular forms							
JNS 13-31	0.16	16.9865	7	15.4925	6	40.5764	19
JNS 16-27	0.18	16.7234	8	15.4700	6	44.5041	21
JNS 17-3	0.06	17.3712	9	15.5368	9	49.1236	28
SP25-1	0.03	17.8013	8	15.5778	7	48.4227	53
JNS 17-73	0.12	17.2144	10	15.5159	10	45.9137	32
SP38-1	0.00	16.9399	6	15.4811	6	40.7712	18
SP38-2	-0.03	16.8993	6	15.4701	7	40.7763	22
SP85-1	0.07	17.0152	8	15.4925	7	41.3270	20
SP85-3	0.04	17.1217	10	15.4762	10	41.6602	34
JNS 19-0	0.15	17.6843	8	15.5746	9	45.4911	26
SP68-1	0.00	17.0752	9	15.5066	8	41.7341	26
JNS 19-3	0.25	16.6464	8	15.4506	8	41.2924	22
JNS 19-77	0.30	17.0952	9	15.5042	9	44.4140	30
SP70-1	0.01	17.3660	6	15.5327	4	44.3411	18

<sup>a</sup> precision  $\pm 0.05\text{‰}$ <sup>b</sup> probability (t -test) 7.3E-07 1.2E-03 2.3E-03 6.9E-01

Table S2: Major and trace elements of the fillings and the host rocks of the circular forms

	unit	Host rocks														$\rho^a$
		JNS 3,31	JNS 16,27	JNS 7,3	SP 25-1	JNS 17,73	SP 38-1	SP 38-2	SP 85-1	SP 85-3	JNS 19,0	SP 68-1	JNS 19,3	JNS 19,77	SP 70-1	
height	m	13.31	16.27	17.3	16.8	17.73	18.3	18.3	18.7	18.7	19	19.6	19.3	19.77	15.8	
SiO <sub>2</sub>	%	58.30	57.81	58.09	57.16	54.74	57.89	57.56	61.27	61.45	62.88	58.21	61.85	58.93	56.76	1.4E-07
Al <sub>2</sub> O <sub>3</sub>	%	18.86	18.60	17.07	20.79	12.06	18.85	17.86	19.06	18.81	18.65	18.30	15.14	16.69	18.68	3.7E-01
Fe <sub>2</sub> O <sub>3</sub>	%	2.36	2.20	2.81	2.46	6.50	2.27	2.32	3.71	4.47	3.44	2.51	3.81	3.69	2.28	1.5E-01
MnO	%	0.24	0.26	0.44	0.28	0.74	0.26	0.27	0.15	0.10	0.07	0.39	0.23	0.49	0.32	6.0E-01
MgO	%	2.86	2.74	3.06	2.71	5.55	2.74	2.74	1.97	1.96	1.96	2.63	3.02	3.43	2.79	3.4E-01
CaO	%	2.18	2.07	2.67	1.52	5.21	1.95	2.14	0.32	0.34	0.37	1.60	0.27	0.23	2.02	2.9E-05
Na <sub>2</sub> O	%	0.38	0.35	0.33	0.41	0.23	0.40	0.39	0.36	0.36	0.39	0.38	0.30	0.34	0.39	1.2E-06
K <sub>2</sub> O	%	3.79	3.73	3.32	4.27	1.47	3.73	3.60	3.71	3.64	3.63	3.62	2.83	2.95	3.71	7.9E-02
TiO <sub>2</sub>	%	0.40	0.39	0.39	0.46	0.32	0.41	0.36	0.40	0.39	0.41	0.39	0.42	0.33	0.40	8.4E-03
P <sub>2</sub> O <sub>5</sub>	%	0.14	0.16	0.13	0.12	0.12	0.13	0.15	0.20	0.17	0.17	0.16	0.20	0.05	0.15	4.0E-01
CaI		74.84	75.16	73.00	77.05	63.57	75.60	74.47	81.31	81.30	80.95	76.59	81.64	82.58	75.36	9.5E-06
As	ppm	0.8	0.8	0.8	1.25	7.0	0.82	1.17	0.75	1.33	10.9	<L.D.	1.4	0.4	0.79	5.9E-01
Ba	ppm	1448	1482	1294	1705	651	1466	1404	1434	1424	1505	1445	1137	1132	1528	2.2E-01
Be	ppm	1.5	1.6	1.3	1.91		1.75	1.68	1.61	1.85	1.5	1.58	1.7	1.3	1.71	2.7E-01
Cd	ppm	0.3	0.7	0.4	0.11	0.4		0.07	0.04	0.05	0.3	0.54	0.1	0.2	0.03	
Co	ppm	5.3	5.1	4.2	6.21	20.1	4.59	5.73	5.76	6.38	8.9	4.86	6.7	5.3	6.47	3.2E-01
Cr	ppm	33.2	33.8	36.3	55.5	40.6	49.9	46.7	51.3	49.9	54.8	49.7	41.7	37.0	49.5	5.1E-02
Cs	ppm	11.0	10.7	8.5	13.8	5.5	12.1	11.3	11.1	11.1	11.1	11.2	9.0	8.0	11.5	4.3E-02
Cu	ppm	57.0	51.9	58.0	20.7	34.6	62.1	64.4	24.8	16.3	56.6	95.5	56.1	40.1	64.0	1.9E-01
Ga	ppm	23.0	23.9	21.3	27.7	17.1	24.5	22.9	23.5	23.8	23.9	23.5	20.0	20.6	24.4	3.9E-01
Ge	ppm	2.5	2.4	2.4	2.66	2.3	2.37	2.22	2.35	2.67	2.1	2.24	2.1	2.0	2.41	8.9E-01
Hf	ppm	4.6	5.0	5.1	2.29	6.8	4.24	4.93	4.58	4.33	5.6	4.78	5.6	3.5	5.04	1.1E-07
Mo	ppm	0.3	0.3	0.3	1.05	0.8	1.04	1.15	1.28	1.39	0.8	1.02	0.3	0.3	1.15	4.8E-03
Nb	ppm	5.3	5.5	5.6	6.14	4.6	5.72	5.28	5.66	5.55	5.9	5.75	5.6	4.1	5.82	3.6E-03
Ni	ppm	33.5	33.9	42.6	55.1	83.2	42.8	43.6	66.7	82.7	60.7	47.2	52.1	48.9	45.8	2.2E-01
Pb	ppm	18.1	12.3	15.0	16.9	13.4	6.14	9.50	5.95	9.38	10.8	3.89	8.4	5.1	6.23	6.5E-01
Rb	ppm	123.8	126.1	108.4	150	53.9	132	122	125	125	125.3	127	105.3	95.2	132	1.6E-01
Sb	ppm	0.3	0.3	0.3	0.37	0.8	0.21	0.28	0.23	0.38	0.5	0.17	0.3	0.2	0.29	9.2E-01
Sc	ppm	8.4	7.9	7.4	9.19		8.53	8.21	8.55	8.73		8.67	7.8	9.3	9.10	7.8E-01
Sn	ppm	4.1	1.6	1.9	1.08	1.3	1.18	2.02	0.82	0.88	1.3	0.91	1.2	0.8	0.87	3.7E-02
Sr	ppm	84.0	85.9	91.6	90.6	70.0	93.7	88.2	83.0	78.5	86.3	88.1	94.2	74.2	90.2	2.7E-05
Ta	ppm	0.5	0.5	0.5	0.50	0.4	0.47	0.47	0.50	0.48	0.5	0.52	0.5	0.4	0.50	2.3E-03
Th	ppm	12.8	13.5	13.5	15.1	10.8	14.2	13.0	13.7	13.8	14.4	15.3	16.0	10.0	14.7	2.6E-01
U	ppm	1.2	1.2	1.2	1.20	1.1	1.17	1.17	1.17	1.16	1.2	1.15	1.3	0.8	1.24	7.9E-03
V	ppm	50.7	50.0	49.5	59.3	32.4	52.0	47.4	46.5	48.3	53.0	46.9	38.7	43.0	52.0	6.2E-01
W	ppm	1.6	1.7	1.8	1.66	1.0	1.29	1.95	1.97	1.89	1.7	1.62	2.1	1.3	1.79	8.4E-02
Y	ppm	14.3	13.6	12.8	11.5	13.8	13.1	13.1	16.3	19.1	14.3	12.9	13.9	10.2	14.4	6.1E-02
Zn	ppm	54.2	53.9	65.6	91.4	150.5	64.1	190	93.1	139	93.9	70.5	82.3	102.4	59.3	3.1E-04
Zr	ppm	179.9	192.2	197.0	81.0	265.4	163	189	172	164	220.0	183	210.1	134.8	190	1.6E-07
La	ppm	41.9	40.2	39.4	41.0	23.5	43.4	40.8	45.1	40.0	43.4	44.4	52.8	30.0	41.1	8.3E-01
Ce	ppm	76.9	74.2	73.9	74.9	44.3	79.5	75.1	83.2	74.4	80.4	81.6	97.1	57.0	76.5	9.3E-01
Pr	ppm	8.2	8.0	8.0	8.09	4.9	8.58	8.10	8.90	8.08	8.7	8.85	10.3	6.2	8.26	8.2E-01
Nd	ppm	28.5	28.0	28.1	28.0	18.2	29.9	28.4	30.7	28.3	30.6	30.4	35.5	22.2	28.8	9.6E-01
Sm	ppm	4.5	4.6	4.5	4.35	3.2	4.70	4.60	4.79	4.29	4.9	4.72	5.4	3.6	4.66	3.8E-01
Eu	ppm	1.0	1.0	1.0	0.984	0.8	1.04	1.00	1.03	1.01	1.1	1.02	1.2	0.8	1.06	3.0E-01
Gd	ppm	3.2	3.4	3.2	3.20	2.6	3.38	3.18	3.48	3.49	3.5	3.27	3.7	2.6	3.40	2.7E-01
Tb	ppm	0.4	0.4	0.4	0.406	0.4	0.426	0.418	0.445	0.467	0.5	0.406	0.5	0.3	0.440	8.4E-02
Dy	ppm	2.3	2.3	2.2	2.04	2.1	2.29	2.23	2.47	2.63	2.4	2.17	2.5	1.8	2.36	1.2E-02
Ho	ppm	0.5	0.4	0.4	0.379	0.4	0.439	0.439	0.495	0.532	0.4	0.427	0.5	0.3	0.471	5.0E-03
Er	ppm	1.2	1.1	1.1	0.930	1.1	1.10	1.12	1.24	1.33	1.2	1.10	1.2	0.9	1.18	2.4E-04
Tm	ppm	0.2	0.2	0.1	0.124	0.2	0.149	0.154	0.161	0.171	0.2	0.145	0.2	0.1	0.157	2.5E-06
Yb	ppm	1.1	1.0	1.0	0.790	1.1	0.964	1.00	1.01	1.09	1.1	0.989	1.1	0.7	1.05	2.4E-07
Lu	ppm	0.158	0.153	0.158	0.112	0.167	0.140	0.145	0.148	0.157	0.159	0.141	0.162	0.110	0.152	3.6E-07



Table S2: continued

		Fillings													
	unit	NS 13-3	NS 16-2	NS 17-3	SP25-1	NS 17-7	SP38-1	SP38-2	SP85-1	SP85-3	NS 19-4	SP68-1	NS 19-3	NS 19-7	SP70-1
SiO <sub>2</sub>	%	52.03	54.24	52.70	47.74	52.00	49.79	53.89	51.89	49.36	53.30	53.02	55.57	55.35	49.79
Al <sub>2</sub> O <sub>3</sub>	%	18.86	18.39	18.48	17.07	18.60	16.15	17.32	19.35	17.80	18.95	19.05	19.23	19.87	19.30
Fe <sub>2</sub> O <sub>3</sub>	%	3.37	2.07	2.83	1.54	2.47	2.14	2.51	2.43	2.31	2.68	2.02	3.87	4.06	2.24
MnO	%	0.30	0.16	0.40	0.21	0.77	0.23	0.27	0.25	0.33	0.77	0.38	0.24	0.15	0.29
MgO	%	2.97	2.63	3.10	2.23	2.74	2.43	2.61	2.59	2.72	2.86	2.68	2.54	1.99	2.74
CaO	%	3.61	3.73	3.95	5.99	3.80	5.62	4.47	4.63	5.93	3.46	3.99	2.51	2.08	4.84
Na <sub>2</sub> O	%	0.85	1.42	1.03	2.21	1.42	1.97	1.25	1.43	1.85	0.82	1.33	1.17	1.19	1.57
K <sub>2</sub> O	%	3.63	3.77	3.61	3.67	3.90	3.38	3.57	4.17	3.88	3.78	4.08	3.67	4.07	4.10
TiO <sub>2</sub>	%	0.36	0.33	0.33	0.32	0.32	0.31	0.32	0.41	0.36	0.37	0.37	0.39	0.39	0.40
P <sub>2</sub> O <sub>5</sub>	%	0.32	0.14	0.14	0.14	0.14	0.19	0.14	0.17	0.16	0.11	0.15	0.12	0.18	0.16
CAI		69.98	67.34	68.27	59.01	67.11	59.57	65.07	65.43	60.43	70.19	66.96	72.39	73.03	64.75
As	ppm	3.772	0.551	<L.D.	0.7	0.888	0.7	1.1	1.0	0.880	2.4	4.9	2.1	0.6	
Ba	ppm	1434	1433	1390	1496	1514	1264	1341	1508	1419	1496	1595	1394	1597	1551
Be	ppm	1.7	1.7	1.6	1.7	1.6	1.7	1.7	1.8	1.6	1.7	1.7	1.3	2.1	1.8
Cd	ppm	0.1		0.0	0.0	0.0		0.0	0.1	0.2	0.0	1.0	0.6	0.2	0.1
Co	ppm	13.5	3.3	4.4	5.6	5.6	5.1	5.3	6.7	6.1	8.9	7.4	17.0	32.8	3.6
Cr	ppm	46.2	46.2	46.9	48.2	48.5	49.2	46.6	60.9	47.5	50.3	50.0	53.7	54.3	51.7
Cs	ppm	7.7	12.2	11.3	12.9	12.1	11.7	11.5	13.0	12.3	12.3	12.9	11.1	13.4	12.8
Cu	ppm	175.0	61.4	62.0	86.9	54.0	86.6	78.2	22.0	27.4	111.0	21.2	54.1	39.8	40.5
Ga	ppm	24.2	23.0	23.1	22.3	24.0	20.8	21.5	24.9	23.1	24.6	24.8	24.2	25.5	25.5
Ge	ppm	2.2	2.1	2.5	1.8	2.1	2.0	2.0	2.5	2.4	2.6	2.4	2.7	2.7	2.3
Hf	ppm	3.3	2.3	2.3	1.8	2.0	2.3	2.6	1.5	1.7	2.3	1.9	2.3	2.1	1.9
Mo	ppm	1.9	1.0	0.8	1.0	1.3	1.3	0.8	1.2	1.6	1.3	1.3	1.5	1.0	1.1
Nb	ppm	5.3	4.9	4.7	4.6	4.8	4.6	4.7	5.3	4.8	5.1	5.1	5.3	5.3	5.4
Ni	ppm	81.5	39.1	49.9	71.2	48.0	48.6	46.9	58.0	51.6	58.4	50.1	82.1	137.2	41.6
Pb	ppm	14.3	5.3	4.2	4.2	5.7	5.7	3.7	10.4	11.7	6.6	20.2	18.1	9.4	6.5
Rb	ppm	120.0	127.2	122.1	128.2	130.9	115.3	117.9	135.1	124.9	133.1	139.7	121.6	139.7	138.3
Sb	ppm	0.8	0.3	0.2	0.2	0.2	0.2	0.1	0.3	0.2	0.3	0.5	0.6	0.5	0.3
Sc	ppm	9.7	7.8	8.1	8.3	7.9	7.4	7.3	7.2	7.2	8.5	8.2	9.5	11.6	7.4
Sn	ppm	5.8	1.1	1.3	5.0	1.2	2.3	1.1	2.5	5.2	4.6	2.3	1.0	1.4	2.5
Sr	ppm	85.2	105.7	106.7	132.1	103.9	113.4	101.0	103.0	109.2	102.6	101.4	93.1	103.7	106.7
Ta	ppm	0.5	0.4	0.4	0.4	0.4	0.5	0.4	0.4	0.4	0.4	0.4	0.5	0.5	0.4
Th	ppm	10.5	13.9	13.5	14.5	13.9	14.0	13.3	11.3	10.6	13.0	14.1	13.4	12.7	12.9
U	ppm	1.0	1.0	0.9	1.1	1.1	1.0	0.9	1.0	1.1	0.9	1.1	1.4	1.0	1.1
V	ppm	51.2	47.8	45.4	51.9	48.7	44.5	46.6	52.8	48.7	46.0	51.9	48.9	49.8	52.0
W	ppm	1.6	1.2	1.4	2.7	1.7	6.4	1.8	4.0	3.7	1.7	1.8	1.6	2.0	4.0
Y	ppm	14.5	10.4	10.0	10.6	10.0	9.5	10.1	10.0	10.2	11.3	9.6	11.4	22.5	10.6
Zn	ppm	205.4	144.8	151.1	180.5	166.8	126.4	119.9	126.5	146.4	151.7	243.3	193.5	321.9	168.6
Zr	ppm	128.6	82.8	84.7	66.9	73.6	83.6	93.4	54.2	60.2	84.8	67.4	87.2	78.2	68.9
La	ppm	33.2	39.7	42.1	46.5	39.7	43.2	41.1	36.4	33.9	43.5	37.2	34.6	49.1	36.6
Ce	ppm	62.4	73.7	78.1	88.9	73.4	79.2	75.4	69.9	64.3	80.3	68.0	64.3	91.3	67.8
Pr	ppm	6.9	8.0	8.4	9.1	7.9	8.5	8.1	7.3	6.8	8.6	7.4	7.1	9.9	7.3
Nd	ppm	25.3	27.9	29.4	31.3	28.0	29.7	28.0	25.2	24.2	30.4	25.6	25.3	36.0	26.0
Sm	ppm	4.25	4.23	4.35	4.42	4.21	4.31	4.15	4.18	3.97	4.54	3.94	4.05	5.61	4.17
Eu	ppm	1.02	0.92	0.94	0.92	0.94	0.92	0.87	0.96	0.96	1.00	0.90	0.93	1.33	0.96
Gd	ppm	3.24	2.90	2.92	3.01	2.89	2.85	2.80	3.12	3.11	3.04	2.79	2.94	4.51	3.13
Tb	ppm	0.42	0.36	0.35	0.37	0.36	0.35	0.34	0.37	0.38	0.37	0.34	0.38	0.58	0.39
Dy	ppm	2.32	1.83	1.77	1.84	1.83	1.83	1.82	1.94	1.91	1.93	1.73	1.95	2.97	2.07
Ho	ppm	0.44	0.35	0.34	0.34	0.34	0.33	0.34	0.34	0.34	0.35	0.32	0.36	0.57	0.36
Er	ppm	1.10	0.85	0.85	0.83	0.84	0.80	0.84	0.80	0.79	0.88	0.77	0.87	1.35	0.87
Tm	ppm	0.14	0.11	0.11	0.11	0.11	0.10	0.11	0.10	0.10	0.11	0.10	0.11	0.15	0.11
Yb	ppm	0.91	0.70	0.70	0.71	0.66	0.68	0.73	0.61	0.64	0.71	0.65	0.74	0.92	0.66
Lu	ppm	0.130	0.102	0.103	0.102	0.096	0.102	0.108	0.090	0.092	0.110	0.093	0.106	0.139	0.098

Table S2: continued

		Host rocks														
	<i>unit</i>	JNS 3,31	JNS 16,27	JNS 7,3	SP 25-1	JNS 17,73	SP 38-1	SP 38-2	SP 85-1	SP 85-3	JNS 19,0	SP 68-1	JNS 19,3	JNS 19,77	SP 70-1	<i>p</i> <sup>a</sup>
Th/U		10.364	10.867	10.955	12.551	10.009	12.075	11.16	11.722	11.903	11.924	13.331	12.121	12.097	11.818	<i>0.11</i>
Lu/Hf		0.034	0.030	0.031	0.049	0.025	0.033	0.029	0.032	0.036	0.028	0.030	0.029	0.031	0.030	<i>1.2E-06</i>
Ce/Ce <sup>*b</sup>		0.96	0.96	0.97	0.96	0.96	0.96	0.96	0.97	0.96	0.97	0.96	0.97	0.97	0.97	<i>0.18</i>
Eu/Eu <sup>*b</sup>		1.15	1.10	1.11	1.11	1.21	1.10	1.11	1.07	1.10	1.10	1.10	1.15	1.15	1.13	<i>0.95</i>
Y/Y <sup>*d</sup>		1.17	1.14	1.14	1.10	1.26	1.10	1.12	1.24	1.36	1.18	1.13	1.09	1.11	1.15	<i>0.26</i>
		Fillings														
	<i>unit</i>	JNS 3,31	JNS 16,27	JNS 7,3	SP 25-1	JNS 17,73	SP 38-1	SP 38-2	SP 85-1	SP 85-3	JNS 19,0	SP 68-1	JNS 19,3	JNS 19,77	SP 70-1	
Th/U		10.1	14.321	15.034	13.657	13.192	13.411	14.238	10.969	9.3088	14.506	12.685	9.9147	12.519	11.528	
Lu/Hf		0.039	0.044	0.044	0.056	0.049	0.044	0.042	0.059	0.054	0.048	0.048	0.045	0.065	0.051	
Ce/Ce <sup>*</sup>		0.96	0.96	0.97	1.01	0.96	0.97	0.97	1.00	0.98	0.97	0.96	0.96	0.96	0.96	
Eu/Eu <sup>*</sup>		1.16	1.10	1.11	1.07	1.14	1.10	1.08	1.12	1.15	1.14	1.14	1.14	1.12	1.12	
Y/Y <sup>*</sup>		1.22	1.10	1.09	1.13	1.07	1.03	1.09	1.03	1.06	1.16	1.09	1.15	1.46	1.03	
Zn <sub>xs</sub> (Fe) <sup>c</sup>		128	94	85	123	110	66	28	66	74	79	187	110	209	110	
Zn <sub>xs</sub> (Zr) <sup>c</sup>		167	122	123	105	125	94	78	97	95	116	217	159	262	147	

<sup>a</sup> probability that the host rock and the filling belong to the same population (*t*-test). In italic, values <0.0003.

<sup>b</sup> Ce/Ce\* = Ce<sub>N</sub>/(La<sub>N</sub>×Pr<sub>N</sub>)<sup>1/2</sup>, Eu/Eu\* = Eu<sub>N</sub>/(Sm<sub>N</sub>×Gd<sub>N</sub>)<sup>1/2</sup>, Y/Y\* = Y<sub>N</sub>/(Dy<sub>N</sub>×Ho<sub>N</sub>)<sup>1/2</sup>

where N indicates normalization to MuQ values of Kamber et al. (2005)

<sup>c</sup> See main text for the Zn excess formula

Supplementary Table S3. C, P, and S contents of the lenticular forms and their host rocks

		C	P	C/P	S
units	sample	mol/100g	mol/100g	mol/mol	ppm
Host rocks	SP38-1	0.1594	0.0020	81	<100
	SP38-2	0.2467	0.0023	109	540
	SP85-1	0.1153	0.0030	38	380
	SP85-3	0.2219	0.0026	86	<100
	SP68-1	0.1451	0.0024	60	<100
	SP70-1	0.1080	0.0023	48	520
	SP25-1	0.1543	0.0018	85	540
	JNS 13,31	0.1472	0.0020	75	481
	JNS 16,27	0.0917	0.0023	41	<100
	JNS 17,3	0.1383	0.0018	75	<100
	JNS 17,73	0.2475	0.0017	146	<100
	JNS 19,0	0.1587	0.0024	66	<100
	JNS 19,3	0.0733			133
	JNS 19,77	0.1832			<100
Lenticular forms	SP38-1	0.1383	0.0029	48	410
	SP38-2	0.2392	0.0021	113	<100
	SP85-1	0.2093	0.0026	82	<100
	SP85-3	0.1567	0.0024	65	<100
	SP68-1	0.3168	0.0023	140	<100
	SP70-1	0.1917	0.0024	79	<100
	SP25-1	0.2219	0.0021	105	<100
	JNS 13,31	0.2955	0.0048	61	3390
	JNS 16,27	0.2683	0.0021	127	<100
	JNS 17,3	0.1658	0.0021	78	<100
	JNS 17,73	0.2023	0.0021	96	<100
	JNS 19,0	0.1733	0.0017	104	<100
	JNS 19,3	0.1886	0.0018	104	2340
	JNS 19,77	0.3503	0.0027	129	510

average and stand. dev. host rocks

76 30

average and stand. dev. infillings

95 27

probability (t -test)

0.038

0.329

0.306

Supplementary Table S4.  $\delta^{13}\text{C}$  data measured on the carbon fractions of LF fillings (1) and host sediments (2).

sample	$\delta^{13}\text{C}$ (‰)
JN-21-63-1	-34.87
JN-21-63-2	-34.93
JN-21-83-1	-34.55
JN-21-83-2	-33.99
JN-21-M13-1	-34.76
JN-21-M13-2	-34.59
JN-21-68.1	-34.93
JN-21-68-2	-34.83
JN-21-M14-1	-34.02
JN-21-M14-2	-34.11

## **Credit author statement**

**Author Contributions:** A.E.A. designed the research. A.E.A., F.A., J.B.T., A.S., and K.O.K. wrote the manuscript. A.E.A, E.C.F, and J.N.G did the field work. J.N.G., C.F., J.N.G., and A.E.A. prepared the samples and performed XRD analyses and models. A.M. performed X-Ray microtomography. A.E.A. analyzed morphology, A.R. analyzed carbon and sulfur concentrations. A.C.P.W. analyzed carbon isotopes. A.L. analyzed Zn and Pb isotope compositions with assistance from J.B.T. A.S carried out the synchrotron experiments and processed the data.