

1 Dark materials: pre-Columbian black lithic carvings from St Vincent and the  
2 wider Caribbean  
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25 **Keywords:** Circum-Caribbean, cannel coal, lignite, carvings, pre-Columbus

26

27 **Highlights:**

- 28 • Analysis of material from two pre-Columbian 'black' carvings from St  
29 Vincent
- 30 • Their chemical composition and biological components are similar to  
31 cannel coal
- 32 • Material for both carvings is therefore likely to have originated in South  
33 America

- 34       • Indicates potential social and trade networks spanning the circum-  
35       Caribbean

36

37   **Disclaimer:**

38   Declarations of interest: none

39

40   **Abstract:**

41   A small number of pre-Columbian black lithic carvings are known to have  
42   been found at archaeological sites across the Caribbean, as well as in parts of  
43   neighbouring mainland South America. The identity of the material used to  
44   create these artefacts is often unknown, but suggestions include lignite, wood,  
45   petrified wood, manja(c)k, jet (or 'jet-like' materials) and hardened asphalt.  
46   These identifications are often historical and lacking any scientific basis, and  
47   as such can be unreliable. However, identification of the material has the  
48   potential to inform on the source of the carving and thereby pre-Columbian  
49   trade routes within the circum-Caribbean region. Four analytical techniques  
50   (reflectance microscopy, FTIR, Py-GC/MS, x-ray fluorescence) were applied  
51   to samples taken from two carvings found on St Vincent and five comparative  
52   materials. Both artefacts were found to be most likely to be carved from  
53   cannel coal, indicating that they originated in South American (where cannel  
54   coal is found extensively in locations in Colombia and Venezuela), as the  
55   material is not found within the Caribbean region.

56

57   **1. Introduction**

58       Pre-Columbian Caribbean archaeology is based overwhelmingly on  
59   ceramic and stone artefacts. Surviving wooden artefacts are rare (e.g.  
60   Ostapkowicz et al., 2012, 2013), and carvings of fossilised wood and other  
61   black organic materials are rarer still. As such, these have remained a largely  
62   unrecognised artistic medium (Ostapkowicz, 2016, Ostapkowicz, in press).  
63   These fine-grained, usually matte, black and black-brown materials have been  
64   used for a variety of carvings, ranging from small anthropo-/zoomorphic  
65   ornaments (Figure 1) to drug-related paraphernalia (Figures 2 and 3) and,  
66   based on current knowledge, have been found at a small selection of sites

67 spanning Trinidad north to Puerto Rico (Figure 4), dating roughly to the  
68 Caribbean's Early Ceramic Age (ca. 400 BC – AD 600).

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72 Figure 1: Anthropo-zoomorphic carvings in dark materials, roughly to scale. **1.**  
73 Carving from Morel, Guadeloupe: H: 27mm; W: 15mm; D: 13mm; courtesy,  
74 Musée Edgar Clerc, 94.14.2. **2.** L'Allée Dumanoir carving, Guadeloupe: H: 22  
75 mm; W: 12mm; D: 14mm; courtesy, Direction Régional des Affaires Culturells,  
76 Guadeloupe, ST3295, 14. **3.** Carving from Sorcé, Vieques, Puerto Rico, H:  
77 14mm; W: 11mm; D: 12mm, S-V, Z-T-B, C-5. **4.** Sorcé, Vieques, Puerto Rico  
78 amulet, H: 8mm; W: 6mm; D: 8mm, S-V, Z-16. **5.** Sorcé, Vieques, Puerto Rico  
79 amulet, H: 7mm; W: 5mm; D: 6mm, S-V, Z-16. Sorcé carvings courtesy  
80 Yvonne Narganes Storde. All photographs: Ostapkowicz. (*Figure to be*  
81 *reproduced in colour*)

82



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84

85 Figure 2. Four views of snuff tube depicting a bird above a monkey, St  
86 Vincent, ca. ~ AD 300-800. H: 86mm; W: 53mm; D: ca. 67mm (max).  
87 Photograph: Ostapkowicz, courtesy Pitt Rivers Museum, University of Oxford,  
88 Acc. No. 1900.44.1. [*Figure to be reproduced in colour*]  
89



90  
91  
92 Figure 3. Plano-convex carving featuring a frog design in its ventral surface. L:  
93 49mm; W: 42mm; D: 14mm. Photograph: Ostapkowicz, courtesy and  
94 copyright St Vincent and the Grenadines National Trust,  
95 2004.0001.0001.0098. [*Figure to be reproduced in colour*]  
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97 Some of the carvings share almost identical iconography, although  
98 they appear at sites hundreds of kilometres apart, such as those found at  
99 L'Allée Dumanoir, Guadeloupe (Etrich, 2002; 300 BC – AD 300) and Sorcé,  
100 Vieques (Chanlatte Baik and Narganes Storde, 1984: 46-47; 400 BC – AD  
101 600) (Figure 1) or Coto, Puerto Rico (Rainey, 1940: 73-74; ca. AD 900-1200).  
102 Their surfaces often have visible structural detail, which have resulted in many  
103 being identified as wood (e.g. Petit Roget, 1995). However, lignite may also  
104 exhibit visible structure (as noted for carvings by Allason-Jones and Jones,  
105 2001), especially if it contains wood pieces, or merely owing to the tranquil  
106 conditions during the accumulation of layer upon layer of organic material.  
107 Some jet and 'jet-like' materials may also show structure (e.g. Kool et al.,  
108 2009), as may cannel coals which originate as layer by layer accumulations.  
109 All of these materials, as well as other dark materials such as asphalt and

110 manja(c)k originating in or around Pitch Lake in Trinidad, could possibly have  
111 been used to produce carvings

112

### 113 1.1 The materials

114         These dark organic materials are a notable departure from the lustrous  
115 exotic minerals such as amethyst, quartz and jadeites that they are  
116 sometimes associated with in the Caribbean archaeological record (e.g.  
117 Chanlatte Baik and Narganes Storde, 1984: 46-47; Etrich, 2002: 26; 2003: 49-  
118 50). They therefore raise a number of questions, first and foremost being the  
119 identification of the material itself and its potential sources, crucial information  
120 that is required before the networks involved in their exchange can be  
121 discussed. Further, what does the presence of such similar artefacts (in the  
122 case of the anthropo-/zoomorphic pendants) on different islands suggest  
123 about the social, cultural and economic links between communities during the  
124 Caribbean's Early Ceramic Age? What does the selective use of black  
125 materials in the creation of artefacts that specifically functioned within ritual  
126 contexts (e.g., drug-related paraphernalia) imply about their significance and  
127 symbolic associations?

128         Small carvings and ornaments in dark materials have also been  
129 documented in mainland South America, in particular Venezuela (e.g.  
130 Spinden, 1916; Kidder, 1944; Arroyo et al., 1971; Antczak and Antczak, 2006,  
131 2011; Falci et al., 2017). They are sometimes described as jet, 'jet-like' or  
132 *azabache* (the Spanish term for jet) (e.g. Arroyo et al., 1971: 154-155; 233),  
133 although one piece previously described as jet (Falci, 2015) was recently  
134 stated to be bituminous coal (Falci et al., 2017), with no explanation given for  
135 this reclassification.

136         The identification of archaeological carved black artefacts as jet or 'jet-  
137 like' often appears to be based solely on the intense black colouration of the  
138 object and its ability to take a high polish, without regard to the actual  
139 definition of jet. Jet is generally considered to be formed from compressed,  
140 waterlogged drifted wood, which has been secondarily impregnated with  
141 bitumen from the surrounding environment (Stach et al., 1982). Only a limited  
142 number of deposits are known worldwide, in particular in Europe, including  
143 Whitby, United Kingdom (e.g. Muller, 1980; Muller and Muller, 2009), Spain

144 (e.g. Suárez-Ruiz and Iglesia, 2007; Gutierrez Blanco et al., 2008) and Utah,  
145 USA (where it is described as a ‘very peculiar coal’ by Traverse and Kolvoord,  
146 1968).

147 The South American carvings described above may therefore be made  
148 of cannel coal, lignite or other hydrocarbon materials, rather than jet. Both  
149 cannel coal and lignite are commonly found in Venezuela and Colombia (e.g.  
150 Orndorff, 1985).

151

## 152 1.2. The carvings

153 The two artefacts explored in this paper were both ‘excavated’ from  
154 historic museum collections – part of the legacy holdings of the Pitt Rivers  
155 Museum, University of Oxford, UK, and the St Vincent National Trust, St  
156 Vincent and the Grenadines. The larger of the two carvings (Figure 2) was  
157 found on a sugar cane plantation in Charlotte Parish, St Vincent, at some  
158 point before ca. 1870, when it was presented by Bishop Michinson, Master of  
159 Pembroke College, Oxford, to the Pitt Rivers Museum. It depicts a bird,  
160 possibly a parrot or macaw, surmounting a crouched monkey with a long,  
161 curled tail. Identified until quite recently as simply a ‘figure’ (Hicks and Cooper,  
162 2013; 45), it is in fact a central component of a snuff tube used to inhale  
163 hallucinogenic snuffs during rituals (Ostapkowicz, in press). It is drilled with  
164 two internal tubes which once emerged as raised spouts from the bird’s back,  
165 now badly broken – these would have been pressed to the nose to deliver the  
166 dose, potentially with the aid of short bird bone tubes bringing the narcotic  
167 snuff directly into the nostrils. Its style of carving places it within the insular  
168 Caribbean’s Barrancoid period – roughly AD 300 to AD 600. As such, it is the  
169 earliest elaborate snuff tube from the region (for further discussion see  
170 Ostapkowicz, in press).

171 The second carving (Figure 3) is held in the collections of the National  
172 Trust of St Vincent and the Grenadines. It is a light-weight, black carving  
173 identified in museum notes as being made of ‘pitch’ (asphalt) or ‘gutta-  
174 percha’, a tree latex. Its potential provenance is equally varied: if asphalt, it  
175 most likely came to St Vincent from Pitch Lake, Trinidad, via prehistoric trade  
176 routes. If gutta-percha, it is thought to have been acquired via Barbados (La  
177 Verne Phillips, per. com 2015). It is understood to have been part of the ‘Old

178 Library' collections, curated by Earl Kirby (b. 1921; d. 2005), St Vincent's first  
179 qualified veterinarian and, in his spare time, keen amateur archaeologist, who  
180 eventually became chairman of the St Vincent Archaeology Society and  
181 Director of the National Museum. Unfortunately, the carving had very little  
182 associated documentation when it was formally accessioned in 2004, with the  
183 hypothetical provenance(s) input at this time.

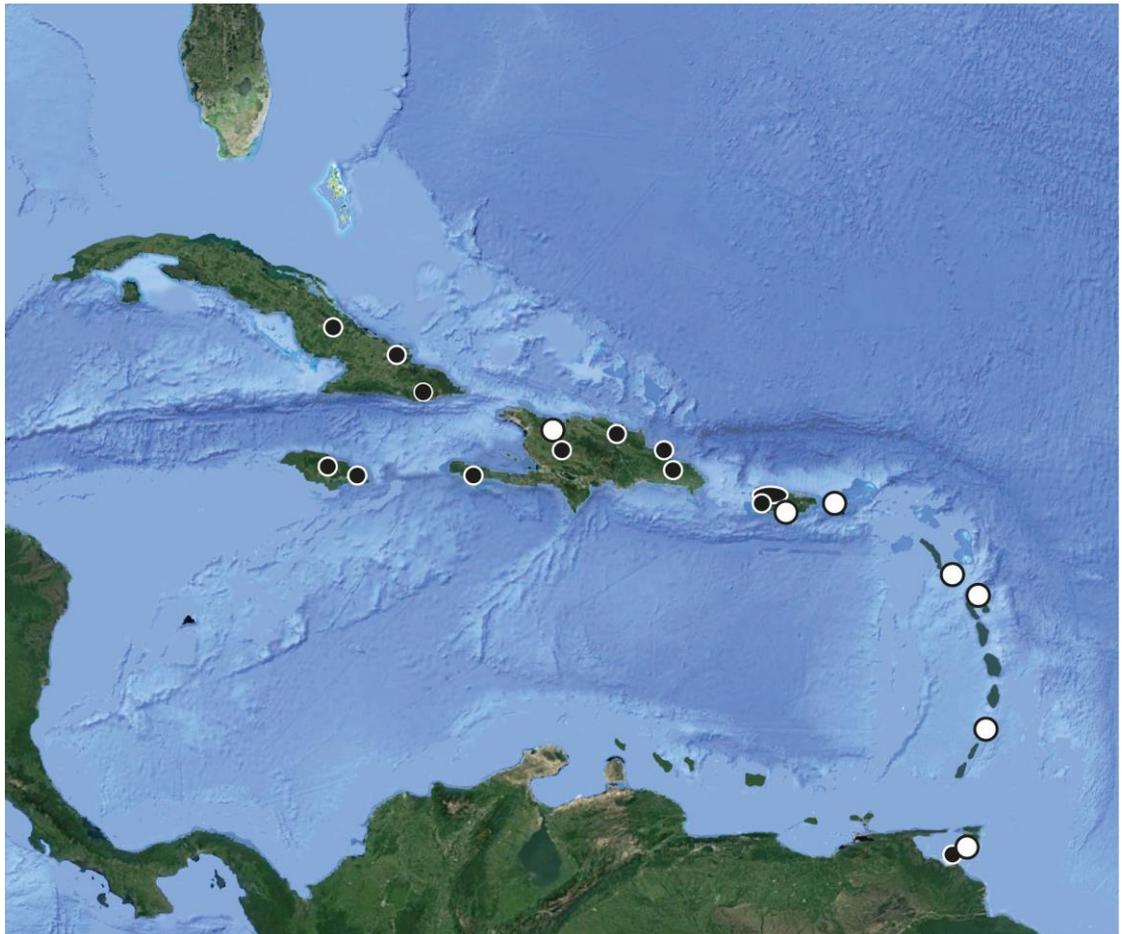
184 A stylised frog's body is depicted on the dorsal surface of the broken  
185 carving (Figure 3) – its remaining left foreleg, round body and hind legs in the  
186 quintessential position of this amphibian depicted in designs common across  
187 the span of the Caribbean from the Saladoid period (~ ca. 500 BC – AD 500),  
188 well into colonial times (~ AD 1500) (Waldron, 2016: 187). It is clear from the  
189 tool marks on both surfaces that the black material was carved rather than  
190 moulded into this shape. The smooth, matte finish of the dorsal surface must  
191 have been achieved by fine-grained sanding and polishing. The ventral  
192 surface appears to be shallowly excavated with a thick rim ridge; together with  
193 its small size and smoothly rounded dorsal surface – which perfectly fits the  
194 palm of the hand – these elements potentially suggesting a personal snuff-  
195 tray for small doses of a potent narcotic substance.

196

### 197 1.3. Geological materials

198 Identification of the materials from which these black Caribbean  
199 carvings are made may help identify their geological origin, and hence  
200 improve understanding of trade and exchange routes in the pre-Columbian  
201 circum-Caribbean. Carvings made of cannel coal, for example, are most likely  
202 to have originated in South America, where it is common (in particular in  
203 Venezuela and Colombia), as deposits are not known to be present in the  
204 Caribbean (Sealey, 1986). The identification of the material as either lignite or  
205 lignitic (i.e. highly mineral-containing) would be less informative, as these  
206 materials occur in both South America (e.g. Orndorff, 1985) and the  
207 Caribbean, where they are found in Trinidad (Orndorff, 1985; Babalool et al.,  
208 2016) and throughout the Greater Antilles, eastwards from Cuba, across parts  
209 of Jamaica, Haiti, the Dominican Republic, and Puerto Rico (e.g. Orndorff,  
210 1985; Iturralde-Vinent and Hartstein, 1998; Iturralde-Vinent, 2001; Sealey,  
211 1986; Graham, 1996) (Figure 4). Most of these lignite and lignitic deposits are

212 not extensive enough (or are found at depth, and hence likely unavailable to  
213 pre-Columbian artisans), or the material is not sufficiently consolidated, to be  
214 suitable for carving (Alan Graham, pers com. 2018). However, it is not  
215 inconceivable that some small, high quality exposed deposits do exist, which  
216 might have been of particular interest to a carver skilled in working other  
217 materials.  
218



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222 Figure 4: Map of the Caribbean, indicating locations of finds of black Pre-  
223 Columbian carvings (white circles) and known locations of lignite (black  
224 markers) (e.g. Orndorff, 1985; Babalool et al., 2016; Iturralde-Vinent and  
225 Hartstein, 1998; Iturralde-Vinent, 2001; Sealey, 1986; Graham, 1996).

226

227 It is also possible that hydrocarbon materials such as asphalt, bitumen,  
228 and manja(c)k associated with Pitch Lake (Trinidad) and the Scotland District

229 (St Andrew's parish) of Barbados (e.g. Sealey, 1986) were carved, as similar  
230 solid hydrocarbons such as albertite are known to have been carved  
231 elsewhere, including Scotland, UK (e.g. Sheridan, 2015). While some of these  
232 materials may not have been suitable for carving once exposed and solidified,  
233 they may have been softer and workable prior to exposure to air, in a similar  
234 manner to that of Turkish black amber or Oltu stone (e.g. Kalkan et al., 2012).  
235 However, Boomert (2016: 40) considered the black carvings found in Trinidad  
236 likely imports from the Lower Orinoco Valley in Venezuela, despite the local  
237 availability of lignite and materials associated with Pitch Lake. Waldron (2016:  
238 37) also describes one black anthropomorphic carving from Montserrat as  
239 'probably hardened asphalt or pyroclastic materials' although the basis for this  
240 identification is unclear, and the original museum accession card records the  
241 piece as 'cannel coal'.

242 The suggestion in the records of the St Vincent National Trust that the  
243 frog carving may be made from 'gutta percha' is intriguing, though likely a  
244 result of historic misattribution. Historically carved for jewels and ornaments  
245 (Prakesh et al., 2005), gutta percha is a tree latex produced by native  
246 Indonesian woods of the Sapotaceae family (Clouth, 1903), and hence  
247 unlikely to be the origin of the Caribbean material. A similar substance, balata  
248 (originally described as 'Surinam gutta-percha') is produced by trees from the  
249 same family found in the Caribbean and South America (Clouth, 1903).  
250 However, historical balata carvings appear dull brown in colour and are  
251 visually very distinct from the black Caribbean carvings of this study (e.g.  
252 Albuquerque, 2018).

253

#### 254 1.4 Material identification

255 The materials that were likely used for both of the St Vincent carvings  
256 (Figures 2 and 3), as well as others found in both the Caribbean and South  
257 America, are all composed of plant material that has been degraded,  
258 compacted, and sometimes heated or impregnated, to varying extents over  
259 many millennia, and with differing degrees of mineral impurities. These  
260 variations in composition result in different properties in terms of carving  
261 ability, resilience and lustre (Teichmüller, 1992). However, the individual  
262 materials cannot be identified by eye, which can be challenging for

263 archaeologists, especially those studying large assemblages of artefacts  
264 carved in a range of materials (e.g. Sheridan, 2017; Woodward and Hunter,  
265 2015).

266 Identification of the carving material can be further complicated  
267 because of variations in the definitions of each of the hydrocarbon materials,  
268 with a lack of clearly defined physical and/or chemical characteristics for each  
269 one. Several studies have used traditional organic petrology techniques (such  
270 as reflected light microscopy and vitrinite reflectance) and/or palynology to  
271 identify archaeological coal artefacts (see Suárez-Ruiz et al., 2012, for a more  
272 detailed review). However, these techniques are often not suitable for  
273 individual archaeological carvings, requiring destructive sampling to allow for  
274 preparation of thin sections, palynology slides or mounting in resin blocks to  
275 be polished. These techniques also require a detailed understanding of  
276 petrographic techniques and comparative local geological samples (e.g.  
277 Kalkreuth and Sutherland, 1998; Kalkreuth et al., 2012), which is often  
278 available for European samples, but not currently for those from the  
279 Caribbean or South America.

280 Current approaches to the identification of materials found in European  
281 black lithic assemblages include consideration of colour and texture, and  
282 degradation, surface polish and fracture characteristics (e.g. Sheridan, 2017;  
283 Woodward and Hunter, 2015), supported where possible by analytical  
284 techniques including x-radiography (e.g. Sheridan et al., 2002) reflected light  
285 and reflectance microscopy (e.g. Allason-Jones and Jones, 2001) and x-ray  
286 fluorescence spectrometry (e.g. Woodward and Hunter, 2015; Gormley,  
287 2017). Various studies have applied a further range of analytical techniques to  
288 European assemblages in efforts to distinguish between different carving  
289 materials (usually including jet, lignite, oil shales, and/or cannel coal) and to  
290 potentially identify source materials, whilst minimising (or removing entirely)  
291 the need for destructive analysis, with varying degrees of success. These  
292 techniques include ESR (Sales et al., 1987; Hunter et al., 1993), <sup>13</sup>C NMR  
293 (Lambert et al., 1992), FTIR (Hunter et al., 1993; Watts and Pollard, 1998),  
294 py-GC/MS (Watts et al., 1999) and LA-ICP-MS (Baron and Gratuze, 2016).

295 This study applies four complimentary techniques (XRF, FTIR,  
296 reflectance microscopy, py-GC/MS) to the two St Vincent carvings, to

297 determine the most suitable techniques to identify the material type with  
298 minimal requirement for destructive sampling<sup>1</sup>. The techniques were applied  
299 to analyse a range of characteristics (trace element and organic composition,  
300 physical structure and biological constituents), to determine what they are  
301 made of, and hence where they might have originated.

302

## 303 **2. Materials & Methods**

### 304 2.1 Samples

305         The two carvings (Figures 2 and 3) were each sampled carefully with a  
306 clean scalpel blade, ensuring the minimum amount of material was taken as  
307 discretely as possible. Small scrapings of the carving were removed from the  
308 margins of an internal crack near the base of the bird/monkey snuff tube (Pitt  
309 Rivers Museum, University of Oxford, UK). The largest piece measured 5 mm  
310 at its widest point and was ca. 2 mm thick.

311         The frog carving (St Vincent and the Grenadines National Trust) was  
312 sampled on the broken surface to ensure a discrete sampling that in no way  
313 affected the carved ventral or dorsal surface (Figure 5). A natural semi-  
314 circular crevice within the break provided good leverage for the scalpel to  
315 extract 12.2 mg of thin, sliver-like fragments. The material was soft and easy  
316 to sample, but also fragmented easily in storage after sampling.

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<sup>1</sup> Several samples from this study are additionally undergoing PIXE-PIGE analysis at the Louvre Laboratory as part of wider study of jet and similar materials under the direction of Dr Lore Troalen, National Museum of Scotland.



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321           Figure 5: The broken surface of the frog carving (tilted slightly to the left  
322 when compared to the central image in Figure 3), showing the sampling target  
323 area (circled) before (left) and after (right) sampling. Photos: Ostapkowicz,  
324 courtesy St Vincent and the Grenadines National Trust,  
325 2004.0001.0001.0098.

326

327           Five comparative source materials were chosen for analysis in this  
328 study, as follows:

329           • Jet from Whitby, Yorkshire, UK (obtained from Yorkshire Coast Fossils,  
330 UK).

331           • Lignite, origin unknown, supplied as part of a reference hydrocarbon  
332 specimen set (obtained from UKGE Ltd., UK.)

333           • Cannel coal from La Pajarita in the state of Táchira, western Venezuela  
334 (sample M13-LP; Hackley et al., 2005).

335           • Solidified surface crust material collected from Pitch Lake, Trinidad.

336           This material is dull, matt, dark grey/black in colour, with a  
337 heterogeneous appearance, and includes small amounts of fresh plant  
338 material.

- 339       • A sample of black, glassy, solidified, weathered pitch-like material  
340           (possibly manjak) collected from a beach along the coast from Pitch  
341           Lake, Trinidad.

342           The two samples from Pitch Lake, Trinidad (henceforth 'crust' and  
343 'beach') were not subjected to all analyses as their visual appearance was too  
344 distinct from that of the carving material: the crust material was too dull and  
345 matt, and the beach sample was too glassy. Neither material appeared  
346 suitable for carving, although they may have been chemically representative  
347 of material that might have been softer prior to hardening on exposure to air.  
348

## 349 2.2. Reflectance microscopy

350           Samples were embedded in resin (EpoFix epoxy supplied by Struers)  
351 and polished (using 60-, 240-, 400-, and 600- grit SiC papers followed by 0.3  
352 micron alumina on Buehler Texmet paper and 0.05 micron alumina on silk) to  
353 provide a surface for study. The blocks were made perpendicular to any  
354 lineation where it was visible within the sample. Polished blocks were viewed  
355 in reflected light under immersion oil (Cargille type A, density 0.923g/cc at  
356 23°C, RI of 1.514) using a Leica reflected light microscope and either × 20 or  
357 × 50 oil immersion objectives.

358           All specimens were examined from side to side and top to bottom (one  
359 transect each) to check for uniformity or variability. Areas with scratches on  
360 the blocks were avoided for photography where possible. All images are  
361 representative of the samples and all were taken under the same lighting  
362 conditions, with the same brightness and contrast settings. Focussing was  
363 difficult, especially in the jet sample, which by its nature is a very low  
364 reflectance material such that edges of features on which to focus are  
365 scarcely visible. Some images (Figure 6) had to be adjusted to make the  
366 features visible in the figure and so not all images are directly comparable  
367 with one another in terms of brightness and contrast as it is seen under the  
368 microscope.

369

## 370 2.3 FTIR

371 The samples were analysed by Fourier Transform Infrared (FTIR)  
372 spectroscopy using a Bruker Alpha mid-IR optical benchtop FTIR equipped  
373 with a standard in-compartment horizontal attenuated total reflectance (ATR)  
374 accessory fitted with a diamond crystal (Platinum ATR).

375 Due to the limited amount of material available for each sample, and  
376 variations in ease with which the material could be roughly crushed, the  
377 samples varied in size from less than a millimetre in largest dimension to well  
378 over five millimetres. A small portion of each sample – sufficient to  
379 substantially cover the surface of the diamond sensor element – was pressed  
380 into intimate contact with the crystal, using the built-in compression anvil, as is  
381 usual. Good contact was judged from the quality of spectral response  
382 observed, using strength of absorbance as the key metric.

383 The mid-infrared response of each sample was recorded between  
384 4000 and 400  $\text{cm}^{-1}$  wavenumbers, at 4  $\text{cm}^{-1}$  spectral resolution. 256 scans  
385 were collected for each sample to achieve high-quality data. Bruker Opus  
386 MENTOR software was used to control the system and to manipulate the  
387 data; this included automatically ratio-ing the sample's spectrum against a  
388 reference spectrum, as is usual practice.

389 Prior to analysis, the background reference spectrum was acquired  
390 with no sample loaded onto the sensor crystal. Both the sensing region and  
391 the tip of the anvil were cleaned with isopropanol before each background,  
392 and before loading each new sample; mechanical abrasion was also used if  
393 residual material from the previous analysis was tenacious. In addition, the  
394 background was re-acquired periodically, to mitigate the impact of any  
395 residual material on subsequent analyses.

396 The data have not been modified, post-collection: no data treatments  
397 have been applied. As a result, care must be taken when comparing the data  
398 to reference spectra collecting using other techniques (such as transmission  
399 through pressed pellets, by external diffuse or specular reflection, or by  
400 photoacoustic means; see Monnier (2018) for further discussion. There are  
401 well-known optical effects to consider when using the internal reflection (ATR)  
402 geometry. We simply note here that in order to compare accurately ATR data  
403 with transmission data, one should correct for the impact of variable  
404 penetration depth on relative signal intensity, as a function of wavenumber;

405 and also correct for asymmetric band shape and apparent shift in band  
406 position, due to the effects of anomalous dispersion in regions of strong  
407 absorption.

408

#### 409 2.4 Pyrolysis-GC/MS

410 Sample material from both carvings and the cannel coal comparative  
411 sample were analysed by py-GC/MS using a Chemical Data Systems (CDS)  
412 5150 pyroprobe pyrolysis unit attached to an Agilent 6890A gas  
413 chromatograph (GC) fitted with a CPSil-5CB fused column (Varian 100%  
414 dimethylpolysiloxane; 50 m, 0.32mm i.d.; 0.45µm film thickness) and a  
415 ThermoElectron MAT95 double focussing mass spectrometer  
416 (ThermoElectron, Bremen) operated in electron ionization (EI) mode (EI  
417 source temperature 200°C, interface 310°C) with helium as a carrier gas (2  
418 mL min<sup>-1</sup>). Samples were pyrolysed in a quartz tube at 610°C for 20 s,  
419 transferred to the GC using a pyrolysis transfer line (310°C) and injected onto  
420 the GC using a split ratio of 10:1; the injector port temperature was  
421 maintained at 310°C. The oven was programmed to heat at 4°C<sup>-1</sup> min from  
422 50°C (held for 4 min) to 300°C (held for 15 min). The MS scanned the range  
423 *m/z* 50–650 at a rate of one scan per second and there was a filament delay  
424 of 7 min. Data were collected using MAT95InstCtrl v1.3.2 and viewed using  
425 QualBrowser v1.3 (ThermoFinnigan, Bremen). Compounds were identified  
426 using the National Institute of Standards and Technology (NIST08) database  
427 and by comparison with spectra from the literature (including Watts et al.,  
428 1999) and an in-house library. A sub-sample of Pitch Lake crust material was  
429 previously analysed by Brock et al. (2017).

430

#### 431 2.5. X-ray fluorescence (XRF) spectrometry

432 Aliquots of all five geological specimens and both carvings were  
433 analysed as powders using benchtop XRF. The benchtop XRF is more  
434 sensitive, but hand-held (HH)-XRF was also used for the bird/monkey  
435 artefact, to investigate its potential for future analysis of similar objects on-site  
436 in collections/museums.

437

438 *2.5.1. XRF (benchtop)*

439 The elemental compositions of all seven samples were assessed by using  
440 a SciMed SEA6000VX X-ray fluorescence spectrometer. Measurements were  
441 taken over a 0.5 x 0.5 mm area in air at the instrument's normal focusing  
442 distance, with its X-ray tube operating at 50 kV, 1000  $\mu$ A without any filtration.  
443 Each spectrum was collected for 1200 s and a semi-quantitative calculation of  
444 concentrations of the metallic components of the samples was obtained by  
445 using the instrument's standard fundamental parameters program with the  
446 balance of the sample assumed to be carbon.

447

448 *2.5.2 Hand-held XRF*

449 Analysis of the surface of the bird/money carving was undertaken on-site in  
450 the Conservation Department at the Pitt Rivers Museum using an Oxford  
451 Instruments XMET 8000 light element handheld XRF. The instrument has a  
452 5mm diameter spot size and analysis areas were selected using a cross-hair  
453 on an in-built positioning camera. Measurements were taken using the Alloy-  
454 LE (light elements) fundamental parameters dual condition set which  
455 alternates between 8kV, 40 $\mu$ A with a 500 $\mu$ m Al filter and 40kV, 8 $\mu$ A with a  
456 25 $\mu$ m Fe filter. The program produces a spectrum for each condition set  
457 which meant that elements ranging from magnesium to uranium could  
458 potentially be identified. 60 second acquisition times were used for all  
459 measurements.

460 A small area (approx. 10mm diameter) of thin wax coating (presumed to be  
461 a historical conservation treatment) was removed from the surface of the  
462 object by swabbing with a mixture of IMS (industrial methylated spirit) and  
463 white spirit to allow analysis of the underlying material. Three measurements  
464 were taken on both the surface coating and the cleaned area so that elements  
465 derived from the coating could be distinguished.

466 Bruker Artax software was used to identify elemental peaks and to  
467 calculate the number of counts that contributed to each peak ('peak area  
468 analysis'). Full quantification of the data was not possible due to the lack of  
469 suitable reference material of the same matrix as the sample.

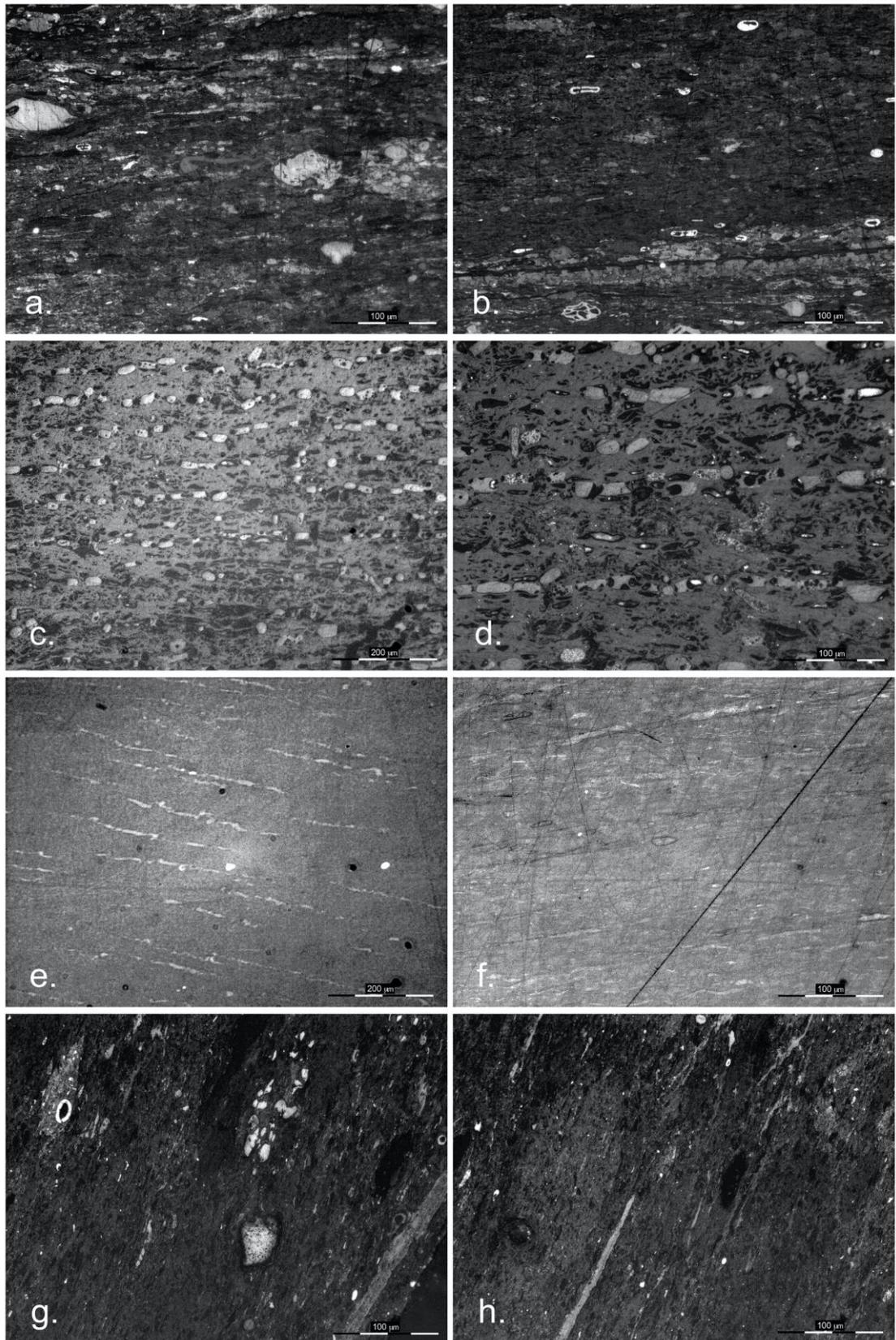
470

471 **3. Results and discussion**

472 3.1 Reflectance

473 Reflectance microscopy of polished blocks under oil is widely used in  
474 the study of coals, lignites and charcoal, and it enables recognition of  
475 structure, tissues and cells in otherwise dark materials (e.g. Allason-Jones  
476 and Jones, 2001). Interpretations here are based on prior experience of one  
477 of the authors (MEC) where the following are examples (Collinson et al.,  
478 2007; Steart et al., 2007; Hudspith et al., 2012; Robson et al., 2015;  
479 Noorbergen et al., 2018 supplementary material).

480 The cannel coal sample (M13-LP) is approximately parallel laminated  
481 at a very fine scale and contains a wide variety of components (Figures 6a,b).  
482 The regions in various dark shades of grey contain various-sized clumps or  
483 layers of material within a darker, almost black, background matrix lacking  
484 obvious plant tissue cell structure. Whilst some of the paler grey regions are  
485 almost structureless, others have well-defined morphology. The single  
486 isolated rings may be derived from plant or fungal material such as isolated  
487 lignified walls of wood cells (separated after decomposition), fungal spores,  
488 pollen, or a mixture of all three. Multicellular fungal sclerotia are also present.  
489 There is no obvious multicellular plant tissue.  
490



491

492

493 Figure 6: Reflectance microscopy images from polished blocks under oil: a, b:

494 cannel coal; c, d: lignite; e, f: Whitby jet; g, h: bird/monkey carving.

495

496           The lignite sample (Figure 6c, d) appears to consist of a single piece  
497 (or organ) of only one type of multicellular plant tissue. This therefore differs  
498 from other lignites which can be formed from multiple types of multicellular  
499 plant tissues. The specimen is uniform throughout showing a repeated  
500 pattern of (i) discontinuous layers (left to right in image), a single cell thick,  
501 where cells have infills (very light grey) and (ii) multiple layers (darker grey) of  
502 varied cell sizes often without infills (black spaces). This is consistent with  
503 considerably decayed wood if the obvious layers with pale infill represent the  
504 parenchymatous rays and the woody xylem cells between have been both  
505 degraded and distorted due to compression with some still having open cell  
506 lumina.

507           Two fragments of Whitby jet were examined and both were extremely  
508 difficult to image or interpret owing to the minimal reflectance observed, which  
509 is typically characteristic of jet (Stach et al., 1982), combined with residual  
510 scratches from the polishing. Unlike the cannel coal sample, the jet  
511 specimens lack multiple distinctive components (such as spores or fungal  
512 sclerotia). The jet samples also do not show the very fine parallel laminations  
513 characteristic of the cannel coal sample.

514           Layering is clearly visible across parts of both jet specimens (Figure  
515 6e, f) – where one type of layer is visible as very pale discontinuous bands  
516 (oblique to the horizontal in the images). The very pale discontinuous bands  
517 (most obvious in Figure 6e) are consistent with strongly compressed former  
518 parenchymatous rays in wood (comparable to the interpretation of the lignite  
519 sample above (Figure 6c, d) as a single piece of wood). In the slightly darker  
520 grey bands, a few elongate oval spaces (interpreted as original cells) are  
521 visible at the microscope, some with infills. Most of the sample is compacted  
522 and appears structureless, i.e. any original cell lumina have been occluded  
523 completely.

524           The Pitch Lake solidified surface crust showed only uniform very dark  
525 material closely resembling its visual appearance in hand specimen. No  
526 physical features could be distinguished. This is completely different from the  
527 lignite, jet and cannel coal comparative samples.

528 Owing to the very small and thin sample (ca. 1 mm) that was available  
529 for the frog carving it was decided not to attempt embedding and polishing for  
530 reflectance microscopy.

531 The largest fragment of material collected from the bird/monkey carving  
532 measured a maximum of 4 mm by 3 mm, and was less than 2 mm thick.  
533 Despite the limited amount of material, a lot of detailed structure is visible  
534 showing multiple components in a very finely laminated sample (laminations  
535 slightly oblique to the vertical in the images; Figures 6g, h). Of the four  
536 comparative dark materials studied (cannel coal, lignite, Whitby jet and Pitch  
537 Lake crust), the bird/monkey sample most closely resembles the cannel coal,  
538 and is clearly not jet or Pitch Lake solidified surface crust.

539

### 540 3.2 FTIR

541 FTIR has the potential to distinguish between different geological  
542 source materials as the spectra reflect both the original plant material and any  
543 additional mineral phases present (Watts and Pollard, 1998). As each sample  
544 is comprised of a mixture of a wide range of organic compounds, individual  
545 peaks cannot be assigned to specific molecules or constituents, but the  
546 spectra can be used to distinguish between material types and to corroborate  
547 other techniques. This approach considers each recorded spectrum to be the  
548 signature of a given sample; generated by the superposition of the unique  
549 spectral contributions from each constituent.

550 The samples of Whitby jet, lignite and cannel coal were analysed both  
551 for comparison with previously published spectra (e.g. Hunter et al., 1993;  
552 Watts et al., 1997; Watts and Pollard, 1998), as well as the spectra of the two  
553 carvings, and the Pitch Lake crust and beach samples. However, natural  
554 variations between specimens of the same type are to be expected due to the  
555 heterogeneous nature of the materials and natural variations between (and  
556 within) deposits. As the lignite specimen appears to be formed from a single  
557 plant tissue (as observed by reflectance microscopy), the sample may be less  
558 heterogeneous than most other lignite specimens.

559 It should also be noted that the spectra presented in Fig 7a, while very  
560 similar to those of Watts and Pollard (1998) cannot be compared directly due  
561 to differences in the techniques used. Watts and Pollard (1998) analysed

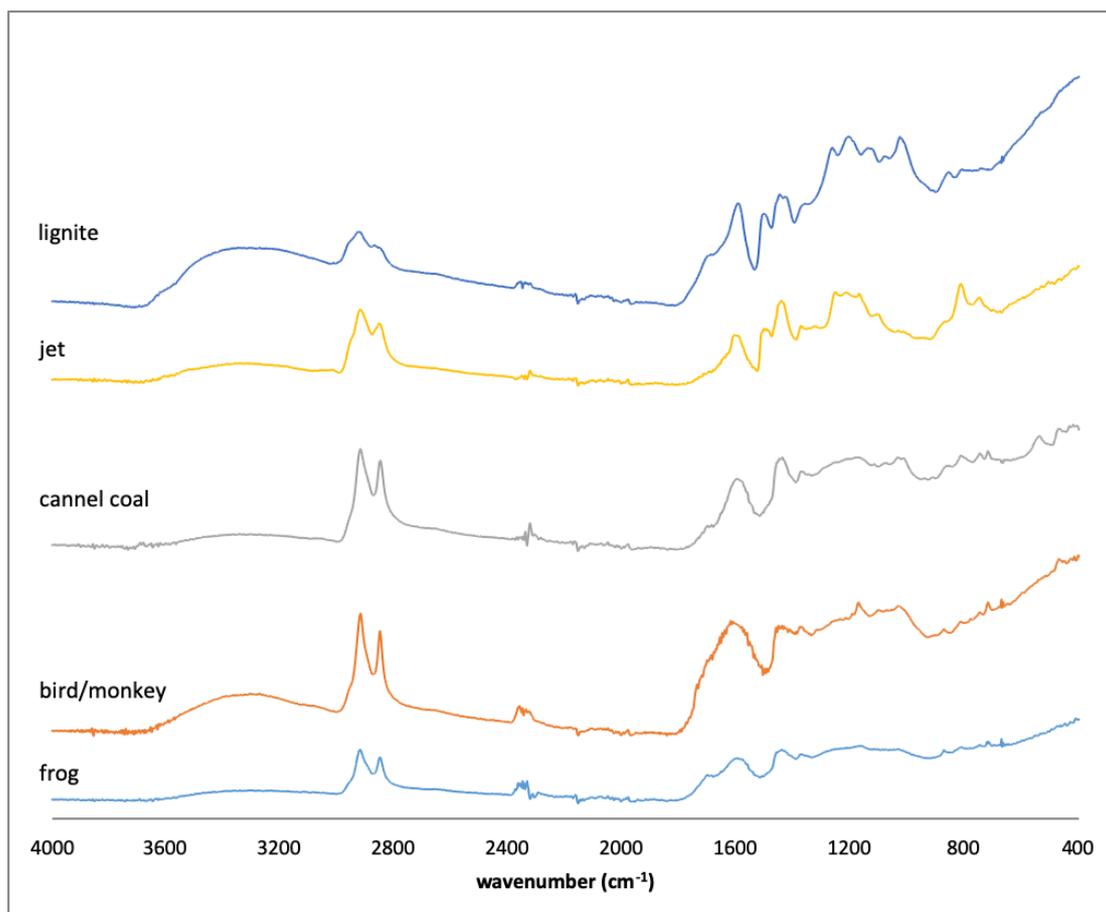
562 powdered samples pressed into KBr pellets and measured in transmission  
563 mode, while this study directly analysed small fragments or rough powders by  
564 ATR in absorbance mode.

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572 Figure 7a. FTIR spectra of lignite, Whitby jet, cannel coal, the bird/monkey  
573 carving and the frog carving.

574

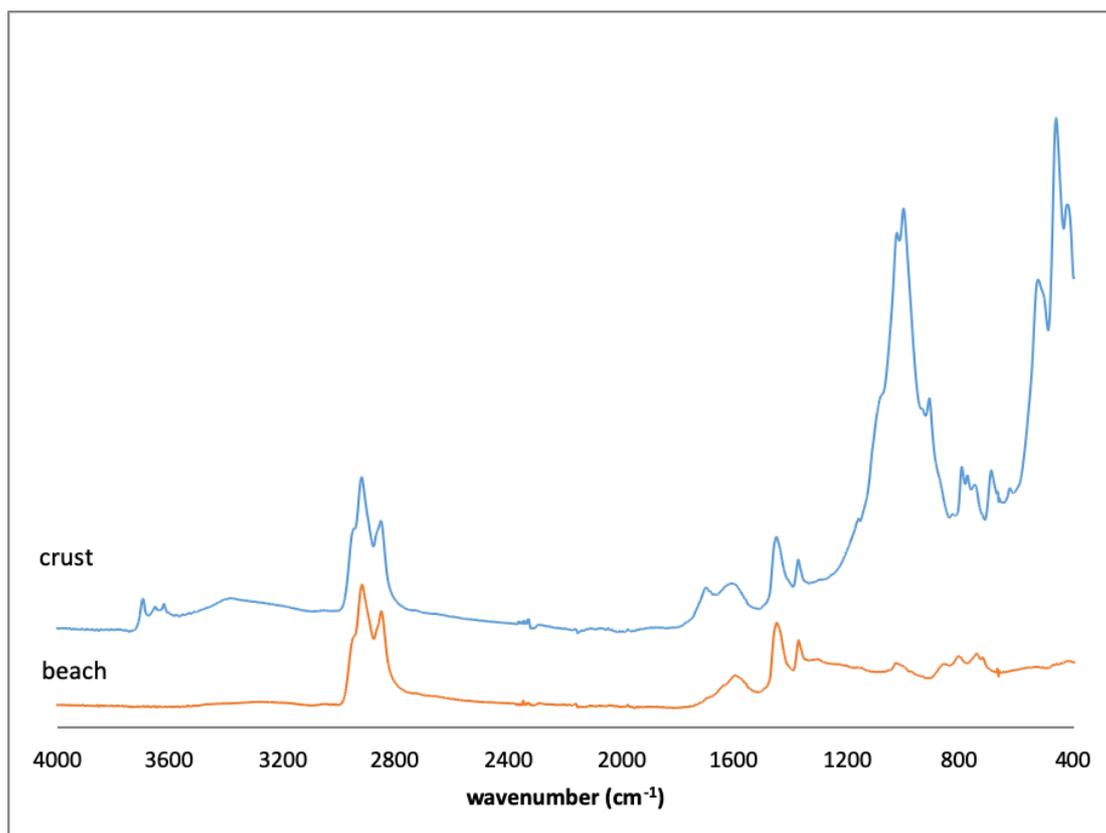
575 The spectra for Whitby jet, lignite and cannel coal (Fig 7a) are  
576 consistent with those published by Hunter et al. (1993) and Watts and Pollard  
577 (1998). The lignite and jet spectra both have a distinct aromatic C=C stretch  
578 at ca. 1500 cm<sup>-1</sup>, which has previously been recorded in the spectra of jets  
579 from Spain, the UK and USA, as well as ‘unusual’ coals (Iglesias et al., 1995;

580 Watts et al., 1997; Traverse and Kolvoord, 1968). This peak is not observed in  
581 most coal samples (Watts et al., 1997; Watts and Pollard, 1998) and is absent  
582 in the cannel coal sample in this study as well as both the bird/monkey and  
583 the frog carvings. There is great variation in the region of C-H deformation  
584 between 900-700  $\text{cm}^{-1}$  (Watts and Pollard, 1998); both the jet and lignite  
585 spectra are more distinctive in this region than the other geological materials,  
586 with jet having a sharp peak at ca. 850  $\text{cm}^{-1}$  absent in all other spectra.

587 In general, the spectra for both the bird/monkey and frog carvings can  
588 be considered to most closely resemble those of the cannel coal, although all  
589 3 of these spectra have small, but distinct, differences. The absorption for the  
590 frog sample is poor compared to the other samples, which may reflect poor  
591 sample contact during analysis. Poor contact between sample and sensor  
592 element is well-known to yield poor spectral response in ATR spectroscopy - it  
593 can be especially troublesome where the material is mechanically hard,  
594 because it is difficult to achieve good contact over a sufficiently large area.  
595 Whilst this can be mitigated by preparation of a fine dispersion by grinding or  
596 milling, care must be taken to avoid processing the material in ways that lead  
597 to structural or compositional changes that would intrinsically alter the spectral  
598 response. It is also vital that there is sufficient material present to ensure good  
599 contact. Analogous concerns apply over preparation of samples for  
600 transmission spectroscopy; any method that requires sample preparation  
601 and/or intimate contact should be used circumspectly.

602 The peak at ca. 1020  $\text{cm}^{-1}$  is most likely indicative of alumino-silicates  
603 (Watts and Pollard, 1998). This is seen to varying extents in all samples  
604 except the Whitby jet sample, but is most distinct in the Pitch Lake crust and  
605 lignite samples. Its presence in the cannel coal spectra is supported by the  
606 presence of high concentrations of kaolinite (hydrated aluminium silicate)  
607 measured in the same specimen by Hackley et al. (2005).

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613

614 Figure 7b. FTIR spectra of Pitch Lake crust material and Trinidad beach  
615 specimen.

616

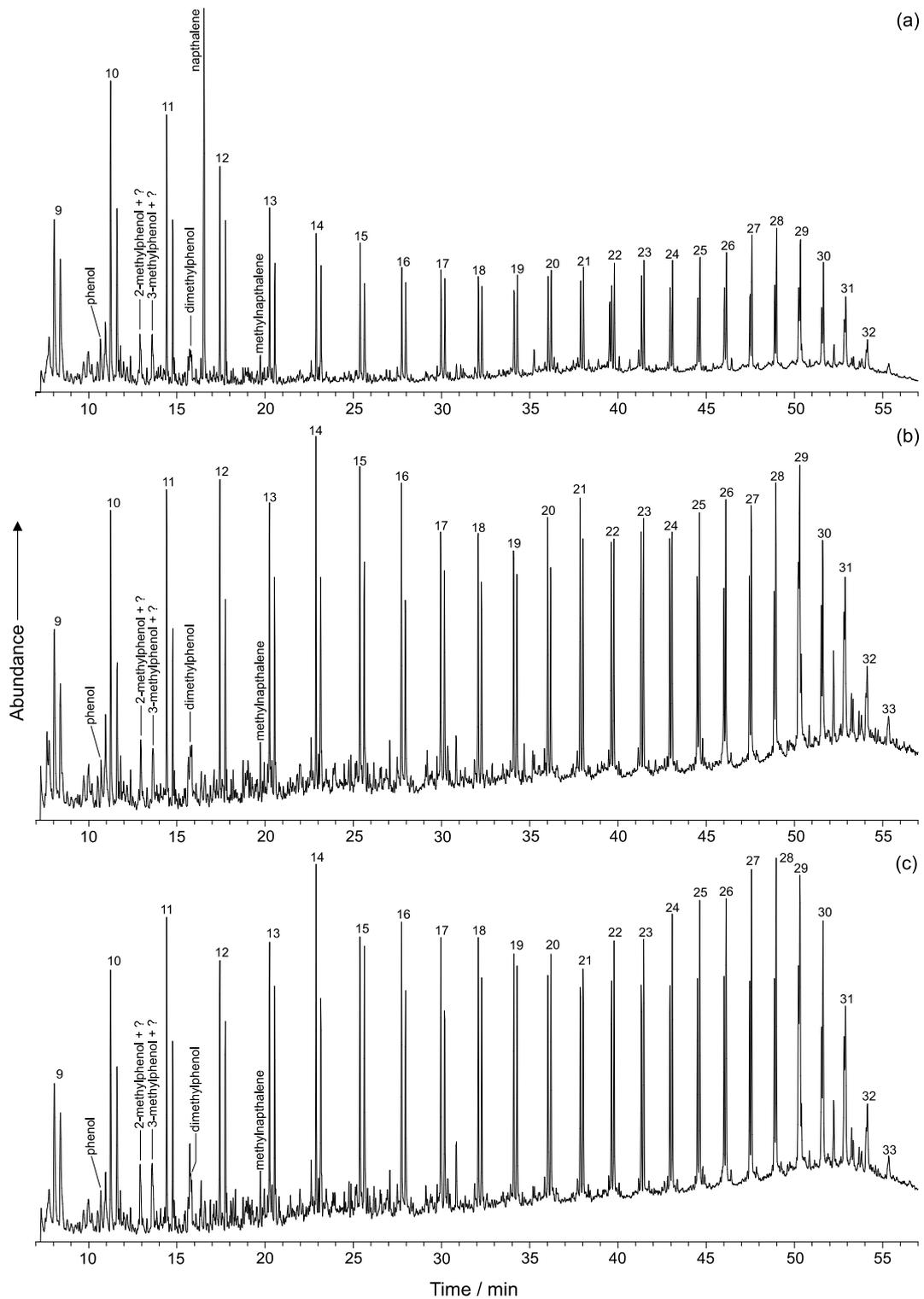
617 The Pitch Lake materials (Fig 7b) are considered separately from the  
618 other samples, as they are visually very distinct from the carvings and are  
619 thus unlikely to be from the same source. The spectra for the crust material  
620 demonstrate a very different mix of constituents from those of all other  
621 samples and the carvings, especially in the 1200 to 400  $\text{cm}^{-1}$  range, most  
622 likely due to higher mineral input, as well as fresh plant material. The  
623 spectrum of the beach specimen is similar to that of the crust in the 3000 to  
624 1300  $\text{cm}^{-1}$  range, but is otherwise distinctive.

625

### 626 3.3 Pyrolysis-GC/MS

627 Figure 8 depicts partial chromatograms for material taken from: (a) the  
628 bird/monkey carving, (b) the frog carving, and (c) cannel coal. All three  
629 chromatograms are dominated by a homologous series of *n*-alkene/*n*-alkane  
630 doublets, ranging in carbon chain-length from  $\text{C}_9$  to  $\text{C}_{33}$ , indicative of the

631 highly aliphatic nature of the materials analysed with little contribution from  
632 aromatic compounds, although low amounts of phenol, 2-methylphenol, 3-  
633 methylphenol, dimethylphenol and methyl naphthalene are present in each  
634 (as identified by comparison with Larter, 1984). The bird/monkey carving also  
635 exhibits a dominant peak which was identified as naphthalene.  
636



637

638 Figure 8: Partial chromatograms obtained by py-GC/MS analysis of: (a)  
 639 bird/monkey carving, (b) frog carving, and (c) cannel coal. Integers indicate  
 640 the carbon numbers of *n*-alkene/*n*-alkane doublets.

641

642           None of the distributions shows an odd-over-even predominance for  
643 the *n*-alkanes. The relative distributions of the *n*-alkene/*n*-alkane doublets for  
644 the frog carving and cannel coal are almost identical with roughly similar  
645 relative amounts of each homologue, barring the peripheral homologues (C<sub>9</sub>,  
646 C<sub>30</sub>-C<sub>31</sub>). In comparison, the low molecular weight homologues (C<sub>10</sub>-C<sub>13</sub>)  
647 observed for the bird/monkey carving dominated over the rest of the  
648 distribution. Previous work by Brock et al. (2017) reported distributions of *n*-  
649 alkene/*n*-alkane doublets observed in partial py-GC/MS chromatograms  
650 obtained for the solidified surface crust material collected from Pitch Lake,  
651 Trinidad. Whilst the homologous series described the same range (C<sub>9</sub> to C<sub>33</sub>),  
652 the distributions determined for the artefacts and cannel coal characterised in  
653 this study exhibit a far more uniform distribution across the range, indicative of  
654 a more terrigenous source of organic matter (Peters et al., 2005).

655           The py-GC/MS results obtained for the cannel coal are consistent with  
656 those obtained in previous work concerned with the provenance of  
657 archaeological artefacts made from various black lithic materials (Watts et al.,  
658 1999). However, the frog carving does not yield results that are consistent  
659 with those observed previously for samples of Whitby and Kimmeridge jet,  
660 lacking the predominance of phenolic over aliphatic moieties materials which  
661 characterises such materials (Watts et al., 1999). Moreover, the close match  
662 between the frog carving and the cannel coal py-GC/MS results strongly  
663 suggests that the carving is made from cannel coal (or some closely related  
664 material) rather than jet or lignite.

665           Whilst the elevated (relative to the whole distribution) low molecular  
666 weight *n*-alkanes (C<sub>10</sub>-C<sub>13</sub>) observable for the bird/monkey carving may  
667 indicate a different source material from that used for the frog carving, it is  
668 also possible that these homologues constitute the additional contamination  
669 associated with conservation treatments previously mentioned. Removal of  
670 them would result in a chromatogram more closely matching those of the frog  
671 carving and cannel coal indicating a similar origin. Similar to the frog carving,  
672 the bird/monkey carving was not manufactured from jet as the chromatogram  
673 does not show the predominance of phenolic over aliphatic moieties so  
674 characteristic of this material (Watts et al., 1999). The occurrence of  
675 naphthalene in the bird/monkey carving is not unsurprising as it is naturally

676 present in some coals, but concentrations may be artificially high due to the  
677 presence of pesticide residues remaining from historic treatments applied to  
678 the Pitt Rivers collection (Charlton et al., 2014).

679

### 680 3.4 X-ray fluorescence (XRF) spectrometry

#### 681 *3.4.1 Benchtop XRF*

682 Previous studies of European jet and similar materials suggested that  
683 XRF was capable of distinguishing between archaeological artefacts of jet,  
684 non-jet, and shale (Pollard et al., 1981; Hunter et al., 1993). These studies  
685 suggested that iron was the most discriminatory element, with very low levels  
686 associated with jet, and higher (but varying) levels in non-jets such as cannel  
687 coal and oil shale. However, more recently Sheridan (2015) reported higher  
688 iron levels in some jet relating to, for example, pyrite inclusions. Most shales  
689 also exhibit high levels of aluminium and silicon (Hunter et al., 1993), allowing  
690 for discrimination between shales and lignite (e.g. Gormley, 2017). However,  
691 natural heterogeneity, both within and between deposits, has been highlighted  
692 as an issue when using XRF data to link carved materials to original source  
693 material (e.g. Penton, 2008; Brassler, 2015).

694 XRF was applied in this study to investigate the variation between the  
695 samples, and to determine its suitability for further studies. Due to a lack of  
696 suitable standard material the data are presented semi-quantitatively (Table  
697 1) with the balance of each sample assumed to be carbon. Only elements  
698 with concentrations >0.1% are included. Figure 9 presents several of the XRF  
699 spectra measured, demonstrating the variation observed between the cannel  
700 coal, the Pitch Lake crust, and the bird/monkey carving.

701

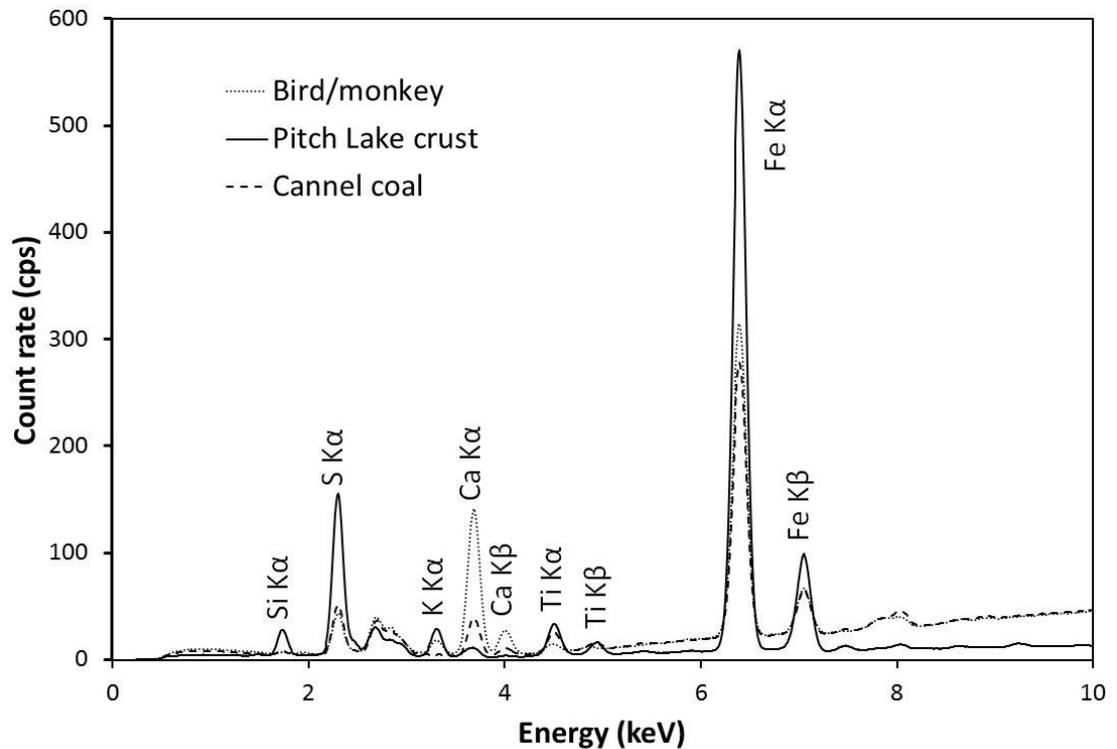
	<b>Fe</b>	<b>K</b>	<b>Ca</b>	<b>Si</b>	<b>S</b>	<b>Ti</b>
Cannel coal	0.21	0.00	0.22	0.69	1.73	0.06
Lignite	0.24	0.07	0.35	5.40	20.52	0.02
Whitby jet	0.89	0.46	0.15	2.20	13.70	1.88
Pitch Lake crust	1.35	0.63	0.11	4.98	8.75	0.21
Trinidad beach	0.11	0.06	0.01	0.59	11.47	0.01
Bird/monkey	0.33	0.12	0.83	0.52	1.41	0.02

Frog	0.17	0.05	3.34	0.70	1.82	0.03
------	------	------	------	------	------	------

702

703 Table 1: Element concentrations as determined by benchtop XRF (all values  
704 as weight percent).

705



706

707

708 Figure 9: XRF spectra of the bird/monkey carving, the Pitch Lake crust  
709 sample, and the cannel coal sample, highlighting the differences in elemental  
710 concentration.

711

712 Other elements were detected in trace amounts as follows: Cannel  
713 coal: nickel, copper; Lignite: arsenic, tungsten, germanium; Jet: vanadium,  
714 chromium, copper, nickel; Pitch Lake crust: nickel, copper, rubidium; Beach:  
715 vanadium, nickel, copper; bird/monkey: copper; frog: copper.

716

717

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719

720

Without a larger comparative dataset, it is difficult to draw a conclusion  
from the data, although some elements, such as copper and calcium, can be  
discarded immediately, having previously been found to be influenced by the  
burial environment of the artefact, rather than the original source material  
(Hunter et al., 1993).

721           However, the greatest variation was observed for sulphur, which is  
722 known to be naturally present in petroleum-based materials. The cannel coal  
723 sample and the two carvings both contained significantly less sulphur (<2%)  
724 than any of the other samples, although due to the aforementioned issues  
725 regarding sample heterogeneity, the data should be treated with caution when  
726 trying to identify the material type of either of the carved artefacts.

727           Variations were also observed for silicon, although at lower  
728 concentrations than sulphur, with concentrations highest for lignite and Pitch  
729 Lake crust material, and lowest for the cannel coal, beach material, and both  
730 carvings. Contrary to the findings of Pollard et al. (1981) and Hunter et al.  
731 (1993) that iron levels were lower in jet than other materials, the jet sample in  
732 this study had higher iron concentrations than all other samples, with the  
733 exception of the Pitch Lake crust.

734

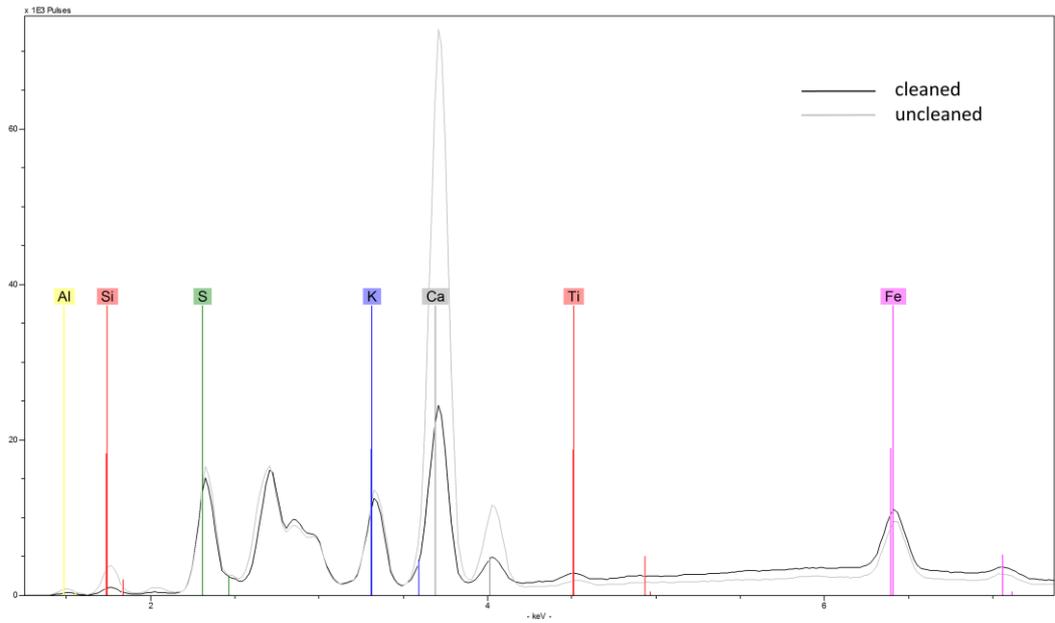
#### 735 *3.4.2 HH-XRF analysis*

736           Hand-held XRF is less sensitive than benchtop analysis, but was  
737 undertaken on the bird/monkey carving as a comparison to determine its  
738 suitability for analysis of artefacts without the need for destructive sampling.

739           Analysis of several spots on the bird/monkey carving detected a wide  
740 range of elements, including high counts for iron, sulphur, calcium, potassium  
741 and strontium, and low levels of aluminium, silicon, phosphorus, titanium,  
742 barium, copper, zinc, lead, rubidium, mercury and bromine (Fig. 10a,b). A  
743 small region of the same area of the artefact was then cleaned to remove any  
744 surface wax and other museum treatments, prior to re-analysis. The cleaning  
745 removed the mercury and bromine, and reduced the levels of lead, aluminium,  
746 phosphorus and calcium, the presence of which may be attributed to the  
747 application of pesticides to the museum collections (Charlton et al., 2014).

748

749



750

751

752 Figures 10a and b. Hand-held XRF spectra of cleaned and uncleaned areas  
753 of the bird/monkey carving highlighting the compositional differences between  
754 the surface and underlying material. *[Images to be reproduced in colour]*

755

756 This comparison of the two XRF techniques highlights the need for  
757 careful consideration of surface analysis where destructive analysis is not  
758 possible, as objects in collections may have either undergone conservation  
759 treatment themselves, or have been cross-contaminated, especially with

760 pesticide residues from historic treatments within ethnographic collections  
761 worldwide.

762

### 763 3.5 Composition and source of the bird/monkey and frog carving material

764 Comparison of fragments from both the bird/monkey and frog carvings  
765 with the five comparative specimens show them to be most similar to cannel  
766 coal. Furthermore, comparison of the FTIR and py-GC/MS data for the  
767 carvings with published data for other specimens of cannel coal, lignite and jet  
768 (Watts and Pollard, 1998; Watts et al., 1999), also supports the conclusion  
769 that these two carvings are most likely made from cannel coal (or similar) and  
770 confirms that they are not made of lignite or jet. Although both carvings  
771 appear very similar, it is not possible to confirm whether they are from the  
772 same source material, especially due to the presence of museum  
773 conservation treatments on the bird/monkey snuff tube.

774 Visual observations and comparison of both sulphur concentration (as  
775 detected by XRF) and the FTIR spectra of the carvings with the solidified  
776 surface crust material from Pitch Lake, suggest that it is unlikely that the frog  
777 carving is made of either pitch or gutta percha, as recorded in the museum's  
778 notes accompanying the object.

779 If both carvings are, as the data imply, made of cannel coal, it is highly  
780 likely that the source material originated in mainland South America, most  
781 likely Venezuela or Colombia, due to the lack of any coal in the Caribbean  
782 island chain. There were quite active trade networks spanning the Lesser  
783 Antillean region during the Early Ceramic Period, between AD 200-800 (e.g.  
784 Hofman et al., 2007; Figures 6-7), encompassing eastern Puerto Rico south  
785 to Trinidad, the latter the main entrepôt through which South American  
786 materials (and people) migrated north along the island chain. Barrancoid  
787 materials - inclusive of ceremonial artefacts, such as the St Vincent  
788 bird/monkey snuff tube – are understood to have spread from the mainland  
789 through to Trinidad and Tobago, perhaps as far as the southern Leewards  
790 between AD 300 and 650/700 (e.g., *ibid*: 252). As far as currently known, the  
791 distribution of the anthropo-/zoomorphic carvings, which appear at both  
792 Huecan (La Hueca, Puerto Rico) and Saladoid (Escape, St Vincent) sites,  
793 spans St Vincent north to Puerto Rico.

794

### 795 3.6. Analytical strategy

796 This study was undertaken to identify the most suitable techniques for  
797 identification of the carving material for similar Caribbean pre-Columbian  
798 carvings. The four complimentary analytical techniques applied here  
799 (reflectance microscopy, FTIR, py-GC/MS and XRF) were chosen to  
800 investigate the chemical composition and biological components of the  
801 samples based on previous studies of archaeological carvings in cannel coal,  
802 lignite and jet. FTIR and XRF were partly chosen due to the availability of  
803 hand-held instruments, which might allow for non-destructive analysis within  
804 museums and other collections in future studies.

805 All four techniques were informative, although the XRF data should be  
806 considered with caution based on sample heterogeneity within individual  
807 geological deposits. Both reflectance microscopy and py-GC/MS require  
808 destructive analysis, although this study demonstrated that they can both be  
809 applied to very small masses of sample. Reflectance microscopy can be  
810 undertaken on small samples, preferably with one dimension at least 2 mm  
811 thick to be readily embedded in resin and polished. The use of such small  
812 samples, however, reduces the available area on which to assess sample  
813 uniformity/variability. Powdered samples can also be studied using reflectance  
814 microscopy if necessary, but are more challenging and time-consuming to  
815 embed. Py-GC/MS requires only ~0.1 mg material for analysis.

816 Hand-held versions of FTIR and XRF are both available, which makes  
817 them appealing for analysis of samples on-site in museum collections, and for  
818 artefacts which cannot be sampled, but these portable instruments often lack  
819 the sensitivity of other techniques, and surface analysis has been shown in  
820 this study to be affected by the presence of museum conservation treatments.  
821 The benchtop FTIR utilised in this study required only 2-3 mg of material for  
822 analysis, which could usually be recovered afterwards and potentially  
823 submitted for py-GC/MS analysis.

824 If further analysis was to be undertaken on other similar Caribbean  
825 carvings, reflectance microscopy, py-GC/MS and FTIR should be considered  
826 together where destructive sampling is allowed, but undertaken alongside  
827 analysis of a considerably larger set of comparative geological specimens

828 from across the region, including neighbouring mainland South America.  
829 Although the two carvings studied here were demonstrated to be most like the  
830 cannel coal sample, the possibility that similar carvings from the region may  
831 be made from less well-characterised materials, such as those associated  
832 with Pitch Lake, cannot be excluded. A larger comparative dataset would also  
833 improve understanding of sample heterogeneity, and enhance the potential  
834 for grouping samples from the same geological source together based on  
835 their biological and chemical components.

836 While XRF is not the most suitable stand-alone technique for  
837 identifying these black lithic materials, concentrations of sulphur, and possibly  
838 also silicon, are worthy of further investigation, especially where non-  
839 destructive analysis is required. However, care must be taken to ensure that  
840 the presence of museum conservation treatments does not influence the  
841 analytical data.

842

#### 843 **4. Conclusions**

844 By comparison with specimens of cannel coal, lignite and jet, and two  
845 materials associated with Trinidad's Pitch Lake, as well as additional  
846 published data (e.g. Watts and Pollard, 1998; Watts et al., 1999) it is  
847 concluded that both the bird/monkey snuff tube and the frog carving found on  
848 the island of St Vincent are most likely to have been carved from cannel coal.  
849 Due to the lack of cannel coal deposits in the Caribbean islands, it is probable  
850 that these artefacts originated in mainland South America, possibly Venezuela  
851 or Colombia, and were traded northwards into the Lesser Antilles during the  
852 Early Ceramic Period. While it is currently not possible to conclude whether  
853 the two artefacts were carved from the same source material, the detailed  
854 interrogation of their structure is a critical first step in efforts to document the  
855 connections which linked communities within the insular Caribbean and  
856 neighbouring South America in an exchange of such ceremonial artefacts.

857

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