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On the structure and chemistry of fossils of the earliest woody plant

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ABSTRACT

Palaeontology relies on the description of fossil morphologies to understand the evolutionary history of life on Earth. Yet, much remains unknown about the impact of fossilization processes, even though these may introduce biases in paleobiological interpretations. Here, we report the characterization of fossilised remains of the earliest woody plant *Armoricaphyton chateaupannense* preserved either in 2D (as flat carbonaceous films) or in 3D (as organo-mineral structures) in early Devonian shales (ca 407 Ma) of the Armorican Massif on the northern margin of Gondwana. To document the fine-scale structure and the chemistry of the tracheids of this ancient plant, we used propagation phase contrast synchrotron radiation X-ray microcomputed tomography (PPC-SR μ CT), transmission electron microscopy (TEM) and synchrotron-based scanning transmission X-ray microscopy (STXM) coupled with X-ray absorption near edge structure (XANES) spectroscopy. PPC-SR μ CT enables digital visualization of cell walls in unprecedented detail for the specimens preserved in 3D revealing structures similar to those observed in extant lignified cells, thereby strongly suggesting that the earliest woody plant *A. chateaupannense* originally contained lignin-like compounds. STXM-based XANES and TEM data show that, whatever the preservation modes (3D vs 2D), the original lignin or lignin-like compounds, if present, did not withstand fossilization processes and were replaced by

35 pyrobitumen compounds containing automorphic Ti-nanomaterials. Altogether, the present study
36 illustrates that anatomical and chemical preservations may not always be correlated.

37
38 Keywords: Earliest Woody Plant, Lignin, Fossilization, Pyrobitumen, Microtomography,
39 XANES spectroscopy .

40

41

42 INTRODUCTION

43

44 The fossil record provides information fundamental to understanding the evolution and
45 diversification of plants on land. One key source of data comes from tissue systems and their
46 preserved cellular constituents. By drawing comparison to modern species, one can infer aspects
47 of function, physiology and chemical composition. In addition, direct chemical analyses of fossil
48 residues could help interpreting the nature of fossilized tissues. However, assessments of
49 chemical signals remain difficult, notably because fossilization processes inevitably modify soft
50 tissues, altering or obscuring their original biochemical structure (Bernard and Papineau 2014;
51 Briggs and Summons 2014), thereby hindering the precise reconstruction of their original
52 chemistry.

53 Here we investigate cell structure and residual chemistry of the most ancient woody plant
54 *Armoricaphyton chateaupannense* (ca 407Ma) from the Armorican Massif, Western France
55 (Strullu-Derrien 2010; Gerrienne *et al.* 2011; Strullu-Derrien *et al.* 2014) Phylogenetically, this
56 plant is closely related to *Tetraxylopteris*, a genus of extinct vascular plants that belonged to
57 Lignophytes, i.e. plants producing wood through a cambium (Strullu-Derrien 2010). In modern
58 woody plants, tracheid cell walls are composed primarily of cellulose, hemicelluloses and lignin.
59 Lignin is a class of complex organic macromolecules that lend rigidity to cell walls making them
60 less permeable to water, thereby improving conductivity within the vascular system. The
61 composition of lignin varies from species to species. What kind of lignin was synthesized by *A.*
62 *chateaupannense* (e.g. the most ancient woody plant) remains an open question.

63 Over the past ten years, the use of advanced techniques has shown that diagenesis does
64 not systematically obliterate all the biochemical information carried by fossils (Bernard *et al.*
65 2007; Lepot *et al.* 2008; Steemans *et al.* 2010; Cosmidis *et al.* 2013b, a; Alleon *et al.* 2016a,
66 2018; Delarue *et al.* 2017, 2018; Abbott *et al.* 2017). In parallel, laboratory experiments have
67 highlighted that burial-induced thermal degradation of organic molecules can be more abstruse
68 than generally believed (Schiffbauer *et al.* 2012; Li *et al.* 2013, 2014; McNamara *et al.* 2013a,

69 *b*; Bernard *et al.* 2015; Alleon *et al.* 2016*b*, 2017; Miot *et al.* 2017; Vinogradoff *et al.* 2018). Yet
70 the impact of advanced fossilization processes remains poorly constrained, limiting the
71 significance of chemical studies.

72 Here, to go further than previous studies conducted on fossil tracheids of different species
73 (Edwards *et al.*, 1997; Boyce *et al.*, 2001, 2002, 2003, 2010; Bernard *et al.*, 2009, 2010 Galvez
74 *et al.*, 2012a; Abbott *et al.*, 2017) we combined non-invasive synchrotron-based
75 microtomography and spectromicroscopy tools to document, at the submicrometer scale, both
76 the cell wall structure and the chemical nature of the organic components of specimens of *A.*
77 *chateaupannense* preserved either in 2D (i.e. as flat carbonaceous films) or in 3D (i.e. as organo-
78 mineral structures). Based on these observations, we reconstruct the fine anatomy of the plant
79 tracheids and constrain the diagenetic history of the fossils and we discuss the significance of the
80 biogeochemical signals retrieved.

81

82 **GEOLOGICAL SETTING**

83

84 Specimens of the early Devonian plant *A. chateaupannense* (407 Ma) preserved in 2D
85 (i.e. as flat carbonaceous films; Fig. 1a) or 3D (i.e. as organo-mineral structures; Fig. 1b) were
86 recovered from the Châteaupanne quarry (47°22'11.73''N/0°49'31.97''W) located in the
87 Armorican Massif (France). The Armorican Massif is the western part of the Variscan Belt that
88 extended throughout central Europe during the Late Paleozoic (Ballèvre *et al.* 2009).

89 The Châteaupanne unit belongs to the South Armorican domain and consists of
90 Ordovician marine sediments unconformably overlain by the Devonian (Emsian Stage)
91 Chalonnes Formation (Fig. 1d). This formation, located on the northern margin of Gondwana
92 during the Devonian, is predominantly composed of massive limestone overlying terrigenous
93 layers (Fig. 1d), suggesting deposition in a nearshore environment (Strullu-Derrien *et al.* 2010).
94 Both types of specimens of *A. chateaupannense* were collected from these terrigenous layers.

95

96 **Mineralogical Context**

97 The mineral matrix surrounding the fossil specimens mainly comprises submicrometric
98 K-aluminosilicates, with Fe-aluminosilicates locally concentrated in thin veins (Figs 2a,b).
99 Quartz (SiO₂), rutile/anatase (TiO₂) and Al-phosphates containing traces of Cerium are also
100 observed (Figs 2b,c). Both specimens of fossil plant possess an organic component, the
101 specimens preserved in 3D are also heavily pyritized.

102

103 MATERIAL AND METHODS

104

105 Propagation Phase Contrast X-Ray Synchrotron Microtomography

106 Propagation phase contrast X-ray synchrotron microtomography (PPC-SR μ CT) was
107 employed to study the three-dimensional structure of the permineralized wood, using the ID19
108 beamline of the European Synchrotron Radiation Facility (ESRF), Grenoble, France (Feist *et al.*
109 2005). The acquired tomographic dataset (0.551 μ m per voxel) was converted to 8-bit grayscale
110 bitmapped images using ImageJ (Abramoff *et al.* 2004). It was then imported using DrishtiImport
111 v2.5 (Limaye 2012) and converted into the proprietary (.pvl.nc) volume format used by the
112 volume exploration and presentation tool Drishti v2.5. Drishti volume renders the dataset voxels
113 into a manipulable 3D model. The volume was false coloured by mapping voxel x-ray attenuation
114 values to colour ranges, each targeting a different mineralogical x-ray attenuation range; this
115 enables the extraction of pyrite from the surrounding matrix through digital thresholding
116 (Spencer *et al.*, 2017). Clipping planes were used to crop the volume to smaller areas of interest.
117 Drishti has built-in scalebars and bounding boxes that were used to measure the real-world size
118 of features within the 3D model space. The Keyframe Editor was used to produce animated image
119 sequences showing the rendered 3D model. The individual animation was produced into a video
120 using the open-source animation package Blender™ (Garwood and Dunlop 2014).

121

122 Preparation of Ultrathin Foils of Samples

123 Focused Ion Beam (FIB) milling is commonly used for preparing ultrathin samples for
124 STXM and TEM investigations since it allows extracting, *in situ*, ultrathin foils of sample with
125 a very high spatial precision (Schiffbauer and Xiao 2009; Wirth 2009). Here, FIB foils (~20 μ m
126 x 5 μ m x 80 nm) were extracted from the organic parts of the specimens investigated using a
127 Zeiss Auriga FIB system (IPGP, Paris, France). The FIB lift-out extraction procedure maintains
128 textural integrity, even in the case of loosely consolidated materials, and prevents shrinkage and
129 deformation of microscale to nanoscale pores, even in the case of highly sensitive materials
130 (Schiffbauer and Xiao 2009; Wirth 2009). Milling at low Ga-ion currents prevents common
131 artefacts like creation of cracks or amorphous layers, redeposition of the sputtered material and
132 significant changes in the speciation of complex carbon-based polymers (Bernard *et al.* 2009;
133 Bassim *et al.* 2012).

134

135 Scanning Transmission Electron Microscopy (STEM)

136 STEM observations were performed with a JEOL 2100 Field Emission Gun (FEG)
137 microscope (IMPMC - Paris, France) operating at 200 kV. Scanning Transmission Electron
138 Microscopy (STEM) Z-contrast imaging was performed using the high-angle annular dark field
139 (HAADF) mode. High-resolution TEM (HRTEM) images were collected using the bright field
140 mode allowing us to resolve the crystalline planes (of the order of 0.1 nm) of the different phases.
141 Elemental compositions of different phases were determined by energy dispersive X-ray
142 spectrometry (EDXS) performed using the JEOL detector with an ultrathin window allowing
143 detection of light elements.

144

145 **X-Ray Absorption Near Edge Structure Spectroscopy (XANES)**

146 XANES data were collected using a scanning transmission X-ray microscope (Cosmidis
147 and Benzerara 2014; Karunakaran *et al.* 2015), on both the 10ID-1 STXM beamline
148 (Kaznatcheev *et al.* 2007) at the Canadian Light Source (CLS) and on the HERMES STXM
149 beamline (Belkhou *et al.* 2015; Swaraj *et al.* 2017) at the synchrotron SOLEIL for all the
150 specimens investigated. At CLS, a 100 nm thick titanium filter was used to remove the
151 contribution of second order light while at SOLEIL, beamline optical elements were exposed to
152 a continuous flow of pure O₂ to remove carbon contamination. Energy calibration was done
153 before measurements using the well-resolved 3p Rydberg peak of gaseous CO₂ at 294.96 eV.
154 XANES data were extracted from image stacks collected at energy increments of 0.1 eV over the
155 carbon (270–350 eV) absorption range with a dwell time of ≤ 1 ms per pixel to prevent irradiation
156 damage (Wang *et al.* 2009). Alignment of images of stacks and extraction of XANES spectra
157 were done using the latest version aXis2000 software. The C-XANES spectra shown in the
158 present contribution correspond to homogeneous carbon-rich areas of several hundreds of square
159 nanometres and were normalized to the carbon quantity by integrating the spectra (after
160 subtraction of a power law background) from the pre-edge region up to the mean ionization
161 energy (e.g. 282-291.5 eV at the C K edge) following the method proposed and validated by Le
162 Guillou *et al.* (2018).

163

164

165

166 **RESULTS**

167

168 **Anatomical Details**

169 Although fine-scale anatomical details of specimens preserved in 2D cannot be observed,
170 specimens preserved in 3D reveal cellular details of the vascular system (Fig. 3). The tracheids
171 have a radial diameter of ca 30–69 μm (\bar{x} 46 μm), a tangential diameter of ca 20–50 μm (\bar{x} 32
172 μm) and a length exceeding 1.2 mm (Figs 3a,b). Virtually removing the pyrite reveals that the
173 tracheids possess scalariform bordered pits (Figs 3b-i), typical of P-type tracheids (Kenrick and
174 Crane 1997; Strullu-Derrien *et al.* 2013). Similarly to modern lignified tissues, the cell walls
175 comprise secondary wall thickenings (ca 5 μm) between the pits, consisting of an external layer
176 (0.4–1.0 μm thick; \bar{x} 0.6 μm) interpreted as decay resistant and an internal hollow (1.7–5.0 μm
177 diameter; \bar{x} 3.1 μm) presumably corresponding to a less resistant layer (Figs 3d,e) (Kenrick and
178 Edwards 1988). In contrast to modern groups, an additional perforate sheet of secondary wall
179 material overlies the pit apertures (Figs 3f,g), as observed in P-type tracheids (Kenrick and Crane
180 1997; Strullu-Derrien *et al.* 2013). The perforations are distributed in a reticulum (Fig. 3g) and
181 have a highly variable shape ranging from 0.9–3.6 μm (\bar{x} 2.3 μm) in diameter. A similar pattern
182 of pitting was observed on the four facets of the tracheid cell walls (Figs 3h,i; movie S1).

183

184 **Organic Carbon Speciation**

185 The specimens investigated, either preserved in 3D or in 2D, are very homogeneous and
186 similar in terms of carbon speciation (Fig. 4a). Their C-XANES spectra show a broad absorption
187 feature at ~ 284.8 eV indicating the presence of aromatic or olefinic carbons, a peak at 286.3 eV
188 that can be attributed to carbons bonded to oxygen or sulfur, and a peak at ~ 288.4 eV, likely
189 corresponding to the presence of ester or carboxylic groups (Bernard *et al.* 2015; Karunakaran *et*
190 *al.* 2015; Le Guillou *et al.* 2018). An additional gentle absorption feature at 287.3 eV that can be
191 attributed to the presence of phenols or ketones was observed for specimens preserved in 3D.

192

193 **Mineral Inclusions**

194 The specimens investigated, either preserved in 3D or in 2D, exhibit needle-shape,
195 automorphic nanocrystals (~ 50 nm) of titanium oxides (likely rutile or anatase) homogeneously
196 and ubiquitously distributed within the organic carbon (Figs 4b,c,e). Of note, all the observed
197 organic material contains these Ti-nanominerals; they are ubiquitous in these fossils. Specimens
198 preserved in 2D also contain submicrometric Ca-nanominerals (likely calcite) and Fe-
199 nanominerals (likely pyrite and iron oxides/hydroxides) (Figs 4d,f).

200

201

202 **DISCUSSION**

203

204 The anatomical details of the specimens preserved in 3D likely results from the early
205 pyritization of the tissues, which was very much less prevalent in the specimens preserved in 2D.
206 Pyritization of plant tissues may remain incomplete, the distribution of pyrite in fossil plants
207 being generally interpreted in terms of differential biodegradability of the original organic
208 constituents of the plant (Kenrick and Edwards 1988; Edwards *et al.* 1997; Grimes *et al.* 2001;
209 Bernard *et al.* 2010; Cai *et al.* 2012; Schiffbauer *et al.* 2014). The pattern of secondary cell wall
210 thickenings interspersed by very regular perforations revealed by tomography (Fig. 3) strongly
211 suggests that *A. chateaupannense* was originally constituted of two different organic phases, one
212 being more easily biodegradable than the other. It may therefore be assumed that, in addition to
213 biodegradable cellulose, the tracheid cell walls of *A. chateaupannense* originally contained
214 decay-resistant lignin-like compounds.

215 Historically, cell-wall biopolymers such as lignin have been seen as intrinsically more
216 resistant to biodegradation and thermal maturation than polysaccharides and proteins for instance
217 (Tegelaar *et al.* 1989; Eglinton and Logan 1991; van Bergen *et al.* 1995; Briggs 1999; Derenne
218 and Largeau 2001). This view has since been challenged by studies that demonstrated that the
219 persistence of organic compounds is not only controlled by their molecular structure, but rather
220 mainly by biological and environmental factors (Schmidt *et al.* 2011; Lehmann and Kleber 2015;
221 Keiluweit *et al.* 2016). Rot fungi in the Agaricomycetes have the ability to decompose lignin
222 (Floudas *et al.* 2012; Krah *et al.* 2018), so do some modern bacteria (Ma *et al.* 2016; Wilhelm *et*
223 *al.* 2018). Although thermodynamic constraints prevent the biodegradation of lignin under
224 anaerobic conditions (Keiluweit *et al.* 2016), fungal or bacterial lineages capable of lignin
225 degradation likely already existed during the early Devonian (Nelsen *et al.*, 2016). It has also
226 been recognized that the primary structure of the lignin molecule may thermally degrade even at
227 relatively low temperature (Cody and Sághi-Szabó 1999), making lignin residues difficult to
228 identify in the fossil record.

229 All the specimens investigated are homogeneous in terms of carbon speciation and exhibit
230 a similar molecular structure (Fig. 4a). These compounds are quite different from modern lignin
231 (Fig. 4a) or thermally degraded lignin (Edwards *et al.* 1997; Boyce *et al.* 2002, 2003, 2010;
232 Bernard *et al.* 2010; Galvez *et al.* 2012b; Karunakaran *et al.* 2015), and rather typical of
233 macromolecular aromatic compounds such as pyrobitumen (Bernard *et al.* 2012b, a; Bernard and
234 Horsfield 2014) (Fig. 4a). In other words, whatever the preservation mode (3D vs 2D), the
235 original lignin or lignin-like compounds, if present, did not withstand fossilization processes and
236 were replaced by pyrobitumen.

237 The presence of Ti-nanominerals within the organic compounds of all the specimens
238 investigated (Figs. 4b,c,e) may help to constrain the geological processes that affected the
239 original organic molecules of the fossils. There is no doubt that these Ti-nanominerals were not
240 originally present within the *A. chateaupannense* vascular tissues. In fact, besides Ti
241 accumulation in plants that grow on Ti-rich soils (Ramakrishna *et al.* 1989), no Ti-rich phytolith
242 has ever been reported. Relatively common in hydrothermal veins (Rumble *et al.* 1986; Craw
243 2002), association of Ti with organic compounds has previously been reported for plant fossils
244 (Pe-Piper *et al.* 2011; Galvez *et al.* 2012a) and other ancient organic fossils (Lekele Baghekema
245 *et al.* 2017; Wacey *et al.* 2018), and interpreted as diagenetic features. Here, the euhedral needle
246 shape, narrow size distribution, and lack of alteration features of the Ti-nanominerals observed
247 within the organic compounds of all the specimens support their authigenic growth rather than a
248 detrital origin.

249 Titanium may be mobile in relatively shallow diagenetic settings in the presence of
250 complexing organic acids (Hausrath *et al.* 2009; Galvez *et al.* 2012a). Here, the biodegradation
251 of organic tissues trapped in the sediment likely produced organic acids that promoted Ti
252 solubility and transport in the form of organic complexes (Huggins and Huffman 2004). These
253 complexes have eventually been trapped into the tracheid scaffolding of the specimens
254 investigated and, during subsequent burial, experienced pyrolytic dissociation into pyrobitumen-
255 like compounds and Ti-nanominerals.

256 The homogeneous chemical composition of the organic component of the specimens
257 investigated, whatever their preservation mode, together with the homogeneous and ubiquitous
258 distribution of the Ti-nanominerals down to the submicrometric scale attest that the original
259 biopolymers of *A. chateaupannense* did not withstand the fossilization processes. In fact, if a
260 significant proportion of the original biopolymers had been preserved in the fossils, some
261 variability might have been expected (Boyce *et al.* 2002, 2010), both in terms of organic
262 speciation and distribution of Ti-nanominerals, which is not the case.

263 Our findings illustrate the difficulty of retrieving information on the primary chemistry
264 of organisms preserved as fossils. Biopolymers inevitably experience degradation depending on
265 the physical and chemical conditions that prevail during fossilization and burial. Here, despite
266 the loss of the original biopolymers and their replacement by pyrobitumen compounds containing
267 Ti-nanominerals, the fine scale cellular structure of the vascular tissues of *A. chateaupannense*
268 is exceptionally preserved. This study shows that pyrite formed during early diagenesis preserved
269 the 3D anatomical framework of the plant tracheids. It also demonstrates that the replacement of
270 biopolymers by pyrobitumen constitutes a diagenetic pathway relevant for the morphological

271 preservation of fossil plant tissues with varied structural outcomes, encompassing fossils in
272 which cellular level details are preserved and those in which they are not.

273

274

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276

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290

291 **AUTHOR CONTRIBUTIONS**

292 **C.S-D, S.B.** and **L.R.** designed and funded the present research. **C.S-D.** collected the specimens
293 investigated. **A.R.T.S.** performed the PPC-SR μ CT reconstructions and interpret them with **C.S-**
294 **D. S.B.** performed the STXM and TEM experiments. **C.S-D., S.B., L.R., P.K.** and **D.D.**
295 interpreted the data and discussed their implications. **C.S-D., S.B** and **D.D.** wrote the present
296 article with critical inputs from the other co-authors.

297

298 [The specimens belong to CS-D's collection and are provisionally housed at the Museum Angers.](#)

299 [The numbers are:](#) CSD-07M-01 (Fig. 1a), CSD-06C-02 (Fig. 1b), CSD-07F-01 (Fig. 2), CSD-
300 017-01 (FIB lamella, Fig. 1e-g), CSD-017-02 (FIB lamella, Fig. 3).

301

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303

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572

573 **EXPLANATIONS OF FIGURES**

574

575 **FIG. 1.** Geological and mineralogical context. **a.** Picture of a specimen of *A. chateaupannense*
576 preserved in 2D as carbonaceous thin films. **b.** SEM image of a transverse section of an axis of
577 a specimen of *A. chateaupannense* preserved in 3D showing the radially aligned tracheids. **c.**
578 Lithostratigraphic column of the Chateaupanne unit (after Strullu-Derrien et al., 2010, 2014). **d.**
579 Location of the plant-rich level containing the specimens investigated (after Strullu-Derrien et
580 al., 2010, 2014). Scale bar is 4 km.

581

582 **FIG. 2.** Composition of the mineral matrix. **a.** STEM image in HAADF mode (z-contrast)
583 showing the heterogeneous nature of the mineral matrix. **b.** STEM image of another area of
584 the mineral matrix and corresponding EDXS maps showing the spatial distribution of silicon,
585 aluminium, iron, potassium, phosphorus and titanium. **c.** EDX spectra of Ti-oxides, Fe-silicates,
586 K-silicates, Al-(Ce-)phosphates and Si-minerals (quartz). Scale bars are 1 μm (a,b).

587

588 **FIG. 3.** Microstructure of the specimens preserved in 3D. **a.** Part of a reconstructed 3D bloc of
589 *A. chateaupannense* preserved in 3D. **b.** Organic structure of the P-type tracheid cells. **c.** Detail
590 of b. **d.** Area showing the scalariform bordered pits of the tracheids. **e.** Detail of d. **f.** Area
591 showing the perforate sheet of secondary wall material overlying the pit apertures. **g.** Detail of f.
592 **h-i.** Inside views of a tracheid. Scale bars: a–d = 100 μm , e–g = 50 μm , h,i= 25 μm .

593

594 **FIG. 4.** Geochemical nature of the investigated specimens. **a.** C-XANES spectra of the organic
595 carbon of a specimen preserved in 3D (red) and of a specimen preserved in 2D (blue). C-XANES
596 spectra of pyrobitumen (Bernard and Horsfield 2014) and lignin (Bernard *et al.* 2010) are shown
597 for comparison. **f.** High resolution STEM image of the organic carbon (dark) of a specimen
598 preserved in 3D showing the automorphic nature of the Ti-minerals (bright). **b.** STEM image of

599 the organic carbon of a specimen preserved in 3D. Organic carbon appears dark while
600 automorphic Ti-nanomaterials appear bright. **c.** STEM image of the organic carbon of a specimen
601 preserved in 2D. Organic carbon appears dark while Ti-, Fe- and Ca-nanomaterials appear bright.
602 **d.** EDXS compositional map of the area located by a red square in c, showing the spatial
603 distribution of organic carbon (carbon appears in black), oxyhydroxide minerals (iron appears in
604 red), calcite minerals (calcium appears in green) and Ti-nanomaterials (titanium appears in blue).
605 **e.** STEM image of the organic carbon of a specimen preserved in 3D. Organic carbon appears
606 dark while Ti-nanomaterials appear bright. **f.** EDX spectra of the organic compounds (similar for
607 the specimens preserved in 2D and in 3D), Ti-nanomaterials (similar for the specimens preserved
608 in 2D and in 3D), Ca-nanomaterials (only observed in the specimens preserved in 2D) and Fe-
609 nanomaterials (only observed in the specimens preserved in 2D). Scale bars are 200 nm (b) and
610 500 nm (c,d,e).

611

612

613 **SUPPLEMENTARY MATERIAL**

614 **MOVIE S1:** 3D view of a tracheid.

615

616 **DATA ARCHIVING STATEMENT**

617 Data for this study are available in the Zenodo repository: [http://dx.doi.org/](http://dx.doi.org/10.5281/zenodo.1290504)
618 10.5281/zenodo.1290504

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