1 # Authigenesis of biomorphic apatite particles from Benguela upwelling zone sediments off

2 # Namibia: The role of organic matter in sedimentary apatite nucleation and growth

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18 ## Abstract

19 Sedimentary phosphorites comprise a major phosphorus (P) ore, yet their formation remains

20 poorly understood. Extant polyphosphate-metabolizing bacterial communities are known to act as

21 bacterial phosphate-pumps, leading to episodically high dissolved phosphate concentrations in

22 pore waters of organic-rich sediment. These conditions can promote the precipitation of

23 amorphous precursor phases that are quickly converted to apatite – usually in carbonate

24 fluorapatite form [$Ca_{10}(PO_4,CO_3)_6F_{2-3}$]. To assess the mechanisms underpinning the nucleation

25 and growth of sedimentary apatite, we sampled P-rich sediments from the Namibian shelf, a

26 modern environment where phosphogenesis presently occurs. The P-rich fraction of the topmost

27 centimeters of sediment mainly consists of pellets about 50 to 400 μm in size, which in turn, are

28 comprised of micron-sized apatite particles that are often arranged into radial structures with

29 diameters ranging from 2 to 4 μm, and morphologies that range from rod-shapes to dumbbells to

30 spheres that resemble laboratory-grown fluorapatite-gelatin nanocomposites known from double-

31 diffusion experiments in organic matrices. The nucleation and growth of authigenic apatite on the

32 Namibian shelf is likely analogous to these laboratory-produced precipitates, where organic

33 macromolecules play a central role in apatite nucleation and growth. The high density of apatite

34 nucleation sites within the pellets ($>10^9$ particles per cm^3) suggests precipitation at high pore

35 water phosphate concentrations that have been reported from the Namibian shelf and may be

36 attributed to microbial phosphate pumping. The intimate association of organic material with the

37 apatite could suggest a possible role of biological substrata, such as exopolymeric substances

38 (EPS), in the nucleation of apatite precursors. Importantly, we do not observe any evidence that

39 the apatite particles are actual phosphatized microbes, contradicting some earlier studies.

40 Nevertheless, these results further evidence the potential importance of microbially-derived

41 (extracellular) organic matter as a template for phosphatic mineral nucleation in both recent and

42 ancient phosphorites.

43

Introduction

45 Phosphorites – rocks that contain >9 wt.% P_2O_5 (Filippelli, 2011) – constitute the largest sink of

46 sedimentary phosphorus (Delaney, 1998). Not only do they remove P from the global

47 biogeochemical cycle, but importantly, they influence Earth's primary production on geological

48 time scales (Tyrrell, 1999). Phosphorites are also a critical non-renewable resource for

49 agriculture, specifically required in the production of phosphatic fertilizer (Cordell *et al.,* 2009).

50 However, despite their economic importance, the origin of these mineral deposits remains

51 enigmatic.

52   The main sites of modern phosphorite formation are major upwelling systems along

53 continental margins where primary production and the flux of sinking organic matter – and thus

54 of P – to the seafloor are relatively high. Indeed, the great majority of modern phosphorites form

55 today in regions of upwelling (Föllmi, 1996), such as on the western coasts of Namibia

56 (Summerhayes *et al.,* 1973; Baturin & Bezrukov, 1979; Baturin, 2000; Compton & Bergh, 2016),

57 Chile and Peru (Veeh *et al.,* 1973; Burnett, 1977; Burnett *et al.,* 2000), Mexico (Jahnke *et al.,*

58 1983; Schuffert *et al.,* 1998), and in the Arabian Sea (Schenau *et al.,* 2000), with some

59 exceptions, such as off-shore eastern Australia (O'Brien & Veeh, 1980; O'Brien & Heggie,

60 1988).

61   The processes necessary for the formation of sedimentary phosphorites begin with

62 weathering of P-bearing minerals, solubilization to the phosphate anion (PO_4^{3-}), and transport by

63 rivers and groundwater to the oceans. Once in seawater, P is rapidly incorporated into biomass or

64 adsorbed to Fe/Mn-oxyhydroxides, both of which are eventually deposited on the seafloor.

65 Heterotrophs take advantage of the high flux of easily degradable organic matter, resulting in

66 oxygen levels in the bottom waters that are low enough to cause a steep (sub)oxic-sulfidic

67 redoxcline in the shallow sediment subsurface. In addition to remineralization of organic matter,

68   these conditions also facilitate redox-sensitive reactions, such as polyphosphate cycling by sulfur-

69   oxidizing bacteria (Schulz & Schulz, 2005) and, to a lesser degree, the reductive dissolution of

70   Fe/Mn-oxyhydroxides (Noffke *et al.*, 2012). These processes all result in the release of phosphate

71   anions into sediment pore waters, which may eventually lead to supersaturation with respect to

72   amorphous apatite precursor phases, and ultimately the transformation into the stable crystalline

73   phase, carbonate fluorapatite (Föllmi, 1996; Goldhammer *et al.,* 2010; Filippelli, 2011;

74   Ruttenberg, 2014).

75   Dissolved phosphate concentrations in pore waters of the topmost few centimeters of

76   organic-rich sediment can reach >400 µM, and thus exceed the solubility product of amorphous

77   apatite precursors (Krajewski *et al.,* 1994; Schulz & Schulz, 2005; Goldhammer *et al.*, 2011;

78   Dale *et al.*, 2013). While sinking organic matter is the main source of P in the sediments, and a

79   large flux is a prerequisite for the formation of phosphorites, it has been shown that simple

80   remineralization of organic matter by heterotrophs is on its own not enough to produce the

81   observed concentrations of dissolved phosphate in sediment pore waters (Froelich *et al.,* 1988;

82   Krajewski *et al.,* 1994). Furthermore, Fe input into sediments in upwelling environments has

83   been found to be low, precluding a significant role of redox-dependent Fe cycling in increasing

84   phosphate concentrations (Brüchert *et al.*, 2006; Noffke *et al.*, 2012). In this regard, several

85   studies have recently highlighted the catalytic role that microbial processes play in mediating

86   apatite precipitation (Schulz & Schulz, 2005; Arning *et al.,* 2008, 2009a; Goldhammer *et al.,*

87   2010; Brock & Schulz-Vogt, 2011). For instance, several genera of sulfur-oxidizing bacteria have

88   been demonstrated to store intracellular polyphosphate granules (*e.g.*, *Beggiatoa*, *Thiomargarita*).

89   Steep (sub)oxic-sulfidic redoxcline conditions are known to provide a habitat for some

90   phosphate-cycling chemolithoautotrophs, which act as "phosphate pumps". These bacteria are

91   capable of accumulating polyphosphate intracellularly under oxic and suboxic conditions, then

92   hydrolyzing the polyphosphate and releasing phosphate under sulfidic conditions in short, but

93   intense, pulses (Froelich *et al.,* 1988; Föllmi, 1996; Schulz & Schulz, 2005; Goldhammer *et al.,*

94   2010; Holmkvist *et al.,* 2010; Brock & Schulz-Vogt, 2011). For example, in the case of the

95   phosphogenic Namibian shelf, Schulz & Schulz (2005) found that, in a 3-cm thick horizon below

96   the sediment-water interface, peak *Thiomargarita* abundance coincided with a peak in dissolved

97   phosphate concentration (>300 µM) and in hydroxyapatite abundance in the solid phase of the

98   sediment. This mechanism suggests that sufficiently high bacterial phosphate "pumping" rates

99   can lead to intermittent supersaturation of pore water with respect to carbonate fluorapatite

100   precursors (Arning *et al.,* 2009b; Goldhammer *et al.,* 2010).

101   In addition to supersaturation, for mineral formation to occur, the activation energy

102   barriers to nucleation need to be overcome. Previous experiments that investigated the

103   precipitation of phosphate minerals have demonstrated that direct precipitation of apatite from

104   supersaturated solution is a very slow process (Krajewski *et al.,* 1994; Golubev *et al.*, 1999;

105   Gunnars *et al.*, 2004). Instead, at sufficiently high levels of supersaturation, more soluble

106   amorphous phases of calcium phosphate, such as octacalcium phosphate (Brown *et al.*, 1984;

107   Gunnars *et al.*, 2004) or amorphous calcium phosphate (Martens & Harriss, 1970; Golubev et al.,

108   1999), begin to nucleate at a much higher rate due to the significantly lower activation energy

109   barriers to nucleation for these phases. The amorphous phases then serve as precursor sites for

110   apatite nucleation and growth (van Cappellen & Berner, 1991; Krajewski *et al.,* 1994; Schenau *et*

111   *al.*, 2000; Golubev et al., 1999; Gunnars *et al.*, 2004; Borkiewicz *et al.*, 2010; Oxmann &

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112 Schwendenmann, 2014). It is plausible that sedimentary bacteria and/or microbially produced

113 organic compounds, such as exopolymeric substances (EPS), may also serve as substrata for

114 nucleation, thus enhancing phosphate precipitation. Experiments aimed at investigating microbial

115 biomineralization show that apatite group minerals can preferentially precipitate on bacterial

116 sheaths and cell walls (*e.g.*, Benzerara *et al.,* 2004), though earlier studies downplay the role of

117 such substrata in the rapid precipitation of apatite precursor phases (*e.g.*, Hirschler *et al.,* 1990;

118 Krajewski *et al.,* 1994).

119 Despite much experimental work, what remains to be determined is whether the

120 experiments represent natural conditions, especially with respect to the influence of organic

121 substrata. In this regard, an ideal study site for the evaluation of the mechanisms underpinning

122 phosphate precipitation are the phosphorites that are currently still forming on the Namibian

123 continental shelf – a site of considerable controversy over phosphorite mining plans, with

124 uncertain implications for the local marine ecosystem (Midgley, 2012; Watson *et al.,* 2014).

125 Previous studies of this location have suggested that phosphate precipitation is microbially

126 influenced (Schulz & Schulz, 2005) and that the physical concentration of apatitic pellets may be

127 due to sediment reworking caused by changes in sea level (Compton & Bergh, 2016).

128 Accordingly, the aim of this work was to study the micro- and nanofabric of those same

129 phosphorites to better understand how sedimentary authigenic apatite forms, and whether the

130 phosphogenesis fossilizes microbial structures.

131

Geological setting

The Namibian shelf is known for its unusual breadth and depth, extending to 400 m water depth. It consists of Proterozoic to Cenozoic basement rocks and a thin Cenozoic sedimentary succession, terminated by an erosional surface on which late Cenozoic to modern sediments were deposited (Compton & Bergh, 2016). The Namibian shelf is influenced by the Benguela Upwelling System, representing some of the strongest upwelling currents in the world. The rising nutrient-rich deep ocean waters fuel the world's most biologically productive eastern boundary marine ecosystem (Carr, 2001), which is associated with intense organic carbon burial (Inthorn *et al.,* 2006). Combined with a modest detrital input (Eckardt & Kuring, 2005), the prolific algal production has led to the accumulation of an up to 15 m thick layer of Pleistocene to modern diatomaceous mud near Walvis Bay (Figure 1; Baturin, 2000). This mud grades into less diatomaceous organic-rich mud towards the south. The nearshore shelf sediments tend to consist of sand and gravel, while the outer shelf hosts carbonates (Figure 1; Compton & Bergh, 2016).

Remineralization of the high flux of sinking organic matter in the coastal upwelling system off Namibia creates fluctuating shelf anoxia and sulfidic water-column conditions, titrating the limited Fe input (Brüchert *et al.,* 2006) and further decreasing the importance of Fe-Mn oxyhydroxides in P cycling. The organic matter also acts to deliver P to the sediments – a primary factor enabling the formation of phosphorites on the inner shelf – while the fluctuating redox conditions facilitate phosphogenic polyphosphate metabolism, driving phosphate concentrations in the pore waters up to levels required for apatite precursor precipitation (Schulz & Schulz, 2005; Brock & Schulz-Vogt, 2011). Phosphorite deposits range in age from late

153 Oligocene to modern (late Miocene to modern off the Namibian coast), and geographically they

154 extend from the southern shelf of South Africa up to the Kunene River. The modern locus of

155 phosphogenesis has, however, shifted northwards since the Pleistocene, to the diatomaceous

156 mudbelt near Walvis Bay (Baturin, 2000; Compton *et al.,* 2002, 2004; Compton & Bergh, 2016).

157 These phosphorites usually occur in the form of apatitic pellets, which are typically a few

158 hundred micrometers in diameter, along with concretionary authigenic forms, phosphatized

159 mollusk molds and occasional recent phosphatic brachiopods (Baturin, 2000).

160   Based on petrologic features, Namibian phosphorites can broadly be divided into two

161 classes: (i) dispersed, authigenic Pleistocene to modern phosphatic concretions and pellets that

162 are still forming in the diatomaceous mud of the inner shelf, at water depth ranges between 50

163 and 140 m (whole sediment P_2O_5 content ~0.8 wt.%; Veeh *et al.,* 1974; Baturin, 2000) and (ii)

164 reworked, late Miocene to Pleistocene-aged phosphatic sediments occurring as P-rich lags on the

165 middle to outer shelf at 180 to 500 m water depth, consisting of a 1–2 m thick P-rich layer, which

166 displays a coarsening upward succession from muddy to increasingly more sandy and gravelly

167 sediment (average P_2O_5 content 19 wt.%; Compton and Bergh, 2016). Aside from phosphorite

168 sand, skeletal fish debris, foraminifera and bivalve shells and terrigenous components co-occur in

169 the sediment pile. Strontium isotope stratigraphy places the formation time of this phosphorite

170 from the late Miocene to Pleistocene, beginning at roughly 5.8 Ma, with the majority of the

171 deposit having formed during the Pliocene and Pleistocene (Compton & Bergh, 2016). Some

172 pellets show evidence of zonation consistent with multiple episodes of phosphorite formation;

173 this, in addition to the sedimentary fabric and different strontium isotope ratios for pellets in the

174 same sample, points to complex sedimentary reworking. Compton and Bergh (2016) explain the

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175   formation of this deposit through changes in sea level that has resulted in the reworking, transport

176   and concentration of previously-formed authigenic phosphorite from the diatomaceous mudbelt

177   to sediments further offshore, similar to what has previously been reported for South African

178   deposits (Compton *et al.,* 2002, 2004; Wigley & Compton, 2006). Authigenic phosphorite

179   formation is interpreted to have taken place during sea level highstands and reworking during

180   lowstands, beginning with the onset of glacial cycles in the Pleistocene (Compton & Bergh,

181   2016). During sampling, none of the coring sites chosen for their location at known areas of

182   phosphorite abundance yielded any phosphorite, while those that did were taken from areas

183   assumed to be low in P content, reflecting the patchy occurrence of phosphorites on the Namibian

184   shelf (Figure 1).

185

Materials and methods

187   The sediment samples used for this study were collected during oceanographic cruises on the

188   research vessel *Mirabilis* in the central-southern shelf sea off the coast of Namibia in May of

189   2015. An Ocean Instruments MC-400 multi-corer was used to sample a variety of unconsolidated

190   sediments, of which two cores were used in this study – core GC4 (21 cm in length, from ~300 m

191   water depth) and core 25005 (25 cm in length, from ~50 m water depth) (Figure 1). The top 10

192   cm of the cores were sectioned and sampled at 1 cm intervals; below that, the intervals were 2 cm

193   in length. The bottom waters and topmost centimeters of sediment sampled by the multi-corer did

194   not smell of H_2S, indicating oxic or suboxic conditions at the sediment-water interface at the time

195   of sampling. The samples were freeze dried following collection. While this process is likely to

196   affect the preservation of amorphous microstructures with high water contents, such as biofilms

197   and other organic substrata, already crystallized apatite structures are not affected, especially if

198   these are seen to still preserve a fine-grained primary microfabric.

199   The mineralogical composition of whole rock samples was studied by X-ray

200   diffractometry (XRD) at the University of Tartu, Estonia. Samples were pulverized by hand with

201   an agate pestle and mortar and unoriented preparations were made. Powders were then scanned

202   on a Bruker D8 Advance diffractometer using Cu Kα radiation and LynxEye positive sensitive

203   detector in 2–70° 2Θ range. The mineralogical composition of each sample, along with their

204   apatite lattice parameters, were interpreted and modeled using the Rietveld algorithm-based

205   program Topaz. Total organic carbon content of core GC4 was estimated by measuring the mass

206   lost on heating several dried GC4 samples at 500°C for 24 hours. Solid-phase P and S

207   concentrations of the sediments in core 25005 were determined using inductively coupled plasma

208   mass-spectrometry (ICP-MS) in multi-acid digested (HNO_3, $HClO_4$, HF, HCl) samples at Bureau

209   Veritas Commodities Canada Ltd in Vancouver.

210   To specifically study the microstructure, several 100–400 μm apatitic pellets were

211   handpicked from bulk samples under a microscope. Impurities of lighter minerals and high

212   porosity did not allow heavy liquid fractionation of the apatitic pellets. The preparation of the

213   pellets was done either by (i) cleaning in an ultrasonic bath, mounting on an adhesive carbon

214   film, and breaking with a scalpel to reveal their inner structure, or (ii) embedding in epoxy resin,

215   then finely grinding down to reveal a cross-section. The polished samples were subsequently

216   milled at the University of Tartu with a Leica EMRES101 Wide Beam Argon Ion Mill to produce

217   a smooth and clean flat surface.

218   For micromorphology studies, the polished pellets were coated with a few nm thick

219   conductive carbon layer, while broken surfaces were coated in platinum. Scanning electron

220   microscope (SEM) imaging was performed using a variable pressure Zeiss EVO MA15 SEM

221   equipped with Oxford X-MAX energy dispersive detector system (EDX) and AZTEC software

222   for element analysis at the University of Tartu; and Zeiss Sigma 300 VP-FESEM equipped

223   Bruker EDX at University of Alberta, Canada. Imaging was done both in back-scattered electron

224   (BSE) and secondary electron (SE) modes.

225   Selected cross-sections of apatitic pellets were investigated using transmission electron

226   microscopy (TEM). The 15 x 5 x 0.15 μm foils for TEM study were cut from embedded and

227   polished samples using Focused Ion Beam (FIB) technique on a FEI FIB200-TEM at

228   GeoForschungsZentrum Potsdam, Germany (locations of the cuts are shown on Figure S1). The

229   foils were mounted on a lacy carbon film and examined with a FEI Tecnai G2 F20 X-TWIN

230   TEM operated at 200 kV with a field emission gun as electron source. The TEM imaging and

231   analysis were done using a Fishione high-angle annular dark-field detector (HAADF), Gatan

232   imaging filter (GIF) Tridiem and EDAX X-ray analyzer with ultra-thin window. Analytical data

233   were processed using the TIA software package. Electron energy-loss (EELS) element maps were

234   performed with C-K and S-K edges using the jump-ratio technique.

235   The laboratory-grown apatite pseudofossils shown in Figure 10 were precipitated in the

236   diffusion gel portion of a double diffusion gradient setup, designed to mimic Ca, F and PO_4^{3-}

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237   interaction in sediment pore water conditions (Crosby & Bailey, 2017). The precipitates

238   suspended in the gel were then removed from the diffusion setup, residue gel dissolved in water,

239   and concentrated precipitates mounted on an adhesive carbon film on top of an SEM stub.

240   Imaging was done on a Hitachi TM1000 Tabletop ESEM operated at 15.0 kV accelerating

241   voltage, and analyzed by EDS using Bruker Quantax 50 software (Crosby & Bailey, 2018).

242

Results

Mineralogy and chemistry

245   Sediments in core GC4 are enriched in organic matter (up to 10–15 wt.%). The sediments can be

246   described as calcareous phosphatic sands (Figure 2a), containing mostly calcite, quartz, some

247   phyllosilicates (glauconite) and abundant apatite (Figure 3a). The content of apatite is relatively

248   uniform (ca. 19–28 wt.%) throughout the core, rising slightly towards the bottom (Figure 3c).

249   Sediments in core 25005 are rich in opalinous diatom frustules (Figure 2b). Mineral

250   composition of the sediment is characterized by quartz, plagioclase, K-feldspar, calcite and

251   glauconite (Figure 3a). Elevated levels of apatite were identified in the upper half of the core

252   down to 8 cm depth, with the highest relative amount (up to 11 wt.%) found at 6 cm depth

253   (Figure 3a). Apatite nearly disappears in the lower part of the core, coincident with the

254   appearance of pyrite (Figure 3d). The distributions of apatite and pyrite determined by X-ray

255   diffraction are consistent with the chemical composition of the sediment, showing a peak in P

256 concentration of 1.9 wt.% at 5 cm of depth, dropping below 0.3 wt.% deeper in the core, while S

257 content rises from near-zero values to 0.6 wt.% over the same interval (Figure 3e).

258 The apatite can be identified by its characteristic XRD pattern as a carbonate fluorapatite

259 mineral. It is poorly crystalline, as evident from the low values of apatite coherent stacking

260 domain sizes which average approximately 31 nm in core GC4 and 23 nm in core 25005. The

261 unit cell parameters of apatite in core GC4 are well constrained, varying between 9.327 and 9.332

262 ± 0.002 Å and 6.885 and 6.889 ± 0.002 Å for a and c parameters, respectively (Figure 3b). These

263 values fall within the field ascribed to sedimentary phosphorites. However, the unit cell

264 parameters of apatite in core 25005 have a much larger variance than in GC4 – between 9.298

265 and 9.337 ± 0.005 Å for a parameter and between 6.865 and 6.900 ± 0.007 Å for c parameter, and

266 hence, they are significantly outside the range of most sedimentary phosphorites. This is possibly

267 due to a more poorly ordered crystal structure with a higher number of defects (Figure 3b).

268

269 **Microscopy**

270 Under optical microscopy and SEM, samples from both cores were found to be dominated by

271 aggregates of mud and organic debris with abundant diatom frustules. In addition, there are

272 ostracod valves and other calcareous shelly fragments, quartz, feldspar and glauconite grains, a

273 small fraction of heavy minerals, and numerous apatitic pellets (Figures 4a, b). The average grain

274 size of the particulate fraction is typically between 100 to 300 μm.

275 Apatitic pellets appear under optical microscopy as dark gray to black in color and are

276 slightly larger compared to other grains. The surfaces of the pellets are usually splotchy and

277   pitted. SEM reveals that most of the studied pellets in the core GC4 are ~200 to 400 μm in

278   diameter and are rounded or slightly flattened with smooth surfaces (Figure 4c). In core 25005,

279   the pellets typically measure 50 to 300 μm in diameter, and have a more pitted surface. These are

280   poorly- to well-rounded and generally elongated (Figure 4d), with numerous pits or pores that

281   open to the pellet surface.

282   At a broken surface, most pellets are composed of a porous apatite aggregate embedding

283   fragments of fossil remains, commonly diatom frustules, as well as terrigenous grains. Fossil

284   detritus is most abundant in pellets from core 25005, but rare in pellets from GC4 where the

285   detritus has mostly been dissolved and only casts remain (Figures 4e–f). Pellets show variable

286   porosity, whereas some of the pores represent either hollow spaces inside well-preserved diatom

287   frustules – suggestive of lumina – or what are possibly dissolved casts of fossils (Figure 4f).

288   Diameters of pores are tens of μm or less. Estimated porosity (relative area of the pores in the

289   pellet's cross-section) is ~1–2% in pellets from core GC4 and ~3–10% in those from core 25005.

290   The apatitic pellets also typically have an irregular patchy inner structure (Figures 5a–b).

291   Backscattered electron images of polished pellets in core GC4 reveal concentric structures

292   composed of layers ca. 10–20 μm thick (Figure 5a). Also, pellets in core 25005 occasionally

293   show a single rim at the pellet's outer perimeter exhibiting a similar concentrically-layered

294   texture (Figure 5b).

295   At higher resolution, the micrographs show that the pellets consist of micron-scale apatite

296   particles that are often arranged into radial structures with diameters ranging from 2 to 4 μm

297   (Figure 5c). The structural details of the apatite particles are revealed at pore margins and within

298   pores, where they are shown to consist of various morphologies, including irregular, colloform,

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299   globular, dumbbell-shaped, and elongated (Figure 6a). The most typical are elongated, rod-

300   shaped apatite particles with rounded ends, generally ca. 0.5 μm to 4 μm in length, and

301   approximately a third of that in diameter (Figure 6b). With few exceptions, the rod-shaped

302   particles are of similar size within any particular pellet, but can vary in size between different

303   pellets or cores.

304   The rod-shaped particles are not single apatite crystallites, but instead are composed of

305   elongated nanocrystallites (tens of nanometers in diameter) which are oriented parallel to the long

306   axis of the particles. In core 25005, the crystallites composing the rod-shaped particles are

307   elongated and anhedral in appearance (Figure 6c), but in core GC4, these are larger in size and

308   possess a distinctly hexagonal morphology characteristic of the apatite crystal habit (Figures 6d,

309   8b). In most cases, the rod-shaped particles occur together with films or filaments composed of

310   organic polymeric macromolecules that could possibly represent dried remnants of organic

311   matrices (e.g., EPS) that have been heavily dehydrated during sample preparation in high

312   vacuum. The organic substance covers the pore wall wherever there are rod-shaped particles

313   present, connecting several structures as filaments or sheets (Figure 6e). Often, the rod-shaped

314   particles also occur together with framboidal pyrite aggregates roughly 0.3 to 3 μm in diameter

315   (Figure 6f).

316   TEM analysis of foils cut from apatite particles reveal that the rod-shaped particles have a

317   heterogeneous inner structure (Figure 7) and are composed of several concentric layers about 50–

318   200 nm thick (Figure 7b). The layers consist of apatite crystallites a few nanometers in diameter.

319   The contrast between the layers could be due to different porosity (electron transparency) and/or

320   due to changes in sulfur and carbon content, likely the result of minor incorporation of the

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321   organic substance covering the pore walls (Figures 7d–f). Furthermore, the electron diffraction

322   patterns indicate that the apatite in the inner layers of the rod-shaped particles has greater

323   crystallinity (i.e. greater long range structural ordering, fewer defects) than in the outer layers,

324   and that the outer layers show smeared reflections, reminiscent of nanoscale misorientation of

325   individual crystallites (Figures 7i–j). However, in several cases, highly crystalline, elongated

326   apatite crystallites are nucleated at the ends of the rod-shaped particles, growing parallel to and/or

327   radiating along the long axis of concentric rod-shaped particles (Figure 7c).

328   The rod-shaped particles frequently intersect one another, or are intergrown at different

329   angles and to different degrees (Figure 8a). They can also form larger radially growing

330   aggregates (Figure 8b). In some rare cases, the rod-shaped particles appear to have nucleated and

331   grown tangentially on solid surfaces, such as diatom frustules (Figure 8c). Most often, however,

332   the walls of pores are composed of intergrown rod-shaped particles (Figure 8d). In addition,

333   progressive growth phases of the rod-shaped particles can be discerned (Figure 9). Rod-shaped

334   particles (Figure 9a) are joined by dumbbell-like structures, being somewhat larger due to their

335   bulging distal ends (Figure 8e, 9b–c). Much of the pore walls are also coated with larger

336   colloform or spherical microstructures (Figure 8f, 9d).

337

338   ### Apatite double-diffusion experiments

339   Beginning within ~30h of the start of the double-diffusion experiments, the ion fronts began to

340   interact and apatite began to precipitate out in a faint band that proceeded to separate into several

341   distinct zones over the next 4 to 5 days. SEM micrographs reveal that within the gel environment,

342   apatite precipitated in a wide variety of morphologies (Figure 10; reviewed in Crosby & Bailey,

343   2018). Most of the structures represent either rod-shaped particles (Figure 10a), variously

344   intersecting dumbbells (Figure 10b, d, e) or closed spheres (Figure 10c). During the later phases

345   of apatite precipitation, larger spheres, which can develop concentric rims tens of μm in

346   thickness, form (Figure 10f).

347

Discussion

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The phosphogenic system

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350   The phosphatic samples from core GC4 represent a large reworked phosphate sand deposit that

351   formed during Pleistocene sea-level low-stands in the Namibian middle-to-outer shelf, where

352   apatite ranges in age from the late Miocene to the Pleistocene (Compton & Bergh, 2016). In

353   contrast, the organic-rich muddy sediments at site 25005, though outside the typical

354   diatomaceous mud province around Walvis Bay (Figure 1), are within the zone most affected by

355   the Benguela Upwelling System and characterized by high organic matter flux. At around 50 m

356   depth, site 25005 is situated within the reported depth range of authigenic phosphorites. The site

357   is shallow enough to have been periodically exposed during most of the Pleistocene (Bintanja *et*

358   *al.,* 2005). However, it is unlikely that the phosphorites at this site are the result of intensive

359   transport and reworking of preexisting phosphatic deposits (as the relict phosphorite deposits of

360   the middle to outer shelf are) because the apatitic pellets co-occur with abundant, well preserved,

361   fragile diatom frustules. This suggests that the apatite in core 25005 is authigenic and represents a

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362   site of very recent phosphogenesis, likely Holocene in age. The lack of obvious giant sulfide-

363   oxidizing bacteria at the site, however, makes it possible that active phosphogenesis at this site

364   ceased, perhaps because the area of most intense upwelling and biomass accumulation had

365   shifted northwards (Compton & Bergh, 2016).

366   Diagenetic pyrite first appears within the apatite maxima zone and increases downward in

367   core 25005. This suggests the establishment of sulfidic conditions and a sharp redoxcline in the

368   shallow subsurface (Figures 3d–e). Such diagenetic conditions are consistent with microbial

369   redox-driven polyphosphate cycling, which invokes active and fluctuating redoxclines

370   (Ruttenberg & Berner, 1993; Brock & Schulz-Vogt, 2011). A possible process which resulted in

371   the apatite enrichment in core 25005 was proposed by Schulz & Schulz (2005), based on a study

372   of the diatomaceous mudbelt to the north of the cores studied here. They found that the peak of

373   sulfur-oxidizing *Thiomargarita* abundance coincided with peak dissolved and solid-phase

374   phosphate concentration in the sediments, suggesting that phosphate pumping by these organisms

375   leads to supersaturation with respect to apatite precursors, as the subsurface environment

376   fluctuates between suboxic and sulfidic.

377   The apatitic pellets in the studied cores are ubiquitously composed of agglutinated,

378   micron-sized, rod-shaped apatite particles that have coalesced into larger aggregates. They show

379   recrystallization and growth from simple rod-shaped particles to dumbbell-shaped, and finally

380   spherical particles (Figures 6, 9). Sequential recrystallization of apatite in the pellets is well

381   illustrated by XRD and electron diffraction characteristics of apatite in the studied cores. They

382   reveal a noticeably lower crystallinity and highly variable unit cell values of the authigenic *in situ*

383   apatite in core 25005 in comparison with the redeposited apatite in the core GC4 (Figure 3b).

384   Similarly, the inner layers of the concentric rod-shaped particles show greater crystallinity

385   compared to those in outer layers (Figure 7i–j).

386   Earlier studies of poorly consolidated phosphatic concretions in the Namibian

387   diatomaceous mud (Baturin, 2000; Compton & Bergh, 2016) have suggested that the concretions

388   initially formed as replacements of carbonaceous shells or infillings of sediment pore space

389   (Compton & Bergh, 2016), possibly via localized and rapid apatite nucleation events triggered by

390   phosphate-accumulating bacteria (Krajewski *et al.,* 1994; Schulz & Schulz, 2005). Our data

391   indicate that sedimentary authigenic apatite is nucleated as ellipsoidal, 50–200 nm-sized electron

392   dense areas. Growth of the rod-shaped particles then proceeds concentrically by addition of

393   layers composed of nanocrystalline apatite. It appears that rod-shaped apatite particles are

394   nucleated simultaneously at numerous sites within sediment pore water, and that apatite growth

395   on individual particles proceeds episodically at different rates. The electron-dense layers in the

396   concentric rod-shaped particles are composed of tightly packed, minute apatite crystallites that

397   possibly represent periods of higher supersaturation (Figure 7b). Higher levels of apatite

398   supersaturation – meaning the extent to which solute concentration exceeds thermodynamically

399   determined solubility – result in higher rates of apatite precursor precipitation, as increasing

400   supersaturation make the precipitation less dependent on distinct nucleation templates and allow

401   for the precipitation of more soluble precursor phases (Krajewski *et al.*, 1994). By contrast, the

402   porous layers are composed of crystallites tens of nm in size and could represent the growth of

403   rod-shaped particles at lower supersaturation levels (Figures 7). Up to 12 alternating concentric

404   layers were found in rod-shaped particles, and typically the electron-dense layers are wider

405   compared to porous layers (Figure 7b). The outer layers of the rod-shaped particles appear wider,

406   possibly due to a geometric effect of the cross-sections cutting through the ellipsoidal rod-shaped

407   particles at different distances with respect to their center (*e.g.*, Cosmidis *et al.*, 2013). Similar

408   nanometer scale autocatalytic self-organization of the precipitates, due to oscillations in the local

409   microenvironment, is known in silica-carbonate biomorphs (*e.g.*, Nakouzi *et al.*, 2015), and can

410   result in formation of intrinsic mineralized banding patterns with the same periodicity (Montalti

411   *et al.*, 2017). Therefore, such layering observed in rod-shaped apatite particles could be the result

412   of alternating levels of phosphate input, in turn, a result of intermittent microbial phosphate

413   pumping by polyphosphate-accumulating bacteria (Schulz & Schulz, 2005; Jones *et al.*, 2016).

414   Alternatively, the pattern might be similar to Liesegang banding, in which case the formation of

415   layers could arise from a supersaturation-nucleation-depletion cycle, or by post-nucleation

416   Ostwald-ripening type processes, without requiring a fluctuating phosphate input (Nakouzi &

417   Steinbock, 2016). However, the thinnest Liesegang bands observed in natural and experimental

418   settings are on the order of a few to 100 μm thick (*e.g.*, Bensemann et al., 2005), much larger

419   than the bands observed in our study.

420   We interpret the concentric rod-shaped particles to be primary phosphatic nuclei, possibly

421   growing episodically at the fluctuating (sub)oxic-sulfidic redoxcline. There is no evidence of a

422   visible substrate for heterogeneous nucleation inside the rod-shaped particles, except for perhaps

423   the organic matter closely associated with the apatite particles. Instead, the high number of rod-

424   shaped particles ($>10^9$ particles per cm^3) seems to be more consistent with homogeneous

425   nucleation from a highly supersaturated solution with dissolved phosphate concentration >400

426   μM (e.g., above the threshold for the nucleation of low interfacial-energy apatite precursor

427   phases), as has been previously suggested for other phosphorites (Krajewski *et al.*, 1994). Such

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428   high dissolved phosphate levels might be the result of phosphate pumping by polyphosphate-

429   accumulating bacteria (Schulz & Schulz, 2005), which may or may not be giant sulfur bacteria

430   (Jones et al., 2016). It is particularly interesting that the density of apatite nuclei in Namibian

431   apatitic pellets is in the same range as in other recent and ancient phosphorites (Lamboy, 1990a),

432   possibly suggesting a universal mechanism behind authigenic apatite precipitation in

433   phosphogenic environments.

434   It has been shown that sedimentary authigenic apatite precipitation involves different

435   metastable fluoride-poor (semi-)amorphous Ca-phosphate precursor phases, such as struvite,

436   octacalcium phosphate or amorphous calcium(-magnesium) phosphate. These phases are

437   subsequently converted into carbonate fluorapatite – the most thermodynamically-stable apatite

438   phase in seawater (Jahnke, 1984; Knudsen & Gunter, 2002) – through a dissolution-re-

439   precipitation process or alternatively directly through solid-phase transitions (Froelich *et al.*,

440   1988; Krajewski *et al.,* 1994; Baturin, 2000; Arning *et al.,* 2009b). The absence of amorphous

441   precursor phases in analyzed samples is consistent with termination of apatite precipitation at the

442   studied sites some time ago. Nonetheless, since the critical role of amorphous precursors in

443   apatite precipitation has been confirmed in both laboratory experiments and in marine settings

444   (van Cappellen & Berner, 1991; Krajewski *et al.,* 1994; Schenau *et al.*, 2000; Golubev et al.,

445   1999; Gunnars *et al.*, 2004; Borkiewicz *et al.*, 2010; Oxmann & Schwendenmann, 2014), we

446   expect these phases must have precipitated first. Changing structural ordering of the Ca-

447   phosphate phase is also suggested by TEM diffraction of the less-matured apatite on the rims of

448   the apatite particles that does show some smearing – a sign of misorientation of individual

449   nanocrystallites, which is a characteristic of mosaic crystals derived from amorphous precursors

450   (Figure 7j). Furthermore, the lath-shaped (well crystallized) crystallites nucleating at the rod-

451   shaped particles and forming larger intersecting dumbbell-to-spherical particles might result from

452   thermodynamically driven recrystallization of nanocrystalline primary apatite involving Ostwald

453   ripening type processes (*e.g.*, Voorhees; 1985) that are suggested as a mechanism in the

454   formation of Liesegang banding (*e.g.*, Kai *et al.,* 1982). The less-well defined apatite matrix

455   might represent the end product of the intergrowth and re-crystallization of primary rod-shaped

456   apatite particles, or could alternatively be a more direct result of the dehydration and

457   recrystallization of amorphous Ca-phosphate mass (Baturin, 2000).

458   The growth of very similar rod, dumbbell and spherical-shaped apatite particles has been

459   previously reported in laboratory experiments conducted at high supersaturation levels

460   (Krajewski *et al.,* 1994; Ruan *et al.,* 2013). An important aspect in understanding the genesis of

461   such apatite microstructures is the occurrence of different types of microstructures forming a

462   sequence of evolving morphologies – from rod-shaped particles with bulged distal ends to

463   dumbbells and semi-spherical particles (Figure 9). A similar assemblage of microstructures

464   termed "fluorapatite-gelatin nanocomposites" has been reported to occur in double-diffusion

465   experiments using a variety of organic substrata (Kniep & Busch, 1996; Busch *et al.,* 1999;

466   Kniep & Simon, 2006; Wu *et al.,* 2010). In double-diffusion experiments investigating the

467   influence of organic materials on the precipitation of apatite, numerous morphologies evolved

468   from prismatic to dumbbell-like to spherical amongst the precipitates that nucleated and grew

469   within a polymeric gelatin gel (Crosby & Bailey, 2017; 2018; Figure 10). Interestingly, many

470   have a distinctly biological appearance despite being abiological, and they resemble features

471   described in the Namibian phosphate pellets. Such a form of fractal-like reorientation of crystal

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472   growth has been found to be controlled by an intrinsic dipolic field generated by organic

473   macromolecules that are incorporated in the nanostructure of the particles (Simon *et al.,* 2006). A

474   very similar form of crystal growth is interpreted to have formed the succession of rod-shaped to

475   dumbbell to spherical/radial microstructures found on the Namibian shelf, although Baturin and

476   Titov (2006) have alternatively explained the formation of spherical particles through the

477   dehydration and recrystallization of amorphous Ca-phosphate gels.

478   The lab-grown nanocomposites possess a distinctive inner structure – crystallites

479   emanating from the core mostly grow parallel to the long axis, but tend to start to orient at an

480   angle as the composites grow (Brickmann *et al.,* 2010). The slightly angled orientation of the

481   crystallites in the Namibian rod-shaped particles is evident in apatitic pellets in both cores

482   (Figures 6c–d, 7). In Namibian phosphorites, the growth of the recrystallized apatite particles

483   composed of radiating lath-shaped crystallites is seeded on concentric rod-shaped particles.

484   Similar to the lab-grown nanocomposites (Figure 10a–b), most of the subsequent growth is

485   concentrated at the distal ends of the rod-shaped particles and directed outward (Figure 7c). This

486   results in bulging of the distal ends of the particles (Figure 9b–c), where cross-sections reveal that

487   the growth layers are widest at the distal ends of the rod-shaped particles (Figure 7b). It further

488   leads to the formation of radial/spherical particles that compose most of the volume of the

489   macroscopic apatitic pellets (Figure 9d, 10c). In addition, besides the very similar morphology,

490   the rod-shaped particles commonly appear in association with substrata composed of organic

491   macromolecules (Figure 6). The latter likely serve as nucleation surfaces for the formation of the

492   fluorapatite-gelatin nanocomposites and may also induce the distal reorientation of crystal growth

493   as noted by Simon et al. (2006). This also suggests that the pellets form by aggregation of

23

494   recrystallizing rod-shaped apatite particles, and that there is not much outward growth of the

495   primary apatitic pellets themselves. However, concentric rims on reworked/matured pellets in

496   GC4 core (Figure 5a, similar to 10f) possibly indicate that Ca-phosphate precipitation has been

497   repeatedly renewed using the surface of the preexisting pellet as the nucleation template.

498

499   The role of biological templates in apatite nucleation and growth

500   The pervasive rod-shaped apatite particles in Namibian apatitic pellets bear a strong superficial

501   resemblance to microbial casts due to their generally similar sizes, and co-occurrence with

502   organic substance that may have once represented microbial EPS (Figure 6). Very similar fabrics

503   have been found in various phosphorites that were previously interpreted as aggregations of

504   microbial casts (Lamboy, 1990a; Zanin & Zamirailova, 2011). Their formation was hypothesized

505   to be the result of nucleation of apatite nanocrystals on microbial cell walls, which are known to

506   provide suitable binding sites for biologically induced phosphate mineral formation (Konhauser

507   *et al.,* 1994). The minerals encrusting the microbes then start to grow and coalesce, until the

508   organic structures are wholly replaced by apatite (*e.g.*, Lepland *et al.,* 2014). Indeed, the fast-

509   growing field of biomineralization research has provided a myriad of experimental evidence to

510   support the importance of microbes in both providing nucleation surfaces and exerting more or

511   less direct control over the precipitation of minerals via extra- or intracellular enzymes, the

512   concentration of ions, or the excretion of EPS material (Konhauser & Riding, 2012). Specifically,

513   functional groups on cell walls and/or polymeric strands of EPS provide suitable binding sites for

514   calcium cations and have thus been shown to promote the nucleation of calcium carbonate

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515 minerals (Benzerara *et al.,* 2004), although the importance of such surfaces on apatite

516 precipitation decreases with higher degrees of supersaturation and higher precipitation rates

517 (Krajewski *et al.,* 1994).

518   Despite many microbes having developed mechanisms to prevent becoming encrusted in

519 authigenic minerals (Schultze-Lam *et al.*, 1992; Phoenix and Konhauser, 2008; Hegler *et al.*,

520 2010), phosphatization is a well-known means by which microbes and metazoans can be

521 preserved as fossils (Crosby & Bailey, 2012). The rapid formation of sedimentary authigenic

522 apatite leads to the phosphatization of widely different biological structures, including nanoscale

523 fibrous organic structures in linguliform brachiopods (Lang *et al.,* 2016), fungal mats (Bréhéret,

524 1991), filamentous cyanobacteria mats and stromatolites (Rao *et al.,* 2000), filamentous sulfur

525 bacteria (Bailey et al., 2013), and other bacterial forms (Krajewski *et al.,* 1994). In microbial

526 structures the mechanism remains the same in most cases – extracellular precipitation of apatite,

527 which tends to produce external molds of microbes. Conspicuous microbial structures have also

528 been found in a wide variety of ancient phosphorites (Krajewski *et al.,* 1994; Crosby & Bailey,

529 2012; Bailey *et al.,* 2013; Cosmidis *et al.,* 2013), up to and including, some of the earliest

530 significant phosphorites in the world, e.g., the 1.7 Ga Jhamarkotra Formation, India (Crosby *et*

531 *al.,* 2014), 1.85 Ga Michigamme Formation, USA (Hiatt *et al.,* 2015), 1.88 Ga Ferriman Group,

532 India (Edwards *et al.,* 2012), and ~2 Ga Zaonega Formation, Russia (Lepland *et al.,* 2014). The

533 very common occurrence of phosphatized microbial cells in phosphatic sediments has been

534 interpreted as evidence of the direct role of microbial surfaces in the nucleation of phosphate

535 minerals (Lamboy, 1990a), the role of microbes in concentrating ions in pore waters (Schulz &

536   Schulz, 2005; Goldhammer *et al.,* 2010), or simply as a consequence of the rapid precipitation of

537   authigenic apatite, which tends to indiscriminately phosphatize surfaces (Krajewski *et al.,* 1994).

538   A controversial class of phosphatic microstructures are the densely-packed aggregates of

539   small rod-shaped particles marked by rounded, non-crystalline appearance and a length of a few

540   µm, which have been reported from a variety of recent and ancient phosphorites (Bremner, 1980;

541   O'Brien *et al.,* 1981; Mullins & Rasch, 1985; Bersenev *et al.,* 1986; Garrison *et al.,* 1987; Rao &

542   Nair, 1988; Garrison & Kastner, 1990; Lewy, 1990; Lamboy, 1993, 1994; Baturin, 2000). Their

543   overall resemblance to phosphatized microbial mats has led many researchers to interpret them as

544   phosphatized casts of rod-shaped bacteria (O'Brien *et al.,* 1981; Lamboy, 1990a, 1990b;

545   Bréhéret, 1991; Zanin & Zamirailova, 2011).

546   A large body of laboratory work has also been conducted on the precipitation of apatite in

547   the field of biomaterials research, motivated by the goal of understanding biomineralization of

548   human bone and teeth, and by possible medical applications, such as re-growing bone tissue

549   (Vallet-Regí & González-Calbet, 2004). Since controlled biomineralization in vertebrates takes

550   place in a complex environment of organic scaffolds and catalysts, the research has focused on

551   the effects of polymers as nucleation templates or additives, while also keeping in mind the effect

552   of inorganic additives, pH and temperature (Bleek & Taubert, 2013). These studies have shown

553   an exceedingly diverse picture of the possible apatite mineral forms capable of growing under a

554   large variety of synthesis conditions (Lin *et al.,* 2014). Densely-packed, rod-shaped particles are

555   often described forming in such experiments (*e.g.* Ruan *et al.,* 2013), and similarly to what is

556   found in Namibian phosphorites, some of this work shows that rod-shaped particles transform

557   into dumbbell-shaped and radial-spherical particles in the presence of organic macromolecules.

26

558 These structures are equally common in calcite, dolomite, and Fe-oxyhydroxide precipitates

559 formed in the presence of organic substances (Meldrum & Hyde, 2001; van Lith *et al.*, 2003;

560 Meldrum & Cölfen, 2008; Tourney & Ngwenya, 2014).

561   Krajewski *et al.* (1994), along with other researchers, expressed a skepticism of all

562 putative bacterial forms in phosphorites (except filamentous cyanobacteria and fungi) and

563 suggested that only morphologies which have been demonstrated to form during experimental

564 mineralization of microbes can be considered as potential microbial fossils. Such forms are

565 mainly empty or partially infilled coccoid to rod-shapes, in essence, forms that contain a hollow

566 lumen (Cosmidis *et al.,* 2013). Microscopic rod-shaped particles in the Namibian phosphorites

567 reported here, and in previous studies (Baturin, 2002; Baturin & Titov, 2006; Titov & Baturin,

568 2008; Compton & Bergh, 2016), bear significant resemblance to phosphatized microbial remains.

569 These appear as rod-shaped dubiofossils with somewhat consistent sizes, attached to pore walls

570 in a microbially active sedimentary environment, surrounded by organic macromolecular

571 structures that possibly represent dessicated EPS (*e.g.*, compare Figure 6b with Figure 7 in

572 Nealson, 1997). There are, however, significant problems with this interpretation, as has

573 previously been pointed out regarding the Namibian phosphorites by Baturin and Titov (2006)

574 and Titov and Baturin (2008). For instance, the nanostructure of the rod-shaped particles, as

575 imaged via TEM in this study, indicate that the particles are not phosphatized microbes (Figure

576 7). A microbe would first be encrusted on the outside, with mineralization reaching the inside of

577 the cell after it has lysed (Konhauser *et al.,* 1994). This would, ideally, result in distinct rim and

578 core structures, representing the different stages of mineralization (*e.g.*, Lepland *et al.,* 2014).

579 The innermost layer of the rod-shaped particles could be construed as a mineralized microbe, if

580   not for its small size – a diameter of <200 nm is much less than that generally attributed for

581   viable non-parasitic bacteria (Luef *et al.,* 2015). Secondly, a significant number of the rod-shaped

582   particles show intersecting/intertwining with respect to one another and/or a common point of

583   origin that is not characteristic of microbial casts (Figures 8a–b). Although this may be the result

584   of post-nucleation growth of what were originally much smaller and non-intersecting apatite

585   particles, in most cases, this appears to be a primary feature possessed by even the innermost

586   layers of the rod-shaped particles, as evident in TEM-micrographs (Figure 7b).

587   The question then becomes how did the apatite precursor phases nucleate, and which, if

588   any nucleation templates were involved. On the one hand, the nanoscale structure of the rod-

589   shaped apatite particles does not incorporate any other mineral components. On the other hand,

590   several lines of evidence point to the role of organic matter in apatite nucleation: (i) the apatite

591   particles commonly appear (almost without exception) in association with organic substances

592   (Figure 6); (ii) the microstructures that form most of the apatite matrix are similar to laboratory

593   fluorapatite-gelatin nanocomposite precipitates, in which organic macromolecules are intimately

594   tied to apatite nanostructure and play a key role in controlling apatite growth (Kniep & Simon,

595   2006; Simon *et al.,* 2006); (iii) the occurrence of porous layers within the rod-shaped apatite

596   particles that are enriched in carbon and sulfur, likely proxies for organic matter (Figure 7d–f).

597   Accepting the identification of the apatite microstructures in Namibian phosphorites as analogous

598   to fluorapatite-gelatin nanocomposites, the crystal growth and formation of this specific

599   morphology seems to be controlled by organic macromolecules of a certain type (*e.g.,* Simon *et*

600   *al.,* 2006).

601   While characterizing the exact nature of this organic substance is beyond the scope of the

602   present study, we can hypothesize that in the Namibian shelf sediments, these substances most

603   likely derive from microbial cell walls, the products of microbial breakdown of sedimentary

604   organic matter, or relicts of bacterially excreted EPS. It is then possible that organic polymeric

605   macromolecules, for example those that comprise the organic portion of EPS, served as the

606   primary nucleation environment during the formation of rod-shaped particles and its precursor

607   phases. EPS is known to provide a template for adsorption of metal cations to which anions are

608   attracted, thus inducing local mineral supersaturation (Tourney & Ngwenya, 2014).

609   Although the abundant rod-shaped particles in Namibian apatitic pellets are not fossilized

610   microbes, the authigenic precipitation of apatite can be seen as having been largely controlled by

611   microbially-produced processes (e.g., phosphate pumping) and substances (e.g., EPS or other

612   microbially-produced organic substances). Since the association of phosphatic facies and strata

613   with organic matter is widely recognized in the geologic record (Krajewski *et al.,* 1994), it may

614   well be that nucleation of calcium phosphate minerals on organic nucleation substrata played

615   similar roles in the formation of authigenic apatite in other recent and ancient phosphorite

616   deposits.

617

Conclusions

619   Microbial influences on sedimentary authigenic apatite precipitation from an area known for

620   modern phosphogenesis were studied. Phosphorus in these sediments is mainly present as sub-

621   mm apatitic pellets, which are, in turn, mainly composed of intergrown ~1 μm long, rod-shaped

622   apatite particles that co-occur with organic substance. The dense distribution ($>10^9$ per cm^3), a

623   lack of visible nucleation templates in the nanostructure, and distinctive growth patterns

624   incorporating organic matter, indicate that the phosphate minerals in the P-rich sediments on the

625   Namibian shelf may have nucleated on organic substrata, such as polymeric strands of EPS, in

626   pore waters supersaturated with respect to an apatite precursor. Furthermore, as similar structures

627   are common in other phosphorites, this potentially represents a general mechanism for the

628   precipitation of P-rich sediments.

629   The apatite microstructures range from rod-shaped to bulged forms, dumbbells and

630   spherical particles, representing a growth continuum very similar to previously reported lab-

631   grown apatite structures in highly-supersaturated solutions in organic matrices – "fluorapatite-

632   gelatin nanocomposites" or phosphatic objects precipitated in the gelatin matrix of a double

633   diffusion gradient apparatus. Considering the similar inner structures of the lab grown

634   microstructures to the apatite structures in the Namibian phosphorites, one can infer that the

635   environmental precipitates formed through a mechanism analogous to that of the lab-grown

636   nanocomposites.

637   The closely intertwined organic matrix in the nanostructure of the apatite is most likely a

638   byproduct of microbially-produced organic matter and might act as a major nucleation template

639   for the apatite precursor phases. This could provide a further indirect microbial control on the

640   formation of phosphorites. However, the superficial resemblance of such rod-shaped apatite

641   particles to microbial casts, as has been previously suggested, is not borne out under closer

642   scrutiny, urging caution when looking for microfossils in similar material.

643

Acknowledgments

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946 **Figure captions**

947 **Figure 1.** Distribution of sediments on the southern part of the Namibian shelf with coring sites.

948 Modified after Baturin (2000).

949 **Figure 2.** Optical micrograph of whole sediment: (a) core GC4 and (b) core 25005. Core 25005

950 contains numerous fragile diatomaceous frustules. Scale bars represent 1 mm.

951 **Figure 3.** (a) characteristic XRD patterns of bulk sediment samples from cores GC4 (depth 10–

952 11 cm) and 25005 (depth 4–5 cm). (b) apatite unit cell parameters for cores GC4 and 25005 in the

953 context of different types of natural apatite. Modified after Nemliher (1999); Vinn & Kirsimäe

954 (2014). (c) apatite and pyrite content in core GC4, XRD quantification; (d) apatite and pyrite

955 content in core 25005; (e) phosphorus and sulfur content in core 25005, as measured by ICP-MS.

956 **Figure 4.** SEM-BSE overview images of whole sediment in (a) core GC4 and (b) core 25005.

957 Both cores contain abundant apatitic pellets. SEM-SE images of single apatitic pellets from (c)

958 core GC4 and (d) core 25005. Pellets from core GC4 tend to be larger and more rounded than

959 those from core 25005. (e–f) SEM-SE images of broken surfaces of apatitic pellets form (a) core

960 GC4 and (b) core 25005. Pellets from core 25005 contain much more pores and detritus.

961 **Figure 5.** SEM-BSE images of polished surface of the pellets: (a) core GC4 and (b) core 25005.

962 Pellets from core GC4 display several 10–20 μm thick rims, those from core 25005 usually have

963 one, if any. (c) SEM-BSE image of a broken surface of a pellet, showing that the material is

964 mainly composed of inter-grown radial microstructures (core 25005).

965 **Figure 6.** SEM-SE images of apatite particles from broken-surface pellets. (a) diverse forms of

966 apatite microstructures (core 25005). (b) abundant apatite rod-shaped particles coat pore walls

967 (core 25005). (c) rod-shaped particles in core 25005 are composed of anhedral apatite

968 nanocrystallites oriented parallel to their long axis. Lighter in tone in the foreground is a spherical

969 pyrite microaggregate. (d) apatite particles in core GC4 are composed of euhedral hexagonal

970   crystallites, oriented in the same manner as in panel c. (e) rod-shaped particles occur together

971   with a film-like organic substance, seen here filling most of the image (core 25005). (f) rod-

972   shaped particles often co-occur with framboidal pyrite (core GC4). Scale bars represent 1 μm.

973   **Figure 7.** TEM images of intergrown rod-shaped apatite particles from core 25005. Large light

974   bands on panels a, b, d–f and g, as well as the dark band covering the left half of panel h,

975   represent carbon filaments, part of the lacy film that the FIB-cut is mounted on. (a, g) high-angle

976   annular dark-field (HAADF) images of entire FIB-foils. (b) HAADF image illustrating the

977   growth of rod-shaped particles in several concentric ~50–200 nm thick layers, originating form

978   an ellipsoidal ~50-200 nm wide inner core, alternating between dense and porous. The layers are

979   thickest at the distal ends of the particles. (c) HAADF image showing elongated apatite

980   crystallites radiating along the long axis of the rod-shaped particles (some examples indicated by

981   dashed lines). (d) HAADF image of a rod-shaped particle with layered internal structure; (e–f)

982   overlayed Electron Energy Loss Spectroscopy jump ratio maps of carbon (i) and sulfur (j) of the

983   same area. (h) bright field image of a rod-shaped particle. (i) Fast Fourier Transformed electron

984   diffraction pattern of inner layer, showing greater crystallinity (sharp reflections). (j) Fast Fourier

985   Transformed electron diffraction pattern of the outer layer of a rod-shaped particle, showing

986   lower crystallinity (diffuse and smeared-out reflections).

987   **Figure 8.** SEM-SE images of broken-surface pellets (b from core GC4, all others from core

988   25005). (a) rod-shaped apatite particles tend to intersect one another. (b) rod-shaped particles

989   often form intergrown aggregates. (c) truncated apatitic particles, which appear to have nucleated

990   tangentially on a pore wall (example of pore wall and apatitic particles is indicated by dashed
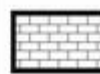
991   lines). (d) individual rod-shaped particles merge into the apatite matrix of the pellets. (e) rod- and

992   dumbbell-shaped apatite particles display varying sizes. (f) spherical apatite particles. Scale bars

993   represent 1 μm.

994   **Figure 9.** SEM-SE (a,b,d) and SEM-BSE (c) images of progressing apatite growth forms from

995   broken-surface pellets (c from core GC4, all others from core 25005). Rod-shaped and other

996   apatite microstructures form a continuum from (a) spindle-shaped elongated rods to (b) rods that

997   start to bulge at their distal ends to (c) dumbbells to (d) spherical particles. Scale bars represent 1

998   μm.

999   **Figure 10.** SEM images of apatite precipitated in organic matrices during double-diffusion

1000 experiments (Crosby and Bailey, 2017; 2018). The resultant apatite morphologies range from (a)

1001 spindle-shaped to (b) dumbbells to (c) spherical microstructures. Such apatite microstructures

1002 often intersect and are composed of smaller lathe or hexagonal shaped apatite crystallites. (d–e) a

1003 consortium of different apatite microstructures, concentrated in the harvesting phase. (f) apatite

1004 overgrowth forming a 10–20 μm thick radial layer over a laboratory-grown apatite sphere broken

1005 to expose complex internal microstructures. Scale bars represent 10 μm.

1006 Figure 1
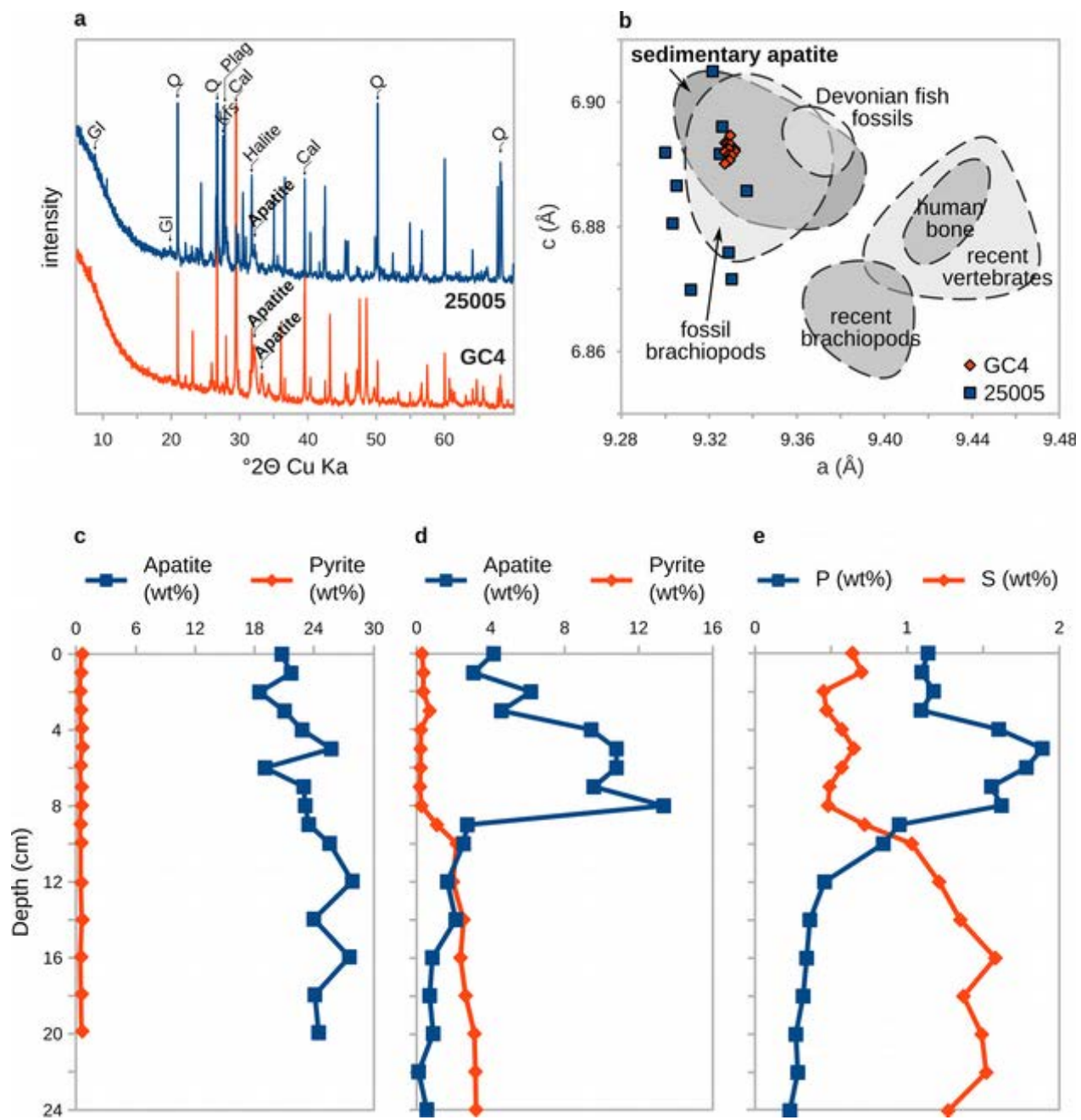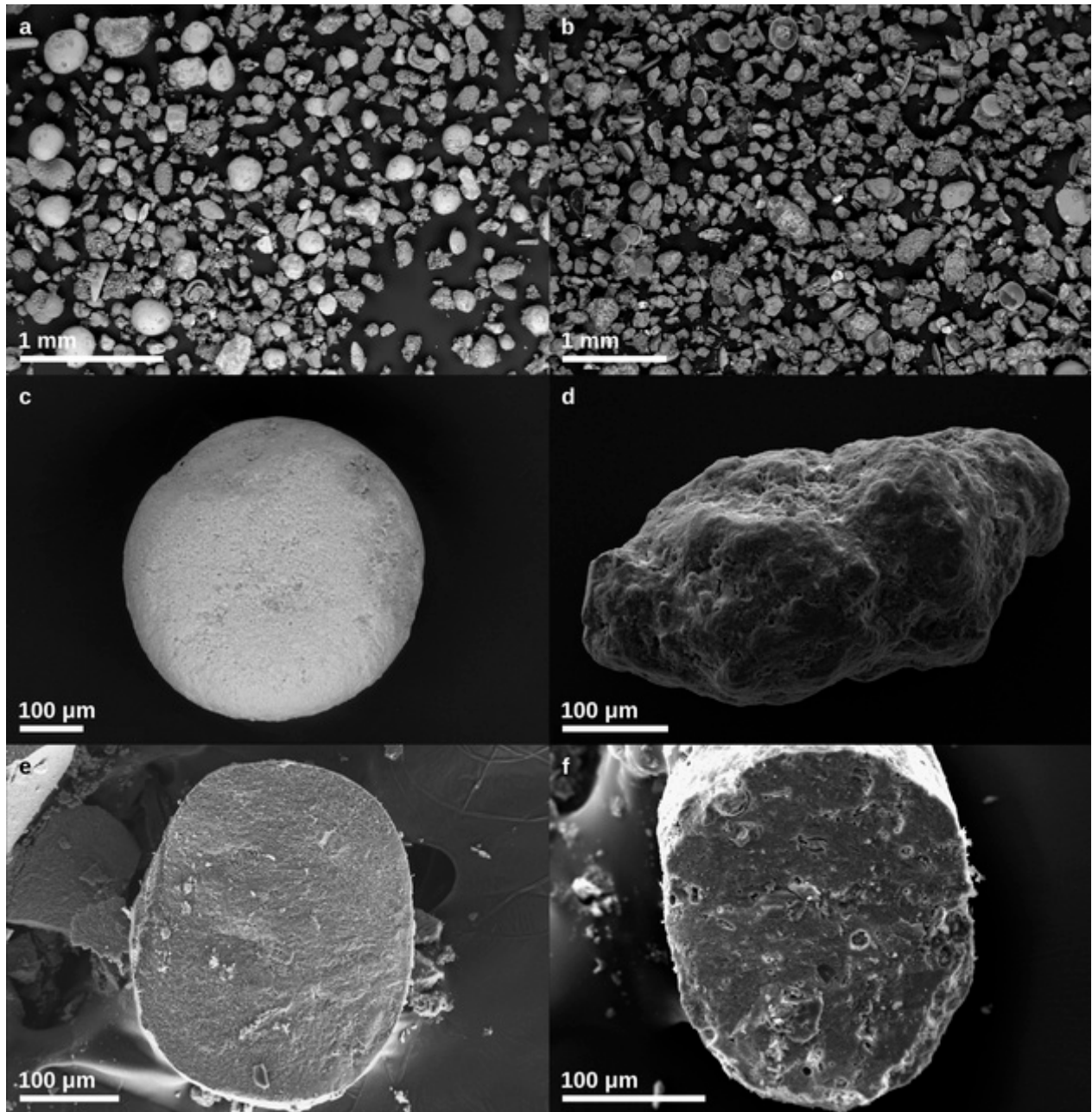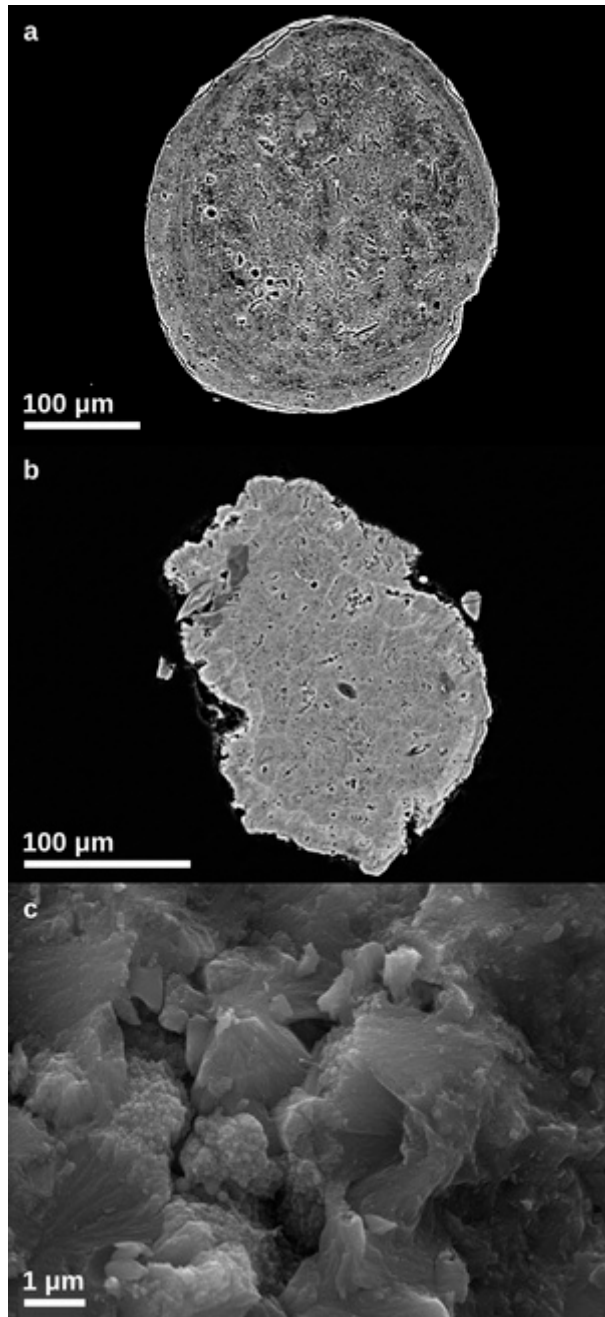
1007

1008   Figure 2

1010   Figure 3
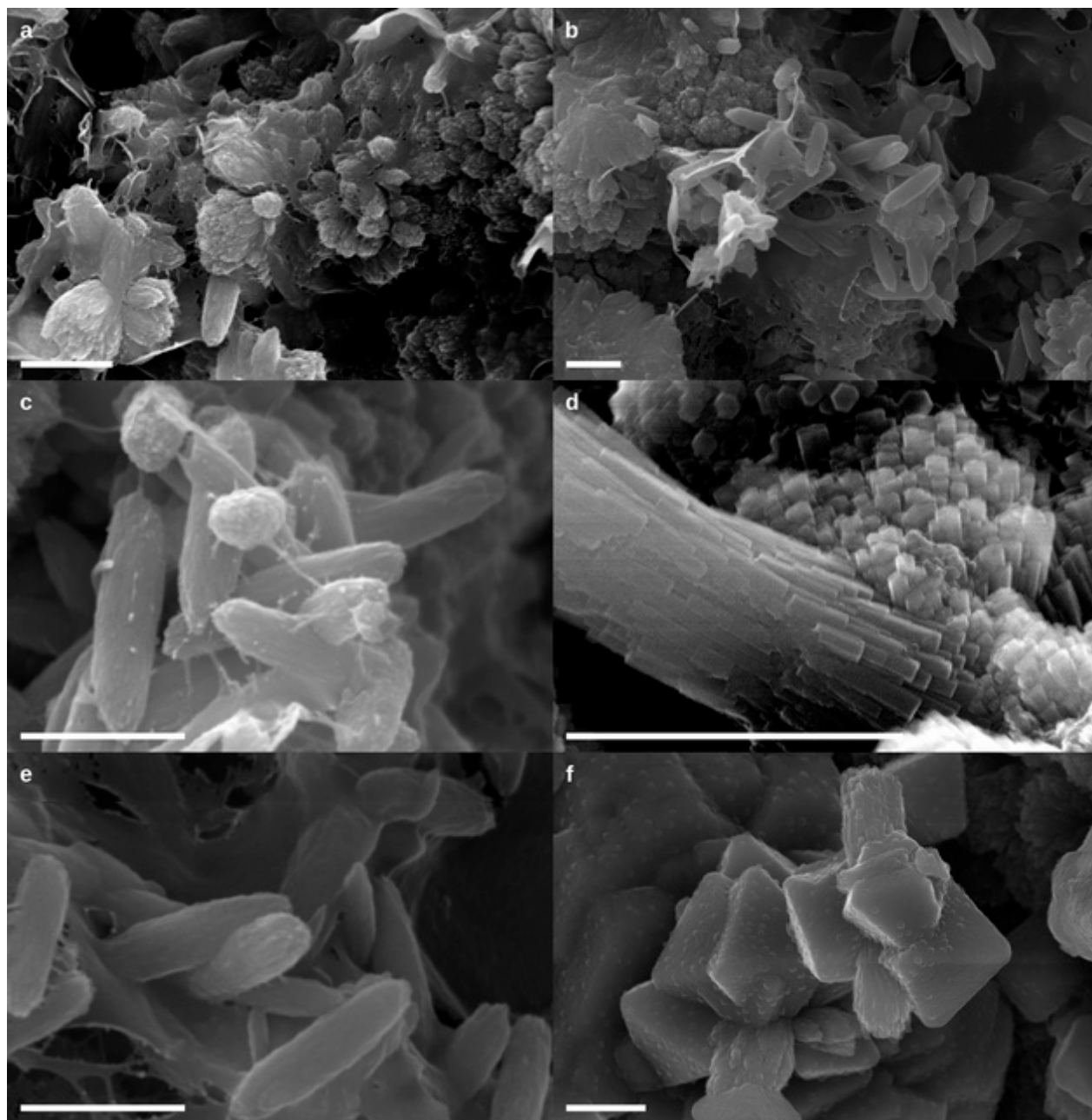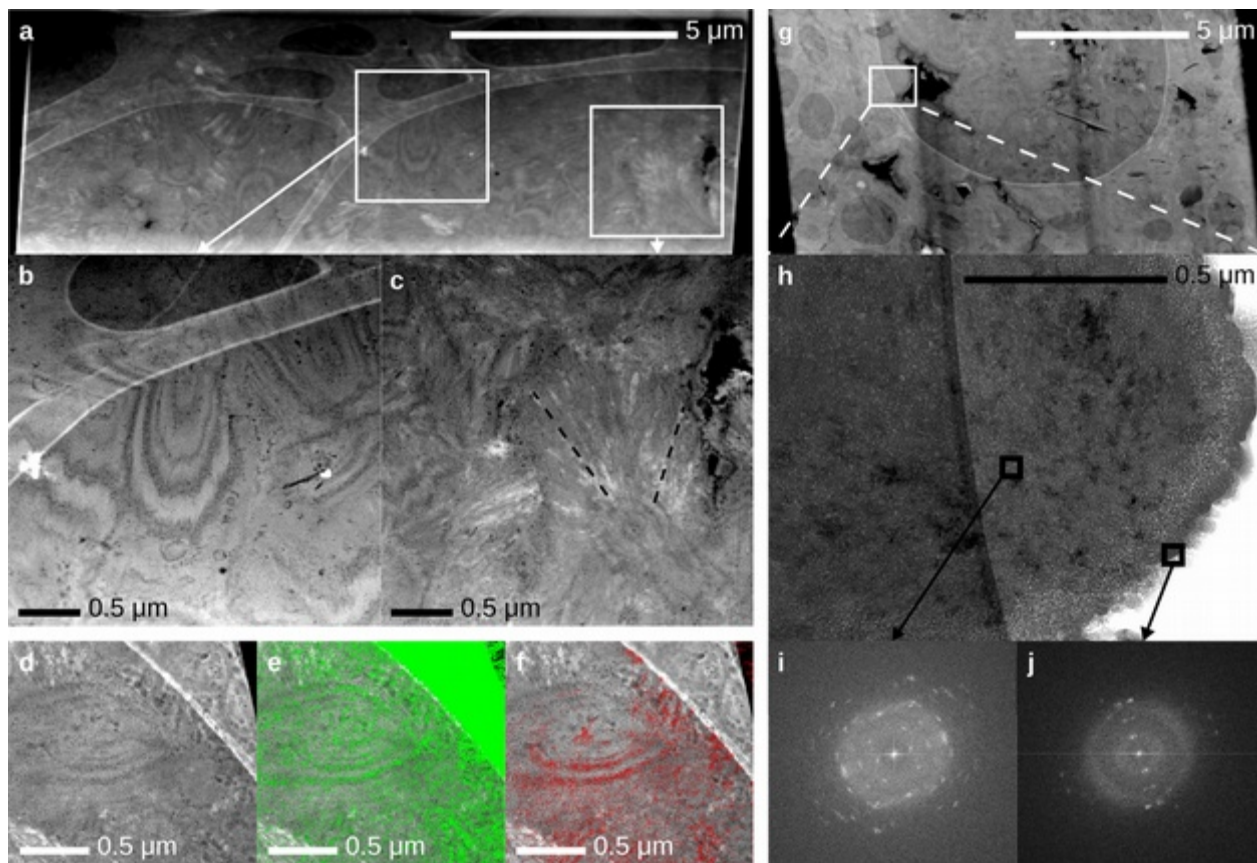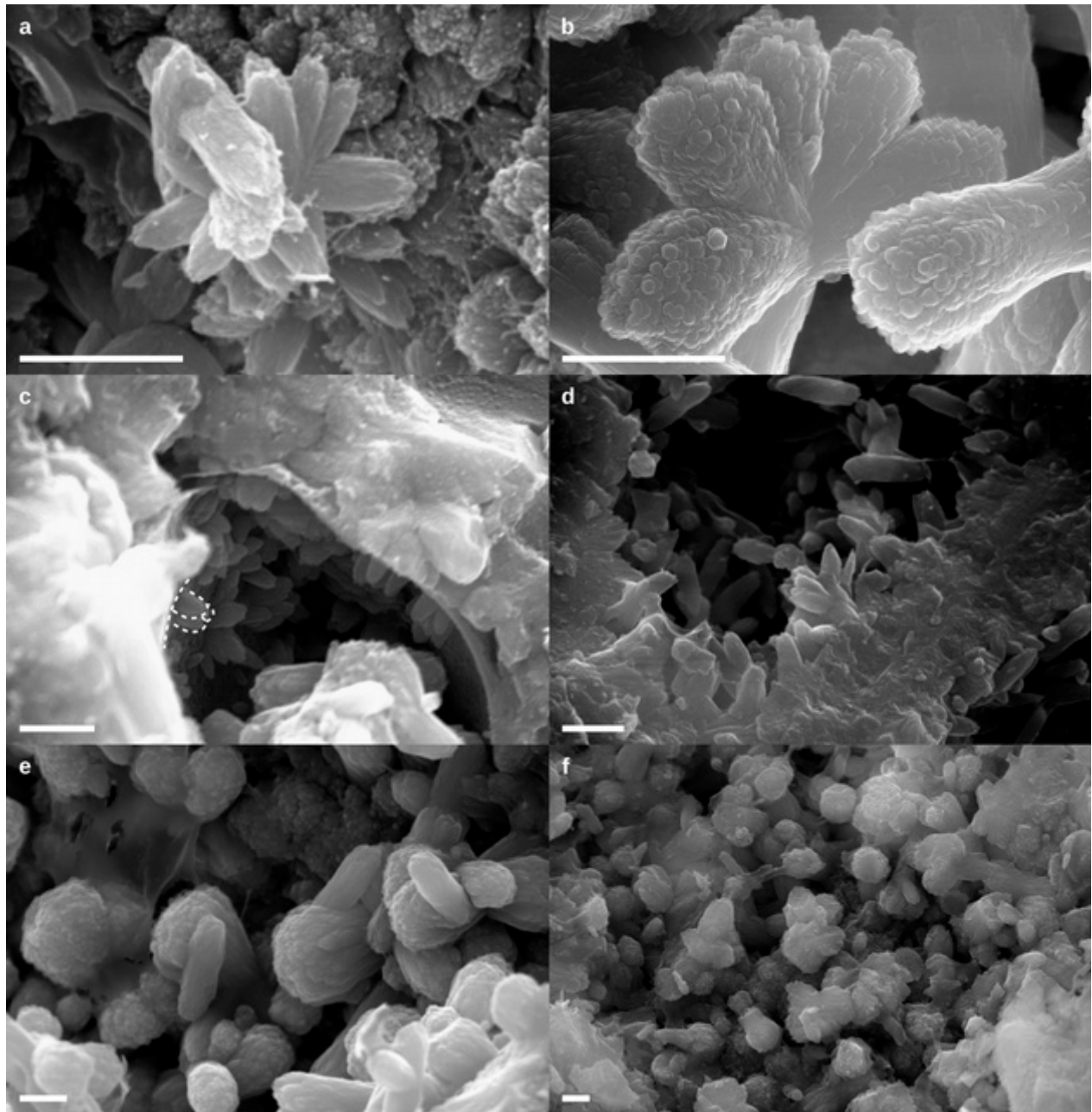

1011

1012   Figure 4

1013

1014   Figure 5

1016   Figure 6

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1018   Figure 7

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1020   Figure 8

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1022   Figure 9

1023

1024   Figure 10

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