

Organic geochemical investigations of an MIS 5 fire in the Palaeolithic deposits of Ormesson (Seine-et-Marne, France): Anthropogenic or natural?

Ivy Notterpek^{1,2,*}, Alexandre Lucquin¹, Samuel Abiven^{3,4}, Pierre Bodu⁵, Tobias Bromm⁶, Bruno Glaser⁶, Henri-Georges Naton⁷, Matthew D. Pickering⁸, Oliver E. Craig¹, Isabelle Théry-Parisot²

¹ BioArch, Department of Archaeology, University of York, Environment Building, Wentworth Way, YO10 5NG, York, UK

² Université Côte d’Azur, CNRS, CEPAM UMR 7264, SJA3, 24 Avenue des Diablos Blue, 06300, Nice, France

³ Laboratoire de Géologie, Département de Géosciences, CNRS – Ecole Normale Supérieure, PSL Université, Institut Pierre Simon Laplace, 24 rue Lhomond, 75005, Paris, France

⁴ CEREEP-Ecotron Ile De France, CNRS – Ecole Normale Supérieure, PSL Université, 11 Chemin de Busseau, 77140, St-Pierre-lès-Nemours, France

⁵ UMR 8068 TEMPS, MSH Mondes – Bâtiment Ginouvès, 21 Allée de l’Université, 92023, Nanterre Cedex, France

⁶ Institute of Agricultural and Nutritional Sciences, Soil Biogeochemistry, Martin Luther University Halle-Wittenberg, Von-Seckendorff-Platz 3, 06120, Halle (Saale), Germany

⁷ GeoArchPal-GéoArchÉon, TEMPS UMR 8068, 30 Rue de la Victoire, 55210, Viéville-sous-les-Côtes, France

⁸ Department of Environment and Geography, University of York, Environment Building, Wentworth Way, YO10 5NG, York, UK

* Corresponding author.

Email: ivynotterpek@palaeome.org

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29 Abstract

30 Despite the central role of fire in Pleistocene and Palaeolithic lifeways, the relationship among
31 hominins, fire, and their environment remains unclear. Ancient combustion residues hold a wealth of
32 molecular data that may help to resolve some of these questions, yet standardised guidelines for
33 reconstructing past fire traces are notably lacking. In this study, we examine extensive combustion
34 residues overlying Middle Palaeolithic deposits from the open-air site of Ormesson (France). To
35 determine whether the combustion residues are of natural or human origin, multiproxy approaches
36 including anthracology, lipid biomarker, and benzene polycarboxylic acid (BPCA) analyses are applied.
37 These techniques are used to characterise organic matter and pyrogenic carbon compositions in the
38 deposits, providing insights into surrounding vegetation, palaeoenvironmental shifts, and the
39 production parameters involved in the formation of the char assemblage. Lipid biomarker evidence
40 suggests that the pre-fire local environment featured abundant coniferous vegetation (e.g., Pinaceae
41 taxa), which is supported by anthracological evidence for a predominance of *Pinus* cf. *sylvestris/nigra*
42 complemented by *Betula* sp. taxa. The post-fire environment saw a contraction of coniferous
43 vegetation, concurrent with an expansion of deciduous taxa, grasses and herbaceous material. The
44 combustion event, which resulted in 67% of the charcoal assemblage exhibiting vitrification, produced
45 PyC contents of up to 362 g/kg OC in soil samples and 443 g/kg OC in charcoal samples, with aromatic
46 condensation values of up to 34%. BPCA-derived predictions of heat treatment temperatures yielded
47 values of approximately 300–400 °C for charcoal samples and 400–550 °C for soil samples in the burned
48 layer, constituting the first instance in which quantitative temperature estimations are obtained from
49 BPCA results. Based on the integrated evidence, we accept the null hypothesis that the studied
50 combustion residues are natural in origin. However, the similarity of archaeometric and geochemical
51 signatures from natural and human-controlled fires underscores the need for interdisciplinary,
52 multiproxy efforts to improve the identification of past fire regimes.

1. Introduction

The habitual and controlled use of fire was integral to the evolutionary development of *Homo*, with numerous biological, social, and technological ramifications. However, the nature and chronology of hominin “habituation to natural fire, use of fire, maintenance of fire, [and] manufacture of fire” (Sandgathe, 2017: 5367) remain clouded by regional variability and the often-fragmentary archaeological record of early sites (see also Gowlett, 2016). Evidence for fire use outside of Africa is limited prior to 0.5 Ma, and becomes markedly more frequent after 400 ka (Goren-Inbar et al., 2004; Fernández Peris et al., 2012; Shimelmitz et al., 2014; Rhodes et al., 2016; Rosell and Blasco, 2019; Sanz et al., 2020; Stancampiano et al., 2023). This intensification may signal the emergence of fire production techniques, rather than the control or maintenance of natural fires, as suggested for earlier contexts (Roebroeks and Villa, 2011; Sandgathe, 2017). Yet in the Middle Palaeolithic, evidence from Neandertal occupation sites in southwest France indicates that fire frequency was higher during warmer than colder periods; this pattern has been interpreted as opportunistic harvesting of naturally occurring fires, likely more common in warmer conditions (e.g., from lightning strikes), rather than independent fire generation (Sandgathe et al., 2011; Dibble et al., 2017, 2018). The ways in which Neandertals used fire (e.g., opportunistic vs. intentional), the technical skills involved (e.g., regulation vs. production), and the implications of these practices for behavioural complexity are subjects of ongoing debate, with direct relevance for understanding the development and diversification of pyrotechnology throughout the Pleistocene.

Resolving these debates requires rigorous analyses of archaeological fire traces at both macro- and micro-scopic scales. Despite decades of multidisciplinary efforts, clear diagnostic guidelines have yet to be established for one of the most essential aspects of reconstructing past fire: determining natural or anthropogenic origins. The distinction of these fire types has been pursued through a number of techniques, including: (i) palaeomagnetism and magnetic susceptibility (Barbetti, 1986; Deldicque et al., 2021); (ii) charcoal reflectance values (McParland et al., 2009; Belcher et al., 2018; Braadbaart et al., 2020); and (iii) the analysis of micro-material including microfaunal remains

(Fernandez-Jalvo and Avery, 2015; Rhodes et al., 2016) and flint debitage (Alperson-Afil, 2012). Researchers have also sought to discriminate these fire types via distributions of polycyclic aromatic hydrocarbons (PAHs) (Brittingham et al., 2019; Bird et al., 2024), or other molecular evidence (Wolf et al., 2013; Jambrina-Enríquez et al., 2019; Stancampiano et al., 2023). Lastly, these fire types have been investigated using temperature estimations (e.g., Marynowski et al., 2011; Walker et al., 2016), often derived through the comparison of ancient material (e.g., charcoal, bone) to thermally altered experimental references (Ferrio et al., 2006; Scott, 2010; Deldicque et al., 2016, 2023). These efforts are predicated on the notion that natural and anthropogenic fires burn at different combustion temperatures, with higher temperatures typically ascribed to human-controlled fires (e.g., Wolf et al., 2013). However in the majority of early-middle Pleistocene and lower-middle Palaeolithic sites, the association of fire traces with hominin activity is more often inferred from stratigraphic and chronological investigations (e.g., Berna et al., 2012; Stahlschmidt et al., 2015) rather than molecular techniques.

The full potential of molecular data in ancient fire traces thus remains largely underexploited, despite significant advances in the study of thermally altered organic matter (OM). Analyses of lipid biomarkers via organic residue analysis and of pyrogenic carbon (PyC) via benzene polycarboxylic acid (BPCA) analysis are particularly promising, as these methods target amorphous organic residues and molecular PyC that can persist far longer than macroscopic charred remains (e.g., Brocks et al., 2005; Kappenberg et al., 2019). Lipid biomarker analysis enables the reconstruction of biogenic sources and processes (Evershed, 2008), with applications ranging from identifying vegetal inputs to soil organic matter (SOM) (e.g., Schäfer et al., 2016) to detecting the organic signature of combustion features used for cooking meat (e.g., Lejay et al., 2019). BPCA analysis, which is one of several methods for characterising condensed aromatic moieties in PyC (Hammes et al., 2007), can be used to reconstruct char production parameters such as heat treatment temperature (HTT) (Glaser et al., 1998; Notterpek et al., 2025). The combined application of these methods to ancient combustion residues, particularly of uncertain origin, has not been reported. This study applies lipid biomarker and BPCA analyses to

combustion residues associated with Palaeolithic archaeological remains in order to assess the analytic and interpretive capabilities of these methods for characterising past fire traces.

Extensive burned deposits directly overlying a Middle Palaeolithic archaeological layer at the multi-stratified open-air site of Ormesson (Seine-et-Marne, north-central France) were analysed, as the anthropic or natural origins of the combustion traces were unknown. These combustion deposits could have resulted from human actions — whether through the deliberate burning of the site, the use of a large fire as a smoke signal, or the accidental spread of an unmanaged combustion feature. Alternatively, these deposits could testify to a previously unknown wildfire in the Paris basin region, or contain anthropogenic fire traces that were masked by a subsequent wildfire. As the natural or anthropic origin of the fire cannot be determined *a priori*, this study evaluated the following principal research question: *Did these combustion residues result from a wildfire, or human activity?* This question was addressed through the examination of: (i) anthracological evidence from the charcoal assemblage, including wood taxonomy and anatomical features indicative of the state of wood at the time of combustion; (ii) SOM composition and its implications for surrounding vegetation and palaeoclimatic conditions at the time of the event; (iii) PyC composition to reconstruct the combustion conditions in which the charred material was produced, namely HTT; and (iv) taphonomic and diagenetic alterations to the biomarker evidence. By detailing these factors through the integration of geological, anthracological, and geochemical data, this study highlights important considerations regarding the capabilities and constraints of geochemical and archaeological approaches for the interpretation of past fire traces.

2. Description of the study site

The site of Ormesson is located approximately 70 km southwest of Paris in a valley perpendicular to the Loing River (Lambert coordinates X: 624.1, Y: 1061.25) (Fig. S1). The site contains at least six Palaeolithic occupations, of which four are located on the eastern portion of the site (Les Bossats à Ormesson). These include Mousterian discoid (c. 42–46 ka cal BP), Châtelperronian (c. 42 ka cal BP), Gravettian (c. 31 ka cal BP), and Middle Solutrean (c. 23.5 ka cal BP) archaeological deposits

(Bodu et al., 2014b, 2014a, 2017; Lacarrière et al., 2015; Bodu and Naton, 2024). In 2021, a test pit (survey 95) was opened on the western portion of the site that led to the discovery of two additional Middle Palaeolithic occupations associated with Levallois lithic technology and faunal remains (Fig. 1).

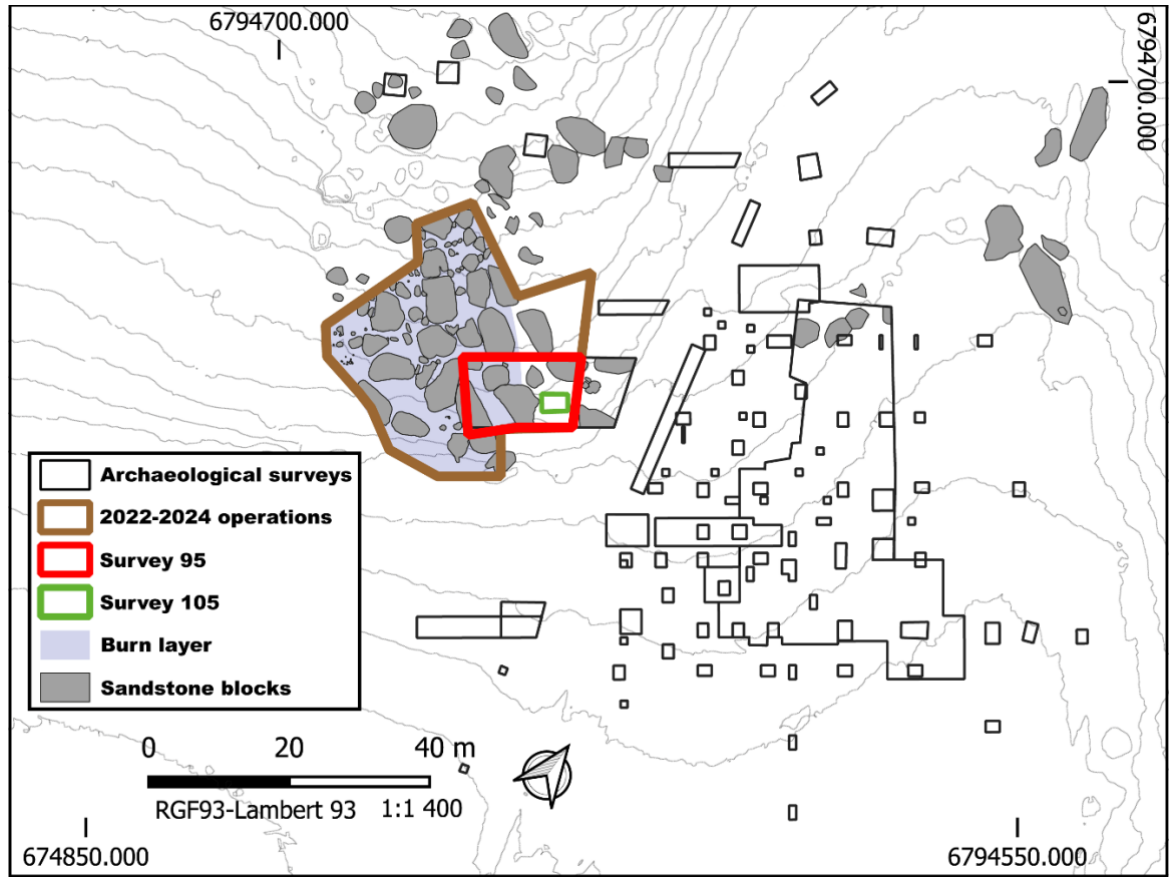


Fig. 1. Map of Ormesson , with the location of survey 95 indicated by a red rectangle (H.G. Naton and L. Heccan, modified by I. Notterpek).

The first occupation, characterised by Levallois point production, was present in the southeast corner of survey 95. Artefacts were found in local aeolian sands dated by optically stimulated luminescence (OSL) to 105.2 ± 5.5 ka (OSL 95-1) (Fig. 2). The second occupation, characterised by preferential Levallois reduction, was identified in the western half of survey 95 directly below extensive burned deposits ranging from 3 to 10 cm in thickness. The massive sandstone blocks were present and in their current tilted positions at the time of deposition. OSL dating of the layered aeolian sands above the burned layer yielded an age of 90.4 ± 6 ka (OSL 95-12), while the underlying geological substratum (Fontainebleau sand) provided an age of > 583 ka (OSL 95-11) (Fig. 2). Together, these results establish a *terminus ante quem* of approximately 90 ka for both the burned layer and the associated Levallois

occupation. These chronometric data place the burned deposits within the morpho-sedimentary framework of the Early Weichselian glacial period, broadly corresponding to Marine Isotope Stage 5 (MIS 5) (dosimetry details of all OSL dates are available in Table S1, sheet 1) (Müller et al., 2003; Helmens, 2014). However, the two Levallois occupations cannot be stratigraphically linked due to a major gully erosion phase that truncated the deposits, with infill sediments dated to 83.5 ± 4.0 ka (OSL 95-10) (Fig. 2). Although the burned layer and associated Levallois occupation likely date between 90.4 ± 6.0 ka and 105.2 ± 5.5 ka, potentially aligning with MIS 5c, this truncation precludes secure correlation between the dated contexts. Accordingly, these deposits are assigned more generally to MIS 5.

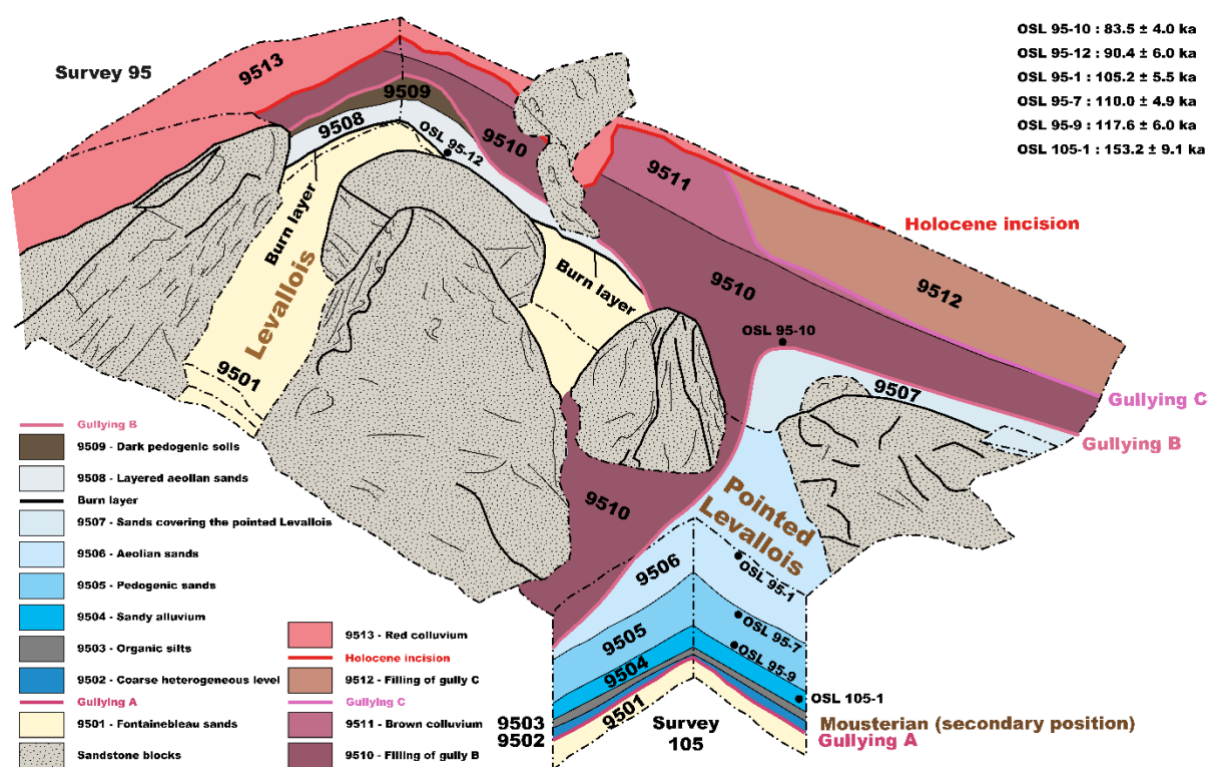


Fig. 2. Schematic drawing of surveys 95 and 105 with geological understandings, the location of optically stimulated luminescence samples, and their chronometric results (H.G. Naton, modified by I. Notterpek).

Extensions of the test pit have since revealed that the burned deposits are substantial, extending over approximately 700 m^2 , and may represent no more than the relic of a much larger burned surface. However, at the time of discovery, only the burned deposits covering approximately 30 m^2 in survey 95 were known. In certain areas, several burned layers were also visible. These

combustion residues therefore required investigation, alongside an assessment of lipid biomarker and BPCA analyses as biomolecular approaches for characterising past fire traces.

3. Materials and methods

3.1. Charcoal samples for anthracological study

All soil from the burned layer(s) was systematically sieved to 2 mm, and burned material was randomly selected from the sieved material for anthracological study. The following units of survey 95 and the number of specimens studied were as follows, for a total of 119 burned fragments: I7 ($n = 1$), I8 ($n = 33$), I9 ($n = 10$), I10 ($n = 11$), I11 ($n = 2$), I12 ($n = 20$), I13 ($n = 1$), I14 ($n = 1$), I15 ($n = 1$), J11 ($n = 6$), L15 ($n = 9$), M15 ($n = 9$), and M17 ($n = 15$) (Fig. 3). The number of samples per square metre does not reflect the total number of charcoal fragments present, but rather the number selected for analysis through random sampling of the charcoal remains.

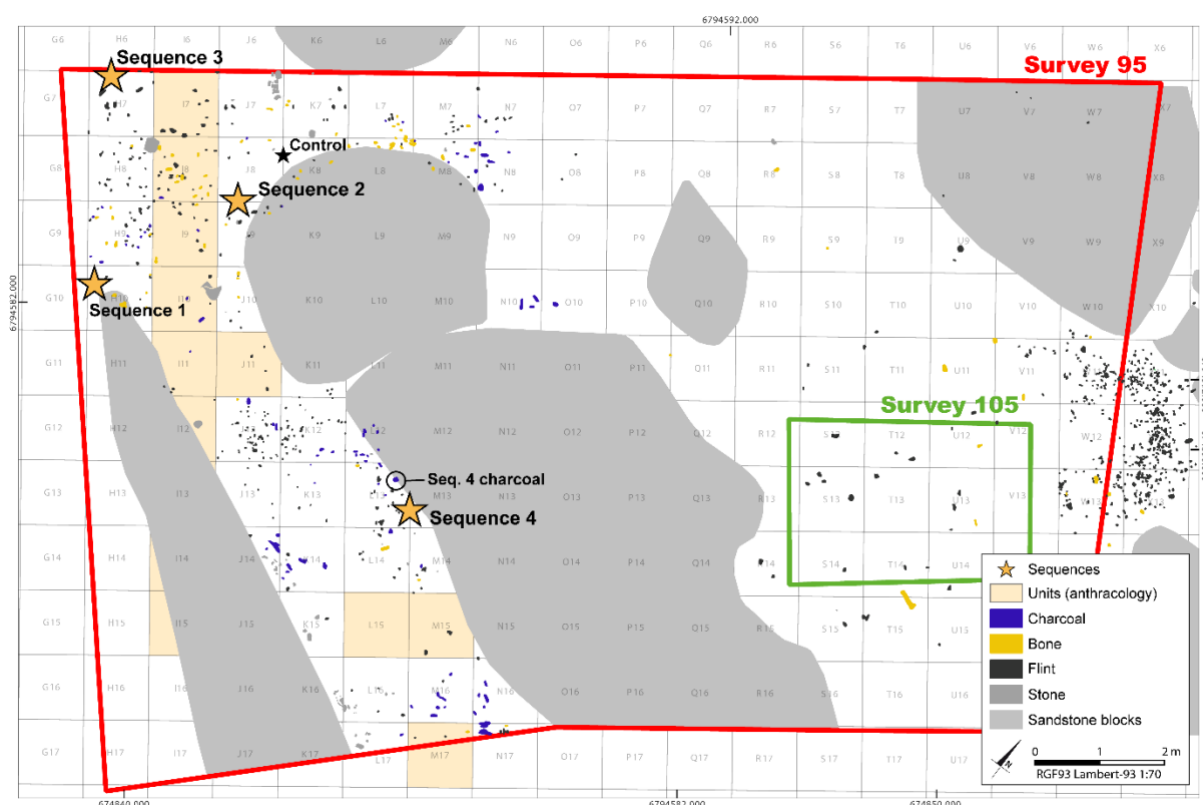


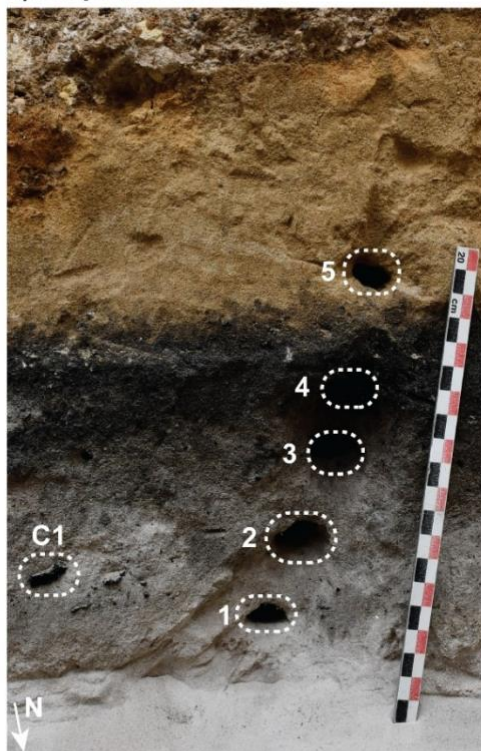
Fig. 3. Map of survey 95 with all sample locations. Units from which charcoal material were randomly selected for anthracological analysis are shaded in yellow. The location of soil sequences is indicated by a yellow star, and the control is indicated by a black star. The in-plan charcoal sample of sequence

4 is plotted and labelled. Archaeological material is shown with charcoal (blue), bone (yellow), flint (dark grey), and stone (grey).

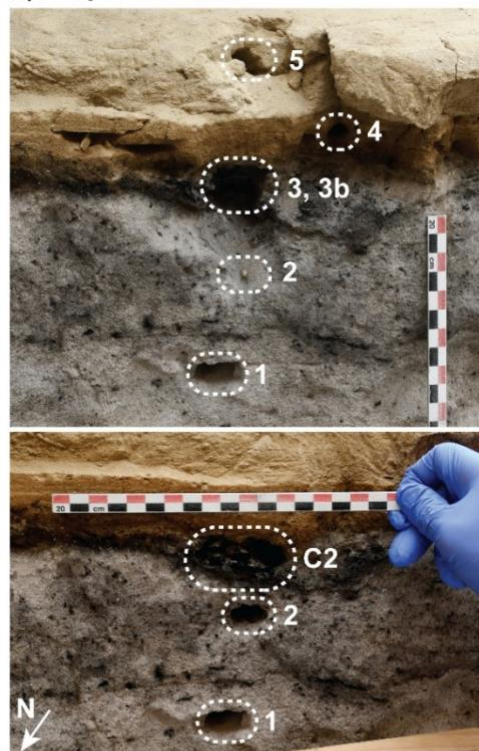
3.2. Soil and charcoal samples for geochemical analyses

For organic geochemical and biomolecular analyses, four sequences of samples were taken from different areas of the burned deposits in survey 95. Each sequence consisted of at least 5 soil samples, collected from bottom to top, that were spaced approximately 2–5 cm apart depending on the area sampled. Sequence 1 was located in the southwestern profile of unit H10 (~77.813–77.964 metres above sea level), sequence 2 in the northern profile of unit J9 (~77.515–77.672 m a.s.l.), sequence 3 in the northern profile of unit H7 (~77.788–77.969 m a.s.l.), and sequence 4 in the eastern profile of unit M13 (~77.673–77.858 m a.s.l.) (Fig. 3). For each sequence, a macrocharcoal remain near the soil sampling zone with an estimated weight of least 10 mg was collected for BPCA analysis (C1–4). Each associated charcoal was sampled in profile (Fig. 4), with the exception of the fourth charcoal (C4). As no macrocharcoal fragments were visible in the profile of sequence 4, a large charcoal in the active excavation surface of unit L13 was collected (Figs 3 and 4). Adhering soil was carefully removed under sterile laboratory conditions and pure charcoal was collected for analysis. For sequence 2, a total of 6 rather than 5 soil samples were gathered. Sample J9 3b was collected at the same elevation of the associated charcoal (C2), but deeper in the profile (Fig. 4). It was retained as a separate sample given its high charcoal content, and was sampled prior to the true soil sample J9 3, again at the same elevation but deeper in the profile. The geological substratum (Fontainebleau sand) was collected as a sterile control in the eastern profile of unit J8, approximately 60 cm beneath the burned layer (77.246 m a.s.l.). Each sequence was photographed before, during, and after sampling, and the elevation of each sample was recorded with a Total Station. All samples were gathered using sterilised stainless-steel tools and were stored in sterile glass tubes to avoid plastic contamination.

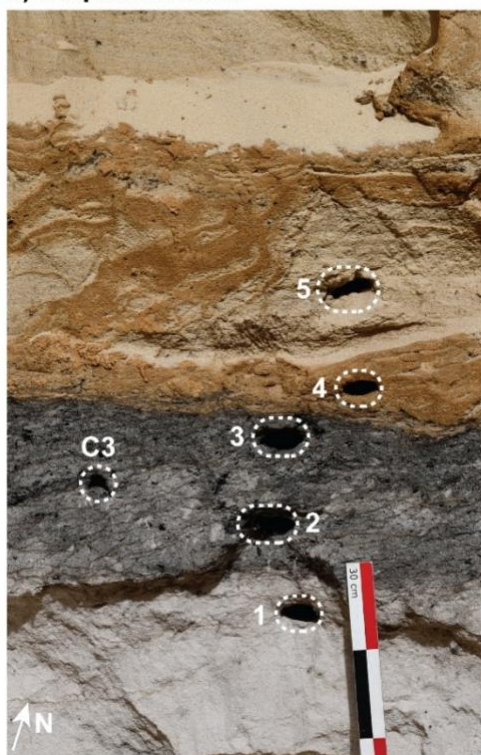
a) Sequence 1: H10



b) Sequence 2: J9



c) Sequence 3: H7



d) Sequence 4: M13



Fig. 4. Samples collected for geochemical analysis. Sequences 1–4, with the location of each sample indicated by a dashed white oval. The associated charcoal for each sequence (C1–4), here prior to sampling, is also shown. In b) sequence 2, the bottom image shows sample 2 and charcoal C2 prior to partial collapse of the profile. The inlay in d) sequence 4 shows charcoal C4 located on the excavation surface of unit L13.

3.3. Methods

Methods included anthracology, bulk elemental and stable isotope analyses, pH measurement, lipid extraction and analysis, and BPCA analysis. Anthracological study was performed on the 119 burned samples described in section 3.1, and the charcoal was studied with microscopy by classical botanical identification based on the three anatomical planes of wood (radial, transversal, tangential). Charcoal collected for geochemical analyses were not studied via anthracology to avoid contamination. Bulk elemental and stable isotope analyses were performed on all samples ($n = 26$), while pH measurement was performed only on the control soil. Lipid extraction and analysis was performed on soil samples ($n = 22$), while BPCA analysis was conducted on both soil and charcoal samples ($n = 26$). Full methodological details are relayed in the supplementary information (SI-1).

Briefly, lipids were extracted from soil samples to characterise OM composition using protocols for solvent extraction with dichloromethane and methanol (modified from Jambrina-Enríquez et al., 2019), and acid extraction using the one-step acidified methanol extraction described by Craig et al. (2013). Analysis of the total lipid extract (TLE) was performed by gas chromatography mass spectrometry (GC-MS). The NIST mass spectra library and MassHunter software (Agilent technologies) were used for compound identification and quantification. Lipid yields are reported as μg per gram dry sample ($\mu\text{g/gds}$), and the various proxies calculated to interpret aliphatic lipid data are relayed in Table 1. These proxies were mobilised to evaluate the contributions of various biogenic sources to SOM, as well as to characterise the preservation state of these compounds, including the detection of microbial reworking or modern lipid input.

Table 1. Summary of aliphatic lipid proxies with formulae, references, and the range of compounds utilised (where applicable).

Proxy	Equation	References, range of compounds
Average chain length (ACL)	$\frac{\sum C_i \times i}{\sum C_i}$, where C_i is the relative amount of n -aliphatic compound with i carbons	General: Poynter et al., 1989. n -Alkanes: C_{16} – C_{35} (this study), ACL_{long} : C_{27} – $C_{33 \text{ odd}}$ (Schäfer et al., 2016). n -Alkanols: C_{22} – C_{28} (Zheng et al., 2009), C_{24} – $C_{32 \text{ even}}$ (Zhang et al., 2006).

Carbon preference index (CPI)	$\frac{(\sum_{i=n}^m C_{2i+1}) + (\sum_{i=n+1}^{m+1} C_{2i+1})}{2 (\sum_{i=n+1}^{m+1} C_{2i})}$, where n is the starting n -aliphatic compound divided by 2 and m is the ending n -aliphatic compound divided by 2	n-Alkanoic acids: C_{12:0}–C_{34:0}, ACL_{long}: C_{20:0}–C_{34:0} even (this study). General: Marzi et al., 1993. n-Alkanes: C₁₆–C₃₂, CPI_{long}: C₂₄–C₃₂ (Knicker et al., 2013). n-Alkanols: C₂₃–C₃₃ (Zhang et al., 2006). n-Alkanoic acids: C_{10:0}–C_{29:0} (Knicker et al., 2013), CPI_{long}: C_{20:0}–C_{31:0} (Wiesenberg et al., 2012).
<u>n-Alkanes</u>		
n -Alkane ratio	$\frac{C_{31} + C_{33}}{C_{27} + C_{31} + C_{33}}$	Schäfer et al., 2016
Odd-over-even predominance (OEP)	$\frac{C_{27} + C_{29} + C_{31} + C_{33}}{C_{26} + C_{28} + C_{30} + C_{32}}$	Hoefs et al., 2002
Ratio of short- to long-chain (R _{s/l})	$\frac{\sum C_{16-24}}{\sum C_{25-33}}$	after Buggle et al., 2010
<u>n-Alkanols</u>		
Alkanol index	$\frac{C_{30}}{C_{28} + C_{30}}$	Zhang et al., 2006
C ₂₄ /C ₂₆	$\frac{C_{24}}{C_{26}}$	Zheng et al., 2009
<u>n-Alkanoic acids</u>		
Even-over-odd predominance (EOP)	$\frac{C_{24} + C_{26} + C_{28} + C_{30} + C_{32}}{C_{23} + C_{25} + C_{27} + C_{29} + C_{31}}$	Schäfer et al., 2016
Ratio of short- to long-chain (FA _{s/l})	$\frac{\sum C_{10-20}}{\sum C_{21-28}}$	Knicker et al., 2013
Palmitic/stearic acid	$\frac{C_{16:0}}{C_{18:0}}$	Eerkens, 2005
C ₁₈ _{unsaturated/saturated}	$\frac{C_{18:1} + C_{18:2}}{C_{18:0}}$	Wiesenberg et al., 2012
Carbon diversity index (CDI)	$\frac{x}{C_{24} + C_{28} + C_{32} + C_{34}}$, where x is C ₂₄ (CDI-C), C ₂₈ (CDI-D), and C ₃₂ +C ₃₄ (CDI-G)	Schäfer et al., 2016

230 Lastly, BPCA analysis was conducted to quantify molecular PyC in soil and charcoal samples,
231 providing information on the aromaticity and aromatic condensation of the charred residues. The
232 procedure followed was that of Glaser et al. (1998) with the modifications of Brodowski et al. (2005),
233 and analyses were performed by GC with flame ionisation detection (GC-FID). BPCA yields were

converted to black carbon or PyC contents using the 2.27 correction factor proposed by Glaser et al. (1998). Results are reported as g BPCA-C/kg dry sample, as well as normalised to sample TOC (g BPCA-C/kg OC). BPCA yields were further processed with the random forest algorithms of Notterpek et al. (2025) to predict HTT and precursor feedstock types (hardwoods, softwoods, grasses). Quantitative HTT uncertainties were calculated at 95% and 68% confidence intervals, with errors for averaged values reflecting the square root of the sum of variances.

4. Results

4.1. Anthracology: taxonomy and state of the wood

Anthracological analysis was conducted on a subsample of 119 burned fragments, of which 114 were charcoal, 4 were bone, and 1 was a seed pericarp. The charcoal assemblage was composed of *Betula* sp. ($n = 7$), *Pinus* cf. *sylvestris/nigra* ($n = 100$), gymnosperm ($n = 3$), and 4 unidentifiable fragments. Several anatomical signatures provide a more precise description of the state of the wood at the time of combustion (Théry-Parisot, 2001; Marguerie and Hunot, 2007; Théry-Parisot and Henry, 2012; Henry and Théry-Parisot, 2014; Vidal-Matutano et al., 2017, 2020). The most predominant characteristic observed was that of vitrification, present in 67% of the charcoal assemblage. Three levels of vitrification were observed: (i) low intensity, characterised by reflective patches with no alteration of the anatomical structure of the wood (Fig. 5a); (ii) intermediate intensity, wherein the anatomical structure was only observable in a small part of the sample (Fig. 5b); and (iii) high intensity, evincing a massive melting of the anatomical structure (Fig. 5c). Elsewhere, 48% of samples showed reaction wood characteristic of branches (Fig. 5d), 13% showed decay characteristic of dead wood (Fig. 5e), and 7% showed shrinkage cracks characteristic of green wood combustion (Fig. 5f).

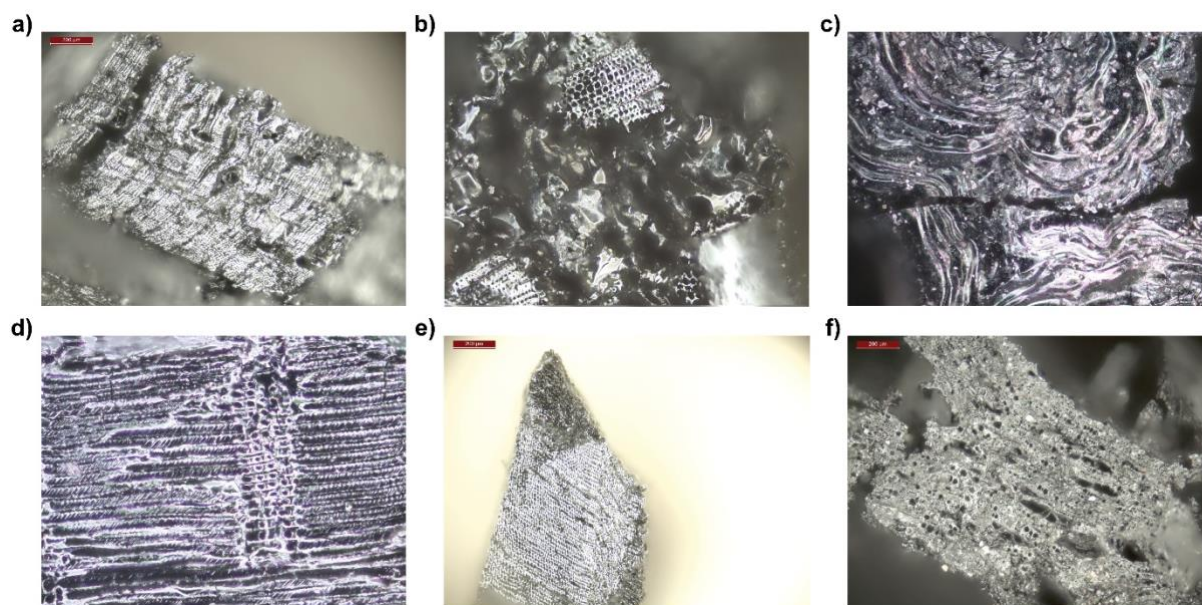


Fig. 5. Anatomical signatures identified in the charcoal assemblage. a) *Pinus* cf. *sylvestris/nigra* (transversal section x100), vitrification with preservation of the anatomical structure of the wood; b) *Pinus* cf. *sylvestris/nigra* (transversal section x100), patches with intense vitrification with the anatomical structure only observable in sections of the sample; c) unidentifiable vitrified sample (transversal section x100) with massive melting of the anatomical structure; d) *Pinus* cf. *sylvestris/nigra* (radial section x100), reaction wood characteristic of branches; e) *Pinus* cf. *sylvestris/nigra*, (radial section x100), dead wood with collapsed cell walls and major cellular deformations, type A.L. 3 (Henry and Théry-Parisot, 2014); f) *Betula* sp. (transversal section x100), wood with radial cracks characteristic of the combustion of green wood (Théry-Parisot and Henry, 2012).

4.2. Lipid biomarkers

Control pH and the bulk elemental and stable isotope results of soil and charcoal samples are relayed in the supplementary information (SI-1 and Table S1, sheet 2). The total lipid yields obtained by solvent and acid extraction are shown in Figure 6 (see also Table S1, sheet 3). The TLE obtained by solvent extraction yielded an average of $2.83 \pm 1.49 \mu\text{g}$ per gram dry sample (gds) for all samples, with contents ranging from 0.75 (H10 1) to 6.14 (J9 3b) $\mu\text{g/gds}$. Sample H7 1 is excluded from this description, as a large plasticiser peak in the silylated solvent extract obfuscated accurate quantification; henceforth, summary statistics for compounds quantified from the solvent extract exclude sample H7 1, while those for compounds quantified from the acidified methanol extract include all samples. The TLE obtained by acid extraction yielded an average of $8.59 \pm 6.75 \mu\text{g/gds}$, with the lowest concentration in the control (1.24 $\mu\text{g/gds}$) and the highest in sample M13 2 (32.82 $\mu\text{g/gds}$). Acid extraction yielded higher lipid contents for all samples, with the exceptions of the control (in

which solvent extraction yields were greater) and sample J9 3b (for which yields between the two extraction techniques were comparable).

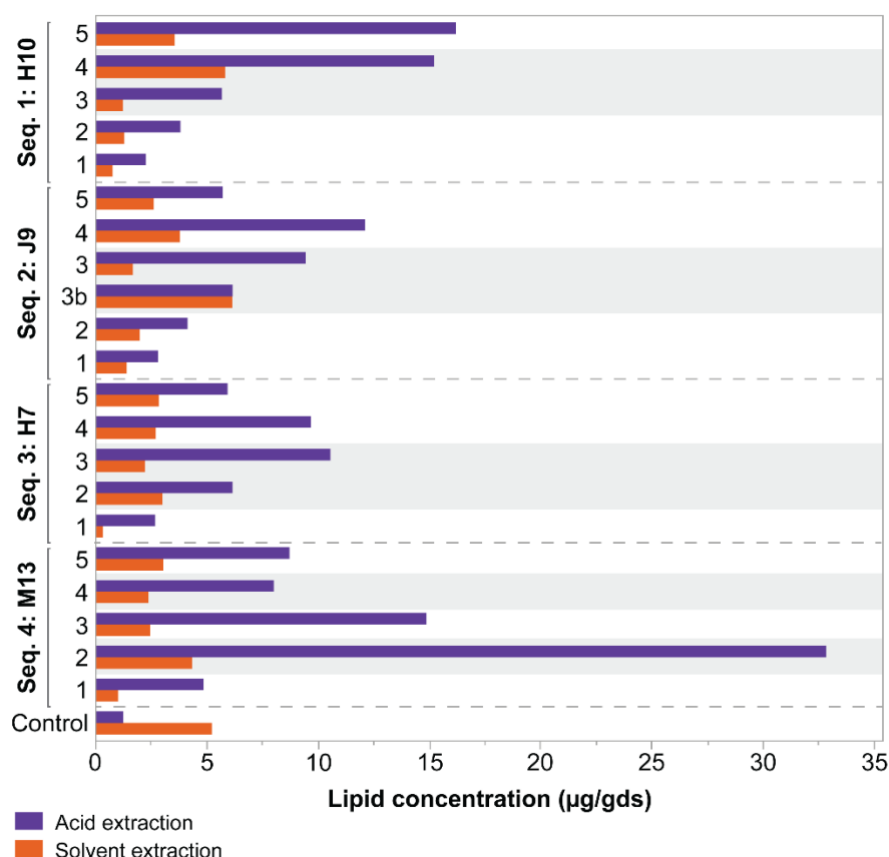


Fig. 6. Total lipid yields in microgram per gram of dry sample (µg/gds) obtained by acid and solvent extraction. The position of the burned layer(s) within each sequence is indicated by a shaded grey bar.

4.2.1. *n*-Alkanes

n-Alkanes ranging from C₁₆ to C₃₅ were identified and quantified in the TLE obtained by solvent extraction (Table S1, sheet 4). Long-chain (> C₂₉), odd-numbered *n*-alkanes were particularly prevalent in samples in and above the burned layer (Fig. S3). Total *n*-alkane yields (µg/gds) ranged from 0.12 to 1.12 with an average of 0.48 ± 0.29 µg/gds for all samples (Fig. 7). The control yielded 0.59 µg *n*-alkane/gds. *n*-alkane ACL values varied from 27.17 to 29.39, and ACL_{long} values from 29.36 to 30.65. When averaged according to sample stratigraphy, both ACL and ACL_{long} increased with ascending elevation on the order of 1.18 for ACL and 0.49 for ACL_{long} (values denote the difference in means between “below” and “above” samples among all sequences, with below samples excluding the control), though a slight dip is observed in the uppermost sample of sequences 2 and 3 (Fig. 7). *n*-

Alkane ratio values ranged from 0.53 to 0.87, and generally increased from samples below the burned layer (0.59 ± 0.05) to those in (0.67 ± 0.10) and above it (0.80 ± 0.06) (Fig. 7). OEP values spanned from 0.79 to 5.01 and values of >3 were obtained for all samples above the burned layer, with the exception of sequence 4, which yielded values between 1 and 2 (Fig. 7). On average, OEP values thus increased from samples below the burned layer (1.14 ± 0.10) to those above it (3.59 ± 0.85). Results of the closely related CPI are relayed in the supplementary information (SI-1). Lastly, $R_{s/l}$ values ranged from 0.09 to 0.44, with the highest average values obtained for samples below the burned layer (0.33 ± 0.05) and the lowest for those above it (0.14 ± 0.04) (Fig. 7).

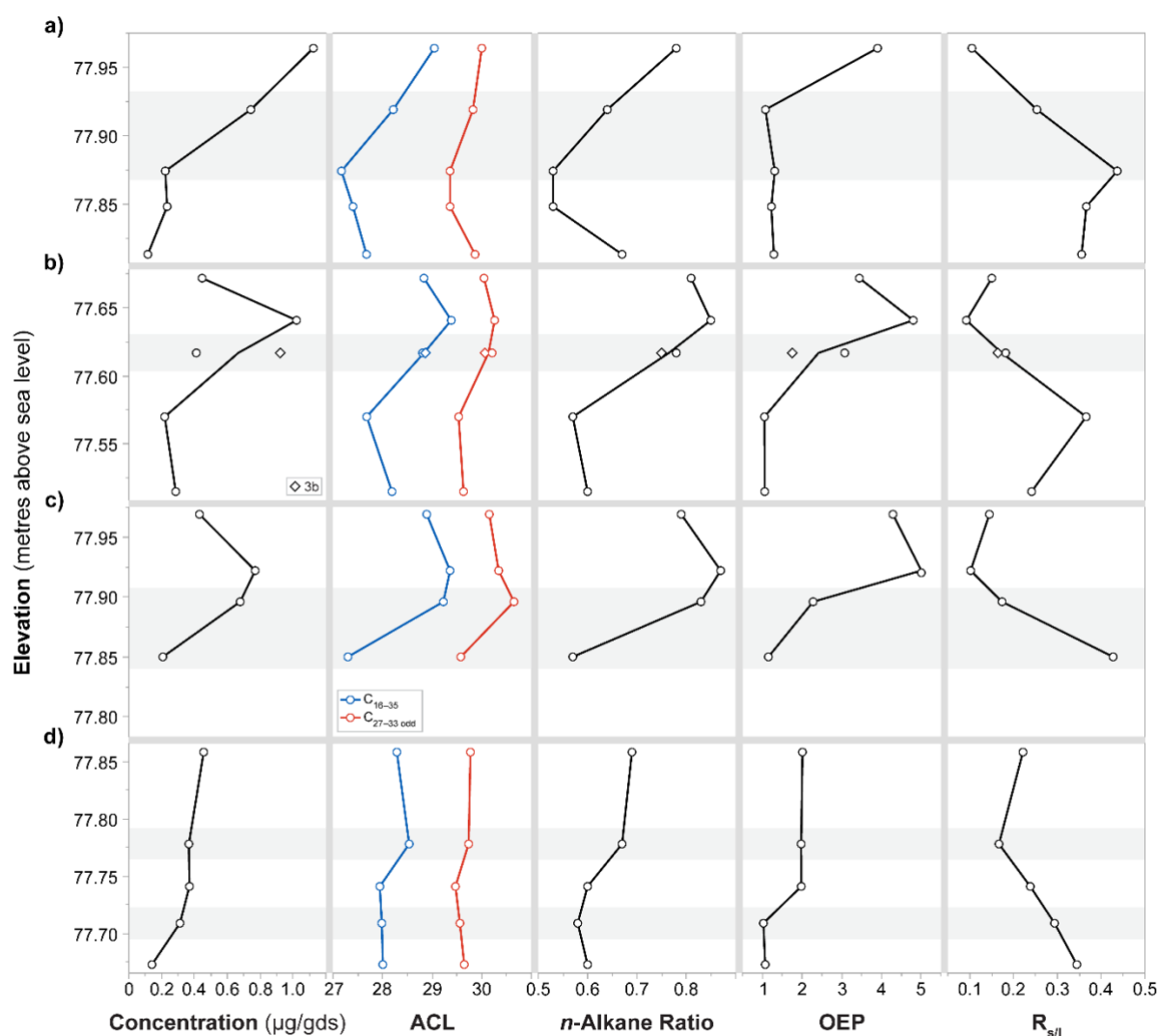


Fig. 7. Quantitative *n*-alkane results for sequences a) 1, b) 2, c) 3, and d) 4. From left to right: (i) concentration ($\mu\text{g/gds}$), (ii) ACL (blue) and ACL_{long} (red), (iii) *n*-alkane ratio, (iv) OEP, and (v) $R_{s/l}$. The position of the burned layer(s) within each sequence is indicated by a shaded grey bar. Sample H7 1 is omitted, and the charcoal-rich sample J9 3b is denoted by a diamond.

4.2.2. *n*-Alkanols

n-Alkanols ranging from 12 to 34 carbons were identified and quantified in the TLE obtained by solvent extraction (Table S1, sheet 5), with the exception of C₁₇ and C₁₉ as these compounds were too close in retention time to C_{16:0} and C_{18:0} *n*-alkanoic acids to be accurately quantified. The recovered *n*-alkanols were predominantly of even-numbered carbon chain length, and as for *n*-alkanes, long-chain *n*-alkanols (> C₂₄) were more abundant in samples in and above the burned layer (Fig. S4). C₁₈ was particularly abundant in the control (~48%) (Table S1, sheet 5). The ACL of *n*-alkanols (C₂₂–C₂₈) ranged from 23.52 to 26.11, with average values of 24.28 ± 0.26 in samples below the burned layer and 25.83 ± 0.25 in those above it (Fig. 8). The ACL of long-chain, even-numbered *n*-alkanols (C₂₄–32 even) also generally increased from samples below (26.69 ± 0.47) to above (27.43 ± 0.25) the burned layer (Fig. 8). The alkanol index yielded values ranging from 0.30 to 0.54, with average values of 0.32 ± 0.01 in samples below the burned layer and 0.46 ± 0.02 in samples above it (Fig. 8). Lastly, C₂₄/C₂₆ produced values spanning between 0.22 and 2.25, with the highest average values in samples below the burned layer (1.20 ± 0.31) and the smallest in those above it (0.30 ± 0.11) (Fig. 8). *n*-Alkanol CPI results are relayed in the supplementary information (SI-1).

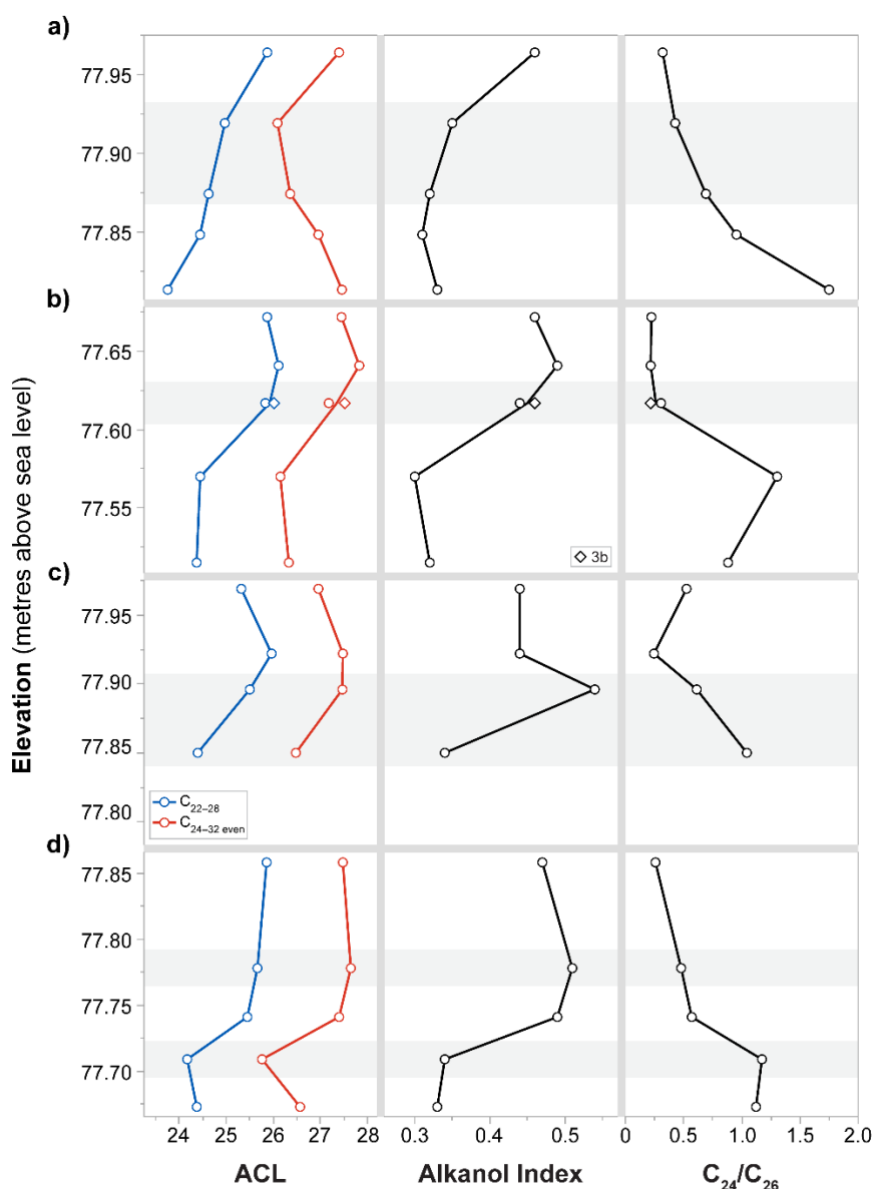


Fig. 8. *n*-Alkanol proxy results for sequences a) 1, b) 2, c) 3, and d) 4. From left to right: (i) ACL C_{22} – C_{28} (blue) and C_{24} – C_{32} even (red), (ii) alkanol index, and (iii) C_{24}/C_{26} . The position of the burned layer(s) within each sequence is indicated by a shaded grey bar. Sample H7 1 is omitted, and the charcoal-rich sample J9 3b is denoted by a diamond.

4.2.3. Saturated and unsaturated fatty acids

n-Alkanoic acids or saturated fatty acids (SFAs) ranging from 8 to 34 carbons were identified and quantified in acid-extracted samples (Table S1, sheet 6). Palmitic ($C_{16:0}$) and stearic ($C_{18:0}$) acid were the most dominant SFAs in all samples, and their relative contributions were more significant in samples below the burned layer, while samples situated in and above the burned layer generally yielded greater relative proportions of medium- to long-chain SFAs (Fig. S5). The unsaturated fatty acid $C_{16:1}$ was identified in 5 samples, $C_{18:1}$ in all 22 samples, and $C_{18:2}$ in 10 samples; $C_{18:3}$ was not identified

in any samples (Table S1, sheet 6). Lastly, two monoacylglycerols (monopalmitin and monostearin) were identified in several samples (Table S1, sheet 7).

Fatty acid ACL values varied from 17.42 to 23.70 with an average of 20.75 ± 1.75 for all samples, while those of ACL_{long} varied from 22.64 to 26.19 with an average of 25.02 ± 0.98 for all samples. The values yielded by these proxies generally increased with ascending elevation, on the order of 3.53 for ACL and 1.70 for ACL_{long} (values denote the difference in means), though a slight dip is similarly observed in the uppermost sample of sequences 2 and 3 (Fig. 9). EOP values ranged from 2.08 to 5.37 with an average of 2.89 ± 0.75 for all samples, and generally decreased from samples below the burned layer (3.43 ± 0.46) to those in (2.56 ± 0.23) and above it (2.45 ± 0.18) (Fig. 9). Fatty acid CPI results are reported in the supplementary information (SI-1). $FA_{s/l}$ values spanned from 0.75 to 108.46, and their average falls to 2.34 ± 1.72 when the high outlier of the control is removed. $FA_{s/l}$ values were highest in samples below the burned layer (4.27 ± 1.87), particularly in sequence 2, and generally decreased with ascending elevation to samples above the burned layer (average: 1.11 ± 0.31) (Fig. 9). The ratio of $C_{16:0}/C_{18:0}$ ranged from 0.51 to 1.05 (average: 0.74 ± 0.14), with the highest values observed in samples from the burned layer (0.80 ± 0.14). Lastly, $C18_{unsat./sat.}$ yielded values ranging from 0.002 to 0.71 (average: 0.18 ± 0.14), which were once more highest in samples from burned layer (0.21 ± 0.20) (Fig. 9).

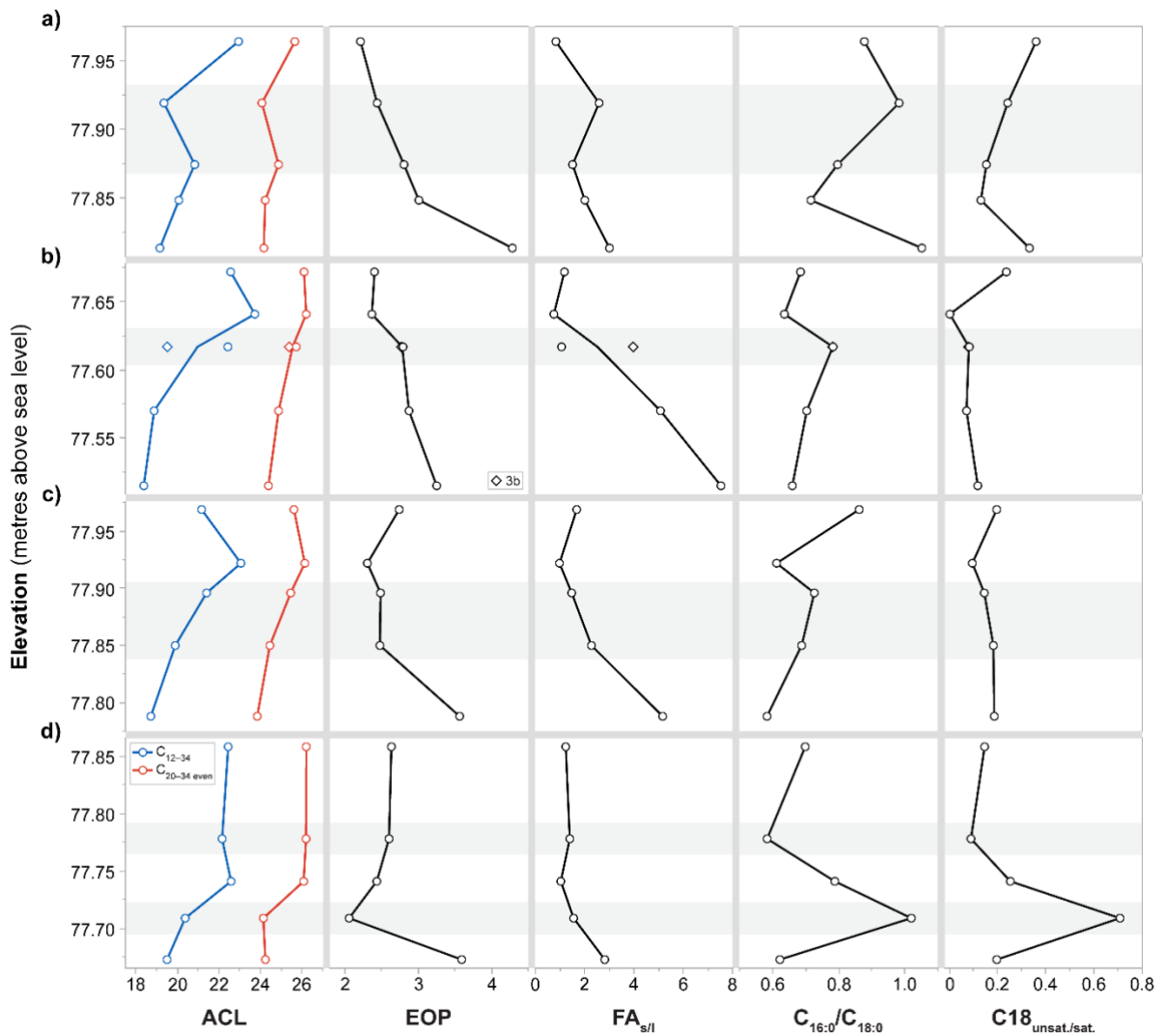


Fig. 9. Fatty acid proxy results for sequences a) 1, b) 2, c) 3, and d) 4. From left to right: (i) ACL (blue) and ACL_{long} (red), (ii) EOP, (iii) FA_{s/l}, (iv) C_{16:0}/C_{18:0}, and (v) C₁₈_{unsat./sat.}. The position of the burned layer(s) within each sequence is indicated by a shaded grey bar. The charcoal-rich sample J9 3b is denoted by a diamond.

The CDI of Schäfer et al. (2016) was calculated to assess contributions of coniferous (CDI-C), deciduous (CDI-D), and grass (CDI-G) vegetation to saturated fatty acids, with values compiled in a ternary plot. As Figure 10 illustrates, the control and samples below the burned layer clustered around CDI-C values of approximately 0.74, CDI-D values of ~0.22, and CDI-G values of ~0.04. Two outliers (samples 1–2 of sequence 2) yielded lower CDI-C (~0.58), higher CDI-D (~0.31), and higher CDI-G (~0.12) values. Burned-layer samples were more variable: four fell within the range of aforementioned control/below values, while four others clustered with samples above the burned layer (Fig. 10).

Samples above the burned layer yielded mean CDI-C values of 0.41 ± 0.05 , CDI-D values of 0.38 ± 0.02 , and CDI-G values of 0.21 ± 0.04 .

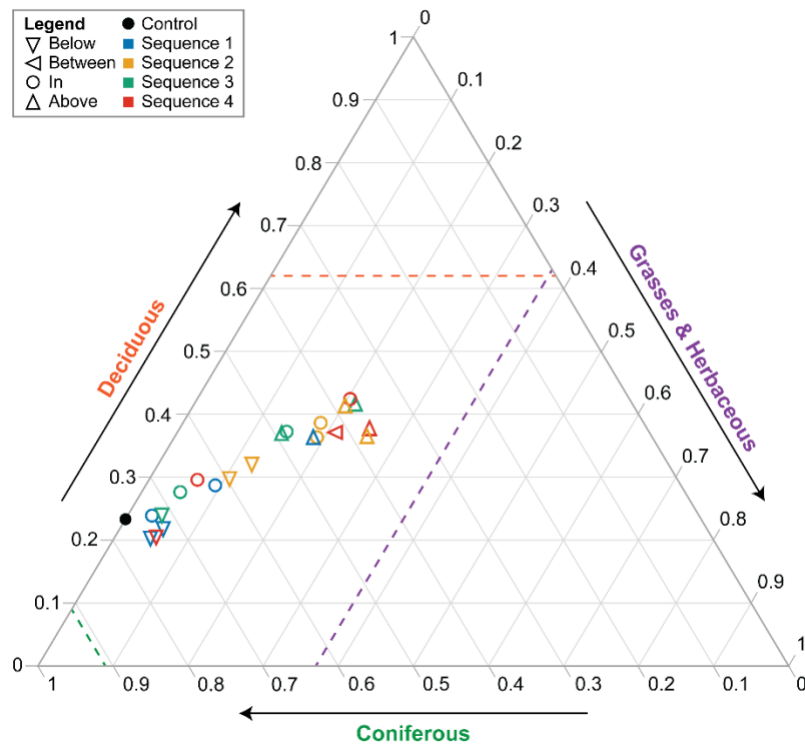


Fig. 10. Ternary plot of the Carbon Diversity Index. Samples are colour coded by sequence, with symbol shapes designating the stratigraphic position of the sample in relation to the burned layer(s). Reference lines are shown for each vegetation type with the maximum values (litter and topsoil) documented in the study of Schäfer et al. (2016).

4.2.4. Phytosterols and terpenoids

The TLE obtained by both solvent and acid extraction yielded various phytosterols and terpenoids (Table S1, sheet 7). A total of eight phytosterols were observed in both the solvent and acid extracts, and include compounds such as stigmast-5-ene, stigmasta-3,5-diene, stigmastanol, stigmasterol, β - and γ -sitosterol, and γ -sitostenone. Four diterpenoids were confidently identified in the solvent extract and include abietic acid, dehydroabietic acid, isopimaric acid, and methyl dehydroabietate. Numerous pentacyclic triterpenoids were also identified in both solvent and acid extracts, including: α - and β -amyrin, olean-13(18)-ene, friedelan-3-one, and D:A-friedoolean-6-ene, lupeol, lupenone, lupa-20,20(29)-dien-28-ol, betulone, betulinic acid, and betulin. Lupane family compounds (including betulin, betulone, and betulinic acid) were particularly abundant in sample M13 2, with only small or trace amounts in other samples. Other identified compounds indicative of plant

sources include a dialkyl ketone (nonacosan-10-one), a hopane, and wax esters of palmitic and stearic acids.

4.2.5. Aromatic biomarkers and selective ion monitoring results

Numerous aromatic hydrocarbons were identified in the solvent and acid extracts (Table S1, sheet 7). These included relatively simple compounds such as benzoic acid (and derivatives) and phthalic acid (derivatives and esters), as well as more complex compounds such as 7-oxo-7H-benzocycloheptene-6,8-dicarboxylic acid and oxirane (2,2'-[(1-methylethylidene)-bis(4,1-phenyleneoxymethylene)]bis). All benzene tricarboxylic acids (hemimellitic, trimellitic, and trimesic acid), tetracarboxylic acids (prehnitic, mellophanic, and pyromellitic acid), and possibly benzenepentacarboxylic acid were identified in the acid extracts of numerous samples. Interestingly, 2,4,6-hydroxy-trimesic acid was identified in a large number of samples. Several classes of PAHs and their derivatives were present, including: naphthalene (e.g., 2,6-naphthalenedicarboxylic acid), phenanthrene (e.g., 4-phenanthrene carboxylic acid, tetrahydroretene), and pyrene. An oxaspiro compound [7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione] and two phenolic compounds [phenol, 2,4-bis(1,1-dimethylethyl)-, phosphite (3:1) and tris(2,4-ditert-butylphenyl)phosphate] were also identified in the majority of samples (see Table S1, sheet 7).

Selective ion monitoring (SIM) was also conducted to target four compound groups of interest: (i) trimethyltridecanoic acids (TMTD), (ii) phytanic acid, (iii) pristanic acid, and (iv) ω -(o-alkylphenyl)alkanoic acids (APAAs) (see supplementary information). TMTD and pristanic acids were not identified in any sample. Trace amounts of phytanic acid isomers (SRR and RRR) were identified in all samples (excluding the control) and the relative abundance of these isomers was very similar, suggesting possible bacterial origins. Trace amounts of C18 APAAs, namely the E and F isomers (Hansel et al., 2004; Evershed et al., 2008; Bondetti et al., 2021), were identified in a number of samples and were particularly clear in sample H7 2.

4.2.6. Diacids and hydroxy fatty acids

A wide range of dicarboxylic acids (diacids) and hydroxy (α -, β -, ω -) fatty acids were identified in the TLE obtained by acid extraction, and to a lesser extent solvent extraction. Diacids of 8 to 32 carbons were identified, and their relative distribution follows a similar pattern to that observed in other aliphatic compounds, wherein longer chain homologues are more prevalent in samples above the burned layer (Fig. S6, see also Table S1, sheet 8). α -Hydroxy fatty acids of 16 to 30 carbons, even-numbered ω -hydroxy fatty acids of 12 to 24 carbons, and numerous β -hydroxy fatty acids were also identified (Table S1, sheet 7).

4.3. Benzene polycarboxylic acids and random forest predictions

BPCA data was obtained for a total of 25 samples, as 1 sample (H10 1) did not yield any BPCAs (Table S1, sheet 9). The total BPCA contents of soil samples normalised to the weight of the sample (g BPCA-C/kg sample) ranged from 0.002 to 36.73 (average: 4.28 ± 8.58), while those of charcoal ranged from 28.53 to 146.46 (average: 62.10 ± 48.88). Total BPCA contents normalised to sample TOC (g BPCA-C/kg OC), which reflect PyC aromaticity, varied from 2.91 to 362.44 in soil samples (average: 175.48 ± 127.79) and from 147.35 to 443.14 in charcoal (average: 290.26 ± 118.96). The control yielded 0.003 g BPCA-C/kg sample or 2.94 g BPCA-C/kg OC, composed entirely of B3CA isomers (trimellitic and trimesic acid). Aromatic condensation values, reflected by the relative abundance of mellitic acid (B6CA% or BPCA_{cond}), ranged from 0 to 33.69 in soil samples (average: 14.65 ± 13.00) and from 20.57 to 29.24 in charcoal (average: 23.84 ± 3.31).

In sequence 1, total BPCA contents (g BPCA-C/kg OC) increased steadily from 161.92 in sample 2 to 291.88 in sample 4, and fell slightly to 270.60 in sample 5 (Fig. 11a). The relative distribution of BPCAs was quite consistent across soil samples, with an average of $8.80 \pm 0.8\%$ B3CA, $32.43 \pm 3.67\%$ B4CA, $35.43 \pm 0.88\%$ B5CA, and $23.35 \pm 4.44\%$ B6CA. The associated charcoal (C1) yielded 443.14 g BPCA-C/kg OC, of which 29.24% were B6CA. Sequence 2 BPCA contents were highest in the burned layer (samples 3 and 3b, average: 353.7 ± 8.74), and decreased by approximately 250 g BPCA-C/kg OC to samples 2 and 4 (Fig. 11b). B6CA contents were significantly higher in samples 3 and 3b ($29.87 \pm$

0.82%) than in all other samples in this sequence, as the relative proportion of BPCAs with a fewer number of carboxylic acid substitutions (B3CA and B4CA) increased with distance from the burned layer. The associated charcoal (C2) yielded 365.14 g BPCA-C/kg OC, of which 23.70% were B6CA.

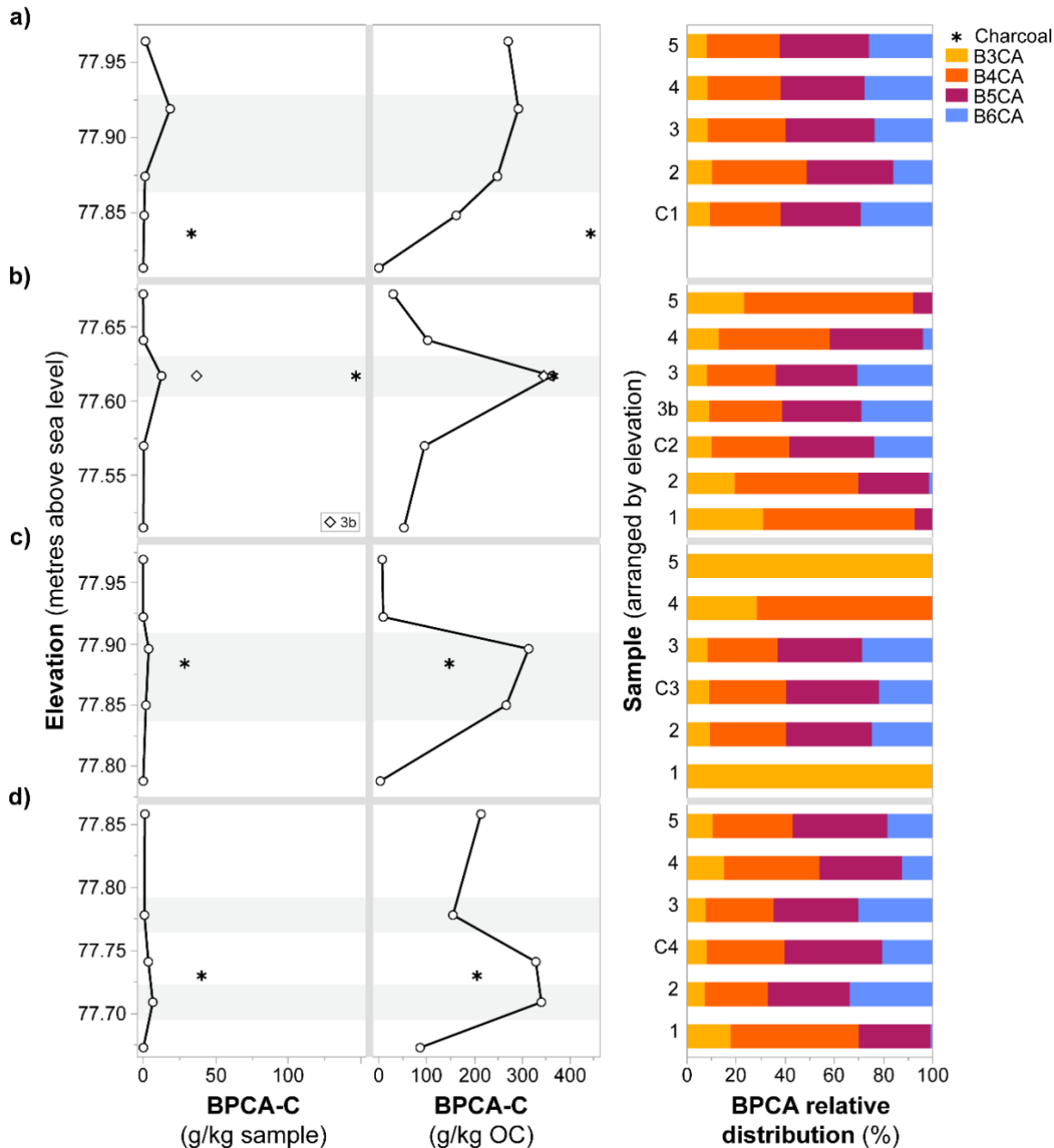


Fig. 11. BPCA results of sequences a) 1, b) 2, c) 3, and d) 4. From left to right: (i) total BPCA-C contents normalised to sample weight (g BPCA-C/kg sample), (ii) total BPCA-C contents normalised to TOC (g BPCA-C/kg OC), and (iii) the relative distribution of BPCAs containing 3–6 carboxylic acid substitutions. The position of the burned layer(s) within each sequence is indicated by a shaded grey bar. The charcoal-rich sample J9 3b is denoted by a diamond, and charcoal samples are denoted by an asterisk (*).

In sequence 3, samples 1 and 5 had the lowest BPCA contents (2.91 and 7.01 g BPCA-C/kg OC, respectively), which were composed exclusively of the B3CA isomer trimesic acid (Fig. 11c). Sample 4 yielded the third lowest BPCA content (9.18 g BPCA-C/kg OC), composed of only B3CAs and B4CAs. The full suite of BPCAs were present in samples 2 and 3, and sample 3 contained both a larger amount of BPCAs (313.38 g BPCA-C/kg OC) and a higher proportion of B6CA (28.73%) than sample 2. The associated charcoal (C3) yielded lower BPCA contents (147.35 g BPCA-C/kg OC) and a lower proportion of B6CA (21.85%) than soil samples located in the burned layer. Sequence 4 was unique in that two burned layers were visible in profile (samples 2 and 4), separated by seemingly unburned deposits (samples 1, 3, and 5). The lower burned layer (sample 2) produced the highest BPCA content in this sequence (339.88 g BPCA-C/kg OC) and the highest B6CA proportion (33.69%) of all samples analysed (Fig. 11d). Values declined slightly in the intervening deposit (sample 3: 328.39 g BPCA-C/kg, 30.33% B6CA) and more substantially in the upper burned layer (sample 4: 155.04 g BPCA-C/kg OC, 12.45% B6CA), before rising again in sample 5 (213.66 g BPCA-C/kg OC, 18.44% B6CA). Sample 1 yielded the lowest values of the sequence, with 86.27 g BPCA-C/kg OC and only 0.76% B6CA. The charcoal recovered in plan (C4) contained 205.40 g BPCA-C/kg OC, of which 20.57% were B6CA.

Quantitative and qualitative HTT predictions were obtained from BPCA results for the 19 samples that yielded B3CA–B6CA (Table S1, sheet 9). At 95% confidence, soil HTT estimates ranged from 159 ± 106 °C to 564 ± 164 °C, with an overall average of 361 ± 172 °C ($n = 15$). Samples from the burned layer produced a higher average of 419 ± 190 °C, which narrowed to 413 ± 98 °C at 68% confidence. These quantitative results are consistent with qualitative probability distributions. For example, while all soil samples were most frequently assigned to the 200–400 °C temperature class (0.60 ± 0.20), burned-layer samples showed higher probabilities of assignment to the 400–600 °C class (0.20 ± 0.08) compared to samples below (0.03 ± 0.02) or above (0.04 ± 0.02) the burned layer (Fig. 12). The four charcoal samples produced HTT estimates ranging from 311 ± 152 to 389 ± 161 °C, with an average of 355 ± 146 °C that is narrowed to 358 ± 84 °C at 68% confidence. Charcoal samples were similarly most frequently assigned to the 200–400 °C temperature class (0.76 ± 0.06). Regarding

precursor feedstock predictions, grasses and softwoods had the highest probabilities of assignment for both soil and charcoal samples, with soil values of 0.36 ± 0.21 (grasses) and 0.37 ± 0.14 (softwoods), and charcoal values of 0.37 ± 0.20 (grasses) and 0.39 ± 0.15 (softwoods) (Fig. 12, Table S1, sheet 9).

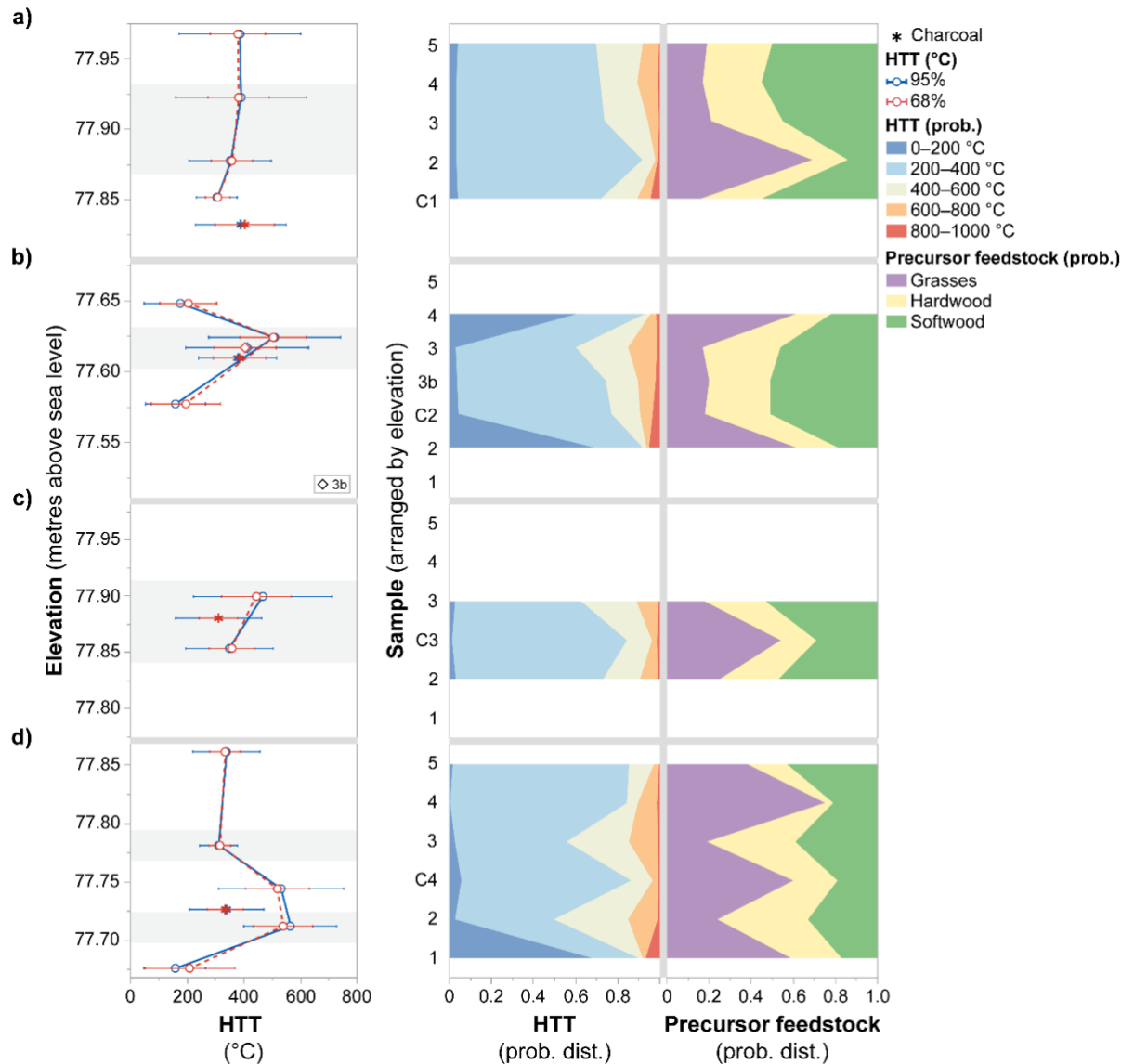


Fig. 12. Random forest predictions of heat treatment temperature (HTT, °C) and precursor feedstock (PF) category for sequences a) 1, b) 2, c) 3, and d) 4. From left to right: (i) quantitative predictions of HTT (°C) with confidence intervals of 68% (red) and 95% (blue), (ii) qualitative predictions (probability distribution) of HTT (°C) in 200 °C increments, where each range is exclusive of the minimum and inclusive of the maximum value; and (ii) qualitative predictions (probability distribution) of precursor feedstock at the level of grasses (purple), hardwoods (yellow), and softwoods (green). The position of the burned layer(s) within each sequence is indicated by a shaded grey bar. The charcoal-rich sample J9 3b is denoted by a diamond, and charcoal samples are denoted by an asterisk (*).

In sequence 1, soil HTT predictions peaked in sample 4 with values of 391 ± 231 °C (95%) and 382 ± 108 °C (68%), though mean estimates for samples 3 and 5 were within 50 °C of these values (Fig.

12a). Charcoal C1 demonstrated high coherence with the soil estimates, and yielded the highest HTT of all charcoal samples (95%: 389 ± 161 °C, 68%: 404 ± 104 °C). Sequence 2 HTT predictions were highest in sample 3 (95%: 509 ± 233 °C, 68%: 504 ± 117 °C), followed by the charcoal-rich sample 3b (95%: 412 ± 217 °C, 68%: 405 ± 110 °C), and decreased substantially in samples 2 and 4 (Fig. 12b). Charcoal C2 produced the second highest HTT among charcoal samples (95%: 379 ± 137 °C, 68%: 385 ± 93 °C), albeit lower than soil estimates from the burned layer. Sequence 3 soil HTT values were limited to the two burned-layer samples and were higher in sample 3 (95%: 467 ± 245 °C, 68%: 445 ± 123 °C) than in sample 2 (95%: 350 ± 154 °C, 68%: 358 ± 80 °C) (Fig. 12c). Charcoal C3 yielded the lowest HTT of all charcoal samples (95%: 311 ± 152 °C, 68%: 310 ± 68 °C). In sequence 4, soil HTT was highest in sample 2, which produced the maximum of all samples at 564 ± 164 °C (95%) and 539 ± 105 °C (68%). Sample 3 predictions also exceeded 500 °C (95%: 532 ± 220 °C, 68%: 518 ± 112 °C), and these estimates decreased to approximately 300–350 °C in samples 4 and 5 (Fig. 12d). Associated charcoal C4 had the second lowest HTT of charcoal samples at 340 ± 131 °C (95%) and 335 ± 63 °C (68%).

5. Discussion

5.1. Post-depositional modifications to the study area and studied residues

The Fontainebleau sands in which the burned deposits at Ormesson were preserved are coarse, porous, and exhibit weak aggregate stability, likely due to the presence of microcrystalline quartz and amorphous silica (French and Worden, 2013). These characteristics favour erosion, as exemplified by gully B, which separated the two Levallois occupations (Fig. 2). Combustion residues were nevertheless preserved in the western portion of survey 95, likely due to a combination of both macro-scale geomorphological factors (e.g., physical protection against erosion by the large sandstone boulders) and finer-scale taphonomic processes that ultimately promoted the persistence of OM and PyC in these deposits, but must be taken into account for the reconstruction of these fire traces.

5.1.1. Pyrogenic carbon preservation

Post-depositional modifications affecting PyC preservation and their relevance to BPCA results are discussed in depth in Notterpek et al. (2025) (see also Vaezzadeh et al., 2023). The most prevalent taphonomic pathways influencing PyC preservation in survey 95 include fragmentation and movement, the extent of which depend upon characteristics of the depositional environment (e.g., soil type, aggregate stability), as well as PyC physical properties (e.g., precursor feedstock type, particle size, surface area) and pyrolysis parameters (e.g., HTT) (Knicker, 2011; Singh et al., 2012; Chrzazvez et al., 2014; Pignatello et al., 2015; Saiz et al., 2018; Bellè et al., 2021). The high porosity and low aggregate stability of Fontainebleau sands facilitate PyC export (e.g., via water erosion, infiltration) compared to finer soils with strong aggregation (Brodowski et al., 2006; Chang et al., 2020; Bellè et al., 2021). Thermal exposure can alter these properties, particularly when followed by rainfall (Certini, 2005; Shakesby, 2011; Moody et al., 2013; Abney and Berhe, 2018), with variable outcomes including heat-induced aggregate breakdown (Jian et al., 2018) or the wash-in of ash/PyC resulting in pore clogging and surface sealing (though this is less common in coarse sands; see Onda et al., 2008; Stoof et al., 2016). PyC turnover is also slower in quartz sands than in fresh soils (Singh et al., 2012), possibly due to the strong sorption affinity of PyC for mineral phases and the mobilisation of mineral-associated OM (Glaser et al., 2000; Schiedung et al., 2020), as well as the greater abundance of non-pyrogenic OM primers (Hamer et al., 2004) that stimulate microbial activity in pedogenic soils (Czimczik and Masiello, 2007).

While lateral displacement of PyC was minimal in protected areas (i.e., the western portion where combustion residues were preserved), vertical movement is evident in the displacement of macrocharcoal fragments (e.g., C1) and in the dissolution of the burned layer with depth (e.g., sequence 3) (Fig. 4). The gradual tapering of BPCA concentrations below the burned layer, particularly when normalised to TOC (e.g., sequences 1 and 2, Fig. 11), provides molecular evidence for the downward infiltration of particulate PyC. In sequence 1, the high BPCA contents (g BPCA-C/kg OC) of sample 5 indicate upward migration of PyC, plausibly via the floating of porous microcharcoal particles

given their high initial hydrophobicity (Rumpel et al., 2015; Abney and Berhe, 2018), though alternative mechanisms such as micro- and meso-faunal bioturbation may also play a role. Within sequence 4, BPCA contents and BPCA_{cond} values fluctuated in a manner unobserved for sequences 1–3. This variability most plausibly reflects localised post-depositional reworking linked to the adjacent sandstone boulder (Fig. 2). The high aromaticity and aromatic condensation of sample 2 (which tapers toward sample 4) suggest that the first burned layer best represents the original burn deposit, with post-fire infilling creating a diluted upper layer (sample 4) that was consequently more exposed to taphonomic alteration. Field observations document heterogeneous and mottled deposits in this zone, consistent with small-scale infilling.

Molecularly, dissolved or non-mineral-protected PyC is more susceptible to diagenetic processes (e.g., oxidation, leaching, and biodegradation) that may preferentially degrade less aromatic and more weakly condensed components, and thereby enrich more heavily condensed BPCAs (see Vaezzadeh et al., 2023; Notterpek et al., 2025, and references therein). Conversely, less-condensed aromatic clusters with functional side chains (including those produced by aging) may interact more effectively with mineral phases, enhancing their stability and retention compared to highly condensed clusters with fewer functional groups (Schiedung et al., 2020; Pignatello et al., 2024). The relatively low mellitic acid yields obtained in this study, particularly compared to modern charcoals (Notterpek et al., 2025), do not suggest post-depositional inflation of heavily carboxylated BPCAs. The consistent relative distributions of BPCAs in sequence 1, and to a lesser extent sequence 4, further suggest that the translocated PyC fraction was primarily particulate rather than dissolved (Abiven et al., 2011; Santos et al., 2022; Vaezzadeh et al., 2023). Particle-size effects may contribute to the greater proportion of weakly condensed BPCAs with distance from the burned layer in sequences 2 and 3, as smaller PyC molecules are more readily transported (Spokas et al., 2014; Hobley, 2019), though additional research is required to clarify the influence of particle size on diagenetic alterations to aromatic condensation, particularly in aged samples (Abiven et al., 2011; Notterpek et al., 2025).

The total BPCA contents here measured substantially exceed those reported in other archaeological or ancient contexts (e.g., Kappenberg et al., 2019; Chu et al., 2022; Wöstehoff et al., 2022, 2023), reflecting favourable PyC preservation. Beyond the fragmentation and physical transport of PyC through various processes (e.g., thermal alteration, erosion, infiltration), diagenetic alterations to the polycondensed aromatic structures from which BPCAs are oxidised appear minimal, particularly for samples within the burned layer. The HTT values here presented may reflect the maximum temperature attained during pyrolysis, given the manner in which BPCA data are reported and the HTT prediction models were constructed (Notterpek et al., 2025). However, they may also represent the average temperature across the entire pyrolysis process, or alternatively, the temperature maintained for the longest duration during pyrolysis. While further experimental work is required to resolve this uncertainty, the absence of molecular evidence for the selective enrichment of heavily condensed PyC indicates that our values do not overestimate HTT. Further, any systematic model biases affecting HTT prediction accuracy should affect the assemblage uniformly. As such, variability in predicted HTT values — grounded in direct measures of PyC aromaticity and aromatic condensation — is interpreted to reflect genuine differences in the combustion conditions that governed PyC formation during the burn event.

5.1.2. Organic matter preservation

Reconstructing past environments or processes through lipid biomarker evidence requires careful interpretation of post-depositional alterations affecting data reliability. In addition to environmental ageing, thermal degradation constitutes an important diagenetic pathway in fire-affected deposits. Lipid preservation was evaluated in this study through proxies indicative of OM maturity, complemented by the identification of degradation markers. While the precise taphonomic process responsible for the observed degradation cannot always be identified given the multitude of potential pathways, several patterns emerge from the available evidence. The results broadly indicate the presence of both thermal and environmental degradation, selective taphonomic pathways

affecting certain compound classes over others, and stratigraphic variation in molecular distributions reflecting a combination of degradation and potential palaeoenvironmental shifts.

Numerous experimental studies have demonstrated that heat-induced cracking of the carbon bonds forming aliphatic hydrocarbon chains reduces chain lengths, thereby lowering ACL and increasing short- to long-chain ratios (e.g., $R_{s/l}$, $FA_{s/l}$) (Almendros et al., 1988; González-Pérez et al., 2008; Wiesenberg et al., 2009; Knicker et al., 2013; Sarangi et al., 2022). Alterations to chain lengths inevitably shift relative proportions of odd and even homologues, measured by the OEP, EOP, and CPI. These values are high in fresh vegetal matter (Eglinton and Hamilton, 1967), and typically decrease with thermal alteration (e.g., CPI_{long} , Wiesenberg et al., 2009). While inter-sequence variation was observed in the present study, shorter-chain homologues were generally more prevalent in deposits beneath the burned layer (Figs S3–S6), reflected quantitatively in the aforementioned proxies. This was most evident for *n*-alkanes in the transition to/from the burned layer (e.g., OEP, Fig. 7), suggesting that thermal alteration was a significant driver for alkane degradation. Attributing a uniquely thermal origin to this degradation is nevertheless complicated by potential precursor feedstock/tissue effects (e.g., leaves versus wood, Jambrina-Enríquez et al., 2018), combustion conditions (e.g., oxygen availability, Wiesenberg et al., 2009; Knicker et al., 2013), and characteristics of the depositional environment (Thomas et al., 2021). Other aliphatic lipids yielded variable signals (e.g., increased $FA_{s/l}$ with increased EOP) indicating compound-specific diagenetic processes. Still, pyrogenic markers such as APAAs (Bondetti et al., 2021) and likely methyl dehydroabietate (Davara et al., 2023) attest to thermally altered OM. Overall, biomarker evidence suggests that heat modified the molecular fingerprints of available biomass, but the extent of these alterations was not uniform across compound classes or zones of the fire-affected area.

Once deposited, the molecular signal of fresh or charred OM can be rapidly altered with integration into the mineral matrix, and variability is once more observed according to molecule type, precursor OM, pyrolysis conditions (if relevant), and depositional characteristics. Generally, open-system studies demonstrate results resembling those produced by thermal degradation, such as

decreasing *n*-alkane OEP or *n*-alkanoic acid EOP with increasing soil residence time (e.g., Hilscher et al., 2009; Knicker et al., 2013; Thomas et al., 2021). The molecular patterns here documented are therefore consistent with both environmental ageing and thermal alteration, making it difficult (and occasionally impossible) to disentangle the two (e.g., Eckmeier and Wiesenberg, 2009; Knicker et al., 2013). Selective preservation processes are also evident, as while *n*-alkanes exhibit more extensive degradation in the lower deposits (e.g., via OEP and CPI values of ~ 1), *n*-alkanol CPI and fatty acid EOP and CPI increase with depth. Intriguingly, $FA_{s/i}$ values also rise in the lowermost deposits, especially within sequence 2 (see also $C_{16:0}/C_{18:0}$, and $C_{18_{unsat./sat.}}$, Fig. 9). While the mechanism(s) behind these patterns remain unclear, these data highlight complex taphonomic pathways differentially affecting each molecule type. Importantly for palaeoenvironmental reconstructions, the enhanced preservation of *n*-alkanols and fatty acids compared to *n*-alkanes supports their use as more robust palaeoenvironmental tracers.

Furthermore, we did not detect lipid input from modern roots (Wiesenberg et al., 2010), algae and photosynthetic bacteria (Brocks and Summons, 2003), or microbes (Dudd et al., 1998; Quénée et al., 2006; Barré et al., 2018). However, the predominance of *n*-alkanol C_{18} in the control sample ($\sim 48\%$) mirrors observations for the sand fraction of forest and cultivated soils (Quénée et al., 2006), and may derive from suberin (Nierop et al., 2003), lower plants, or microbial spore lipids (Naafs et al., 2004). This control, located well below the burned layer, provides clear evidence of extensive environmental degradation without pyrogenic interference. Additional evidence for environmentally degraded, plant-derived OM was observed in specific markers, including: dehydroabietic acid from pine resin (Aveling and Heron, 1998); long chain diacids (C_{20} – C_{32} , Fig. S6) and ω -hydroxy acids (C_{20} – C_{24} , Table S1, sheet 7) from suberin (Otto and Simpson, 2006; Lin and Simpson, 2016); and mid-chain ω -hydroxy acids (C_{12} , C_{14}), potentially from cutin (Spielvogel et al., 2014).

Assembled, the diagenetic evidence suggests that the post-depositional translocation of thermally degraded OM down the soil profile provides a more plausible explanation for increased degradation than *in situ* heating during the combustion event. While thermal alteration up to 10 cm

below the soil surface has been reported in both wildfires and experimental studies, the recorded temperatures are generally low (e.g., 95 °C for surface fires, Campbell et al., 1995; Busse et al., 2005; ~200 °C in controlled experiments, Aldeias et al., 2016) and/or insufficiently sustained to account for the observed lipid transformations (see also Jambrina-Enríquez et al., 2018). Instead, vertical translocation of thermally altered OM (principally downward) appears more consistent with the data. Although the hydrophobicity of lipids renders leaching improbable, transport of particle-bound OM via percolating groundwater remains plausible. Lipids may also have been adsorbed by microcharcoal particles and particulate PyC, whose translocation is evidenced by BPCA yields and distributions (section 5.1.1). Such redistribution may have partially masked the endogenous OM signature in the pre-fire deposits, complicating the interpretation of aliphatic lipid distributions, yet not all compound classes were affected equally. Fatty acids and *n*-alkanols exhibit enhanced preservation compared to *n*-alkanes, potentially reflecting preferential stabilisation within organomineral complexes (e.g., Lin and Simpson, 2016; Chang et al., 2020). These findings thus indicate that while *n*-alkane signals require cautious interpretation, fatty acids and alkanols constitute more robust tracers for palaeovegetal and palaeoclimatic reconstructions in these deposits.

5.2. Palaeoenvironmental reconstructions from lipid biomarker evidence

Palaeoenvironmental reconstructions must account for the diagenetic processes outlined in section 5.1. By integrating multiple biomarkers and prioritising those shown to be more resistant to post-depositional alterations, we can extract the most reliable evidence for past vegetation and environmental conditions. The lipid biomarkers here identified provide robust evidence for significant OM input from higher terrestrial plants, including epicuticular waxes. This is supported by aliphatic lipid data indicative of degraded vegetal matter (section 5.1.2), as well as the presence of phytosterols common to higher plants (e.g., stigmasterol, stigmastanol, β -sitosterol) (Volkman, 2005). Together, these data indicate a vegetation shift from a conifer-dominant forest with scattered deciduous species (e.g., boreal forest) to a more mosaic post-burn landscape with greater contributions from deciduous trees, grasses, and herbaceous taxa (e.g., temperate broadleaf or mixed forest).

5.2.1. Palaeoenvironmental conditions prior to and at the moment of the combustion event

Anthracological evidence from survey 95 demonstrates that the biomass affected by the burn event, and thus established in the landscape at the time of the fire, was composed mainly of pine (*Pinus* cf. *sylvestris/nigra*) with sparse birch trees. This assemblage suggests a relatively open environment with cool climatic conditions.

Among the biomolecular evidence, terpenoids provide the most taxonomically informative data and corroborate anthracological identifications. The detected abietane-class compounds (e.g., abietic acid, dehydroabietic acid, methyl dehydroabietate) are tricyclic diterpenoids, which are common in gymnosperms and particularly prevalent in pine resins (Otto and Simoneit, 2001; Hjulström et al., 2006; Diefendorf et al., 2012; Davara et al., 2023). Dehydroabietic acid is frequently the most abundant resin acid in soils and sediments beneath pine forests (Almendros et al., 1988; Nierop et al., 2006), and its concentration has been shown to increase with heating (Diefendorf et al., 2015b; Davara et al., 2023). Methyl dehydroabietate may further indicate the “hard heating” of pine wood, rather than resin alone (Davara et al., 2023). Pentacyclic triterpenoids are typically found in angiosperms, and while often not family-specific, lupane and lupane-type markers are especially abundant in birch bark (Simoneit, 1986; Aveling and Heron, 1998). In the study of archaeological adhesives, the co-occurrence of these markers (e.g., betulin, lupeol, betulinic acid) is diagnostic of birch bark tar (Lucquin et al., 2007; Koch et al., 2024). Several of the identified markers (e.g., betulone, lupa-2,20(29)-dien-28-ol) are experimentally associated with the “soft heating” of birch bark, though they may also derive from natural decay (Aveling and Heron, 1998), and no markers associated with “strong heating” were detected (Rageot et al., 2019).

Although aliphatic lipid data is often less taxonomically specific than terpenoids or anthracology, *n*-alkane and *n*-alkanoic acid results similarly indicate a forested pre-fire landscape with minimal input from grasses and herbaceous materials. For example, *n*-alkane distributions (Table S1, sheet 4 and Fig. S3) and ACL values (Fig. 7) below the burned layer trend toward the dominant homologues documented in trees (C₂₇ and C₂₉) rather than those observed in grasses (C₃₁ and C₃₃)

(Poynter et al., 1989; van Bergen et al., 1997). *n*-Alkane ACL_{long} values in and below the burned layer (including the control and M13 2) align with those reported by Schäfer et al. (2016) in coniferous litter (~28.6–29.8) and topsoil horizons (~29.8–30.3), as well as deciduous forest horizons (particularly topsoil, ~29.0–29.7), from sites in central and southeast Europe. *n*-Alkane ratios similarly correspond to reference values for coniferous and deciduous forest horizons, particularly deciduous forest topsoils at 0–3 cm depth (~0.17–0.68) (Schäfer et al., 2016).

The variability of conifer values reported in the literature (e.g., Schäfer et al., 2016; Nezhad et al., 2024) reflects the difficulty of detecting this vegetation type via *n*-alkanes, given their lower abundance in conifers compared to angiosperms (Diefendorf et al., 2011, 2015a). Accordingly, other aliphatic compounds such as *n*-alkanoic acids provide more reliable evidence for conifer contributions to OM. The pre-fire presence of conifers is supported by fatty acid CDI results, which cluster toward the maximum value observed in coniferous forest horizons in the study of Schäfer et al. (2016): 0.91 (Fig. 10). For comparison, maximum values of 0.62 were documented in deciduous forests (CDI-D) and 0.37 in grasslands (CDI-G); higher values are systematically associated with stronger correlations to these vegetal sources and a greater ability to distinguish between them, even across different soil horizons (Schäfer et al., 2016). These results therefore suggest that pre-burn OM contributions were predominantly tree-derived, with greater input from conifers than deciduous species, and very minimal contributions from grasses.

n-Alkanol distributions are similarly consistent with higher plants (Kolattukudy, 1980), particularly suberized tissues (C_{16} – C_{24}) in samples below the burned layer (Kolattukudy, 2001). While primarily reflective of vegetal inputs to SOM, *n*-alkanols have also been proposed as palaeoclimatic indicators given potential correlations between *n*-alkanol proxies (ACL, CPI, alkanol index) and magnetic susceptibility. Higher magnetic susceptibility is positively correlated with warmer interstadial conditions and increased precipitation (Maher, 1998; Herries, 2006; Balsam et al., 2011), and has been observed to correlate with lower CPI, higher ACL, and higher alkanol index values (Zhang et al., 2006). Further, the ratio C_{24}/C_{26} may be inversely correlated with precipitation (Zheng et al., 2009). In the

present study, *n*-alkanol results below the burned layer are consistent with cold and arid climatic conditions, as evidenced by: (i) low ACL (< 28 , ΣC_{24-32} even) and alkanol index (< 0.35) values, which are consistent with those observed for glacial periods (MIS 6 and 4) in the loess sequence studied by Zhang et al. (2006); (ii) high CPI values (supplementary information); and (iii) elevated C_{24}/C_{26} values.

However, these palaeoclimatic interpretations must remain tentative given the limited number of studies exploring *n*-alkanol–climate relationships, many of which derive from environmental contexts far removed from the present study area (e.g., Rommerskirchen et al., 2003; Zhang et al., 2006; Zheng et al., 2009). Further studies are needed to corroborate these observations, particularly in fire-affected terrestrial records (for palaeovegetal studies in lacustrine and peat deposits, see Zheng et al., 2007; Zhou et al., 2010; Zhang et al., 2021, and references therein). Acknowledging the need for local calibration and the potential effects of diagenetic alteration on the observed signal (section 5.1.2), the evidence for cool and dry climatic conditions is nevertheless consistent with anthracological impressions of a *Pinus*-dominated boreal forest.

A final evidentiary lens, indicative of palaeovegetation at the moment of the combustion event, is that of BPCA-derived precursor feedstock predictions. While predictions extend beyond the macroscopic burned layer(s), this is likely due to the translocation of microcharcoal particles and molecular PyC (section 5.1.1), with all BPCAs derived from pyrogenic OM. Non-pyrogenic interference — for instance from petrogenic sources, humic acids, or plant biopolymers with non-condensed aromatic structures (e.g., lignin) (review in Vaezzadeh et al., 2023; Notterpek et al., 2025) — is negligible as: (i) petrogenic source material and humic acids were absent from the studied layers; (iii) sample OC contents were limited (Kappenberg et al., 2016; Di Rauso Simeone et al., 2024), and (iv) potential contributions, such as B3CA from lignin (Di Rauso Simeone et al., 2024), are mitigated by the full BPCA distribution being required for the random forest model (Notterpek et al., 2025). However, the accuracy level of this algorithm is lower than that of HTT (qualitative), at approximately 60% versus 80% (Notterpek et al., 2025). The results (Fig. 12 and Table S1, sheet 9) also demonstrate a possible conflation with HTT, as low-temperature samples tend to yield higher grass probabilities. These

limitations underscore the need for caution whilst model accuracy and taxonomic coverage are improved. Nonetheless, this method holds potential in its ability to estimate precursor feedstock contributions to microcharcoal and molecular PyC that are not amenable to anthracological study.

5.2.2. Post-fire palaeoenvironmental conditions: temperate broadleaf or mixed forest

While no anthracological data is available for the post-fire deposits, lipid biomarkers indicate a shift in OM contributions in samples overlying the burned layer marked by a contraction of coniferous vegetation, alongside the expansion of deciduous trees and grasses/herbaceous taxa.

Post-fire grass expansion is suggested in *n*-alkanes by increased C₃₁ and C₃₃ contributions above the burned layer (Fig. S3) (Poynter et al., 1989; van Bergen et al., 1997). Both ACL_{long} and *n*-alkane ratios correspond to grassland topsoil values (ACL_{long}: ~30.1–30.4, *n*-alkane ratio: 0.73–0.83) in these overlying samples, with the exception of M13 5 (Fig. 7), which overlaps with the high end of coniferous and deciduous forest values reported by Schäfer et al. (2016). These patterns may partly reflect taphonomic effects and highlight the difficulty of interpreting degraded Pleistocene samples (indicated by low OEP values) using modern references and calibration curves, as demonstrated by the erratic results produced by end-member modelling of grass contributions (Zech et al., 2013; Schäfer et al., 2016) (Table S1, sheet 4). Fatty acids, being better preserved than *n*-alkanes in survey 95 (section 5.1.2) and more sensitive to vegetation change involving conifers, provide stronger evidence for this shift. Compared to the pre-fire deposits, CDI results above the burned layer are tightly clustered (Fig. 10) and indicate reduced conifer input (lower CDI-C), additional deciduous contributions (higher CDI-D), and increased grass/herbaceous input (higher CDI-G).

The increase in *n*-alkanol chain lengths above the burned layer reinforces these trends, with the predominance of C₂₆ (Fig. S4) likely reflecting enhanced grass input (van Bergen et al., 1997; Naafs et al., 2004). This increase, expressed in ACL and alkanol index results, may also signal broader palaeoclimatic changes. Specifically, increasing ACL (on the order of ~0.74 with the calculation of Zhang et al., 2006; and ~1.56 with that of Zheng et al., 2009), decreasing CPI (supporting information), and alkanol index values typical of interstadial periods (> 0.4, Zhang et al., 2006) suggest a shift toward

warmer climatic conditions following the burn event. A concurrent decrease in C_{24}/C_{26} indicates increased moisture or humidity (Zheng et al., 2009). While these signals cannot be interpreted as direct climatic evidence without local calibration and complementary data, they contrast with the pre-fire signal and are consistent with vegetation changes indicated by other aliphatic lipids, involving a retraction of conifers (namely *Pinus*) and expansion of deciduous taxa, grasses and herbaceous plants.

Taken as a whole, palaeovegetal and palaeoclimatic data indicate a transition from a cool, *Pinus*-dominant boreal forest ecosystem to a warmer, more humid environment with temperate broadleaf or mixed forest characteristics. While chronometric control of the studied deposits are limited, with a *terminus ante quem* of 90.4 ± 6 ka, these shifts suggest a transition from stadial or cool interstadial periods to warmer interstadial conditions. If the deposits can be more narrowly constrained to MIS 5c, associated with the Brörup interstadial (Müller et al., 2003), the observed shifts may correspond to specific warming events. Based on the available data, we tentatively propose the transition from St. Germain Ia, which includes a short cold phase known as the Montaignu event (Woillard, 1978) marked by *Pinus* expansion (Müller et al., 2003; Helmens, 2014), to St. Germain Ic (Wohlfarth, 2013). Given the large number of fluctuations observed in Greenland ice-core records between ~90 and 110 ka (Rasmussen et al., 2014), and the limited chronological resolution of deposits, we do not attempt to link the studied sequence to individual stadial–interstadial events. Instead, this hypothesis rests on broader palaeovegetal and palynological data observed in nearby terrestrial records such as La Grande Pile (Woillard, 1978) and Les Echets (Beaulieu and Reille, 1984). Further refinement will require both higher-resolution chronometric data and palaeoclimatic evidence derived from additional methods.

5.3. Reconstructing the fire event in survey 95

With the data at hand, the natural or anthropogenic origins of these combustion traces can be evaluated through three primary lenses: (i) macroscopic and anthracological evidence, (ii) molecular evidence, and (iii) char production parameters, specifically HTT.

5.3.1. Macroscopic and anthracological evidence

From a geological and archaeological point of view, the quantity of combustion residues and their characteristics support the hypothesis of a wildfire. For instance, no macroscopic evidence for a concentrated zone of combustion residues surrounded by more dispersed areas (as could be envisioned for certain anthropogenic fires) were identified. This does not, however, negate the possibility of *in situ* combustion features masked by a subsequent natural fire, or of large-scale anthropogenic fires for other intended purposes (e.g., smoke signalling, site abandonment). Because wildfires (including ground, surface and crown fires) generate diverse macroscopic charcoal remains, closer examination of the anatomical features of the charcoal assemblage may provide a more reliable basis for distinguishing these fire regimes.

Ground fires consume heterogeneous, small-calibre fuels (e.g., roots) and other SOM below the ground surface under limited oxygen supply, resulting in a high degree of incomplete carbonisation (Rein et al., 2008; Watts and Kobziar, 2013). Surface fires involve the combustion of dead litter accumulations and low-lying surface biomass (i.e., brush, twigs) under low to medium oxygenated conditions, and generally produce large quantities of charcoal (Albini, 1993; Stocks and Kauffman, 1997; Scott, 2010). Crown fires describe the combustion of canopy biomass, often initiated by surface fires or lightning strikes, and are common in conifer forests (Van Wagner, 1977). They typically burn only twigs and needles, generating significant amounts of microcharcoal in smoke but limited macrocharcoal remains (e.g., partially charred tree trunks) (Komarek et al., 1973; Stocks and Kauffman, 1997). Ground fires may accompany crown fires, particularly in areas where underlying soils contain substantial humus or peat deposits, and can burn for prolonged periods (Komarek et al., 1973; Pyne et al., 1996; Scott, 2010).

For all wildfire types, the degree of fuel heterogeneity is contingent upon the diversity of available biomass. As the assemblage of survey 95 is strongly *Pinus* dominated, wood taxonomy provides limited insight into fire type, highlighting the importance of anatomical features. However, direct comparisons between contemporary fire observations and ancient charred remains must be

811 treated with caution. Interpretations of anatomical signatures should carefully consider the range of
812 post-depositional processes that may have altered the original charcoal assemblage, which was
813 formed in a biased and incomplete manner. Nevertheless, the anthracological data from Ormesson
814 casts doubt on the likelihood of a crown fire given the abundant macrocharcoal remains, which feature
815 a high proportion of branch wood (48%) and small proportion of green wood (7%). Yet based on this
816 evidence, we cannot negate the possibility that the charcoal assemblage was formed by the
817 combustion of surface vegetation during a crown wildfire. The high proportion of branch wood and
818 low proportion of dead wood (13%) further indicate a distinctive formation process, particularly as
819 dead wood generally constitutes the majority of fuel utilised by Palaeolithic societies (Théry-Parisot,
820 2001).

821 The primary anatomical feature observed in the charcoal assemblage was vitrification, the
822 origins of which remain debated. Although vitrification is closely associated with combustion (i.e., it
823 cannot occur without carbonisation), other factors such as the characteristics of the wood (e.g.,
824 physiological state) and/or particular combustion conditions appear necessary to produce cellular
825 fusion. Several hypotheses have been proposed for vitrification, including high pyrolysis temperatures
826 (McParland et al., 2010), high wood moisture content (Prior and Alvin, 1986; Henry, 2011), oxygen-
827 starved combustion (Fabre, 1996), or other specific combustion conditions (Vidal-Matutano et al.,
828 2019, 2020; Courty et al., 2020). However, these hypotheses currently lack strong experimental
829 support (Théry-Parisot, 2001; McParland et al., 2010). The high proportion of vitrification here
830 observed (67%) is notable compared to other archaeological contexts, where it is typically observed in
831 less than 5% of the charcoal assemblage. While the high frequency of vitrification and low proportion
832 of dead wood attest to the unique nature of the combustion event, these features are insufficient to
833 determine whether the fire was natural or anthropogenic, or to identify the wildfire type best
834 correlated with the macroscopic charcoal remains.

5.3.2. Molecular evidence

The molecular discrimination of natural and human-controlled fires has been principally pursued through the analysis of PAH and BPCA distributions (e.g., Wolf et al., 2013; Brittingham et al., 2019; Stancampiano et al., 2023). Pyrogenic lipid biomarkers formed within precise temperature ranges are also informative, as they may aid reconstructions of HTT (e.g., Jambrina-Enríquez et al., 2019). For instance, as APAAs are formed by the heating of unsaturated fatty acids at temperatures above 270 °C for 1 h or 200 °C for 5 h (Hansel et al., 2004; Admiraal et al., 2019; Bondetti et al., 2021), the trace presence of these compounds provides molecular evidence for the thermal alteration of unsaturated fatty acids above at least 200 °C. However, these pyrogenic markers attest only to pyrolysis, not to the specific origin of the combustion process.

In the case of BPCA analysis, recent work (Notterpek et al., 2025) has shown that the ratio of B5CA/B6CA is indeed correlated with HTT, but is not reliable for the reconstruction of past fire regimes (Wolf et al., 2013). Other BPCA outputs are more significantly correlated with HTT, and robust HTT reconstruction requires integrating multiple quantitative outputs (Notterpek et al., 2025). Furthermore, we must reckon with the heterogeneity of combustion events and develop methods to account for this heterogeneity in ancient samples, both in relation to the initial combustion event and subsequent post-depositional alterations. Archaeological interpretations of PAH distributions (light versus heavy) to reconstruct hominin fire activity (e.g., Brittingham et al., 2019) are subject to the same caveats, as these distributions must be interpreted in light of taphonomy as well as understandings of wildfire particle emissions that continue to be refined (e.g., Denis et al., 2012; Argiriadis et al., 2018).

A greater abundance of heavy PAHs or heavily carboxylated BPCAs reflects PyC characteristics, such as increased aromatic condensation (due to high HTT, oxygen-starved combustion, etc.), rather than the origin of these pyrogenic markers. No unambiguous “anthropogenic” fire markers have yet been identified, and even if seemingly anthropic markers were detected, their presence could be explained by non-human factors — for instance, heated animal fats from carcasses, or resin acids from conifer trees naturally present in the fire-affected area. Molecular evidence for pyrolysis at Ormesson

is therefore inconclusive, though such data may acquire greater discriminatory power when supported by additional studies of molecular heterogeneity in natural and human-controlled fires, and the effects of environmental diagenesis on these molecular signals.

5.3.3. Char production parameters (HTT)

The final evidentiary lens with the potential to distinguish natural and anthropogenic fires is that of char production parameters, which broadly encompass factors such as precursor feedstock type, oxygen availability, combustion duration, and HTT. This prospect is complicated, however, by the substantial variability of these parameters within a single combustion event (whether natural or anthropogenic) and the difficulty of disentangling these variables in molecular or other archaeometric analyses. Among these factors, HTT currently appears most promising given the extensive experimental measurements available for wildfires and human-controlled combustions, which constitute a robust reference corpus against which HTT estimates from unknown samples can be compared.

To contextualise HTT values, it is constructive to consider the range of temperatures reported for different wildfire types. Ground fires have relatively low combustion temperatures of $\leq 300\text{ }^{\circ}\text{C}$ (Rundel, 1981, 1983), though higher temperatures of up to $600\text{ }^{\circ}\text{C}$ (averaging $400\text{ }^{\circ}\text{C}$) have been documented (Usup et al., 2004; Rein et al., 2008). Surface wildfires reach temperatures of approximately $\leq 350\text{ }^{\circ}\text{C}$ in the litter layer (median: $283 \pm 134\text{ }^{\circ}\text{C}$ per Wolf et al. 2013), including grasses and other herbaceous materials (Albini, 1993; Stocks and Kauffman, 1997), but may reach higher temperatures ($\sim 600\text{ }^{\circ}\text{C}$) elsewhere that persist for several hours (Pyne et al., 1996). Shrubland surface fires are associated with higher combustion temperatures of approximately $450\text{ }^{\circ}\text{C}$ (median: $503 \pm 211\text{ }^{\circ}\text{C}$ per Wolf et al. 2013). Crown fire combustion temperatures vary widely in the literature, but these fires generally burn hotter (approximately $800\text{--}900\text{ }^{\circ}\text{C}$) than ground or surface fires, with reports of air temperatures peaking as high as $1330\text{ }^{\circ}\text{C}$ (Butler et al., 2004; Doerr et al., 2018). Acknowledging the diversity of actualistic wildfire combustion temperatures due to environmental factors (e.g.,

atmospheric humidity), we can generally predict temperatures of < 600 °C for ground and surface fires and > 800 °C for crown fires.

Experimental archaeological research has documented a wide range of temperatures associated with different hearths, with average and maximum combustion temperatures (as well as flame duration, luminosity, radiative heat output, etc.) conditioned by a host of factors not limited to: hearth shape and size, fuel type and condition, environmental constraints, and maintenance behaviours (Sievers and Wadley, 2008; Braadbaart et al., 2012; March et al., 2014; Aldeias, 2017). Nevertheless, average combustion temperatures of 250–550 °C and maximum temperatures of 460–800 °C are documented in conventional open-air hearths (Théry-Parisot et al., 2025). Per the review of Wolf et al. (2013), domestic fires were associated with higher median temperatures of 797 ± 165 °C.

Consequently, expected temperature ranges for anthropogenic hearths and ground/surface wildfires overlap between 250 and 550 °C. The BPCA-derived HTT estimates here presented fall precisely within this range, at approximately 300–400 °C for charcoal samples and 400–550 °C for soil samples. These values are therefore consistent with surface wildfire temperatures, including those coinciding with crown fires, as well as human-controlled, open-air hearths. While reconstructed temperature data has been utilised to identify low-temperature surface fires, with sporadic high measurements attributed to possible canopy combustion (Marynowski et al., 2011), the ability of HTT to discriminate between anthropogenic fires and most wildfire types thus appears limited. This limitation is compounded by diagenetic alterations to the material from which HTT estimations are derived, which impact the reliability of HTT predictions, as shown for elemental analysis (Mouraux et al., 2022) and the Raman–HRTEM method (Deldicque et al., 2023; Delarue et al., 2024) in charcoal. As discussed in section 5.1.1, uncertainty also persists regarding the specific temperature measured by these proxies. Further research is required to resolve these uncertainties and, as for molecular distributions, to develop approaches that account for heterogeneity in combustion processes and their resultant residues.

6. Conclusion

Our multiproxy analyses have demonstrated several key points for the interpretation of these fire traces, notably that:

- The charcoal assemblage is dominated by *Pinus* cf. *sylvestris/nigra*, with some *Betula* sp. and gymnosperm taxa. The charcoals exhibit a significant degree of vitrification (67%) with high amounts of branch wood (48%), and smaller amounts of dead wood (13%) and evidence for green wood combustion (7%).
- Higher terrestrial plants are a significant contributor to SOM, with biomolecular evidence for the presence of conifer trees (e.g., Pinaceae, via diterpenoid resin acids) and angiosperm species (e.g., birch, via lupane-family pentacyclic triterpenoids). Following the burn event, the local environment likely saw a reduction in conifer species and an increase in deciduous trees and grassy/herbaceous vegetation.
- The combustion produced significant quantities of PyC, with BPCA contents of up to 362 g BPCA-C/kg OC in soil samples and 443 g BPCA-C/kg OC in charcoal samples, and aromatic condensation values of up to 34%. HTT predictions derived from BPCA results indicate combustion temperatures of approximately 300–400 °C in charcoal samples and 400–550 °C in soil samples from the burned layer.

Mobilising this data to determine the nature of the combustion event requires careful consideration of the identification criteria for past fire traces, yet this study has demonstrated the substantial equifinality of archaeometric and geochemical data from natural and anthropogenic fires. This highlights a broader methodological issue, in that clear diagnostics for differentiating these fire types do not currently exist. Past fire traces are often interpreted on the basis of geological and archaeological observations, without geochemical and molecular support, despite the abundance of molecular data held within soil and sedimentary matrices. This can be justified in cases such as clearly structured hearths within the archaeological deposits of a cave site. However, cases such as Ormesson featuring extensive combustion residues in an open-air context, or the Caune de l'Arago with scattered fire traces in a cave site (Deldicque et al., 2021), encourage rigorous engagement with the null

hypothesis: that the combustion residues are non-anthropogenic in origin. In light of all available evidence, we accept this null hypothesis and thus do not attribute an anthropic origin to these combustion residues.

This wildfire, in a landscape dominated by *Pinus* spp., was likely intense given the sheer quantity of combustion residues and PyC produced. However, BPCA-derived temperature estimates fall in the expected ranges for both anthropic and natural fire types. Further research is needed to better characterise alterations to the BPCA signal through environmental degradation and to determine how post-depositional processes, such as the selective preservation of weakly condensed PyC (via organomineral interactions), may impact HTT estimates. Experimental research into the factors producing charcoal vitrification will also help clarify the exceptional combustion conditions of this previously unknown wildfire in the Paris Basin region during the Early Weichselian glacial period (MIS 5). More broadly, archaeological and environmental scientists must establish rigorous, systematic guidelines for interpreting past fire traces that address the challenges of equifinality. In doing so, we will be able to harness the full potential of macroscopic, microscopic, and molecular data in ancient and archaeological combustion residues. This is particularly important for analysing the often-ephemeral fire traces of the Pleistocene, so critical to understanding the evolution of pyrotechnology among Pleistocene and Palaeolithic hominins.

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1425

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1429 **Data availability**

1430 All data is contained within the submission. Table S1 and raw chromatograms are also available for
1431 download from the Zenodo repository (doi: 10.5281/zenodo.15113743).