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1 Organic signatures of fireplaces: experimental references
2 for archaeological interpretations

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17

18 ABSTRACT

19 The use of fire is a well-established human practice, at least from the Late
20 Pleistocene. The variability in fuel type highlights complex practices
21 regarding fire technology throughout this period. This contribution provides
22 the organic signatures from fireplaces and is based on a set of experimental
23 studies using different types of fuel, notably bone and/or wood. Soil layers
24 affected by fire operation were compared with soils unaffected by heating
25 and soils impregnated with unburned bone fat. The carbon content, and
26 lipid and bulk organic matter (OM) composition were determined through

27 organic carbon measurement, gas chromatography-mass spectrometry (GC-
28 MS), as well as TMAH-assisted pyrolysis coupled to GC-MS.

29 With the exception of the wood-fueled fireplace, an increase in organic
30 carbon content was caused by fireplace operation. The products of
31 triacylglycerol degradation (diacids, oxo-acids, and glycerol derivatives)
32 reflected the contribution from animal fat affected by the oxidation process
33 with or without thermal alteration. The branched unsaturated C_{9:0} and C_{10:0}
34 acids were detected only in py(TMAH)-GC-MS of soil impregnated with bone
35 fat that was not thermally altered. The branched diacids, ketones, lactones
36 detected in lipid extract, and short chain acids and *n*-alkane/*n*-alkene
37 doublets detected in py(TMAH)-GC-MS, were produced by thermal
38 alteration of animal fat. Finally, in the fireplace fueled with wood only,
39 phenolic compounds, benzoic acids and benzene derivatives were detected
40 and reflected the contribution of charred and uncharred plant OM.

41 The results from lipid and bulk OM characterization permitted to advance
42 the organic signatures obtained as an experimental reference dataset
43 specifically for the identification of fuel type used in fireplaces.

44

45 **Highlights**

46 Bone fires lead to a significant increase in soil OC content, whereas no
47 variation was noticed for wood fire

48 Soil lipid and bulk OM distributions reflected the type of fuel used for
49 experimental fires

50 Characterization of soil lipids and bulk OM permitted identification of
51 byproducts of thermal alteration

52 Organic signatures from experimental fireplaces provide a reference for
53 archaeological applications.

54

55

Keywords

56 Fireplace, Prehistory, Experimental References, Organic signature, Soil

57 1. Introduction

58 The use of fire by hominins is a classic field of study within the prehistoric
59 discipline history and has provided a suite of publications, debates, and
60 controversies since the 19th century (see Roebroeks and Villa, 2011 and
61 Sandgathe et al., 2011 for recent examples). Dating the earliest fire use has been
62 a key question since the beginning of the discipline. Moreover, during the last few
63 decades an increase in interest regarding the study of fire related remains has
64 been observed, likely due to the fact that these remains represent both
65 technologically and sociologically significant shifts. The pyrotechnology of ancient
66 societies is most often investigated through several approaches, including
67 anthracology (Théry-Parisot, 2001), ash studies (Canti, 2003), taphonomy (Théry-
68 Parisot et al., 2010), ethnography (Henry and Théry-Parisot, 2014), magnetic
69 susceptibility (Bellomo, 1993), and micromorphology (Mentzer, 2012 and
70 references therein).

71 These studies have significantly improved our understanding of fireplace
72 operation (e.g. type of fuel, re-use and structure management) and proposed
73 several ethnographically-based models of utilization (e.g. specialized vs.
74 multipurpose, expedient vs. curated). However, direct interpretation of
75 archaeological vestiges remains difficult (Coudret et al., 1989) as archaeological
76 data are rarely explicit. The necessity for an experimental dataset, based on the
77 production and utilization of experimental fireplaces, thus seems apparent if we
78 wish to construct an interpretative tool for the deciphering of the archaeological
79 data.

80 Experimental investigations of prehistoric pyrotechnology are a well-established
81 trend in archaeological science; the production of reference databases is regularly
82 used to tackle taphonomic and functional questions (March et al., 2014; Mallol et
83 al., 2013 and references therein). Unfortunately, the numerous parameters
84 inherent in fireplace operation (e.g. type, state and quantity of fuel, type and
85 state of underlying sediment, operator intervention or not, extinction, re-use)
86 combined with the attempt to reconstruct different types of use (e.g. fireplace
87 morphology and layout, different cooking methods, different types of cooked

88 products) result in complex experimental data, within which it is often difficult to
89 isolate and characterize individual aspects (Aldeias et al. 2016). More specifically
90 these attempts to obtain reference collections rarely took into account the
91 thermal alteration of the organic matter (OM) in archaeological contexts.
92 Ultimately, databases from early experiments were rarely completely published
93 and this lack of documentation hampers our ability to move forward. We are thus
94 faced with the necessary task of systematizing, documenting, and publishing
95 these experimental approaches.

96 Regarding the investigation of OM in archaeological remains through chemical
97 methods, the exploration of prehistoric fireplaces is less advanced than other
98 domains of archaeological chemistry, the analysis of residues in pottery for
99 example (Evershed et al., 2001; Barnard and Eerkens, 2007; Evershed, 2008;
100 Steele, 2013; Reber et al., 2015). In these studies, the main objectives were to
101 recognize the content and use of the containers, despite the numerous processes
102 that might confound interpretation of the chemical data, such as complex ancient
103 practices, taphonomic modifications, or methodological issues (e.g. Reber and
104 Evershed, 2004; Barnard et al., 2007). Even though they provide methodological
105 and interpretative guidelines, results obtained from pottery analysis cannot be
106 directly transferred to fireplace studies due to the differences that are expected in
107 the archaeological context and then in the processes of organic residue formation
108 and preservation.

109 Concerning fireplace investigations, pioneering studies identified lipids in cave
110 fireplaces, using gas chromatography (GC) and thin-layer chromatography
111 (Rottländer, 1989). The latter recognized the presence of reindeer fat and horse
112 fat via comparison with actual reference sets, but he could not determine if their
113 presence was related to fireplace operation (e.g. fuel type) or their utilization (e.g.
114 cooking, animal carcass processing). With the spread of GC-mass spectrometry
115 (GC-MS) in the 1990s, studies in all aspects of archaeological chemistry
116 multiplied (Regert, 2011) and the study of fireplaces became more frequent (e.g.
117 March et al. 1989; March, 1995 ; Buonasera, 2005; Lucquin, 2007; Kedrowski et
118 al., 2009). More recent researches in the field also involved isotopic investigation

119 including bulk (e.g. Heron et al., 2010) and compound specific $\delta^{13}\text{C}$ analysis (e.g.
120 March, 2013; Buonasera et al., 2015).

121 These studies highlighted recurrent conservation of organic compounds in hearth
122 sediments, and attempted to associate them with their natural sources (e.g. plant
123 or animal, terrigenous or marine) even sometimes evoking their specific origin.
124 Moreover, recent studies (Regert, 2011; Kaal et al., 2014) mentioned and
125 illustrated the potential interest of pyrolysis-GC-MS, possibly performed with *in*
126 *situ* tetramethylammonium hydroxide derivatization [py(TMAH)-GC-MS], as a
127 tool for the characterization of archaeological OM in pottery. The technique
128 allows determination of the molecular composition of non-extractable OM, which
129 is often the case for thermally altered fireplace residues. It therefore provides a
130 good opportunity to document an OM fraction usually ignored in GC-MS based
131 studies of solvent extracts.

132 This study focuses on the type of fuel used to stoke fireplaces in Late Pleistocene
133 French open air sites. Most of the sites suffered post-depositional phenomena
134 that frequently destroyed the upper part of fire structures, and particularly their
135 fuel remains. As the resulting vestiges are limited mainly to mineral elements
136 showing thermal alteration (e.g. underlying sediment and surrounding stones),
137 their interpretation is challenging. In addition, the recurrent presence of burned
138 bones residues (i.e. from slightly charred to completely calcinated) within the
139 sites, but not always directly on fireplaces, raises the question of their frequent
140 use as a common fuel by Paleolithic societies (Perlès, 1977, Villa et al., 2002).
141 Despite experimental data ascertained the practicability of this use (Théry-
142 Parisot, 2001 and 2002; Théry-Parisot and Costamagno, 2005; Costamagno et al.,
143 2009), the interpretation of archaeological artefacts is still equivocal as numerous
144 others anthropogenic and natural processes can produce burned bones (see
145 Costamagno et al., 2009 for a review).

146 The objectives were thus to establish the geochemical signatures of fireplaces
147 fueled with different materials and to provide a reference dataset for further
148 interpretation of archaeological fireplaces. Experimental fireplaces were realized
149 using wood and/or bone as fuel and compared with the soil layer unaffected by

150 human practices. The role of the thermal alteration of OM was also tested by
151 analyzing the chemical signature of the soil layer impregnated with unburned
152 animal fat. The chemical composition was determined through organic carbon
153 content (C_{org}) measurement, GC-MS analysis of the lipid extract and py(TMAH)-
154 GC-MS of the bulk OM.

155 **2. Experimental**

156 *2.1. Study site and sampling*

157 The study was conducted on the aurignacian site of Régismont-le-Haut (ca. 30 Ky
158 BP, southern France; Pradeau et al., 2014) where an experimental protocol has
159 been in place since 2012. The site is at the base of a strongly eroded Miocene
160 calcareous hill, which provides most of the colluvial and aeolian deposits forming
161 the sediment under study. During the Late Pleistocene, these colluvial and
162 aeolian sediments slowly infilled paleochannels carved into the underlying
163 marlstone. This context and the relatively arid climatic conditions led to the
164 formation of a colluvic and calcaric Regosol (IUSS Working Group WRB, 2015;
165 *Colluviosol calcaire et carbonaté*: AFES, 2008), with few pedogenic features
166 except those linked to the dissolution and precipitation of $CaCO_3$.

167 Experimental fires were set up to mimic several contexts of hypothetical
168 archaeological operation; the main parameter that was varied was fuel type
169 (wood and/or bone). To emulate the context of archaeological fireplaces and avoid
170 modern agricultural induced bias, the experiment was run in realistic open air
171 conditions on a sterile area of the excavated archaeological level, ca. 50 cm under
172 the plow zone. All experiments and subsequent sampling occurred between
173 August 27th and September 11th, 2012. No significant precipitation was recorded
174 on site during this interval; the local meteorological station of Sètes recorded a
175 mean maximal temperature of 28.6 °C in August and of 23.8 °C in September and
176 a mean minimal temperature of 21.5 °C in August and of 17.6 °C in September.
177 Prior to the experiment a sample of unaffected sediment was collected as a
178 control for the natural organic content and composition in the area (*Control*).

179 Experiments involved the use of bone and/or pine wood of local origin. The former
180 consisted of up to 15 cm fragments of steer long bones and pelvic bones (*Bos*

181 *taurus*). The wood included parasol pine (*Pinus pinea*) dry twigs, small branches
182 and 50 cm long and up to 10 cm in diameter logs. For the first experiment, 10 kg
183 of fragmented steer bones were deposited on the surface of the soil in order to
184 imitate OM impregnation by way of percolation through the sediment. A sample
185 (*Soil with bone OM*) was collected after a week. The second experiment was with
186 a bone-fueled fireplace (*Bone fire*) in which 10 kg of fragmented steer bones were
187 burned. It is noteworthy that a small quantity of pine wood (< 1 kg) was
188 necessary to initiate combustion in this type of hearth (Théry-Parisot and
189 Costamagno, 2005). It operated during 131 min. The third experiment was with a
190 wood-fueled fireplace (*Wood fire*), in which 5 kg of dry pine wood were burned
191 during a total operating time of 137 min. Finally, the last experimental fire
192 involved the use of both 5 kg of pine wood and 3 kg of bone (*Wood+bone fire*), to
193 emulate a mixed-fuel fireplace. The total operating time was of 118 min.

194 For the 4 experiments, sampling was conducted following visual distinction of
195 layers (Fig. 1a). Sampling first concerned the altered soil (Upper sub sample,
196 Table 1) but also the underlying and seemingly unaltered soil (Lower sub sample,
197 Table 1). The micro-local organic content was measured to test the significance of
198 the visual layer distinction.

199 Samples were air-dried over two days at 35 °C (Froilabo-AC120 oven). After
200 manual removing of the most fragile coarse elements (calcitic nodules and
201 organic macroscopic remains such as roots), samples were sieved and the > 2 mm
202 fraction was discard. Samples were then ground with a mortar and pestle, and
203 eventually with a Retsch-PM200 planetary ball mill (6 min, at 450 rpm), to pass
204 a 250 µm sieve.

205 2.2. *C_{org} measurement*

206 Due to the naturally high carbonate content of the sediment, acid fumigation was
207 carried out prior to elemental analysis, following Harris et al. (2001). After
208 weighing the samples in Ag foil capsules, they were humidified (15 µl deionized
209 water) and placed in a desiccator under vacuum, with a beaker of HCl (12 M),
210 during 6 h. Lastly, the sample was air-dried for 12 h at 40 °C.

211 The C_{org} was measured on fumigated samples using an elemental analyzer (Vario
212 PYRO cube, Elementar). To allow C_{org} quantification, two Ag capsules of the
213 same sample were added for a single analysis. The resulting reproducibility was
214 assessed to be between 0.3% (instrumental) and 0.8% (methodological).

215 *2.3. Lipid extraction and GC-MS*

216 Samples for lipid analysis were extracted using an accelerated solvent extractor
217 system (Dionex-ASE100). Between 5 and 7 g of sediment were placed in a 10 ml
218 Inox cell topped with sterile glass fiber. The extraction program ran at 60 °C,
219 with a static time of 20 min, using dichloromethane/methanol (DCM/MeOH) (2:1,
220 v/v). The extract was concentrated using a rotary evaporator and dried under a
221 gentle N₂ flow, dissolved in DCM in a 1,5 ml vial with a PTFE screw cap and
222 stored at 4 °C until analysis (adapted from Quénéa et al., 2012)

223 Each extract was analyzed with an Agilent 6890 gas chromatograph coupled to
224 an Agilent 5973N mass spectrometer using electron ionization at 70 eV. The GC
225 instrument was equipped with a 30 m Restek 5 Sil MS column (i.d. 0.25 mm, film
226 thickness 0.5 µm). The carrier gas was He, at a constant flow rate of 1 ml/min.
227 Samples were injected splitless with the injector at 300 °C. The oven temperature
228 was programmed from 80 °C (0.5 min) to 100 °C at 10 °C/min then to 320 °C at 4
229 °C/min. Compound assignment was based on comparison with published data
230 (references thereafter in the text) and the NIST mass spectral library.

231 The whole device was operated with a Gerstel multipurpose sampler (MPS) and
232 Gerstel Maestro software. The workflow included derivatization of extracts by
233 adding 10% (v/v) BSTFA [N,O-bis(trimethylsilyl)trifluoroacetamide] and heating
234 at 60 °C for 10 min to obtain trimethylsilylated (TMS) derivatives.

235 *2.4. py(TMAH)-GC-MS*

236 Bulk OM from the upper subsample was characterized through Curie-Point
237 pyrolysis (Pilodist) coupled to a GC (Thermo Trace – 30 m RXI 5 Sil MS capillary
238 column, i.d. 0.25 mm, film thickness 0.5 µm with Integra guard column) and a
239 MS (DSQ). Samples mixed with TMAH (25% w/v in MeOH) were loaded in a
240 ferromagnetic tube and pyrolyzed for 9.9 s at 650 °C under a 1 ml/min He flow

241 (adapted from Quénéa et al., 2005). The pyrolysis products were separated in the
242 GC system, where the temperature of the GC oven was held at 50 °C for 10 min,
243 before an increase at 2 °C/min to 310 °C. The ion source of the mass spectrometer
244 was at 220 °C, which was set to scan from m/z 35 to 800. The total ion current
245 (TIC) trace was recorded and products of pyrolysis identified using comparison
246 with published data (references thereafter in the text) and the mass spectral
247 NIST library.

248 **3. Results and discussion**

249 *3.1. Macroscopic features and C_{org} variations*

250 The *Control* displayed general features illustrative of the local soil type: a
251 homogenous sandy loam with numerous calcitic features and few organic macro-
252 elements (Table 1). An expected low C_{org} (0.3%) was measured and was consistent
253 with that of the four lower subsamples ($0.3 \pm 0.1\%$) collected below each
254 experimental structures. This result validated the visual identification of fire-
255 affected soil layers and supported the low soil variability needed to track
256 variables influenced by the experimental parameters.

257 On the contrary, most of the experiments led to an increase in the organic
258 content of upper subsamples (Table 1). In the *Soil with bone OM*, a 2 cm deep
259 impregnation of the sediment was observed on the surface (Fig. 1b) and in
260 section. During the experiment, OM (likely bone marrow) leaked from the bone
261 fragments and was responsible for the impregnation, as well as the increase in
262 C_{org} , which reached 4.7%. The macroscopic visual aspects of the *Bone fire*
263 consisted of an irregular shaped darkened and hardened hearth covered with
264 carbonized to calcinated bones. Vertically, the sediment was affected by the
265 combustion down to 4 cm depth, displaying darkening and reddening. During the
266 operation, a significant leakage of organic fluid was observed around the
267 structure (Fig. 1c) and was also noted vertically on the structure's periphery. The
268 leakage resulted in a slightly lower increase of C_{org} (2.3%) than for the *Soil with*
269 *bone OM*. The phenomenon can likely be explained by a shorter interaction time
270 between the soil and the bone OM, as well as the combustion process that likely
271 degraded part of the bone marrow, thereby limiting its influence on C_{org} . The

272 operation of the *Wood fire* resulted in a circular (ca. 50 cm diam.) collection of ash
273 and charcoal overlying a reddened sediment (Fig. 1e). This reddening was 0.5 to
274 1.5 cm deep. No significant difference was detected in the C_{org} of this reddened
275 sediment compared with the *Control*, likely because the coarse fraction, which
276 may have included some combustion residue, was discarded during sample
277 collection and preparation. The results of the *Wood+bone fire* experiment were,
278 unsurprisingly, intermediate between those from other experimental fireplaces.
279 A superficial covering, consisting logically of a mix of wood and bone combustion
280 residue, capped the structure (Fig. 1d). Vertically, the structure displayed a 1 to
281 2.5 cm deep reddening, whose first 1 cm was heavily influenced by the
282 combustion residues, leaving a darkened layer whose reddened nature was not
283 visible to the naked eye (Table 1). Despite the C_{org} (0.9%) did not prove to be
284 significantly higher than the C_{org} of the *Wood fire* (or *Control*), the value was
285 intermediate between the *Wood Fire* and the *Bone fire*, what seemed coherent
286 with the field observation of a lower input of bone OM due to 1) a lower quantity
287 of bone used as fuel and 2) the formation of wood embers that might have
288 prevented OM leakage into the soil by increasing the efficiency of combustion.

289 3.2. Local organic background

290 In accord with its low C_{org} , the *Control* did not present any detectable component
291 from py(TMAH)-GC-MS analysis. No phenol, lignin-derived components, or long
292 chain alkanes/alkenes and acids, traditionally seen in the pyrolysis products of
293 natural soil OM (Hempfling and Schulten, 1990), were visible in the
294 archaeological soil layer. Lipids detected from GC-MS were diverse, yet present
295 in such low concentration as to render them negligible. The identification of such
296 a diversified lipid fraction was made possible through a higher concentration of
297 sample during preparation. The absence of a significant organic signal confirmed
298 its suitability as a control for the experiments that followed.

299 3.3. Sources of organic compounds

300 3.3.1. Non-diagnostic

301 The saturated *n*-acids from $C_{6:0}$ to $C_{18:0}$, dominated by $C_{16:0}$ and $C_{18:0}$, and
302 monomethylated acids, were ubiquitous in both lipid extracts and

303 thermochemolysis products (Figs. 2 and 3, Tables 2 and 3). Their presence in all
304 the samples might reflect animal, plant and microbial biomass origins.
305 Nevertheless, the C chain distribution appeared more specific, especially the high
306 relative proportion of short-chain fatty acids in *Soil with bone OM*, and is
307 discussed later.

308 Due to its widespread occurrence in animal tissue (Christie, 2014) cholesterol can
309 be considered as an indicator of an animal contribution to lipid extracts, but a
310 fungal or even bacterial origin cannot be completely excluded (Huang and
311 Meinschein, 1976; Volkman, 2005; Christie, 2014). These last two elements were
312 likely the source of cholesterol [25] in the *Control* (Fig. 2a) and the *Wood fire* (Fig.
313 2e).

314 The significant contribution of Me-C₁₅ and Me-C₁₇ acids (iso and anteiso) to the
315 lipids and py(TMAH)-GC-MS trace of the *Soil with bone OM* (Figs. 2b and 3a),
316 the *Bone fire* (Figs. 2c and 3b) and the *Wood+bone fire* (Figs. 2d and 3c), might
317 point to a fungal and bacterial OM signature (Saiz-Jimenez and De Leeuw, 1986;
318 Dudd et al., 1998; Kanthilatha et al., 2014; Spangenberg et al., 2014). However
319 those branched acids can also be produced by bacteria in ruminant intestines
320 (Dudd et al., 1999; Christie, 2014) and an animal origin can not be ruled out in
321 the context of these experiments.

322 The presence of squalene [24], a precursor of numerous sterols, might have a
323 natural origin in the extract of the *Control* (Fig. 2a) and the *Wood fire* (Fig. 2e).
324 However, it is also a broadly-used plasticizer, so in-situ or handling
325 contamination could not be totally dismissed (Evershed, 1993; Heron et al.,
326 2010).

327 3.3.2. *Plant OM*

328 The presence of stigmasterol [26] and sitosterol [28], both common phytosterols
329 (Huang and Meinschein, 1976), and of taraxerone [27], α -amyrone [29], and
330 lupenone [30] in the extract of the *Control* (Fig. 2a) point to a significant
331 contribution from plant OM (Vilegas et al., 1997; Mathe et al., 2004; Simoneit,
332 2005; Hernández-chávez et al., 2012). The contribution of aliphatic compounds

333 with relatively long chains is commonly considered to reflect a plant-derived OM
334 origin. In the extract of the *Control* (Fig. 2a) and *Wood fire* (Fig. 2e), the *n*-
335 alkanes (C₂₁, C₂₉, C₃₁ and C₃₃) might be attributed to an plant epicuticular wax
336 origin (Spangenberg et al., 2014), whereas *n*-alcohols longer than C₁₇, and
337 saturated *n*-acids longer than C₁₈, support the assignment of slightly altered
338 plant derived compounds (Evershed et al., 1999; Poirier et al., 2005). Finally,
339 phenol derivatives [4 and 8] and benzoic acids [1 and 3] in the *Wood+bone fire*
340 (Fig. 2d) and the *Wood fire* lipids (Fig. 2e) highlight byproducts of lignin
341 degradation (Simoneit et al., 1993; Quenea et al., 2004; Simoneit, 2005; Regert et
342 al., 2006; Shadkami and Helleur, 2010).

343 As the phenolic and benzoic compounds were only recovered in *Wood+bone fire*
344 and *Wood fire* (Table 4), they may be illustrative of the contribution of the wood
345 OM used as fuel to the organic signatures of these experiments (March et al.,
346 2014).

347 3.3.3. *Thermally-altered plant OM*

348 Aromatic compounds such as benzene derivatives ([5] to [10]) in the py(TMAH)-
349 GC-MS trace of the *Wood+bone fire* (Fig. 3c) and the *Wood fire* (Fig. 3d), as well
350 as naphthalene [10] in the extract of the *Wood fire* (Fig. 2e), reflect a high degree
351 of OM carbonization (Simoneit et al., 1993; Knicker et al., 2005; Kaal et al., 2009;
352 Alexis et al., 2012; De la Rosa et al., 2012). This type of compounds could also
353 result from artefact production by Curie point pyrolysis from carbohydrates, as
354 observed by Pastorova et al. (1994). However it is noteworthy that in the present
355 study, the benzene and naphthalene derivatives were only detected in the
356 experiments involving wood as dominant fuel and that the numerous furan and
357 pyranone derivatives expected in cellulose pyrolysis were not detected (Table 4).
358 This result suggests that they likely come from carbonized wood residues.
359 Moreover the absence of odd C chain predominance in the alkane series in the
360 *Wood fire* extract (Fig. 2e) could also be indicative of the thermal alteration
361 process of wood fuel OM (Eglinton and Calvin, 1967; Wiesenberg et al., 2009; De
362 la Rosa et al., 2012; March et al., 2014).

363 Many of these compounds were readily documented in GC-MS and py-GC-MS
364 studies of forest fire sediments (e.g. Knicker et al., 2005). Their observation in
365 fireplace context validates the crossing of results between these close fields of
366 research. Finally, their association in wood fueled fires with compounds specific
367 of uncharred wood OM (Table 4) provides a good overall signature for this type of
368 fire operation.

369 3.3.4. Bone OM

370 In the *Soil with bone OM* and the *Bone fire*, the dimethoxypropanol [1],
371 trimethoxypropane [2], saturated and unsaturated *n*-acids, diacids, epoxy- [13],
372 and (di)hydroxyacids ([12] and [14] to [17]) were detected from py(TMAH)-GC-MS
373 (Figs. 3a and b). Monoacylglycerol [15, 17, 19 to 23] and diacylglycerol [31 and 32]
374 were observed in the extract (Figs. 2b and c). These compounds likely resulted
375 from triacylglycerol degradation (Dudd et al., 1998; Evershed et al., 2002; Van
376 Den Berg et al., 2002). They could originate from plant (Van Den Berg et al.,
377 2002; Maher and Bressler, 2007) or animal fats (Evershed et al., 2002; Ben
378 Hassen-Trabelsi et al., 2014). However, the presence of *n*-acid C_{18:1}, one of the
379 most important *n*-acid in animal fat (Malainey et al., 1999; Nieuwenhuysen et al.,
380 2015), points to the latter origin. Moreover, several compounds likely reflect the
381 contribution of fat degraded by hydrolysis or oxidation. The short chain *n*-acids
382 (C₈ and C₉) and monomethyl branched unsaturated acids (Me-C₉ and Me-C₁₀) in
383 the py(TMAH)-GC-MS products (Figs. 3a and b), as well as the short chain
384 diacids (C₄ to C₁₁) and *n*-acid (C₈ and C₉) in the lipid extract (Figs. 2b and c),
385 could originate from drying and/or oxidation of unsaturated *n*-acids (Wexler,
386 1964; Mills, 1966; Erhardt, 1998; Van Den Berg et al., 2002; Rontani and Aubert,
387 2008).

388 These compounds were all present in the *Soil with bone OM* and occasionally
389 present in *Bone fire* and *Wood+bone fire* (Table 4). Those results were in
390 accordance with existing references on animal fat (e.g. Evershed et al., 2002),
391 despite short-chain methyl branched acids have been rarely described in such
392 context. Moreover, the functioning of the fire seems to induce an important
393 reduction of the number of recovered diagnostic compounds.

395 In the py(TMAH)-GC-MS TIC traces of the *Bone fire* (Fig. 3b) and of the
396 *Wood+bone fire* (Fig. 3c), the short chain *n*-alkane/*n*-alkene doublets could be
397 related to thermal degradation processes (Almendros et al., 1988; Nawar, 1989;
398 Simoneit, 2002; Eckmeier and Wiesenberg, 2009; Wiesenberg et al., 2009). In the
399 extract of the same samples (Figs. 2c and d), the series of short chain
400 monomethyl branched diacids (C₄ to C₁₀), short chain *n*-alcohols (< C₁₇), oxoacids,
401 as well as ketones (C₁₄ to C₁₇ and C_{29, 31, 33} and ₃₅) and lactones [13 and 14] were
402 also common markers of, more specifically, animal OM thermal degradation
403 (Nawar, 1989; Evershed et al., 2002). Ketones and γ -lactones are frequently
404 reported in thermally altered OM and are usually attributed to animal-fat and
405 meat degradation by heating (Nawar, 1969; Evershed et al., 1995). In this
406 context, the triacylglycerols and *n*-acids are both sources of the long chain
407 ketones, whereas short chain methyl ketones are considered to be secondary
408 products formed during more intense heating. Besides, the γ -lactones are formed
409 by cyclisation of hydroxyacids following dehydration upon thermal stress (Nawar,
410 1969). The disappearance of 10, ω -dihydroxyoctanoic acid [16], in parallel with the
411 formation of γ -lactones [13 and 14] in *Bone fire* (Fig. 2c) compared with *Soil with*
412 *bone OM* (Fig. 2b) might be illustrative of this process.

413 The *Bone fire* and *Wood+bone fire* provide a signature specific to the use of bone
414 as fuel (Table 4). It is characterized by markers of animal fat heating, resulting
415 from the melting and the burning of marrow initially contained in the bones. Yet,
416 it is noteworthy that, to our knowledge, the formation of short monomethyl
417 branched diacids (C₄ to C₁₀), short chain *n*-alcohols (< C₁₇) and oxoacids is little
418 known in this context.

419 3.4. Archaeological implications

420 In order to apply this reference dataset to archaeological contexts, the recovery of
421 previously identified organic signatures has to be questioned. As stated by March
422 et al. (2014), post-depositional processes may occur, namely the potential
423 pollution through input of more recent OM and the degradation processes that
424 likely affect the archaeological organic residues.

425 First, the pollution issue regards both natural and anthropogenic agents. Natural
426 ones are mostly linked to sedimentary covering of archaeological site and
427 pedogenic processes such as bioturbation and are unavoidable. Additionally, this
428 type of pollution will most likely correspond to vegetal OM lacking thermal
429 alteration byproducts and displaying a weak maturity allowing its recognition
430 (March et al. 2014). Anthropogenic pollution can be related either to agricultural
431 practices or to contamination related to archaeological excavation and sampling.
432 As for agricultural input, markers are generally well known and easily
433 identifiable. They may correspond to modern practices (chemical fertilized),
434 which will not interfere with our compounds of interest, and to manuring (like
435 coprostanol; Evershed et al., 2001). However, conjoint collection of control
436 samples both in stratigraphy and planimetry allows definition of the local soil
437 organic background (e.g. Heron et al., 1991).

438 Secondly, the ability of the signatures to be preserved over time is uncertain.
439 Except from the work of March et al. (2014), this central matter has been rarely
440 explored in the specific case of fireplaces, despite substantial documentation
441 exists in the field of the aging of fire affected soil OM (e.g. Knicker, 2011) and
442 organic residues in pottery (e.g. Malainey, 2007). Labile compounds such as
443 unsaturated *n*-acids or short-chain saturated *n*-acids are unlikely to survive long
444 period of time (Eglinton et al., 1991). In contrary, due to their relative
445 recalcitrance, aromatic compounds originating from lignin (benzoic acids,
446 phenols) and from charring processes (benzene and naphthalene derivatives) are
447 expected to remain in soil at long timescale (Baldock et al., 2004; Lützow et al.,
448 2006; Marschner et al., 2008). Lipids were also reported to present decreasing
449 stability following the order: alkanes, alkanones, sterols, *n*-alkanoic acids
450 (especially > C₂₀), *n*-alkanols and *n*-alkenoic acids (Cranwell, 1981). Based on this
451 chemical property, among previously identified signatures the best candidates for
452 recovery after millennia are 1) ketones and *n*-alkane/*n*-alkene doublets for *Bone*
453 *fire*, 2) saturated *n*-acids longer than C₁₈, benzoic acids, ketones, benzene
454 derivatives and *n*-alkane/*n*-alkene doublets for *Wood and bone fire* and 3)
455 saturated *n*-acids longer than C₁₈, *n*-alkanes, benzoic acids, phenolic compounds

456 and benzene derivatives for *Wood fire*, whereas no compound is expected to
457 remain in *Soil with bone OM* (Table 4).

458 Nevertheless, the relevance of recalcitrance alone to predict the residence time of
459 compounds has been widely discussed (Marschner et al., 2008; Bol et al., 2009;
460 Kleber et al., 2011). Rather, the spatial inaccessibility or the organo-mineral
461 interactions seem determinant for preservation at long timescale or in subsoil
462 horizon (Lützow et al., 2006). More specifically, in calcareous soils like at
463 Régismont-le-Haut, the high polyvalent cation content may induce the formation
464 of cation bridges, leading to stabilization of organic residues (Lützow et al., 2006;
465 Grünewald et al., 2006). However, no effect of CaCO₃ and pH on mineralization
466 could be observed by Bertrand et al. (2007), questioning the significance of this
467 stabilization mechanism. In this fireplace context, the association with charcoal
468 might also limit the decomposition (Hernandez-Soriano et al., 2016), in this case,
469 mainly through physical protection. Finally, as the substrate limitation can be
470 considered as the main contributing factor of organic matter stabilization in deep
471 soil horizons (Marschner et al., 2008), burial underwent by archaeological level
472 could then have favored various compound preservation. For example, in
473 prehistoric contexts, diacids were documented through GC-MS, in addition to
474 long chain ketones and γ -lactones in Pincevent site fireplace sediments and
475 heated stones (ca. 14 Ky cal. BP, Lucquin, 2007). Short chain diacids were also
476 mentioned in the GC-MS study of sediments related to thermal fat processing in
477 Alaska (ca. 5 Ky BP, Buonasera et al. 2015). In the same geographical context,
478 the study of sediments from fireplaces (ca. 14 Ky cal. BP, Kedrowsky et al. 2009)
479 illustrated the preservation of several branched *n*-acids interpreted as resulting
480 from lipid degradation by bacteria or from ruminant fat. The recovery of
481 compounds similar to those detected in this work, but with various intrinsic
482 recalcitrance, could illustrate the importance of physical conditions for the record
483 of organic signatures.

484 **4. Conclusion**

485 This study provides the organic signature of different experimental fireplaces and
486 demonstrates that they allow distinguishing if bone and/or wood were used as

487 fuel. It confirms that the thermal alteration of OM significantly modifies the
488 initial signature of the unburned material, limiting the direct use of markers
489 from unaltered sources to reconstruct fuel nature in archaeological fireplaces. In
490 contrary, several byproducts of thermal degradation can serve as indicators of
491 fuel type and, in this respect, the use of Py(TMAH)-GC-MS for the identification
492 of non-extractable compounds proved particularly adapted. However, because of
493 the variable organic components that constituted the organic signatures of the
494 fireplaces, their differential preservation has to be expected. Their intrinsic
495 recalcitrance, as well as the local environment and depositional context, might
496 influence the recovery of the chemical signatures under investigation.
497 Consequently, when applying this type of reference dataset to archaeological
498 samples, which likely underwent substantial post-depositional processes, caution
499 is needed. Nevertheless, as many identified compounds were found within non-
500 extractable or recalcitrant OM fraction in our study, and subject to the collection
501 of control samples, the reconstruction of archaeological interpretable signatures
502 based on this referential dataset seems possible.

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Table 1

Sample description, experimental parameters and organic carbon content (C_{org}) of upper subsamples (visually-identified as affected by the experiment) and of lower subsamples (visually unaffected by the experiment).

Name	Subsample	Description	C _{org}
Control	-	Yellow sandy loam with frequent calcitic features (e.g. hypocotings, nodules)	0.3 %
Soil with bone OM	Upper	Yellow to brown sandy loam with frequent calcitic features and organic fluids impregnation ; 2 cm thick	4.7 %
	Lower	Similar to control	0.2 %
Bone fire	Upper	Reddened and carbonized sandy loam with frequent calcitic features and fine carbon coatings/infillings ; 4 cm thick	2.3 %
	Lower	Similar to control	0.3 %
Wood+bone fire	Upper	Reddened and carbonized sandy loam with frequent calcitic features and fine carbon coatings/infillings ; 2.5 cm thick	0.9 %
	Lower	Similar to control	0.3 %
Wood fire	Upper	Reddened sandy loam with frequent calcitic features and rare combustion residues on surface ; 1.5 cm thick	0.2 %
	Lower	Similar to control	0.2 %

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Table 2

Compounds in extract of the samples. The molecular weight (MW) and the main mass fragments of TMS derivatives are reported (with decreasing contributions). Compound numbers are reported in Fig. 2. The same peak number may correspond to several co-eluting compounds.

Peak #	Main fragments (<i>m/z</i>)	MW	Name
1	179, 105, 77, 135, 194	194	Benzoic acid, TMS
2	73, 147, 205, 293	308	Glycerol, TMS
3	193, 119, 149, 91, 208	208	2-Methylbenzoic acid, TMS
4	151, 73, 210, 195, 117, 167	210	2-Phenoxy-ethanol, TMS
5	71, 89, 56, 43, 173, 143	216	Propanoic acid, 2-methyl-, 2-ethyl-3-hydroxyhexyl ester
6	43, 71, 145, 83, 161, 98	304	1,3-Diisobutyrim, TMS
7	227, 75, 143, 129	242	3-Methyldecen-1-ol, TMS
8	194, 193, 73, 209, 224	224	Vanillin, TMS
9	57, 71, 83	242	Octyl ether
	257	257	Dimethylbenzoacridine
10	195, 210, 180, 165	210	Naphthalene, 1,2,3-trimethyl-4-propenyl-, (E)-
11	195, 119, 73, 103	252	2-Acetoxy-benzoic acid (TMS)
12	88, 101, 157, 284, 239	284	Hexadecanoic acid, ethyl ester
13	85, 236, 192, 97	254	γ -Palmitolactone
14	85, 97, 220, 264	282	γ -Stearolactone
15	343, 73, 147, 227, 431, 371, 205	446	1-Monomyristin, TMS
16	317, 73, 215, 147	532	10, ω -Dihydroxy-octadecanoic acid, TMS
17	129, 218, 73, 147, 103, 313, 459, 403	474	2-Monopalmitin, TMS
18	369, 73, 129, 147, 55, 370, 457	472	1-Monopalmitolein, TMS
19	371, 73, 147, 459	474	1-Monopalmitin, TMS
20	103, 129, 73, 218, 147	500	2-Monoolein, TMS
21	129, 218, 147, 341, 103, 487	502	2-Monostearin, TMS
22	397, 73, 129, 147, 103	500	1-Monoolein, TMS
23	399, 73, 147, 129, 267, 487	502	1-Monostearin, TMS
24	69, 81, 137, 95, 121	410	Squalene
25	329, 129, 368, 458	458	Cholesterol, TMS
26	83, 129, 484, 394, 255	484	Stigmasterol, TMS
27	204, 300, 133, 285, 424	424	Taraxerone
28	129, 357, 396, 486, 255	486	Sitosterol, TMS
29	218, 424, 203	424	α -Amyrone
30	424, 205, 189, 409	424	Lupenone
31	129, 145, 313, 329, 385, 625	640	1,2-Dipalmitin, TMS
32	371, 372, 73, 385, 625	640	1,3-Dipalmitin, TMS

Table 3

Compounds from py(TMAH)-GC-MS analysis of bulk OM. The MW and main mass fragments of original compounds or methylated derivatives are reported (with decreasing contribution). Peak numbers are reported in Fig. 3. The same peak number may correspond to several co-eluting compounds.

Peak #	Main mass fragments (<i>m/z</i>)	MW	Name
1	45, 75, 88, 102	120	1,3-Dimethoxy-2-propanol
2	59, 45, 89, 102	134	1,2,3-Trimethoxypropane
3	55, 41, 68, 84, 112	112	Cycloheptanone
4	41, 57, 70, 82, 98, 114, 124	142	Nonanal
5	119, 134, 91, 115	134	1,2,3,5-Tetramethylbenzene
6	119, 134, 91, 77, 65	134	1,2,4,5-Tetramethylbenzene
7	133, 148, 105, 91, 115	148	Pentamethylbenzene
8	147, 162, 91, 119, 105, 77	162	1,2,4-Trimethyl-5-(1-methylethyl)benzene
9	147, 162, 133, 91, 105	162	1,2-Diethyl-3,4-dimethylbenzene
10	147, 162, 91, 105, 119, 131	162	Hexamethylbenzene
11	101, 88	298	Heptadecanoic acid, ethyl ester
12	71, 183, 95, 294	326	8-Methoxy-9-octadecenoic acid, methyl ester
13	71, 227, 163, 81, 294	340	12,13-Epoxy-11-methoxy-9-octadecanoic acid, methyl ester
14	71, 213, 169, 294	326	10-Methoxy-8-octadecenoic acid, methyl ester
	71, 169, 227, 294	326	9-Methoxy-10-octadecenoic acid, methyl ester
15	131, 71, 241	328	4-Methoxy-octadecanoic acid, methyl ester
	83, 145, 201	302	6,10-Dihydroxyhexadecanoic acid, methyl ester
	229, 143	328	11-Methoxy-octadecanoic acid, methyl ester
16	55, 74, 155	330	9,10-Dihydroxyoctadecanoic acid, methyl ester
17	69, 201, 83, 137,	358	9,18-Dimethoxyoctadecenoic acid, methyl ester

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Table 4

Summary of specific components in the extracts (GC-MS) and in the bulk soil OM composition [py(TMAH)-GC-MS], and possible origins. In grey, compounds with an expected long-term preservation due to their recalcitrance (according to literature, see §3.4).

	<i>Control</i>	<i>Soil with bone OM</i>	<i>Bone fire</i>	<i>Wood + bone fire</i>	<i>Wood fire</i>	Possible origin
Saturated <i>n</i> -acids > C ₁₈	X			X	X	Plant OM
<i>n</i> -Alcohols > C ₁₇	X				X	Plant OM
<i>n</i> -Alkanes	X				X	Plant OM
Phytosterols	X				X	Plant OM
Terpenes	X					Plant OM
Benzoic acids				X	X	Plant OM
Phenolic compounds					X	Plant OM
Other aromatic compounds					X	Thermal alteration of plant OM
Diacids		X	X	X		Animal fat
(di)Hydroxyacids		X				Animal fat
Monomethyl branched dicarboxylic acids < C ₁₀			X			Slight thermal alteration of animal fat
Oxoacids			X	X		Thermal alteration of animal fat
Monomethyl branched acids < Me-C ₁₂			X	X		Thermal alteration of animal fat
<i>n</i> -Alcohols < C ₁₇			X	X		Thermal alteration of animal fat
Ketones			X	X		Thermal alteration of animal fat
Lactones			X	X		Thermal alteration of animal fat
Benzene derivatives				X	X	Thermal alteration of plant OM
Monomethyl branched unsaturated C ₉ and C ₁₀ acids, high C ₈ and C ₉ saturated <i>n</i> -acids		X				Animal fat
Diacids		X	X			Animal fat
(di)Hydroxy-, epoxy-saturated and unsaturated acids		X	X			Animal fat
Glycerol derivatives		X	X			Animal fat
<i>n</i> -Alkane/ <i>n</i> -alkene doublets			X	X		Thermal alteration of animal fat

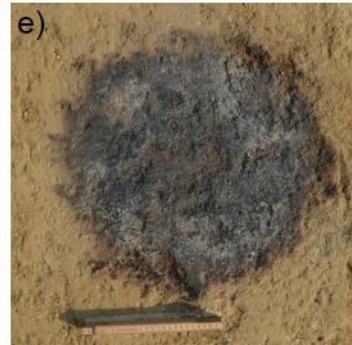
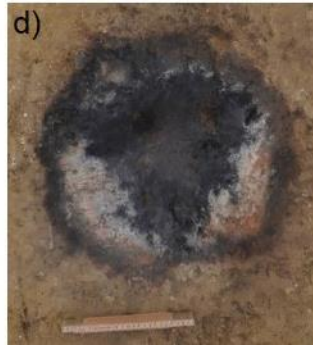
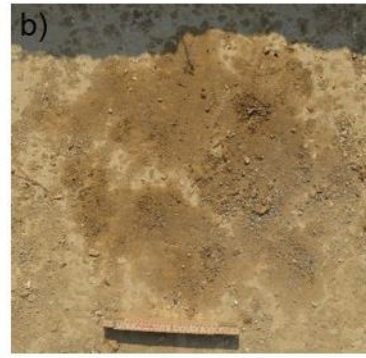
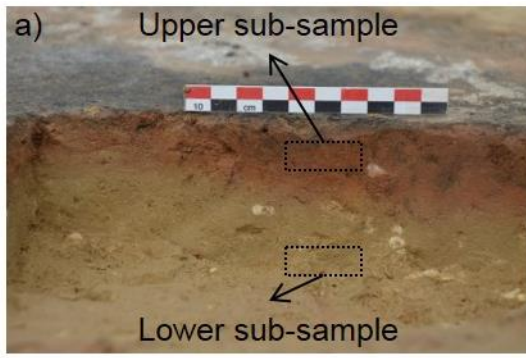
864 **List of figures:**

865 **Fig. 1.** Pictures of Regismont-le-Haut (France) experimental structures during
866 summer 2012 experimental session; (a) section of an experimental fireplace with
867 the localization of upper and lower subsamples, (b) *Soil with bone OM*
868 experiment after removal of bone fragments, (c) *Bone fire* experiment after
869 removal of combustion residues, (d) *Bone+wood fire* experiment after removal of
870 combustion residues, (e) *Wood fire* experiment after removal of combustion
871 residues. The scale is 10 cm long in (a), 24 cm long in (b), (c), (d) and (e).

872 **Fig. 2.** Total ion Chromatogram (TIC) of silylated extract of the (a) *Control*, (b)
873 *Soil with bone OM*, (c) *Bone fire*, (d) *Wood+bone fire* and (e) *Wood fire*. Numbers
874 refer to Table 2; p, plastic derivative; c, column peak. C_x indicates number of
875 carbons in the linear chain.

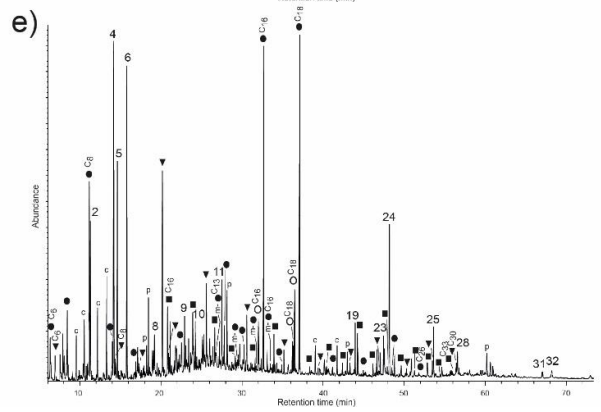
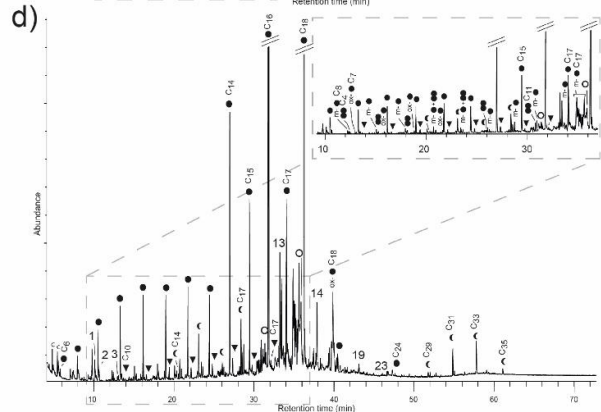
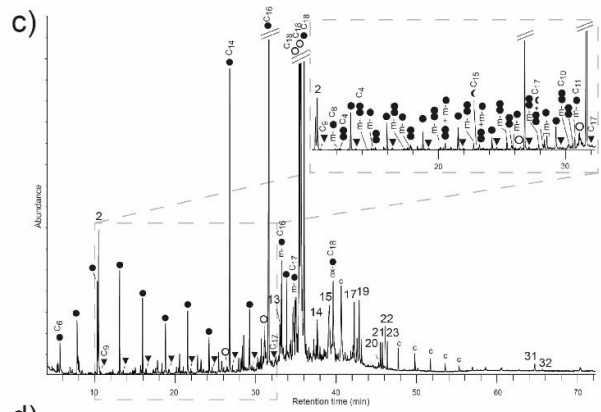
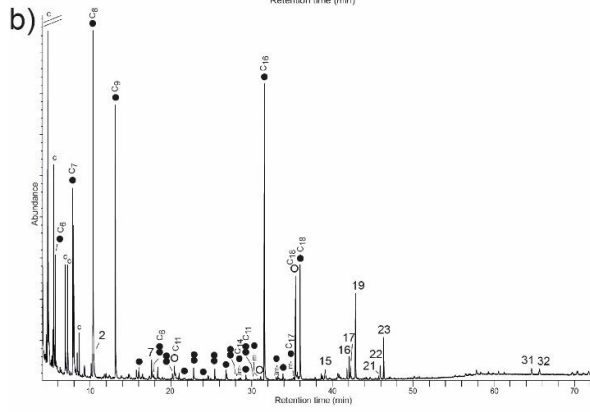
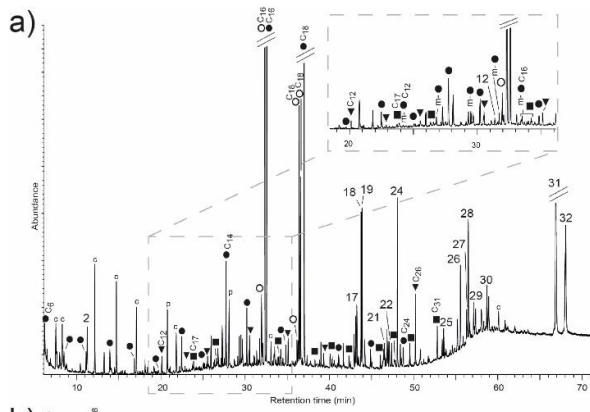
876 **Fig. 3.** TIC trace from py(TMAH)-GC-MS analysis for (a) *Soil with bone OM*, (b)
877 *Bone fire*, (c) *Wood+bone fire* and (d) *Wood fire*. Numbers refer to Table 3. C_x
878 indicates number of carbons in the linear chain.

879



880

881



- Saturated n-acids
- Unsaturated n-acids
- Diacids
- m- Monomethyl branched
- ox- Oxo-
- ▼ n-Alcohols
- n-Alkanes
- ◀ Ketones

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