

1 **FOSSILIZATION OF THE EOCENE “MONKEYHAIR” LATICIFER TREE FROM**  
2 **GEISELTAL, GERMANY: A DEEPER UNDERSTANDING ENABLED BY MICRO CT**  
3 **AND PYROLYSIS GC/MS ANALYSIS**

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26 *RRH: FOSSIL LATICIFERS*

27 *LLH: V.E. MCCOY ET AL.*

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29 ABSTRACT: Although the fibrous plant material called *Affenhaar* from the middle Eocene  
30 lignites of Geiseltal in Germany has been repeatedly studied for over 172 years, modern imaging  
31 and chemical analyses have enabled a deeper understanding of its chemical composition and  
32 preservation within the parent plant. Known in English as “monkeyhair,” the fibrous material  
33 represents a very rare case of fossil laticifers, the latex-bearing ducts of plants. Here we use high-  
34 resolution X-ray microcomputed tomography (micro CT) for the first time to elucidate the  
35 anatomy of tissues and their differential degradation within the monkeyhair tree. Even in large,  
36 fairly intact stem axes, the center cylinder of secondary xylem inside the trunks or branches is  
37 completely lacking, presumably due to diagenetic degradation. Nevertheless, there is a  
38 moderately well-preserved outer layer of bark and mats of excellently preserved laticifers in the  
39 extraxylary zone beneath the bark. Previous chemical analyses revealed that the latex in these  
40 laticifers was dominated by natural rubber (*cis*-1,4-polyisoprene), but also included various  
41 triterpenoids. These fossil laticifers also contained large amounts of organic sulfur, suggesting  
42 the rubber may have been naturally vulcanized. Pyrolysis GC/MS is also applied to the fossil  
43 laticifers for the first time to identify the organic sulfur constituents of this ancient latex. The  
44 chemical analysis yields 12 major sulfur compounds, mostly thiophenes, consistent with  
45 vulcanized rubber. The vulcanization of these laticifers most likely occurred during early  
46 diagenesis, before the degradation of the wood, at low temperatures, and may have been  
47 facilitated with other compounds that serve as accelerators, activators, and fillers.

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49 Key words: *Affenhaar*, Apocynaceae, *Coumoxylon*, fossil laticifers, latex canals, natural  
50 vulcanization

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## INTRODUCTION

52

53 One of the most unusual fossils in the paleobotanical world are the fossil laticifers from  
54 the middle Eocene brown coals in the Geiseltal in eastern Germany. Nicknamed *Affenhaar* by  
55 German miners for their superficial appearance to simian hair, these coarse yet flexible, brown-  
56 colored fibers (Fig. 1, Fig. 2) have been known as paleobotanical remains for over 172 years  
57 (Hartig 1848). The Geiseltal “monkeyhair,” as it is known in English, has since been repeatedly  
58 studied for nearly a century (Gothan 1924, 1927; Kindscher 1924; Jurasky 1928, 1930;  
59 Kirchheimer 1935; Krumbiegel et al. 1983; Mahlberg and Störr 1989; Wilde and Riegel 2010.  
60 However, important details regarding the fossilization of the monkeyhair tree, its anatomy, and  
61 latex-filled laticifers have still remained elusive.

62 The monkeyhair laticifers occur in the middle Eocene deposits in the Geiseltal (Geisel  
63 Valley), in eastern Germany near the city of Halle (Saale), which are characterized by thick  
64 lignite deposits of over 100 m. The lignite was mined in open pits from the 17th century onwards  
65 through 1992 when the brown coal deposits were exhausted (Eissmann 2002; Wilde and Riegel  
66 2010). Mining operations have produced exceptionally well-preserved fossils of plants,  
67 invertebrates, and vertebrates (Krumbiegel 1959; Krumbiegel et al. 1983; Eissmann 2002).  
68 Based on the fossil fauna and flora of this ecosystem and other nearby fossil sites, the lignites are  
69 thought to represent a warm, humid, tropical to subtropical, peat-forming environment (Riegel et  
70 al. 1999; Eissmann 2002; Wilde and Riegel 2010).

71 The Geiseltal monkeyhair are branched, non-articulated laticifers (Fig. 2D), which are  
72 preserved in large fascicles that can be found preserved with some bark, but virtually no wood  
73 (Fig. 1, Fig. 2) (Mahlberg et al. 1984; Mahlberg and Störr 1989). Branched, non-articulated  
74 laticifers are known in many families of living plants (Mahlberg et al. 1984; Hagel et al. 2008;

75 Pickard 2008; Konno 2011); however, study of the few associated wood fragments and gross  
76 morphology of the bark (Gottwald 1976) suggest the botanical affinity of the Geiseltal laticifers  
77 to the family Apocynaceae (dogbanes and milkweeds). Anatomy of the fossil wood is similar to  
78 the wood of the extant genus *Couma* (Gottwald 1976), a tree native to northern South and  
79 Central America today (Williams 1962). The Eocene Geiseltal wood, bark, and laticifers were  
80 thus recognized as pertaining to a new genus, *Coumoxylon* Gottwald 1976. Palynology does not  
81 reveal any strong associations between the monkeyhair tree and apocynaceous pollen.  
82 Nevertheless, the Eocene record of Geiseltal may be heavily weighted towards wind dispersed  
83 pollen (which would exclude the Apocynaceae), even if anemophilous plants were rare in the  
84 ecosystem (Wilde and Riegel 2010). Other Eocene brown coals in the general vicinity of the  
85 Geiseltal also preserve isolated laticifers which, based on their chemical and morphological  
86 similarity to the Geiseltal laticifers, were most likely produced by the same trees living in one  
87 continuous environment (Mahlberg and Störr 1989; Wilde and Riegel 2010).

88 In our investigation, high-resolution X-ray microcomputed tomography (micro CT),  
89 coupled with macroscopic study, is applied to well-preserved specimens from Geiseltal that  
90 include both laticifers and associated tissues to better interpret the anatomy of these more  
91 complete specimens and to understand differential tissue degradation within the monkeyhair tree.  
92 Furthermore, pyrolysis GC/MS is used to investigate the macromolecular structure of these fossil  
93 laticifers, with a specific focus on the organic sulfur compounds, for two purposes. The first  
94 purpose is to complement previous chemical analyses, which did not yield information about  
95 organic sulfur compounds (Mahlberg et al. 1984; Collins et al. 1995; Otto et al. 2001; Simoneit  
96 et al. 2003) to develop a more complete understanding of the chemical composition of isolated

97 fossil laticifers. The second purpose is to help understand the details of the process of natural  
98 vulcanization that contributed to the unique preservation of these laticifers.

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## 100 Laticifers and Latex

101 Laticifers are highly specialized plant cells that produce and store secondary metabolites  
102 (the components of latex), which undergo extreme elongation during growth, allowing  
103 development into tubes or ducts to transport the latex throughout the plant (Mahlberg 1993;  
104 Hagel et al. 2008; Pickard 2008). They can be subdivided into four morphological groups  
105 (Mahlberg 1993; Hagel et al. 2008): non-articulated unbranched, non-articulated branched,  
106 articulated non-anastomosing, and articulated anastomosing. As mentioned above, the laticifers  
107 from the Eocene of Geiseltal are branched, non-articulated laticifers. Not all laticifers are  
108 elongate canals, however; some plant groups have laticiferous cells or cavities (Hagel et al.  
109 2008). Nonetheless, whether elongate canals, cells, or cavities, by definition, laticifers are filled  
110 with latex.

111 Latex is a plant exudate used primarily as a physical and chemical defense against insect  
112 herbivores (Dussourd and Denno 1991; Dussourd 2003, 2017). As a sticky viscous liquid, latex  
113 can gum up and immobilize insect mouthparts, and many of the chemical components are highly  
114 bioactive (Helmus and Dussourd 2005; Hagel et al. 2008; Agrawal and Konno 2009; Konno  
115 2011; Mithöfer and Boland 2012). Latex consists of a complex mixture of chemicals that varies  
116 from species to species (Hagel et al. 2008; Konno 2011; Mithöfer and Boland 2012).  
117 Economically important laticiferous plants include the modern rubber tree, *Hevea brasiliensis*, a  
118 member of the Euphorbiaceae (spurge family), which has latex dominated by natural rubber, *cis*-  
119 1,4-polyisoprene (Hagel et al. 2008). In general, eight of 22 laticiferous plant families produce

120 natural rubber, although in most plants, the natural rubber concentrations or molecular weight is  
121 too low to make economic production viable (Hagel et al. 2008; Agrawal and Konno 2009;  
122 Konno 2011; Venkatachalam et al. 2013). More generally, latex can contain other secondary  
123 metabolites, including terpenoids, alkaloids, and cardenolides, which provide a chemical defense  
124 against insects (Hagel et al. 2008; Konno 2011).

125 <sup>13</sup>C-NMR analysis of the Eocene Geiseltal fossil latex indicates that it too is dominated by  
126 rubber (Mahlberg et al. 1984), while lipid extraction and GC/MS analysis has revealed the  
127 presence of hydrocarbons (Mahlberg et al. 1984), particularly triterpenoids (Collins et al. 1995;  
128 Otto et al. 2001; Simoneit et al. 2003). These compounds most likely represent the most stable  
129 compounds in the latex or stable compounds produced by bacteria as they decay the latex  
130 (Collins et al. 1995); other, more labile compounds may have been lost during diagenesis.

131 Ducts or canals containing exudates, still in place within labile plant tissues such as leaves,  
132 sometimes are found in fossil sites with exceptional preservation of soft tissues; these fossil ducts  
133 include laticifers, an interpretation based on comparisons to extant relatives or chemical analyses  
134 (Call and Dilcher 1997; Wilde et al. 2005). Multiple fossil species of the genus *Eucommia*,  
135 which also includes living laticiferous species (Tangpakdee et al. 1997), from North American  
136 Lagerstätten preserve latex and laticifers in their leaves and seeds (Call and Dilcher 1997), for  
137 example. Silicified wood also is known to contain duct systems that are apparent in thin section,  
138 some of which appear to be laticifers based upon their cellular structure (e.g., Boonchai et al.  
139 2015; Baas et al. 2017; Moya et al. 2018). However, these laticifers in silicified wood appear to  
140 be empty, suggesting that in these cases, the latex did not fossilize. The Geiseltal (and similar  
141 Western European) laticifers are unusual in that the laticifers are abundantly preserved and most  
142 commonly occur in the absence of associated well-preserved plant tissues such as wood and bark

143 (Mahlberg et al. 1984; Mahlberg and Störr 1989; Wilde and Riegel 2010). Collins et al. (1995)  
144 found that the Geiseltal fossil latex is rich in sulfur, indicating that the rubber was naturally  
145 vulcanized (Gothan 1927; Jurasky 1928; Mahlberg et al. 1984; Simoneit et al. 2003), which  
146 explains its exceptional resistance to degradation, particularly compared to the fossil wood and  
147 bark of the monkeyhair tree.

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## MATERIAL AND METHODS

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### Materials

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Eight specimens of fossil laticifers (Table 1) from the middle Eocene brown coals of the Geiseltal region from the Geiseltal Collections at the Martin-Luther-University in Halle-Wittenberg, Germany, were studied. Two of these specimens, GMH LIX20 and GMH Y74, are exceptionally well-preserved; they retain the morphological appearance of laterally compressed stem axes (such as a flattened trunk or large branch) from a good-sized, laticiferous tree (Fig. 1). These two specimens were analyzed non-destructively using micro CT. The other five specimens GMH PB39, GMH PB99, GMH PB37, GMH PB36, and GMH PB101 exhibit the style of preservation more typically found at Geiseltal in which the laticifers are preserved as a fibrous mat with little to no other tissues (similar in appearance to Fig. 2C). Small (~1 mg) samples were taken from five of these specimens—GMH LIX20, GMH PB39, GMH PB99, GMH PB37, GMH PB36—and also from the exceptionally well-preserved specimen GMH LIX20 for pyrolysis GC/MS. Laticifers from GMH PB101 were examined and photographed under a light microscope.

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## Micro CT

167 To study the internal layers within the monkeyhair tree in a nondestructive manner, micro  
168 CT was carried out on the two larger specimens of monkeyhair. Each specimen was wrapped in  
169 tissue paper, mounted between two thick slabs of styrofoam, and secured with packing tape to  
170 orient them for tomography in the optimal upright position. Each specimen was then scanned  
171 with the 240 kV/320 W microfocus tube of a phoenix v|tome|x s 240D CT scanner (General  
172 Electric Measurement & Control Solutions, Wunstorf, Germany). A new feature, multi-scan, in  
173 which two halves of a tall specimen are scanned in separate sessions, was used to automatically  
174 merge projections. Scan parameters for each specimen are listed in Table 2. Image stacks of each  
175 specimen were created in one transverse and two longitudinal planes of section using VG Studio  
176 Max (version 3.2). Single sections, or orthoslices, were selected from the image stacks for image  
177 analysis. Micro CT imagestacks have been archived in morphosource ([morphosource.org](http://morphosource.org)),  
178 project number P1069.

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## Pyrolysis GC/MS

181 Each sample for pyrolysis GC/MS (Table 1) was pyrolyzed in the presence of  
182 tetramethylammonium hydroxide (TMAH) at 610°C for 15 seconds using a CDS pyroprobe  
183 1000. The pyroprobe was interfaced to a Perkin Elmer Clarus 500 gas chromatograph with a 30  
184 m Rxi-5Sil MS column (0.25 mm ID, 0.25 µm film thickness), coupled to a Clarus 500 mass  
185 spectrometer. The injector temperature was 280 °C and the transfer line temperature was 310 °C.  
186 The GC program had an initial temperature of 40 °C for 5 minutes that ramped up to 310 °C at a  
187 rate of 4 °C/minute, where it was held for 10 minutes. The resulting chromatographs were

188 imported into AMDIS for spectral deconvolution, and major peaks were identified and  
189 confirmed using NIST-MS and retention indices.

## 190 RESULTS

### 191 Anatomy of the Parent Plant and Its Laticifers

192 Both of the two larger, well-preserved fossil specimens are wide, flat pieces of fossil stem  
193 axes. GMH LIX20 measures 44 cm long at its longest point, 11.5 cm wide at its widest point,  
194 and 1.5 cm thick at its thickest point. GMH Y74 measures 32.5 cm long at its longest point, 20.5  
195 cm wide at its widest point, and 2 cm thick at its thickest point; a flap of bark and laticifers  
196 measuring roughly 8.5 x 12 cm has folded in on itself along the open edge of the specimen.  
197 Inside each specimen, a mat of laticifers forms an internal scaffolding on which the crumbling  
198 pieces of bark are attached. Hence, the extent of the laticifer mats commonly extends beyond the  
199 extent of the bark.

200 The width of each specimen roughly represents the minimum diameter of the original stem  
201 axis, as there would have been little deformation in the horizontal plane in a cylinder of solid,  
202 rigid tissue (cf. Rex and Chaloner 1983). The original width of the two stem axes would have  
203 thus measured at least 11.5 cm and 20.5 cm, respectively. Given these diameters, in conjunction  
204 with the compressed thickness of the respective specimens, the compaction ratio is 7.7:1 in GMH  
205 LIX20 and 10.25:1 in GMH Y74.

206 The two well-preserved specimens each has three layers (Fig. 2, Fig. 3). The outermost  
207 layer is composed of a dense, crumbly, dark brown to black material with a corrugated texture  
208 and mat surface, which is denser than all but the smaller particles inside the specimens (Fig. 2A,

209 Fig. 3). This is very similar in gross morphology to tree bark and has been interpreted as such in  
210 other specimens by previous researchers (Gottwald 1976; Wilde and Riegel 2010). The thickness  
211 of the bark varies throughout our specimens; in some places, it is missing, but at its thickest, it  
212 makes up close to 60% of the thickness of the tissues remaining in flattened stem axis. This layer  
213 wraps around the specimen so that it is present on three sides, enclosing the inner layers. In both  
214 specimens, the fourth side lacks bark, producing a long, natural, slit-like opening.

215         Immediately within the bark is a layer of less dense, fibrous, lighter brown material which  
216 is composed primarily of laticifers. Sometimes the laticifers are embedded in a dark, pasty  
217 organic material (Fig. 2B, 2C, Fig. 3), which has been previously described as “gel” and a  
218 product of biodegradation (Mahlberg and Haubold 1989). This dark, organic material can appear  
219 fairly solid, with the laticifers densely packed into the organic matter. There is then a smooth  
220 transition without any sharp separation from this solid layer to a compact mat of laticifers devoid  
221 of any dark, organic material. This innermost mat of laticifers varies in thickness, comprising  
222 from ~ 25%–33% of the total thickness of the specimens. The mats of laticifers that are  
223 composed of free laticifers or laticifers embedded in organic matter are fairly robust, especially  
224 when compared to the more fragile nature of the bark, and serve to hold together the length of  
225 the monkeyhair tree specimens. The mats may contain thousands of laticifers (see also Mahlberg  
226 et al. 1984), and each laticifer strand in the mat runs more or less parallel to the long axis of the  
227 stem axis.

228         In the center of both specimens is a hollow longitudinal cavity comprising ~10–18% of the  
229 entire thickness of the specimens. This cavity is mostly empty space, but does contain some  
230 dense particles that appear as the lightest colors in the CT slices (Fig. 3). These include small,  
231 angular pieces of carbonaceous mudstone of variable size, which are especially found in GMH

232 Y74. There are also minute chips of vitrinitic coal that occur in the hollow center, but also  
233 between the layers of internal tissue, especially in GMH LIX20.

#### 234 Pyrolysis GC/MS

235 The chromatograms of the five samples are very similar, with minor differences in in peak  
236 intensity in the peaks of the major sulfur compounds, and more variability in the other peaks  
237 (Fig. 4). Twelve major organic sulfur compounds, mostly thiophenes, could be identified (Fig. 4,  
238 Fig. 5, Table 3): dimethyl disulfide; 2,4-dimethylthiophene; 2,3-dimethylthiophene; 2-(1-  
239 methylethyl)-thiophene; 2,3,4-trimethylthiophene; 2,5-diethylthiophene; 3-[(E)-2-butenyl]-  
240 thiophene; 2-ethyl-5-(2-methylpropyl)-thiophene; 3-isopropylthiophenol; 2,6-  
241 dimethylbenzo[b]thiophene; 2-ethyl-5-hexylthiophene; and 2-dodecyl-5-ethylthiophene.

242 Sixteen additional organic compounds, including minor sulfur compounds (the peak  
243 barely visible above the background) and non-sulfur compounds could be identified (Fig. 5,  
244 Table 3): 1,3,5-cycloheptatriene; 2,7-dimethyl-1,7-octadiene; 1-ethenyl-4-methylbenzene; 1-  
245 methyl-3-propylbenzene; 3,4-diethylthiophene; 4-(1,1-dimethylethyl)-benzenethiol; 2,4-  
246 diethylbenzo[b]thiophene; methyl tetradecanoate; methyl ester hexadecanoic acid; methyl  
247 stearate; methyl ester tetracosanoic acid; squalene; methyl ester hexacosanoic acid; dinor-oleana-  
248 1,3,5(10)-triene; 23,25-bisnorlupan-1,3,5(10),12-tetraene; 22R-17a(H),21a(H)-homohopane.

#### 249 DISCUSSION

##### 250 Anatomy and Fossilization of Tissues in the Monkeyhair Tree

251 Previous morphological investigations have identified three basic patterns of preservation  
252 in the Geiseltal monkeyhair fossil remains.

253 (1) Large stem axes (i.e., trunks or branches) covered with an outer bark layer and  
254 containing mats of laticifers which are sometimes embedded in a “gel” resulting from degraded  
255 stem tissues (Mahlberg and Haubold 1989). Extensive amounts of wood are not present in the  
256 axes (Gottwald 1976; Mahlberg et al. 1984), although, rarely, cellular structure in small wood  
257 fragments can be observed (Gottwald 1976; Mahlberg and Haubold 1989).

258 (2) Isolated laticifers with an occasional piece of bark clinging to them, and some very  
259 small amounts of degraded organic material (Mahlberg et al. 1984; Mahlberg and Haubold 1989;  
260 Wilde and Riegel 2010).

261 (3) Isolated laticifers with little to no other tissues (e.g., Mahlberg et al. 1984; Mahlberg  
262 and Störr 1989). This is most common occurrence of the Eocene laticifers.

263 The two well-preserved specimens in our study pertain to the first category above, as they  
264 resemble flattened stem axes. Their diameters of 11.5 cm and 20.5 cm, respectively, would  
265 correlate with a large-sized branch or moderately-sized tree trunk. In other studies, other fossil  
266 monkeyhair axes have been reported as even greater in girth, at 25 cm or greater in diameter  
267 (Mahlberg and Haubold 1989). In comparison, living trees in the Apocynaceae such as *Couma*  
268 *macrocarpa*, for example, can reach a trunk diameter of 40 to 60 cm, which correlates to a height  
269 of 18 to 24 m (World Timbers Inc., 2008–2015). While the two largest fossil specimens in our  
270 study are less than a half meter long each, other mats of the monkeyhair laticifers have been  
271 reported as often being several meters long (Mahlberg and Haubold 1989).

272 On our two well-preserved specimens, bark is present on the outer surface of both sides of  
273 the compressed stem axes. Immediately within the bark are laticifers embedded in the degraded,  
274 organic-rich “gel,” followed by mats of only laticifers without any degraded organic material.

275 The center region of the monkeyhair specimens is hollow, because the tissues in the center of the  
276 stem axes have not been preserved; these tissues were presumably made up of wood originally.  
277 The small, loose pieces of carbonaceous mudstone inside the hollow region likely washed into  
278 the axes after the wood in the center had decayed. The tiny chips of vitrinite found between the  
279 laticifer mats and occasionally in the hollow center may have derived from the original wood in  
280 the stem axes.

281 The three major stem tissues that originally made up the monkeyhair trunks and  
282 branches—periderm or cork (commonly referred to as bark), laticifers, and secondary xylem  
283 (wood)—were differentially prone to degradation. As mentioned before, the laticifers preserved  
284 very well and occur in all specimens. The bark underwent more degradation than the laticifers,  
285 though far less than the wood. The relatively poorer fossilization of the bark compared to the  
286 laticifers is especially evident when observing the relationship of the bark layer to the laticifer  
287 mats in the two larger specimens studied. The laticifer mats form a framework or scaffolding on  
288 which the crumbly pieces of bark are attached, and the extent of the laticifer mats is often greater  
289 than the extent of the bark layer in the two specimens. Moreover, mats of laticifers or isolated  
290 laticifers without bark are commonly found preserved in the Geiseltal lignites. In these cases, it  
291 is highly likely that the outer bark, as well as inner wood, of the monkeyhair stem axes had been  
292 degraded or abraded away, while the laticifers remained intact.

293 The dark pasty “gel” in which some laticifer stands are found embedded is likely  
294 structureless organic matter formed from the degradation of extraxylary tissues found between  
295 the large cylinder of wood in central of the stem axes and the outermost surface layer of bark.  
296 This likely included the tissues that held the laticifers in the living monkeyhair tree, such as the  
297 phloem, cortex, the inner layers of the periderm, and perhaps even some wood. With exception

298 of wood, the cells in these tissues do not have secondary walls which aid in strengthening the  
299 tissue; however, the proximity of these tissues to the robust laticifer latex may have lent them  
300 some resistance to complete degradation.

301 The laticifers themselves are quite sturdy, surviving in intact mats although the hard tissue  
302 of wood adjacent to them inside the monkeyhair trunks and branches have completely rotted  
303 away. As mentioned earlier, they are so tough that they can exist without an outer protective  
304 layer of bark and hence, are found as isolated strands and mats in Geiseltal. The reason behind  
305 their hardy preservation has long been attributed to the vulcanization (Gothan 1927; Jurasky  
306 1928; Mahlberg et al. 1984; Simoneit et al. 2003), which is further discussed and confirmed in  
307 the following section.

308 Another unusual observation regarding fossilization is that the two stem axes in our study  
309 are highly compressed. The compaction ratio in lignite ranges from 2:1– 4:1 (Ting 1977; Widera  
310 2015). This is greatly exceeded by the compression ratios of 7.7:1 in GMH LIX-20-1993 and  
311 10.25:1 in GMH Y-74. This large compaction in the vertical size of the stem axes is certainly  
312 due to the extensive degradation and loss of wood in the center portion of the stem. A similarly  
313 extreme compression of the laticifer layer would have been unlikely due to the robustness of  
314 vulcanized rubber, assuming that vulcanization happened early in the diagenetic process; the  
315 zone of laticifers was probably not more extensive than what is found in the fossil stem axes  
316 now.

317 There is hardly any evidence now of what must have been a great volume of wood in the  
318 stem axes. As in most trees, wood makes up a huge proportion of the stem tissues—the older and  
319 broader the woody stem, the larger the percentage of secondary xylem. In a 20-cm diameter

320 stem axis such as GMH LIX20, whether it be a trunk or branch, it would be expected that most  
321 of the stem would be filled with wood. Yet, the compacted state of GMH LIX20 measures only  
322 2 cm in thickness. If only the cross-sectional area is considered, approximately 18 cm, or 90%,  
323 of the wood is missing; the remaining 10% is comprised of bark and laticifers. When  
324 extrapolated to the cylindrical shape of a log, the surface area to volume ratio will continue to  
325 decrease the longer the log is. Thus, the taller the trunk or longer the branch, the greater the  
326 increase in the wood relative to bark and laticifers, and thus, in the case of the monkeyhair trees,  
327 the more wood that had been lost.

328         The reason for the preferential degradation of wood in the monkeyhair tree is puzzling.  
329 Fossil wood occurs overwhelmingly more often than bark, which is rare in the geological record  
330 (Ash and Savidge 2004). Wood is well-known as one of the most decay and degradation-  
331 resistant nonmineralized tissues (Van Bergen et al. 1995) and remains intact in recently dead  
332 trees long after the bark has been peeled off the trunk and branches (Gee, pers. obs.). Moreover,  
333 the wood of a living apocynaceae tree such as *Coumea macrocarpa*, for example, is not  
334 especially light or soft; it has a hardness rating of medium and can thus be used for indoor  
335 furnishings and light construction. However, the wood of *C. macrocarpa* has been reported to  
336 have little resistance to decay (Williams 1962).

337         In general, most modern woods are broken down by wood fungi, and to a lesser extent,  
338 bacteria, as well as by insects in tropical regions and marine borers in seawater (Zabel and  
339 Morrell 1992). However, in the case of the monkeyhair tree, it is most likely that chemical  
340 processes during diagenesis in the Eocene lignites was been the reason behind the degradation of  
341 the normally solid tissue of wood.

342

## 343 Sulfur Compounds in Fossil Latex

344 Pyrolysis GC/MS of naturally vulcanized organic matter commonly yields short chain  
345 alkylated (C<sub>0</sub>-C<sub>6</sub>) thiophenes (Sinninghe Damsté et al. 1998; Van Kaam-Peters et al. 1998; Kok  
346 et al. 2000b; van Dongen et al. 2003a, 2003b, 2006; McNamara et al. 2016). In particular,  
347 thiophenes are common pyrolysis products of purely sulfur-crosslinked rubber (Kaminsky and  
348 Mennerich 2001); many of the compounds we identified have previously been reported (Pakdel  
349 and Roy 1994; Arabiourrutia et al. 2007; Gagol et al. 2015). These pyrolysis GC/MS results are  
350 generally consistent with sulfur vulcanized rubber, but have also been found through pyrolysis  
351 GC/MS of other sulfur-rich organic material (Sinninghe Damsté et al. 1998; Van Kaam-Peters et  
352 al. 1998; Kok et al. 2000b; van Dongen et al. 2003a, 2003b, 2006; McNamara et al. 2016). Based  
353 on these results alone, it is possible that some of the organic sulfur compounds may have  
354 originated from the surrounding sulfur-rich coal (Mahlberg et al. 1984), or from algae or bacteria  
355 that had colonized the laticifers at some point during burial, fossilization and diagenesis (Collins  
356 et al. 1995). However, there are a number of previous results that strongly indicate natural  
357 vulcanization of rubber and hence, that these organic sulfur components are the pyrolysis  
358 products of vulcanized rubber: the stabilization of the fossilized latex to such an extent that it  
359 preserves even when very robust tissues such as wood do not (Mahlberg and Störr 1989; Wilde  
360 and Riegel 2010); the high concentrations of rubber in the fossils (rubber is not found in bacteria  
361 or algae) (Mahlberg et al. 1984); the localization of the organic sulfur in the rubber particles in  
362 the latex (Mahlberg and Störr 1989); and the higher concentrations of sulfur in the laticifers than  
363 in the surrounding remnants of tissue (Mahlberg and Störr 1989).

364 The differences between the pyrolysis products of the Geiseltal laticifers and the pyrolysis  
365 products of commercially vulcanized rubber are likely due to a variety of factors. First,

366 commercially vulcanized rubber is entirely produced from the rubber-rich latex of *Hevea*  
367 *brasiliensis*, a mixture of compounds somewhat different from Apocynaceae latex (Konno 2011;  
368 Venkatachalam et al. 2013). Vulcanization of purified rubber is very consistent, but  
369 vulcanization of latex (containing rubber and other constituents) varies from plant to plant, due  
370 to the effects of the various other components (Ramos-De Valle 1981; Santangelo and Roland  
371 2001; Junkong et al. 2017). Consequently, vulcanized apocynaceae latex may have a  
372 somewhat different end-product than vulcanized (and often purified) *Hevea* rubber. Second,  
373 vulcanization includes many intermediate steps in which sulfur crosslinks of rubber chains to  
374 other compounds occurs within the original mixture, and occasionally these pendent groups are  
375 not removed during the later stages of vulcanization (Parks et al. 1970, 1972; Joseph et al. 2015).  
376 Third, some organic sulfur compounds may be the result of sulfur binding to degraded rubber or  
377 the product of degraded vulcanized rubber, causing many chain modifications and changes to the  
378 sulfur crosslinks during the degradation process (Joseph et al. 2015).

379 During commercial vulcanization, other ingredients are added to the sulfur and rubber  
380 mixture, which, like other constituents of latex, can influence the process and the end-product of  
381 vulcanization. These ingredients are carefully selected to maximize the removal of pendent  
382 groups and minimize degradative changes to the rubber (Parks et al. 1972; Coran 2003; Joseph et  
383 al. 2015). In a natural system, with less efficient vulcanization, there would be additional  
384 chemical variation among organic sulfur compounds.

385 All five samples of monkeyhair analyzed are very similar in the presence and relative  
386 abundance of the 12 major sulfur organic compounds (Fig. 4), which are most likely the  
387 pyrolysis products of naturally vulcanized rubber. The higher variability between the samples in  
388 the minor sulfur compounds and other organic compounds might represent original

389 compositional variability in the latex (and sulfurization of compounds other than rubber), or  
390 variable production of other organic compounds during decay and degradation. The fossilization  
391 process—in this case, natural vulcanization of rubber in the latex—is therefore likely very  
392 similar for all the laticifers in this environment.

393

#### 394 Vulcanization of the Geiseltal Laticifers

395

396 Natural vulcanization, or sulfurization, is an important process for the preservation of  
397 organic carbon in the sedimentary record (Brassell et al. 1986; Kohnen et al. 1990; Wakeham et  
398 al. 1995; Sinninghe Damsté et al. 1998; Van Kaam-Peters et al. 1998; Kok et al. 2000a, 2000b;  
399 Werne et al. 2000; van Dongen et al. 2003a, 2003b, 2006; McNamara et al. 2016). Reduced  
400 inorganic sulfur commonly binds to organic compounds, including lipids (Sinninghe Damsté and  
401 De Leeuw 1990; Wakeham et al. 1995), carbohydrates (Sinninghe Damsté et al. 1998; Kok et al.  
402 2000b; van Dongen et al. 2003a, 2003b, 2006), and other compounds (Valisolalao et al. 1984;  
403 Brassell et al. 1986; Kohnen et al. 1990; Kok et al. 2000a; Werne et al. 2000; McNamara et al.  
404 2016) during early diagenesis. The sulfur linkage helps to stabilize the organic compounds and  
405 prevent degradation. Experiments have found that sulfurization occurs relatively quickly, within  
406 a few thousand years, and is commonly found in algal and bacteria-derived organic matter  
407 (Sinninghe Damsté et al. 1998; Kok et al. 2000b; van Dongen et al. 2003a). Much of the organic  
408 sulfur compounds in the sedimentary rock record also are consistent with an algal or bacterial  
409 source (Valisolalao et al. 1984; Brassell et al. 1986; Sinninghe Damsté et al. 1998; Van Kaam-  
410 Peters et al. 1998; Kok et al. 2000a).

411 Sulfur-vulcanized rubber is natural rubber that is crosslinked with sulfur, which increases  
412 the elasticity, toughness, tear strength, and resistance to degradation of the rubber (Coran 2003;  
413 Heideman et al. 2004; Joseph et al. 2015). Vulcanization is a complex process that involves  
414 many components, including rubber and sulfur as well as a wide variety of additional compounds  
415 (Joseph et al. 2015). At its simplest, vulcanization— also called unaccelerated vulcanization—  
416 involves the reaction of natural rubber and elemental sulfur, typically at elevated temperatures, a  
417 process that takes a few hours at 140–160°C (Joseph et al. 2015). In commercial vulcanization  
418 (accelerated vulcanization), various accelerators, activators, fillers and reinforcing agents also  
419 are included to influence the time and temperature of vulcanization as well as the physical  
420 properties of the resulting vulcanized rubber (Coran 2003; Joseph et al. 2015). The process of  
421 vulcanization involves three basic steps (Joseph et al. 2015): (1) acceleration, in which  
422 interactions among the accelerators, activators and sulfur lead to development of an active  
423 sulfurating agent; (2) crosslinking, in which the active sulfurating agent interacts with the natural  
424 rubber to produce crosslink precursors and polysulfidic crosslinks; and (3) postcrosslinking,  
425 which involves major chain modifications, including shortening of the polysulfidic crosslinks.  
426 Even in commercial vulcanization, where all ingredients are carefully controlled and relatively  
427 pure, the exact chemical process is incompletely understood (Joseph et al. 2015).

428 The vulcanization of the Geiseltal laticifers most likely occurred before degradation of the  
429 wood (Mahlberg et al. 1984). This timing is likely, because without either a solid central cylinder  
430 of wood or the stabilization provided by vulcanization, the laticifers would be unlikely to hold  
431 their shape. Plant cells that line the laticifers are not particularly robust compared to wood (Hagel  
432 et al. 2008; Pickard 2008), and nonvulcanized latex typically is a liquid or a plastic solid.  
433 Moreover, natural rubber also is more susceptible than vulcanized rubber to bacterial decay and

434 physical degradation (Rook 1955; Tsuchii et al. 1985; Bode et al. 2001; Coran 2003; Heideman  
435 et al. 2004; Rose and Steinbüchel 2005; Joseph et al. 2015). Although isolated droplets of latex  
436 have been identified in the Geiseltal lignites, these features are interpreted to have been produced  
437 while the wood was still present and possibly result from wounds made during the life of the  
438 laticiferous tree rather than from laticifers that had lost their support from the wood in the stem  
439 axes (Wilde and Riegel 2010).

440       The early vulcanization of the laticifers and later loss of the wood, along with a diagenetic  
441 history of the Geiseltal lignites that involved the absence of extensive heating (Linke 1977),  
442 suggests three things about the process of fossilization for the Geiseltal laticifers. First,  
443 vulcanization occurred at low temperatures. Second, vulcanization occurred on a shorter time  
444 scale than wood degradation. Third, if vulcanization of the Geiseltal latex involved accelerators,  
445 activators, or fillers, the most likely source would have been organic compounds in the wood or  
446 other tree tissues, although the waters in the peat-forming environment may have also influenced  
447 vulcanization.

448       Commercial vulcanization is typically carried out at temperatures ranging from 150°C–  
449 180°C (Mukhopadyay and De 1979; Joseph et al. 2015). However, elevated temperatures are not  
450 required for vulcanization, if all other process variables are equal. Elevated temperatures simply  
451 decrease the time necessary for extensive crosslinking. Depending on accelerators, activators,  
452 sulfur source, type of rubber, and method for introducing the sulfur to the rubber, sulfur  
453 vulcanization can occur, and even happen rapidly, at room temperature (Fisher 1961; Versloot et  
454 al. 1995; Palaty and Joseph 2000). Most studies of room temperature vulcanization focus on  
455 silicone rubber, which easily can vulcanize at low temperatures (Shit and Shah 2013), but natural  
456 rubber also vulcanizes at room temperatures. With the accelerator piperidinium N-

457 pentamethylenedithiocarbamate (technically, an ultra-accelerator), the activator zinc oxide, and  
458 powdered elemental sulfur milled into natural rubber, complete vulcanization occurs after 5 days  
459 (Ostromyslenski 1915), although the tensile strength of the resulting vulcanized rubber is low  
460 (Fisher 1961). Similar results are found using instead the accelerator dimethyl-ammonium N-  
461 dimethyldithiocarbamate; after 33 to 60 days, during which the rubber had vulcanized but  
462 possessed low tensile strength (Fisher 1961). Without milling, or with different accelerators and  
463 activators, the time to vulcanization is much longer: 8.5 weeks with the accelerator piperidinium  
464 N- pentamethylenedithiocarbamate and the activator zinc oxide, or 17 weeks with the addition of  
465 the accelerator quinone dioxime and the activator mercuric oxide (Fisher 1961). Xanthate  
466 accelerators can vulcanize rubber at room temperature in less than a day, although increasing the  
467 temperature to 60°C improves the physical properties of the end product (Palaty and Joseph  
468 2000). Unaccelerated sulfur vulcanization can also occur at room temperature, and this process is  
469 most strongly influenced by the sulfur source. Fisher (1961), who used powdered sulfur without  
470 an accelerator or activator, found no evidence for the production of sulfur crosslinks in natural  
471 rubber. However, with other sulfur sources, such as sulfur dioxide gas and hydrogen sulfide gas  
472 rather than powdered sulfur, a thin sheet of raw rubber can be vulcanized in 10 minutes at room  
473 temperature, or, in the presence of benzene, at 10°C (Bedford and Sebrell 1921; Fisher 1961).  
474 Even these prolonged periods of time for these experiments at room temperature, vulcanization is  
475 well within the likely time interval for wood decay, and therefore within the time frame for  
476 vulcanization of the Geiseltal laticifers. As mentioned earlier, wood is one of the toughest, most  
477 decay and degradation resistant of nonmineralized tissues (Van Bergen et al. 1995), and under  
478 the right conditions of low oxygen and absence of colonization by fungi, wood can retain  
479 structural integrity for millennia (Fengel 1991; Chairkina 2010).

480 Accelerators are compounds added to a rubber and sulfur mixture to increase the rate or  
481 decrease the temperature of vulcanization (Coran 2003; Heideman et al. 2004; Joseph et al.  
482 2015). Accelerators that contain sulfur also can be the sulfur donor for vulcanization, thus  
483 removing the requirement for a separate source of sulfur (Joseph et al. 2015). Most commonly,  
484 accelerators contain nitrogen and sulfur, often with a N=C–S functionality, such as  
485 benzothiazoles, benzothiazolesulfenamides, thiazoles, thiuram sulfides, and dithiocarbamates  
486 (Coran 2003; Heideman et al. 2004; Joseph et al. 2015). However, other groups of compounds,  
487 such as guanidines, xanthates and morpholines, also can act as accelerators (Joseph et al. 2015).  
488 The vast majority (up to 90%) of sulfur in plants, including in wood, is in the form of two amino  
489 acids, cysteine and methionine, both of which include nitrogen, and are primarily bound into  
490 proteins (Giovanelli et al. 1980; Giovanelli 1987; Leustek and Saito 1999). Latex itself can  
491 contain proteins (Konno 2011), which could include these same sulfur-bearing amino acids.  
492 Neither of these amino acids has the structure or functionality found in most accelerators;  
493 nevertheless, many variable compounds can act as accelerators, and the processes by which  
494 accelerators influence vulcanization are still a matter of debate (Joseph et al. 2015).  
495 Consequently, these compounds cannot be ruled out as accelerators.

496 The direct evidence for plant compounds as vulcanization accelerators is mixed. Altman  
497 (1948), for example, found evidence that the amino acid fraction from *Hevea brasiliensis* rubber,  
498 among other organic components, does accelerate vulcanization. By contrast, Bedford and  
499 Winkelmann (1924) found that amino acids do not accelerate vulcanization whereas other  
500 components do. Sulfur and nitrogen also are incorporated into other plant metabolites, including  
501 intermediates between free cysteine and methionine and between protein cysteine and  
502 methionine (Giovanelli et al. 1980; Giovanelli 1987; Leustek and Saito 1999). Moreover, wood

503 is permeable, particularly as it starts to degrade (e.g. Emaminasab et al. 2015), and other sulfur  
504 compounds from the environment may have infiltrated plant tissues and influenced  
505 vulcanization. Interestingly, Altman (1948) found that degraded rubber vulcanized more quickly  
506 than fresh rubber, as long as the degraded rubber was not sterilized, suggesting that bacterial  
507 activity, or the products of bacterial activity, may play a major role in vulcanization. The  
508 presence of hopane derivatives in the fossil laticifers suggests they were at one point colonized  
509 by bacteria which were most likely degrading with the latex itself or surrounding tissues (Collins  
510 et al. 1995), and this may have influenced vulcanization.

511 Pyrolysis GC/MS typically will provide some information about accelerators. For  
512 commercially vulcanized rubber, which were vulcanized with accelerators incorporating both  
513 sulfur and nitrogen (Harada 2016), pyrolysis GC/MS typically yields thiazoles, which are  
514 heterocyclic compounds containing nitrogen and sulfur (Kaminsky and Mennerich 2001). These  
515 constituents most likely are due to formation of pendent groups. During step 2 of rubber  
516 vulcanization, crosslink precursors are formed, in which the active sulfurating agent—developed  
517 through the interactions of the sulfur donor, the accelerator, and the activator—is connected to  
518 the rubber chain (Parks et al. 1970 1972; Joseph et al. 2015). As vulcanization proceeds, these  
519 precursors react further so that eventually the sulfurating agent is replaced by another rubber  
520 chain, creating a sulfur crosslink between rubber chains (Parks et al. 1970, 1972; Joseph et al.  
521 2015). However, vulcanization is not ideally efficient, and often some crosslink precursors fail to  
522 develop into a crosslink, but remain as a pendent group (Parks et al. 1970, 1972; Joseph et al.  
523 2015).

524 The lack of thiazoles in our pyrolysis GC/MS results may be due to a number of factors,  
525 for example: (1) the nitrogen-containing pendent groups have degraded during the past 50

526 million years, (2) some organic compounds lacking nitrogen may have acted as an accelerator, or  
527 (3) Geiseltal laticifers represent unaccelerated sulfur vulcanization. At room temperature,  
528 unaccelerated, sulfur vulcanization of natural rubber occurs most easily by exposing the rubber  
529 to sulfur dioxide and hydrogen sulfide gas (Fisher 1961). Hydrogen sulfide is a common product  
530 of decay, at least from animal soft tissues, which can be expected in abundance in the  
531 depositional environment of the Geiseltal as evidenced by commonly occurring pyrite ( $\text{FeS}_2$ )  
532 within or adjacent to the fossils, due to anaerobic decay (e.g., Chou 2012). While volcanoes are  
533 the major source of atmospheric sulfur dioxide, it has been measured in some sedimentary  
534 environments, too (e.g., Briggs et al. 1996; Azad et al. 2005; Muyzer and Stams 2008;  
535 Brimblecombe 2013).

536       Activators are compounds that increase the efficiency of vulcanization by influencing  
537 which vulcanization structures form and how they change as the vulcanization reactions proceed  
538 (Coran 2003; Heideman et al. 2004; Joseph et al. 2015). Metal oxides, particularly ZnO, are the  
539 most commonly discussed activators, although fatty acids, most notably stearic acid, and zinc  
540 salts of fatty acids also are useful activators, which often are used in conjunction with ZnO in  
541 commercial vulcanization (Heideman et al. 2005; Joseph et al. 2015). Zinc and other metals are  
542 essential nutrients for plants, and especially in environments with high metal concentrations in  
543 the soil, these elements will accumulate in the plant tissues (Weiss et al. 2005; Álvarez-Ayuso et  
544 al. 2013). Moreover, plants can take up and accumulate metal oxides from the soil (Zhu et al.  
545 2008; Wang et al. 2016), and such compounds could act as activators. Additionally, it has been  
546 suggested that some types of latex contain natural activators. Under identical conditions, latex  
547 from *Hevea brasiliensis* vulcanizes more quickly than that from *Parthenium argentatum*,  
548 suggesting that *Hevea* latex contains an unidentified natural accelerator (Ramos-De Valle 1981).

549 However, the Geiseltal laticifers of the Apocynaceae are from a different family unrelated to  
550 *Hevea* of the Euphorbiaceae or to *Parthenium* of the Asteraceae, so it is unclear if latex from the  
551 Apocynaceae also would contain an activator. The role of activators such as zinc oxide typically  
552 cannot be established by pyrolysis GC/MS.

553         Fillers and reinforcing agents are substances, typically inorganic, that are added to  
554 vulcanized rubber as stabilizers (Mukhopadyay and De 1979; Joseph et al. 2015). These  
555 substances do not bind with the rubber, but rather permeate the rubber as dispersed particles  
556 (Salaeh and Nakason 2012). Zinc oxide, now commonly used as an activator, was originally a  
557 filler. Currently, the most common filler added to commercially vulcanized rubber is carbon  
558 black (Mukhopadyay and De 1979; Salaeh and Nakason 2012; Joseph et al. 2015). There also are  
559 other effective fillers such as clay, silica, and lignin (Mukhopadyay and De 1979; López-  
560 Manchado et al. 2003; Košíková et al. 2007; Jiang et al. 2013). As wood decays, hemicellulose  
561 and cellulose quickly disappear, leaving behind more robust lignin (Fengel 1991; Briggs and  
562 Summons 2014). Therefore, it seems likely that lignin fillers helped to stabilize the vulcanized  
563 Geiseltal laticifers at some point. Lignin is a complex, heterogeneous, organic polymer  
564 composed of combinations of three basic monolignol compounds (Ciesielski et al. 2014;  
565 Rencoret et al. 2016; Siddiqui et al. 2017). As such, lignin has no clearly defined structure; its  
566 composition is highly variable, and its exact chemical structure in wood is unknown (Boerjan et  
567 al. 2003; Vanholme et al. 2010; Heitner et al. 2016). However, pyrolysis GC/MS of lignin  
568 typically yields a variety of simple phenols and lignin monomers (Ralph and Hatfield 1991;  
569 Mullen and Boateng 2010; Zhang et al. 2012; Rencoret et al. 2016), which were not present as  
570 major peaks in our pyrolysis GC/MS analysis of the Geiseltal laticifers. If lignin did act as a filler  
571 at some point, it has since been largely degraded.

572           The scarcity of isolated laticifer fossils at other localities in the world may be due to  
573 variations in latex composition, such that other ancient latex material is unable to effectively  
574 vulcanize, or due to a lack of the special chemical conditions within the Geiseltal peat-forming  
575 environment. Alternatively, if the composition of the latex is less rich in rubber, even if the  
576 rubber vulcanizes, it might be too diffuse to retain the original shape of the laticifer. Finally, if  
577 the surrounding plant tissues do not degrade, then the laticifers would not be found as isolated  
578 mats, even if they were to get preserved.

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## CONCLUSIONS

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The *Coumoxylon* monkeyhair tree that grew in peat-forming habitats during middle Eocene times in what is now the Geiseltal had a good-sized trunk or thick branches. Like most woody plants, the stem axes were covered with a relative thin layer of bark. Beneath the bark was an extensive zone of latex-containing ducts called laticifers that were branched and non-articulated. Like many trees that produce copious amounts of latex, the zone of laticifers lay directly under the bark, located adjacent to or contained within the extraxylary tissues (phloem, cortex, the inner layers of the periderm). In the center of the stem axes was a central cylinder of secondary xylem—the greater the girth of the stem axis, the greater the volume of wood.

The three major tissues in the monkeyhair trees—bark, laticifers, and wood—were prone to differential rates of degradation and preservation. Strangely, the wood is rarely found in the monkeyhair stem axes, although it must have been present in large quantities in the living tree. The bark is better preserved than the wood, but the laticifers and latex are best preserved, excellently fossilized through natural vulcanization.

594           The vulcanization of the Geiseltal lignites most likely occurred before significant wood  
595 degradation and at low temperatures, most likely in accordance to the following scenario. Sulfur  
596 compounds—such as hydrogen sulfide which is a very effective sulfur source for promoting rapid  
597 vulcanization at room temperature—were produced during early anaerobic decay of the organic  
598 matter in the waters of the peat-forming environment, including the organic tissues of the tree  
599 and particularly of the latex itself. Exposure to these compounds resulted in vulcanization of the  
600 degraded, rubber-rich latex, a process that was possibly further influenced by some components  
601 of the latex and wood of the monkeyhair tree which acted as accelerators or stabilizers. The  
602 hopane derivatives, bacterial biomarkers, were then incorporated into the vulcanized rubber.  
603 After vulcanization, the latex became more resistant to disintegration than all other plant tissues.  
604 Consequently, the laticifers were fossilized in an unusually well-preserved state, even as the  
605 other tissues in the stem axes degraded.

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608

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## FIGURE CAPTIONS

923 FIG. 1.— Well-preserved *Coumoxylon* stem axes with fossil latex canals (“monkeyhair” or  
 924 *Affenhaar*) from the middle Eocene Geiseltal lignites. **A, B**) Photographs of both sides of  
 925 laterally compressed specimen of GHM LIX20. **C, D**) Photographs of both sides of laterally  
 926 compressed specimen of GHM Y74.

927 FIG. 2.— Detail views of the well-preserved specimens with bark, wood, and latex canals. **A**)  
 928 GMH LIX20, outermost surface showing dark material with a corrugated texture interpreted as  
 929 bark; latex canals are visible underneath. **B**) GMH Y74, latex canals contained within degraded  
 930 tissues of the stem axis. **C**) GMH LIX20, isolated mat of latex canals without any associated  
 931 enclosing bark or degraded organic material. **D**) GMH PB101, one latex canal at a branch point  
 932 under a light microscope.

933 FIG. 3.— CT orthoslices and schematic interpretations of well-preserved *Coumoxylon* stem axes  
 934 with preserved latex canals (“monkeyhair” or *Affenhaar*) from the middle Eocene Geiseltal  
 935 lignites. Dark brown = bark, medium brown = zone of laticifers, black = larger pieces of rock .  
 936 **A, B, C, D**) Specimen GHM LIX20. **A**) CT orthoslice along a longitudinal plane of section,  
 937 736/1925. **B**) Reconstruction of the three identified layers in (A). **C**) CT scan orthoslice along a  
 938 median transverse plane, 535/1019. **D**) Reconstruction of the three identified layers shown in  
 939 (C). **E, F, G, H**) Specimen GHM Y74. **E**) CT orthoslice along a median longitudinal plane of  
 940 section, 2181/4363. **F**) Reconstruction of the three identified layers in (A). **G**) CT scan orthoslice  
 941 along a median transverse plane, 1012/2023. **H**) Reconstruction of the three identified layers  
 942 shown in (C).

943 FIG. 4.— Pyrolysis GC/MS chromatograms of five samples of fossil latex canals. The major

944 sulfur compounds are indicated by numbers in circles; numbers correspond to those in Table 3.

945 **A)** GMH LIX20. **B)** GMH PB39. **C)** GMH PB99. **D)** GMH PB37. **E)** GMH PB36.

946 FIG. 5.— Structures of compounds identified; see Table 3 for more information about each  
 947 compound. **A)** Dimethyl disulfide. **B)** 1,3,5-cycloheptatriene. **C)** 2,4-dimethylthiophene. **D)** 2,3-  
 948 dimethylthiophene. **E)** 2,7-dimethyl-1,7-octadiene. **F)** 2-(1-methylethyl)-thiophene. **G)** 2,3,4-  
 949 trimethylthiophene. **H)** 1-ethenyl-4-methylbenzene. **I)** 1-methyl-3-propylbenzene. **J)** 2,5-  
 950 diethylthiophene. **K)** 3,4-diethylthiophene. **L)** 3-[(E)-2-butenyl]-thiophene. **M)** 2-ethyl-5-(2-  
 951 methylpropyl)-thiophene. **N)** 3-isopropylthiophenol. **O)** 4-(1,1-dimethylethyl)-benzenethiol. **P)**  
 952 2,6-dimethylbenzo[b]thiophene. **Q)** 2-ethyl-5-hexylthiophene. **R)** 2,4-diethylbenzo[b]thiophene.  
 953 **S)** Methyl tetradecanoate. **T)** Methyl ester hexadecanoic acid. **U)** 2-dodecyl-5-ethylthiophene. **V)**  
 954 Methyl stearate. **W)** Methyl ester tetracosanoic acid. **X)** squalene. **Y)** Methyl ester hexacosanoic  
 955 acid. **Z)** Dinor-oleana-1,3,5(10)-triene. **AA)** 23,25-bisnorlupan-1,3,5(10),12-tetraene. **AB)** 22R-  
 956 17a(H),21a(H)-homohopane.

957

#### 958 TABLE CAPTIONS

959 TABLE 1.— All specimens included in the study

960 TABLE 2.— Scan parameters for micro CT

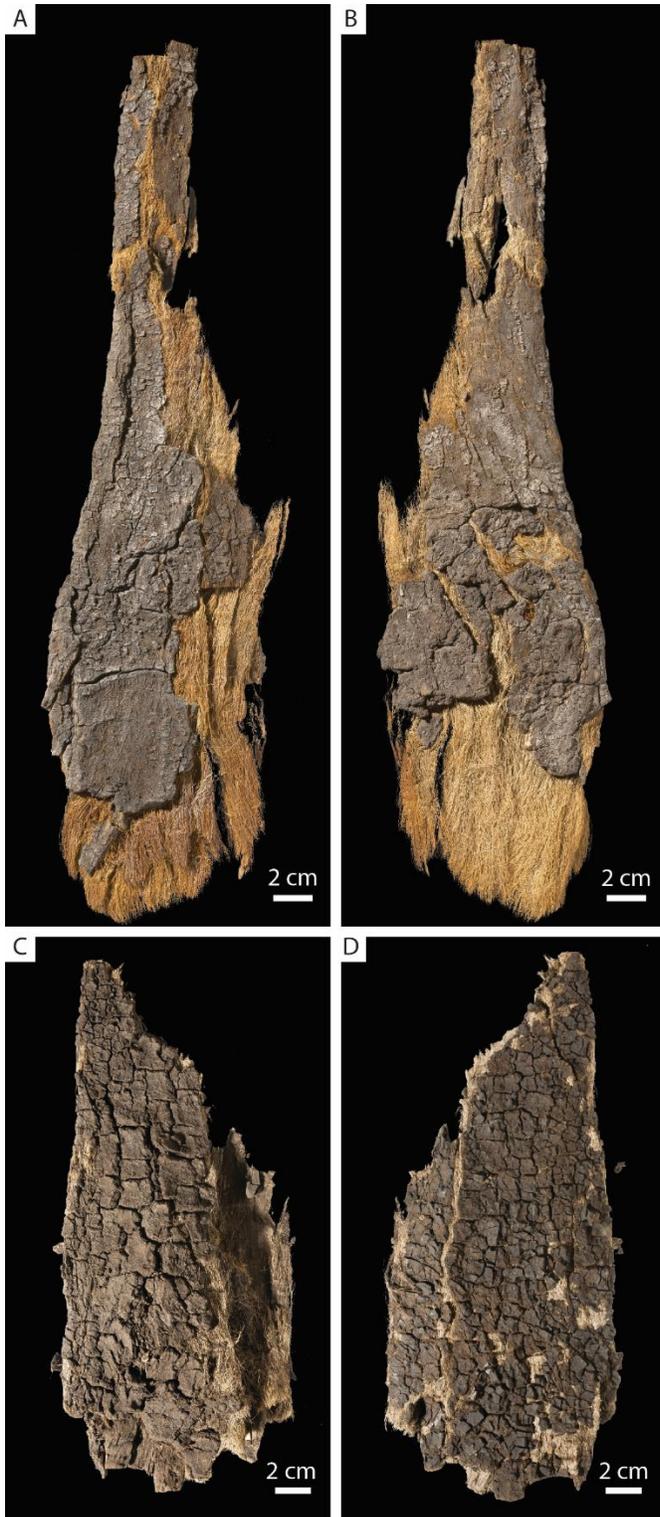
961 TABLE 3.— Table of compounds identified

962

963

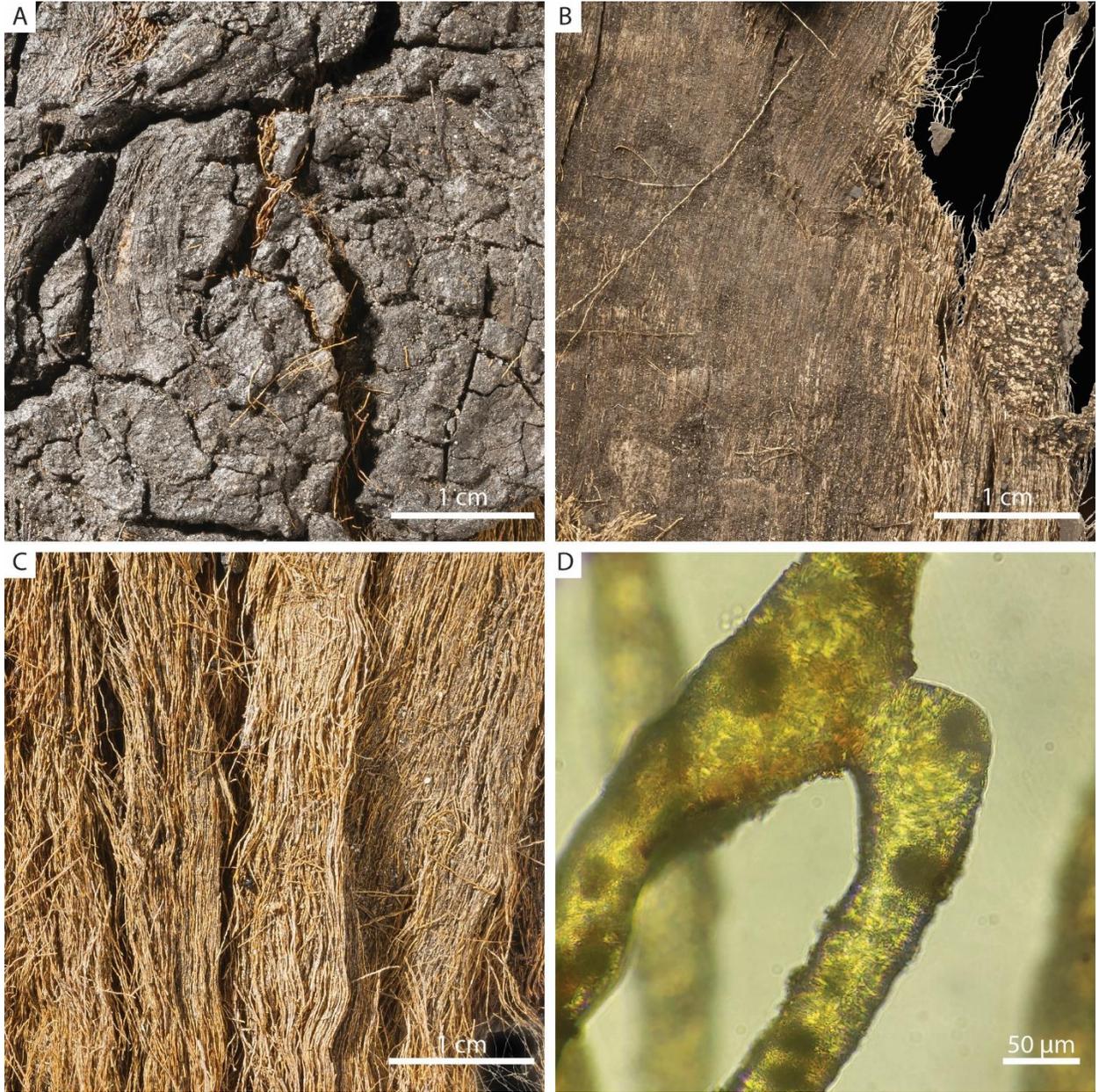
FIGURES

964 FIG. 1.



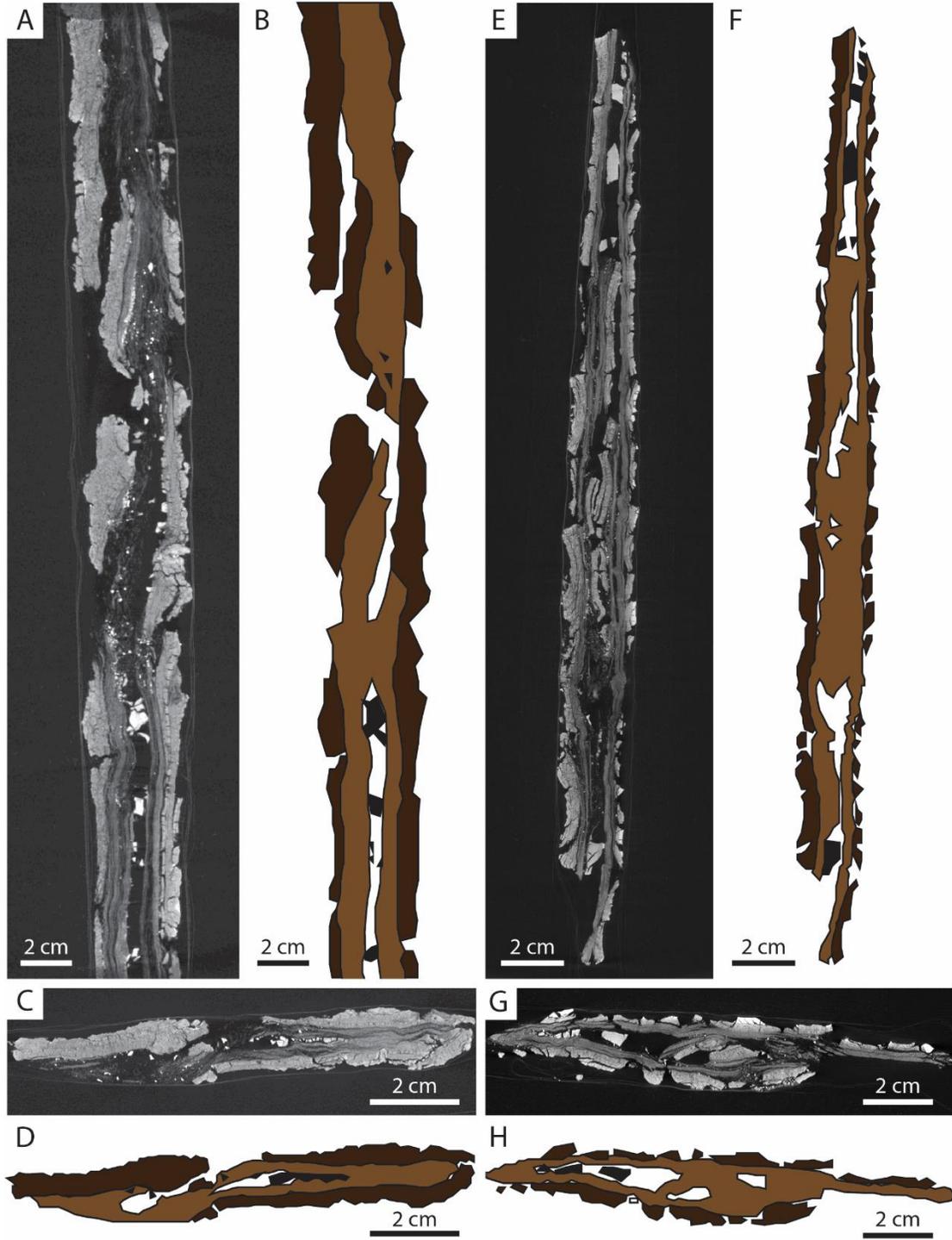
965

966 FIG. 2.  
967



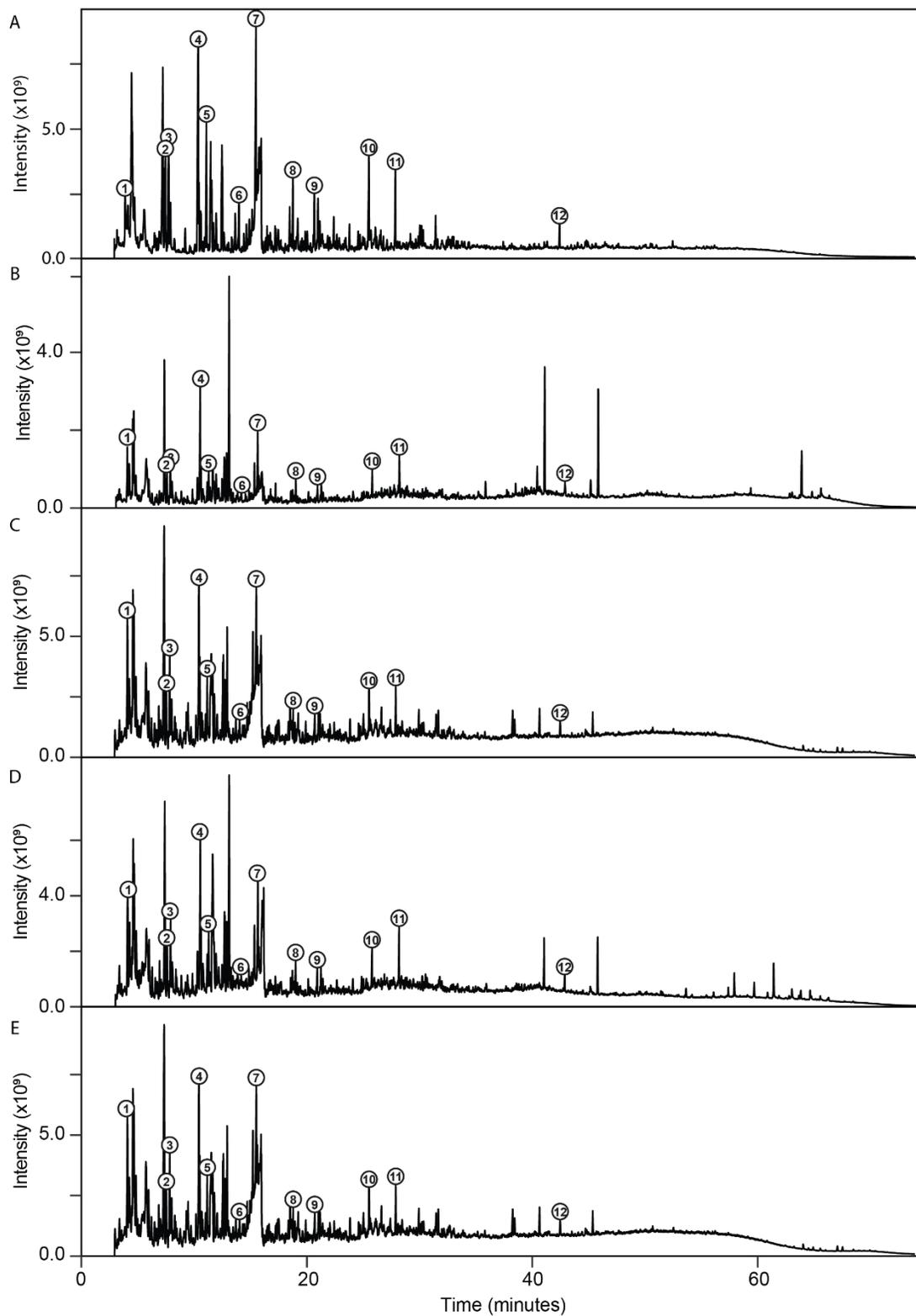
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974 FIG. 4.  
975



976  
977



982 TABLE 1  
983

| Specimen Number* | Description  | Analysis                      |
|------------------|--|-------------------------------|
| GMH LIX20        | Well-preserved with laticifers and remnants of wood and bark | Micro CT and pyrolysis GC/MS  |
| GMH Y74          | Well-preserved with laticifers and remnants of wood and bark | Micro CT                      |
| GMH PB39         | Mat of isolated laticifers                                   | Pyrolysis GC/MS               |
| GMH PB99         | Mat of isolated laticifers                                   | Pyrolysis GC/MS               |
| GMH PB37         | Mat of isolated laticifers                                   | Pyrolysis GC/MS               |
| GMH PB36         | Mat of isolated laticifers                                   | Pyrolysis GC/MS               |
| GMH PB101        | Mat of isolated laticifers                                   | Light microscopy, photography |

\*GMH refers to the Geiseltal Museum Halle, which is part of the NaturalSciences Collections of the Martin Luther University Halle-Wittenberg

984

985 TABLE 2  
986

| Scan parameter        | GMH LIX201993 | GMH Y74 |
|-----------------------|---------------|---------|
| Voltage (kV)          | 120           | 100     |
| Current ( $\mu$ A)    | 300           | 200     |
| Exposure time (ms)    | 333           | 500     |
| Number of projections | 1500          | 1000    |
| Points of density     | 3             | 3       |
| Run time (hour)       | 1:07          | 1:40    |
| Voxel size ( $\mu$ m) | 125.15        | 82.558  |

987

988 TABLE 3  
989

| RI     | Name                                    | Mass | Molecular formula                              | Label Fig. 4 | Label Fig. 5 |
|--------|---|------|--|--------------|--------------|
| 782.1  | Dimethyl disulfide                      | 94   | C <sub>2</sub> H <sub>6</sub> S <sub>2</sub>   | 1            | A            |
| 796    | 1,3,5-cycloheptatriene                  | 92   | C <sub>7</sub> H <sub>8</sub>                  |              | B            |
| 878.7  | 2,4-dimethylthiophene                   | 112  | C <sub>6</sub> H <sub>8</sub> S                | 2            | C            |
| 886.6  | 2,3-dimethylthiophene                   | 112  | C <sub>6</sub> H <sub>8</sub> S                | 3            | D            |
| 927.1  | 2,7-dimethyl-1,7-octadiene              | 138  | C <sub>10</sub> H <sub>18</sub>                |              | E            |
| 959.3  | 2-(1-methylethyl)-thiophene             | 126  | C <sub>7</sub> H <sub>10</sub> S               | 4            | F            |
| 979.4  | 2,3,4-trimethylthiophene                | 126  | C <sub>7</sub> H <sub>10</sub> S               | 5            | G            |
| 996.7  | 1-ethenyl-4-methylbenzene               | 118  | C <sub>9</sub> H <sub>10</sub>                 |              | H            |
| 1048.1 | 1-methyl-3-propylbenzene                | 134  | C <sub>10</sub> H <sub>14</sub>                |              | I            |
| 1057.5 | 2,5-diethylthiophene                    | 140  | C <sub>8</sub> H <sub>12</sub> S               | 6            | J            |
| 1069.2 | 3,4-diethylthiophene                    | 140  | C <sub>8</sub> H <sub>12</sub> S               |              | K            |
| 1098.1 | 3-[(E)-2-butenyl]-thiophene             | 138  | C <sub>8</sub> H <sub>10</sub> S               | 7            | L            |
| 1188   | 2-ethyl-5-(2-methylpropyl)-thiophene    | 168  | C <sub>10</sub> H <sub>16</sub> S              | 8            | M            |
| 1241.8 | 3-isopropylthiophenol                   | 152  | C <sub>9</sub> H <sub>12</sub> S               | 9            | N            |
| 1333.9 | 4-(1,1-dimethylethyl)-benzenethiol      | 166  | C <sub>10</sub> H <sub>14</sub> S              |              | O            |
| 1386.5 | 2,6-dimethylbenzo[b]thiophene           | 162  | C <sub>10</sub> H <sub>10</sub> S              | 10           | P            |
| 1461   | 2-ethyl-5-hexylthiophene                | 196  | C <sub>12</sub> H <sub>20</sub> S              | 11           | Q            |
| 1579.7 | 2,4-diethylbenzo[b]thiophene            | 190  | C <sub>12</sub> H <sub>14</sub> S              |              | R            |
| 1722.1 | Methyl tetradecanoate                   | 242  | C <sub>15</sub> H <sub>30</sub> O <sub>2</sub> |              | S            |
| 1924.5 | Methyl ester hexadecanoic acid          | 270  | C <sub>17</sub> H <sub>34</sub> O <sub>2</sub> |              | T            |
| 1998.6 | 2-dodecyl-5-ethylthiophene              | 284  | C <sub>18</sub> H <sub>32</sub> S              | 12           | U            |
| 2125.3 | Methyl stearate                         | 298  | C <sub>19</sub> H <sub>38</sub> O <sub>2</sub> |              | V            |
| 2726.7 | Methyl ester tetracosanoic acid         | 382  | C <sub>25</sub> H <sub>50</sub> O <sub>2</sub> |              | W            |
| 2805.5 | Squalene                                | 410  | C <sub>30</sub> H <sub>50</sub>                |              | X            |
| 2928.6 | Methyl ester hexacosanoic acid          | 410  | C <sub>27</sub> H <sub>54</sub> O <sub>2</sub> |              | Y            |
| 3079.1 | Dinor-oleana-1,3,5(10)-triene           | 378  | C <sub>28</sub> H <sub>42</sub>                |              | Z            |
| 3138   | 23,25-bisnorlupan-1,3,5(10),12-tetraene | 376  | C <sub>28</sub> H <sub>40</sub>                |              | AA           |
| 3238.2 | 22R-17a(H),21a(H)-homohopane            | 426  | C <sub>31</sub> H <sub>54</sub>                |              | AB           |

