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3

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16

17

18 **ABSTRACT**

19 **Exceptional preservation through phosphatization is primarily controlled by a reduction in**  
20 **pH, favoring the precipitation of apatite over that of calcite. Laboratory experiments**  
21 **suggested that phosphatization results from anoxic decay. Here we report results of the fine**  
22 **scale mineralogical characterization of Cretaceous phosphatized fossils of teleost fishes and**  
23 **crustaceans from the Jebel oum Tkout Lagerstätte (Morocco). Data collected using**  
24 **complementary laboratory and synchrotron-based X-ray techniques reveal that oxidative**  
25 **conditions were established at a certain step of decay. Supporting these conclusions are the**  
26 **presence, covering and embedded in the phosphatized tissues, of Fe(III)-rich mineral**  
27 **phases which precipitation was likely biologically-induced during decay. In contrast to the**  
28 **general belief, the present study highlights that the establishment of oxidative conditions**  
29 **during decay can be compatible with exceptional preservation of fossils through**  
30 **phosphatization.**

31

32 **INTRODUCTION**

33 Soft tissue phosphatization, *i.e.*, calcium phosphate mineralization occurring prior to the  
34 degradational collapse of cellular tissues, provides the most spectacular fossils of animals, still  
35 exhibiting sub-cellular details (Martill, 1990; Briggs, 2003). Most of the time, soft tissues are  
36 pseudomorphically replaced by francolite (a carbonate-rich fluorapatite), as is the case of the  
37 ~110-Ma fossil fishes from the Santana Formation (Brazil) (Martill, 1988). Closed systems, such  
38 as those built by biofilms growing around carcasses, promote apatite precipitation by trapping  
39 phosphorus (Williams and Reimers, 1983; Martill, 1988; Briggs and Kear, 1993; Wilby et al.,  
40 1996). Laboratory experiments suggested that phosphatization results from a decay-induced fall

41 in pH under anaerobic conditions, the decrease of pH being responsible for a switch from  
42 carbonate to phosphate precipitation (Allison, 1988; Briggs and Kear, 1993; Briggs and Wilby,  
43 1996; Sagemann et al., 1999). However, authigenic phosphates such as francolite may precipitate  
44 under a number of redox conditions, including oxic to suboxic conditions (Föllmi, 1996 and  
45 references therein). Phosphatization requires a sufficient concentration of phosphorous (Martill,  
46 1988; Briggs and Kear, 1993; Briggs, 2003), and oxic conditions are known to enhance the  
47 release of phosphorus (e.g., Meunier-Christmann et al., 1989). Here, we report an in-depth and *in*  
48 *situ* assessment of the redox conditions having prevailed during the phosphatization of  
49 “exceptionally preserved” Cretaceous fossils of fishes and crustaceans from the Jebel oum Tkout  
50 (OT1) Lagerstätte of Morocco.

51

## 52 **METHODS**

53 A combination of advanced characterization tools, including X-ray diffraction (XRD),  
54 scanning electron microscopy (SEM) and infrared (IR) spectroscopy was used to achieve a  
55 micro-geochemical characterization of a series of fossils. In addition, major-to-trace elemental  
56 composition was determined using synchrotron-based micro X-ray fluorescence ( $\mu$ XRF)  
57 mapping at a spatial resolution of 60–100  $\mu$ m and at detection limits of a few tens of ppm  
58 (Gueriau et al., 2014, 2018). Samples were scanned in air using a 17.2 keV beam allowing  
59 detection of elements from chlorine to uranium. At this energy, X-rays penetrate up to a couple  
60 of millimeters, but only the XRF photons from the first hundreds of microns can be collected  
61 (see Gueriau et al., 2018). The deconvolution of  $\mu$ XRF data allowed estimating the  
62 concentrations of all detected elements, including rare earth elements (REEs) that were then  
63 normalized to the Post-Archean Australian Shale (PAAS) reference (McLennan, 1989) to

64 reconstruct REE patterns, ratios and anomalies in the fossils at “local”, submillimeter scales  
65 (Gueriau et al., 2015). Finally, the redox states of Fe and Ce were determined using synchrotron-  
66 based micro-X-ray absorption spectroscopy ( $\mu$ XAS) at a 3–10  $\mu$ m spatial resolution. For Fe,  
67 continuous Cauchy wavelet transformation of the spectra was performed to establish a more  
68 robust determination of the speciation (Munoz et al., 2003). Additional details on Methods are  
69 provided in the GSA Data Repository<sup>1</sup>.

70

## 71 **GEOLOGICAL AND PALEOENVIRONMENTAL CONTEXT**

72 The Upper Cretaceous (Cenomanian, ~95 Myr) OT1 Lagerstätte from south-eastern  
73 Morocco (Fig. 1A) yielded a rich and well-preserved soft-bodied fauna including mollusks,  
74 insects, crustaceans, elasmobranchs and actinopterygian fishes embedded in a pale beige  
75 laminated mudstone carved by mudcracks (Fig. 1B). Absence of marine organisms and the  
76 presence of mudcracks, unionids and larvae of insects restricted to freshwater environments,  
77 strongly suggest a low-energy seasonally dried freshwater deposition environment (Dutheil,  
78 1999; Garassino et al., 2006). A paleoenvironmental model of the whole Kem Kem area is  
79 available in Ibrahim et al. (2020).

80

## 81 **MINERALOGY**

82 Remarkably, many fossils exhibit soft tissues (muscles, cuticles and gills - Figs. 1C–E -  
83 Dutheil, 1999; Garassino et al., 2006; Gueriau et al., 2015) pseudomorphically replaced by  
84 nanometric apatite crystallites (< 30 nm), identified as francolite by infrared spectroscopy (Fig.  
85 1F). XRD analyses on oriented preparations indicate that illite and quartz are the main  
86 constituents of the bulk sedimentary matrix, with some interstratified illite-smectite minerals and

87 kaolinite. These minerals are mainly detritic, except for the accordion-like automorphic crystals  
88 of kaolinite. Low trace metal concentrations (Fig. DR1C) with very low degree of enrichment  
89 (PAAS-normalized enrichment factors for V, Ni, Cu, Zn  $\leq$  1.1, Cr  $\sim$ 1.9) and chemical index of  
90 alteration of  $\sim$ 78 (Nesbitt and Young, 1982; low range for illite), indicate very moderate  
91 weathering. The gypsum crystals filling mudcracks (Fig. 1B and DR5) and the Fe-rich clay  
92 minerals displaying plate-like or sheet-like habits forming roses on the sample surface (Figs. 3I  
93 and DR5) are clearly secondary (and rather recent), highlighting that sampling and storage  
94 conditions have slightly tampered with the samples.

95

## 96 **REMAINS OF BIOFILMS**

97 Just as in a textbook case, fossil biofilms can be observed at the OT1 Lagerstätte. They  
98 consist in large (tens of cm<sup>2</sup>) reddish cracked films lying a few millimeters above each of the  
99 fossiliferous layers (Fig. 2A). The morphological similarities between these films (Figs. 2B–D)  
100 and modern microbial mats (Fig. 2E) strengthened their identification as well-preserved fossil  
101 colonies of microorganisms. Moreover, the fossil skeleton, cuticles and soft tissues (white-to-  
102 yellowish in color) are largely covered by similar reddish (to sometimes bluish) thin (a few tens  
103 of  $\mu$ m) films (Figs. 1B, 1C, 3A and DR2A) that are interpreted as remains of biofilms. Reddish  
104 patches are also found embedded within the phosphatized soft tissues (Figs. 3E, 3F and DR2C),  
105 suggesting that their precipitation was concomitant to phosphatization.

106 A few hundreds of mg of fossil biofilm materials were extracted and milled into powder  
107 for XRD analyses, revealing that these mats are composed of Fe(III)<sub>2</sub>O<sub>3</sub> (iron oxide) minerals  
108 (Fig. 2F).  $\mu$ XRF mapping reveals that the iron-rich reddish films covering and embedded within  
109 the fossils of teleost fishes and penaeid shrimps *Cretapenaeus berberus* contain trace metals

110 (Figs. 3A–C, DR1 and DR2), while  $\mu$ XAS investigations at the Fe K-edge reveals that the redox  
111 state of iron in these films is identical to that of iron in the mats (+III; Fig. 2G). The spectrum of  
112 this Fe-rich mineral is consistent with ferrihydrite ( $\text{Fe}_2\text{O}_3 \cdot 0.5\text{H}_2\text{O}$ ) (Figs. 3G, 3H and DR3), less  
113 consistent with goethite ( $\alpha\text{-FeO(OH)}$ ) or lepidocrocite ( $\gamma\text{-FeO(OH)}$ ), and rather inconsistent with  
114 hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) or illite ( $((\text{K},\text{H}_3\text{O})(\text{Al},\text{Mg},\text{Fe})_2(\text{Si},\text{Al})_4\text{O}_{10}[(\text{OH})_2,(\text{H}_2\text{O})])$ ).

115

## 116 ANTIQUITY OF FE-OXIDES

117 The observed Fe(III) hydroxides surround skeleton tissues and are found around *and*  
118 *within* the phosphatized soft tissues (Figs. 3E and DR2C), suggesting that they precipitated  
119 concomitantly with phosphatization. Although some Fe-rich phases in the matrix have been  
120 interpreted as resulting from the oxidation of pyrite (e.g., Gabbot et al., 2004; Osés et al., 2016),  
121 this is not the case for the observed Fe(III) hydroxides for which a primary origin is more likely.  
122 Instead of a cubic or framboidal habit typical of pyrite weathering products, the observed Fe(III)  
123 hydroxides show a honeycomb-like morphology, rather typical of microbial mats (e.g., Frankel  
124 and Bazylinski, 2003; Davies et al., 2016). In particular, one can observe spherical imprints  
125 (Figs. 3J, 3K and DR5), possibly created by coccoid-shaped bacteria (e.g., Iniesto et al., 2016) or  
126 gas bubbles having been produced within the microbial mats (e.g., Davies et al., 2016). The  
127 fossil biofilms discussed here have thus not been exposed to significant weathering or  
128 recrystallization. In other words, the observed Fe(III) hydroxides are likely primary, i.e. they  
129 precipitated during the life of the microbial mats, thereby indicating slightly oxic conditions  
130 during early diagenesis.

131

## 132 REDOX CONDITIONS DURING PHOSPHATIZATION

133           Synchrotron-based  $\mu$ XRF analyses of the phosphatic fossil tissues reveal that they  
134 incorporated REEs as well as strontium, yttrium and thorium (Fig. 3C). The incorporation of  
135 REEs, which substitute for calcium in apatite minerals, generally occurs during diagenesis, with  
136 concentrations increasing by three to four orders of magnitude within  $10^3$ - $10^4$  years depending  
137 on diagenetic conditions (Herwartz et al., 2013). The obtained REE patterns display a very  
138 limited enrichment in intermediate REEs (“bell-shaped” patterns) and a slightly negative Ce  
139 anomaly (Fig. DR4A; Gueriau et al., 2015). The PAAS-normalized La/Yb vs La/Sm values  
140 confirm that the fossils investigated underwent very limited weathering and recrystallization  
141 (Fig. 3D; Reynard et al., 1999; Lécuyer et al., 2003). The observed negative Ce anomaly thus  
142 reflects the early diagenetic redox conditions of burial (German and Elderfield, 1990) and points  
143 to slightly oxic conditions, consistent with the precipitation of Fe(III) hydroxides. Ce L<sub>3</sub>-edge  
144 spectroscopy confirms that Ce has a mixed valence (Gueriau et al., 2015), with oxidized Ce (i.e.,  
145 Ce(IV)) contributing to 20 at.% of the total Ce (Fig. DR4B).

146

## 147 **CONCLUSION**

148           Instead of a fall in pH under anoxic conditions, the fine-scale micro-geochemical  
149 characterization conducted here strongly suggests that (slightly) oxic conditions prevailed during  
150 phosphatization. This conclusion is fully consistent with recent experiment results evidencing  
151 that chemical microenvironments generated by microbial mats may turn oxic after several weeks  
152 despite initially anoxic conditions (Iniesto et al., 2015). One could argue that the observed Fe(III)  
153 hydroxides may have been produced by anaerobic neutrophilic iron oxidizers (e.g., Miot et al.,  
154 2009; Hedrich et al., 2011). This would not be inconsistent with the present interpretation, i.e.  
155 the establishment of slightly oxic conditions during phosphatization, since neutrophilic iron



156 oxidizers require the presence of nitrates to survive, i.e., slightly oxic conditions (anaerobic and  
157 anoxic are not strict synonyms). Altogether, in contrast to the standard view, the present results  
158 establish that exceptional preservation through phosphatization and oxidative conditions are not  
159 antithetic.

160

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177

178

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287

288 **FIGURE CAPTIONS**

289

290 Figure 1. The Jebel oum Tkout Lagerstätte (Cenomanian, Morocco). A: Location and map of the  
291 Kem Kem area, southeastern Morocco; gray areas denotes the outcrops of the Kem Kem beds.  
292 Note the presence of another, slightly younger and marine Lagerstätte at Gara Sbaa (Martill et  
293 al., 2011), ca. 15 km southwest of OT1. B: Optical photograph of a gray illitic layer exhibiting  
294 mudcracks and topped by a reddish microbial mat. In the center, a paraclupeid fish is visible. C,  
295 D: Optical photograph of another paraclupeid (Poi-SGM 10) and SEM images (SE mode) of its  
296 finely phosphatized muscles (after Dutheil, 1999: figs. 5 & 6). E: SEM images (SE mode) of  
297 mineralized muscles from the penaeid shrimp *Cretapenaeus berberus* (MNHN.F.A24633) (after  
298 Garassino et al., 2006: fig. 5). F: Infrared spectrum of mineralized muscles from *C. berberus*.  
299 Scale bars: B = 5 cm; C = 5 mm; D = 10  $\mu\text{m}$ ; E = 50  $\mu\text{m}$ .

300

301 Figure 2. The fossil microbial mats from the Jebel oum Tkout Lagerstätte (Cenomanian,  
302 Morocco). A: Optical photograph of an OT1 microbial mat. B–D: SEM images (SE mode) of  
303 OT1 microbial mats. E: SEM image (SE mode) of a modern microbial mat for comparison. F: X-  
304 ray powder diffraction diagrams of the fossil mat (mat) and of the clayey sedimentary matrix  
305 (clay); abbreviations: Qz, quartz; I, illite. Scale bars: A = 1 cm; B–E = 10  $\mu\text{m}$ .

306

307 Figure 3. Synchrotron-based  $\mu\text{XRF}$  mapping and Fe K-edge  $\mu\text{XAS}$  spectroscopy. A: Optical  
308 photographs of the teleost fish MHNM-KK-OT 10. B: False color overlays of neodymium (red),  
309 yttrium (green) and iron (blue) distributions from the dotted white box area in A. C: Average  
310 XRF spectrum and main elemental contributions from the fish dorsal fin muscles (white box in

311 B). D: PAAS-normalized La/Yb ratios versus La/Sm ratios in OT1 fossils from XRF and ICPMS  
312 quantifications reported in the diagrams proposed by Reynard et al. (1999) and Lécuyer et al.  
313 (2003). E: Optical photograph of a loose sample containing soft tissues and bone from MHNM-  
314 KK-OT 10 (origin: white star in B). F: SEM image (BSE mode) of muscle fibers preserved on  
315 the sample in E. G: Normalized  $\mu$ XAS spectra at the Fe K-edge of reference materials (illite,  
316 hematite, goethite, lepidocrocite and ferrihydrite) and of iron-rich grains covering the teleost fish  
317 (origin: blue star in E) and the penaeid shrimp *Cretapenaeus berberus* (MHNM-KK-OT 01, see  
318 Fig. DR2). Spectra were vertically shifted for increased readability. H: Fourier transform  
319 magnitude and  $k^3$ -weighted  $\mu$ XAS spectra from the iron-rich grains covering the teleost fish  
320 (blue) and the shrimp (orange, as well as ferrihydrite (dotted black) and goethite (dotted gray)  
321 reference materials. I–K: SEM images (SE mode) of iron oxides (origin: arrows in E). Scale  
322 bars: A–B = 5 mm; E = 500  $\mu$ m; F = 10  $\mu$ m; I–K = 1  $\mu$ m.

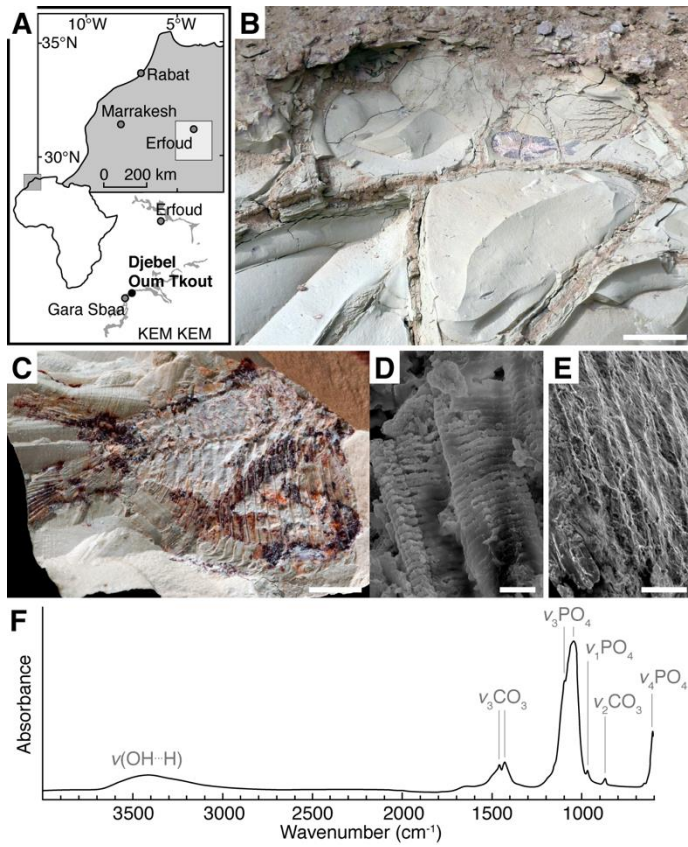
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325 <sup>1</sup>GSA Data Repository item 202Xxxx, methods, additional synchrotron X-ray fluorescence  
326 maps, spectra and main elemental contributions, REEs patterns, Ce L<sub>3</sub>-edge spectra, Fe K-edge  
327 CCWT modulus, SEM images, precise locations of the point analyses, is available online at  
328 [www.geosociety.org/pubs/ft20XX.htm](http://www.geosociety.org/pubs/ft20XX.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or  
329 Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

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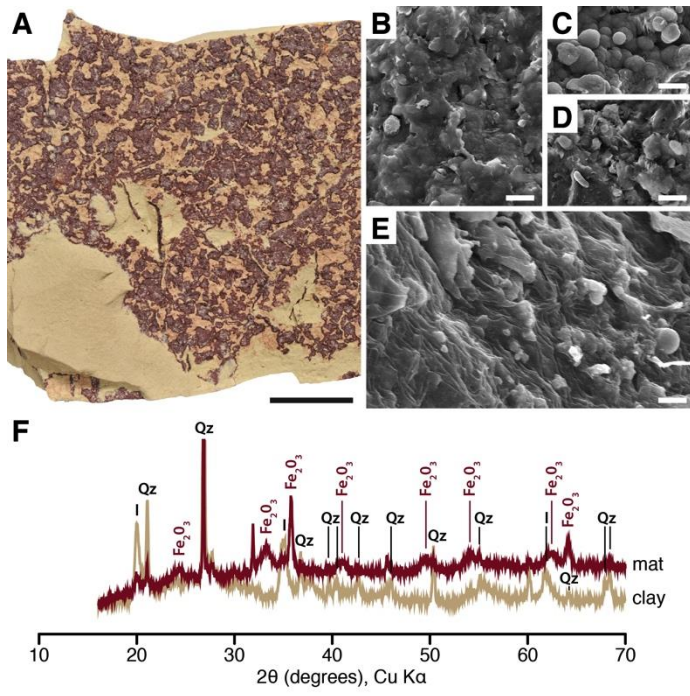


331

332 Figure 1.

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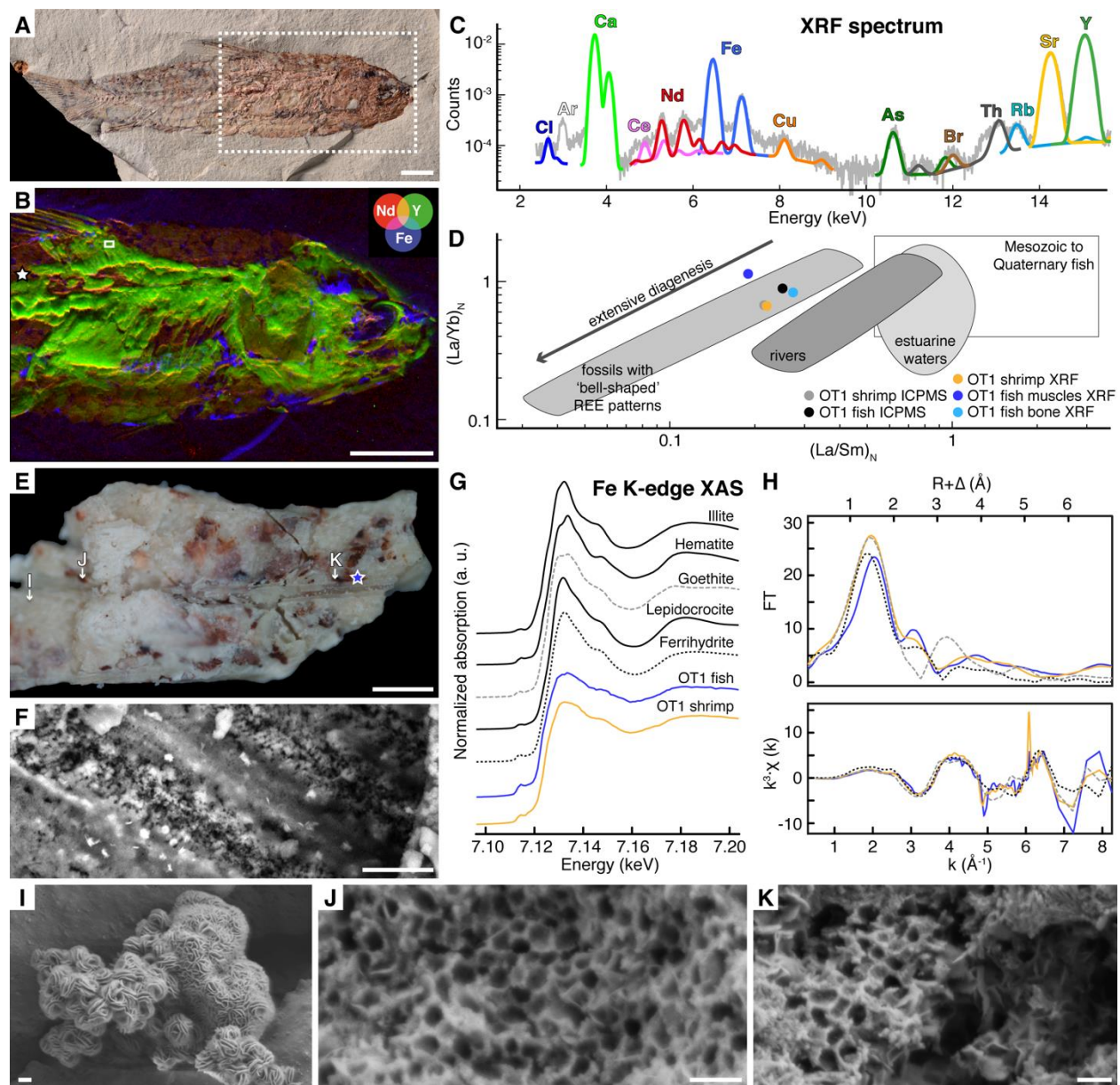
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335

336 Figure 2.

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338

339 Figure 3.