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Resinous deposits in Early Neolithic pottery vessels from the northeast of the Iberian Peninsula

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ABSTRACT

The use of resinous substances, certainly one of the earliest technologies developed by humans, was well-known by Holocene hunter-gatherers at the onset of the Neolithisation process across Europe. Recent research has revealed the use of birch bark tar in the central Mediterranean far from this taxon's endemic regions both in the Paleolithic and Neolithic periods and shows that the first farmers from the Fertile Crescent hafted lithic tools and waterproofed artefacts using bitumen.

The generalised absence of these natural products in south-western Europe may have thus forced a reformulation of Early Neolithic technologies by exploring and benefitting from existing knowledge in local European hunter-gatherer societies. However, information on resin use from the western Mediterranean is still scarce. Here, we report on the analysis of organic residues from 168 pottery sherds by gas chromatography and gas chromatography-mass spectrometry from 10 archaeological sites in this region dating from the second half of the VIth millennium to the first half of the Vth millennium cal BC. In a limited number of samples, minor amounts of several diterpenoids diagnostic of aged Pinaceae resins were detected as mixtures with fats.

The presence of pine in the palynological and carpological record supports the human exploitation of this taxon, but its minimal incidence in the anthracological record suggests that other species were selected as fuelwood. This supports the hypothesis that Pinaceae resins were used in association with pottery sporadically but ubiquitously either as its contents, or as post-firing treatments to waterproof the vessels. This demonstrates the development of adhesive technologies and resin-involved labour processes specific to Early Neolithic societies.

1. Introduction

In the Neolithic period (here referring to approx. 7000–3500 cal. BC), archaeological evidence suggests that resinous substances were multifunctional materials used as waterproofing agents, adhesives and decorative materials (Rageot et al., 2021, 2016). There is a significant body of research supporting the widespread use of bitumen in the Fertile Crescent (ex: Connan and van de Velde, 2010; Breu et al., 2022) which predates the introduction of agriculture and pastoralism (Bar-Yosef, 1987; Rosenberg and Chasan, 2021). Nevertheless, in Neolithic Europe, mainly birch bark tar and tree resins were chosen for the same applications (Chen et al., 2022; Rageot et al., 2016, 2021; Urem-Kotsou et al., 2018) although bitumen was still used in southern Italy, where accessible deposits existed (Nardella et al., 2019). Whether newly arrived

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Neolithic groups developed the technology to produce birch bark tar independently or they adopted it after contacts with local communities is a question still unresolved.

Data on hafting adhesives from hunter-gatherer populations are scarce in Europe. Analyses indicate birch bark tar was already extensively used (Aveling and Heron, 1998; Fletcher et al., 2018; Mazza et al., 2006; Niekus et al., 2019), and studies from southern Italy suggest Pinaceae resins were exploited (Degano et al., 2019) at least in the Middle Palaeolithic. Nonetheless, the exact strategies used by Epipaleolithic groups remain unknown. The choice of resinous substances adopted by Neolithic groups would certainly be affected by the varied environment contexts in Europe. As detected for other plant resources, there were significant differences between Neolithic groups in the western Mediterranean and in Northern Europe and the Balkans (de Vareilles et al., 2020).

Archaeological evidence supporting the use of resins from species other than birch is not substantial (Rageot et al., 2021). Before the IVth millennium, remains of Pinaceae adhesives in the Mediterranean region are scarce. Only 10 pottery vessels out of 70 (14%) from Greece and the Balkans (Makriyalos, Toumba Kremastis Koliadas, Drenovac and Dikili Tash)(Garnier and Valamoti, 2016; Mitkidou et al., 2008; Urem-Kotsou et al., 2018) presented evidence of abietane diterprenoids. In the Pendimoun rock shelter (southern France), 16 vessels from a sample of 52 (30%) presented minimal amounts of diterpenoids which were not analysed further due to the absence of pine in the anthracological record from the site (Drieu et al., 2021).

The Early Neolithic in the northeast of the Iberian Peninsula is characterised by small communities comprising round huts with underground silos to store farming produce and, later, debris from everyday life (Prats et al., 2020). Herds were mainly composed of ovicaprines and, to a lesser extent, bovines and suines (Saña Seguí et al., 2021). Domestic cereals including wheat and barley were farmed intensively (Antolín et al., 2015). Fruits including *Corylus avellana, Quercus* sp. and *Pinus* sp., amongst others, (Antolín et al., 2018) were gathered across the territory. Terrestrial animals, including *Cervus elaphus*, *Sus scrofa*, *Capreolus capreolus* and *Capra pyrenaica*, were seldom hunted (Antolín et al., 2018). Marine shell was used extensively as raw material by craftspeople for ornamental purposes and as tools to decorate vases by potters.

The arrival of the Neolithic in the Iberian Peninsula presents a singular case regarding resin use, as birch was extremely scarce in this region (Revelles et al., 2018; Riera et al., 2016). While Pinaceae resins would have been more readily available, there is an absence of compelling evidence proving their use in the Early Neolithic archaeological record. Only two visible residues from the site of La Draga indicate the presence of a birch bark tar glue in a marble bracelet and a Pinaceae hafting adhesive (Rageot et al., 2021; Tresserras, 2000). Following the pattern of Pinaceae resin scarcity seen in other Early Neolithic Mediterranean regions hitherto, evidence of diterpenoid resins in the Iberian Peninsula has only been reported in two out of 26 ceramic samples (8%) from layer IV in Cueva del Toro (5280–4780 cal BC) (Tarifa-Mateo et al., 2019). Additional evidence is only found in Bronze Age Argaric pottery: two vessels from Peñalosa (Manzano et al., 2015), three vessels from La Bastida, one vessel from La Almoloya (Molina, 2015) and one vessel from Castro dos Ratinhos (García, 2010) were reported to contain diterpenes from Pinaceae resins.

Therefore, further analyses are necessary to assess whether resins were a commonly exploited substance by the first farmers and herders of the Iberian Peninsula. Assessing whether the generalised European pattern of birch bark tar use reached Iberia is key to better understand the socioeconomic and technological relationships developed between different Mediterranean regions within the *Impressa*, Cardial and Epicardial spheres and possible local preceding hunter-gatherer groups. To this end, this paper reports on the results of gas chromatography and mass spectrometry (GC–MS) analyses evaluating the presence of biomarkers from resinous substances in Early Neolithic pottery from the northeast of the Iberian Peninsula. The three main aims are:

- To better understand the conditions under which pottery vessels might have been exposed to resinous substances.
- To approximate how intensively were resins used in pottery though vessel lifetime.
- To explore which resin-producing species present in the pollen and carpological records might have been exploited.

Throughout the results, discussion, and conclusion sections of this paper, we will argue that Neolithic technologies in the northeast of the Iberian Peninsula included the infrequent but ubiquitous collection and use of Pinaceae resins in contact with pottery.

2. Materials and methods

2.1. Materials

To achieve the stated objectives, 168 ceramic samples (Table 1) were obtained from 10 Early Neolithic (Cardial and Epicardial) sites (Fig. 1). These were located along the north-eastern coast of the Iberian Peninsula and dated between 5500 and 4500 cal BC. (available ^{14}C dates and chronologically diagnostic pottery types for each site can be found in the supplementary materials (SI1). In this period, while the most intense occupations have so far been detected on plains and lowlands (La Draga, Caserna de Sant Pau-Carrer Reina Amàlia, Guixeres de Vilobí, El Molló, El Cavet), caves in highlands and planes were also frequently used (Cova de Sant Llorenç, Cova de Can Sadurní, Cova de la Guineu, Cova de la Font major). In consequence, the sites sampled in this study are representative of the occupation pattern in the region.

Regarding the archaeological context, the first third of the samples was recovered from pit silo refills at four sites, the second third of the samples belonged to the refilling of sunken huts from two sites and the last third was recovered from cave (17%) and open air (16%) occupation layers at six sites (Table 1). While most of the samples date to the Cardial period (n = 102, seven sites), 66 Epicardial vases from four sites were also studied.

The sampled ceramic assemblage, composed of rims and wall fragments, presented smoothed surfaces and impressed Cardial decorations using toothed seashells. In Epicardial sherds, decoration was incised or made via the application of cords in orthogonal dispositions. Pottery was made using mainly local clays through coiling and was fired completely in combustion structures with scarce control over the input of oxygen. The main forms included small to medium bowls, hemispheric and subspherical pots and necked S-shaped vases. (Binder et al., 2010; Clop, 2005; Gómez et al., 2008; Morales and Oms, 2008; Oms et al., 2016).

2.2. Methods

After removal of the vessel's interior surface (1–2 mm) and collection of roughly 1 g of pottery powder, all samples were spiked with 10 μg *n*-tetratriacontane (internal standard 1) and prepared using an acidified methanol extraction (Correa-Ascencio and Evershed, 2014). Before injection, all samples were spiked with 10 μg of *n*-hexatriacontane. For this assemblage, the analysis of the vessel's exterior to further study potential contamination was not advised. Early Neolithic pottery fragments were usually too fragmented to withstand two different extractions, and, the destructive nature of the analyses was not compatible with the necessary preservation of impressed, incised or applied decorations. Extracts were screened using gas chromatography with flame ionisation detection (GC-FID) to identify samples with significant quantities of lipids. These were total lipid extracts above the 5 $\mu g \cdot g^{-1}$ stablished thereshold (Evershed et al., 2008), which is the most frequently used for samples in the Iberian Peninsula (Breu et al., 2021; Cubas et al., 2020; Tarifa-Mateo et al., 2019). Selected cases were further analysed through gas chromatography-mass spectrometry (GC–MS) to identify the

Table 1
Detail of all the studied sites, their chronologies, sampled archaeological contexts and the number of vessels analysed using GC-FID and GC–MS.

Archaeological site	Region	Period	Archaeological context	Number of samples	
				GC-FID	GC–MS
Caserna de Sant Pau	Barcelona plain	Cardial	Silo pit refilling	24	24
Carrer Reina Amàlia	Barcelona plain	Epicardial	Sunken Hut refilling	52	52
Cova de Sant Llorenç	Garraf	Cardial + Epicardial	Cave occupation layers	4	4
Can Sadurní	Garraf	Cardial + Epicardial	Cave occupation layers	7	7
La Serreta	Penedès	Cardial	Silo pit refilling	12	6
Guixeres de Vilobí	Penedès	Cardial	Settlement occupation layers	22	5
Cova de la Guineu	Penedès	Cardial	Cave occupation layers	13	2
El Cavet	Camp de Tarragona	Cardial	Silo pit refilling and occupation layers	22	7
Cova de la Font Major	Conca de Barberà	Cardial	Cave occupation layers	5	2
El Molló	Ebro	Epicardial	Hut and silo pit refilling	7	7
Total		Cardial + Epicardial		168	116

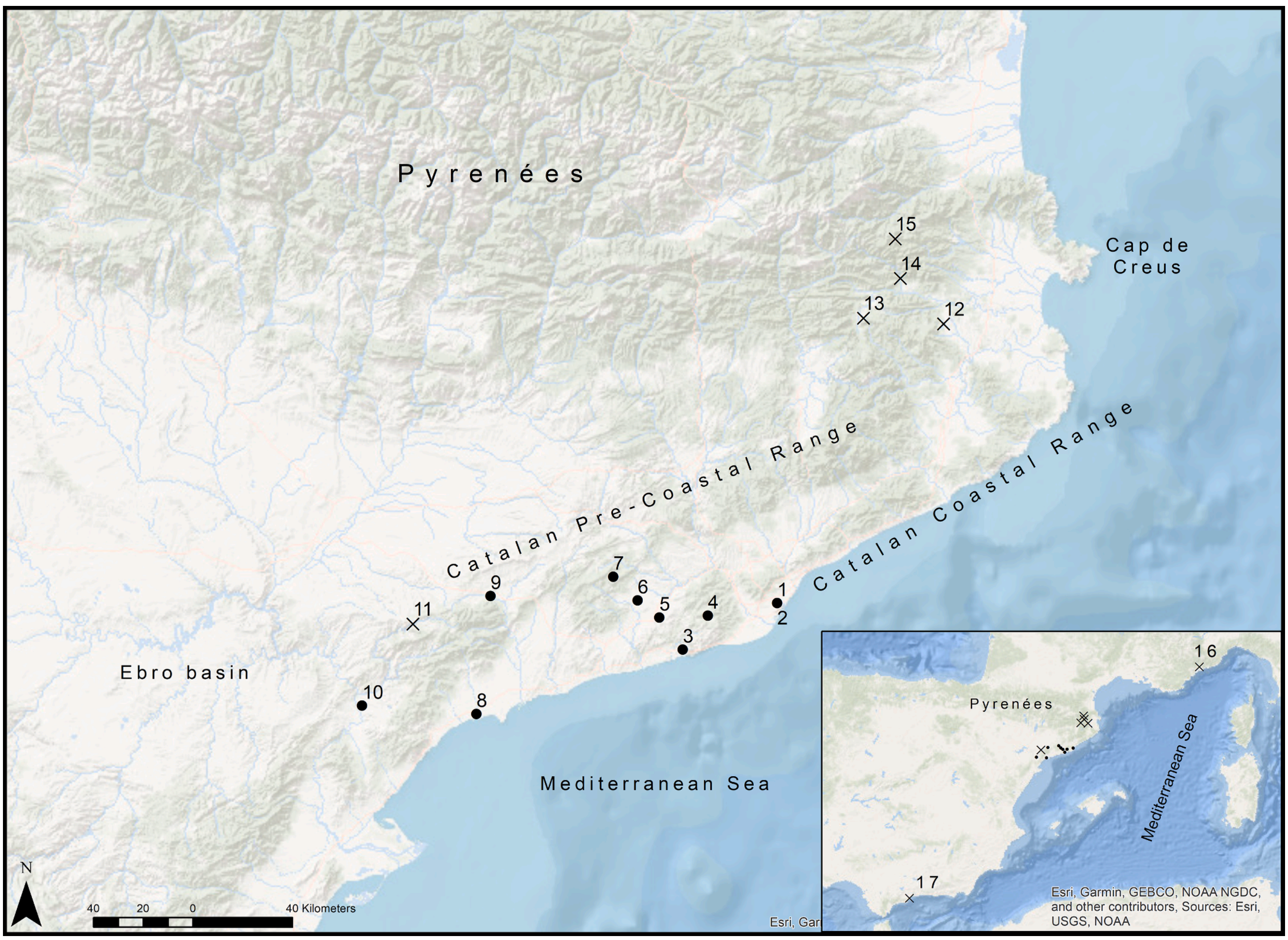

Fig. 1. Map of all the sampled sites from this study. (1) Caserna de Sant Pau, (2) Carrer Reina Amàlia, (3) Cova de Sant Llorenç, (4) Cova de Can Sadurní, (5) La Serreta, (6) Guixeres de Vilobí, (7) Cova de la Guineu, (8) El Cavet, (9) Cova de la Font Major and (10) El Molló. (Breu et al., 2021; Fontanals et al., 2008a; Blasco et al., 2011; Borrell et al., 2014; Cebrià et al., 2014; Gibaja et al., 2018; Gómez and Molist, 2017; González et al., 2011; Molist et al., 2018; Oms et al., 2016, 2014; Piera et al., 2016) and sites mentioned in the text: Coves del Fem (11), La Draga (12), Codella (13), Bauma del Serrat del Pont (14), Cova 120 (15), Pendimoun (16) and Cueva del Toro (17).

presence of resin biomarkers (see analytical details in supplementary SI2).

While birch bark tar can be identified through the detection of triterpenoids such as betulin, lupeol and other related compounds (Aveling and Heron, 1998), the most abundant molecule in aged Pinaceae resins is usually dehydroabietic acid (**IV**), a diterpenoid resulting from the oxidative dehydrogenation of abietane and pimarane (**I**) acids (Pollard and Heron, 2008; Weser et al., 1998). Further oxidation may lead to the appearance of 7-oxodehydroabietic acid (**VI**) and 15-methoxydehydroabietic acid (**V**) (Izzo et al., 2013), which is likely a methoxy substitution of the hydroxy group in 15-hyroxydehydroabietic acid occurring during the extraction process (Lough, 1964). Strong heating will produce triaromatic defunctionalised diterpenoids such as retene (**II**) (Pollard and Heron, 2008; Robinson et al., 1987) and further dehydrogenation will also produce additional compounds such as didehydroabietic acid (**III**) and 7-oxo-didehydroabietic acid (**VII**) (Baumer et al., 2009; Colombini et al., 2005) The presence of these compounds was evaluated in all GC–MS analysed samples.

Identifications were performed according to the compound's characteristic ions (Table 2) and validated using the NIST library. All reported compounds were identified as their methyl esters.

Although diterpenoids originating from aged Pinaceae resins have been reported in analysis of pottery organic residues using an acidified methanol extraction (Drieu et al., 2021; Oras et al., 2017; Reber et al., 2018; Bondetti et al., 2020), this procedure presents several limitations. Free diterpenoid acids and methyl esters already present in the sample cannot be distinguished. Additionally, the existence of false negatives should not be ruled out as the technique is not optimised for the single extraction of resin biomarkers. To better understand these limitations, 10 samples from Carrer Reina Amàlia (CRA) were extracted using both a dichloromethane/methanol (DCM/MeOH) (see supplementary materials 2 for further details) and an acidified methanol extraction on separate subsamples. Under DCM/MeOH, 30% of the samples presented only dehydroabietic acid (TMS ester). All the acidified methanol samples contained methyl dehydroabietate. This is consistent with the observed higher lipid yields of the second technique as reported in other investigations (Correa-Ascencio and Evershed, 2014; Papakosta et al., 2015).

A scoring system based on the number of distinct diterpenoid compounds present in the sample was implemented to qualitatively assess the likelihood that an aged Pinaceae resin had been in contact with the vessel. This value was used to distinguish samples with a partial or limited diterpenoid fingerprint from those with a comprehensive suite of compounds potentially degraded by time. Following the criteria laid out in Table 3, a score from 0 to 5 was assigned to each sample. Scores of 3 or higher, where a suite of at least three distinct compounds is present, were considered an unambiguous resinous residue based on criteria similarly applied elsewhere (Drieu et al., 2021; Oras et al., 2017; Reber et al., 2018; Bondetti et al., 2020).

Additionally, an estimation of abundance within the recovered residue was obtained by calculating the proportion of diterpenoids as a percentage of the total lipid extract. This was obtained by dividing the sum of all the areas of the diterpenoid peaks by the sum of all the areas of the lipid peaks and multiplying this figure by 100.

3. Results

Interpretable amounts of lipids (see 2.2 methods) were recovered from 139 of the 168 studied vessels, 83% of the analysed assemblage. From these, 116 vessels (69%) were further studied by GC–MS. Lipid extracts were dominated by free fatty acids (FFA) ranging between 10 and 28 carbons atoms. In all cases, the two main recovered compounds were palmitic and stearic acids. The total amount of lipids recovered varied between 1 $\mu g \cdot g^{-1}$ to 4832 $\mu g \cdot g^{-1}$ (median 17 $\mu g \cdot g^{-1}$; standard deviation 539 $\mu g \cdot g^{-1}$). Modern contamination from phthalate plasticisers was minimal and did not interfere with the analysis of the results.

Evidence of triterpenoids indicating the presence of birch bark tar was not recovered in any of the extracts. Alternatively, dehydroabietic acid (DA) was detected in 97 of the studied vessels (70%) while 7-oxo-dehydroabietic acid (7ODA) was only present in 37 samples, 35 of which also contained DA. Didehydroabietic acid (DDA) was identified in 19 cases, 74% of which already included DA and 7ODA, and retene was found in 40 vessels always accompanied by DA and, in 72% of the cases, by other additional compounds (7ODA or DDA). Evidence of pimarane diterpenoids (8 samples) always coincided with extensive evidence of oxidation and dehydrogenation and matched with high quantities of other diterpenes. Additional biomarkers such as 15-methoxydehydroabietic acid and 7-oxo-didehydroabietic acid were only detected in samples with a score of 5: CS11 from Can Sadurní (Fig. 2) and CV3003 from El Cavet.

Residues with a score of 1 only contained DA. While a score of 2 was reached because of a combination of DA with DDA (19%), 7ODA (28%) or Retene (52%), 94% of the samples with a score of 3 achieved it with a combination of DA, 7ODA and Retene. Only a total of 13 samples (9%) from Caserna de Sant Pau, Guixeres de Vilobí, Can Sadurní, El Cavet and Carrer Reina Amàlia (Table 4) reached higher scores. These were achieved because of the presence of additional diterpenoids accompanying the common DA-7ODA-Retene pattern, namely DDA (92%) and pimaranes (61%).

The quantity of diterpenoids in samples scoring 3 or higher varied between 0.02% and 9.4% of the total lipid extract with a median of 0.7% and a standard deviation of 1.7%. In 15 cases, these represented less than 0.7% of the total residue and only in 3 samples from three different sites (CS11, CV3003 and CSP3) diterpenoids were more than 2% of the lipid extract. Higher diterpenoid scores (4 and 5 compared to 3) coincided with higher percentages of diterpenoids in the residue (Mann-Withney test, N:32, U:63, p(same) = 0.017) (Fig. 3).

High and low diterpenoid scores were equally detected in rim, wall and base fragments; decorated and undecorated sherds; straight and closed rim shapes and both in vessels cooked in reducing, oxidising and mixed atmospheres.

When describing the presence of diterpenoid resins across different regions (Table 1), the percentage of vessels presenting a score of 3 or higher varied somewhat: Barcelona Plain (21%), Garraf (27%), Penedès (15%) and Southern Catalonia (Camp de Tarragona, Conca de Barberà and Ebro) (33%). Notable differences were found at sites in similar environmental contexts. Despite being adjacent sites, 58% of Caserna de Sant Pau's samples had a score of 3 or higher while this figure was only 4% at Carrer Reina Amàlia ($X^2 = 29.33$, df = 1, N = 76, p(no association) = $1.2 \cdot 10^{-7}$). In other regions, differences were less clear. In the Penedès, none of the samples from La Serreta contained high (≥ 3) diterpenoid scores, but both Guixeres de Vilobí and Cova de la Guineu presented at least 2 samples with high values. This was also the case in Southern Catalonia, where, despite significant landscape and resource accessibility differences, only one out of seven samples in El Molló contained any diterpenoids while 33% of the samples from El Cavet and two samples from Cova de la Font Major presented high scores for these compounds. Therefore, based on this data, a strong correlation between the detection of resin diterpenoids and the location of the site in the prehistoric landscape should not be assumed.

Diachronically, a statistically significant decrease in the number of

Table 2
Range of diterpenoids detected in archaeological samples in this study (bp = base peak; M^+ = molecular ion), highlighting characteristic fragment ions corresponding to methyl ester derivatives.

Elution order	Compound	Characteristic ions (*m/z*)
I	Pimarane diterpenoid	241(bp), 256, 301, 316(M^+)
II	Retene	205, 219(bp), 234(M^+)
III	didehydroabietic acid	197, 237(bp), 312(M^+)
IV	Dehydroabietic acid	239(bp), 299, 314(M^+)
V	15-methoxydehydroabietic acid	269, 329(bp), 344(M^+)
VI	7-oxodehydroabietic acid	187, 253(bp), 328(M^+)
VII	7-oxodidehydroabietic acid	211, 251(bp), 326(M^+)

Table 3
Scoring system used to qualitatively evaluate the presence of diterpenoid resins and their heated derivatives in this study.

Score	Requirements	Compounds
0	No evidence of diterpenoids	None
1	Presence of dehydroabietic acid	IV
2	The requirements from score 1 and limited evidence of diagenesis (detection of one oxidised or dehydrogenated compound)	
3	The requirements from score 2 and additional evidence of diagenesis (at least two compounds)	II, III, V, VI, VII
4	The requirements from score 3 and additional evidence of diagenesis (at least three compounds)	
5	Detection of five or more diterpenoids including extensive evidence of oxidation and dehydrogenation.	I, II, III, IV, V, VI, VII

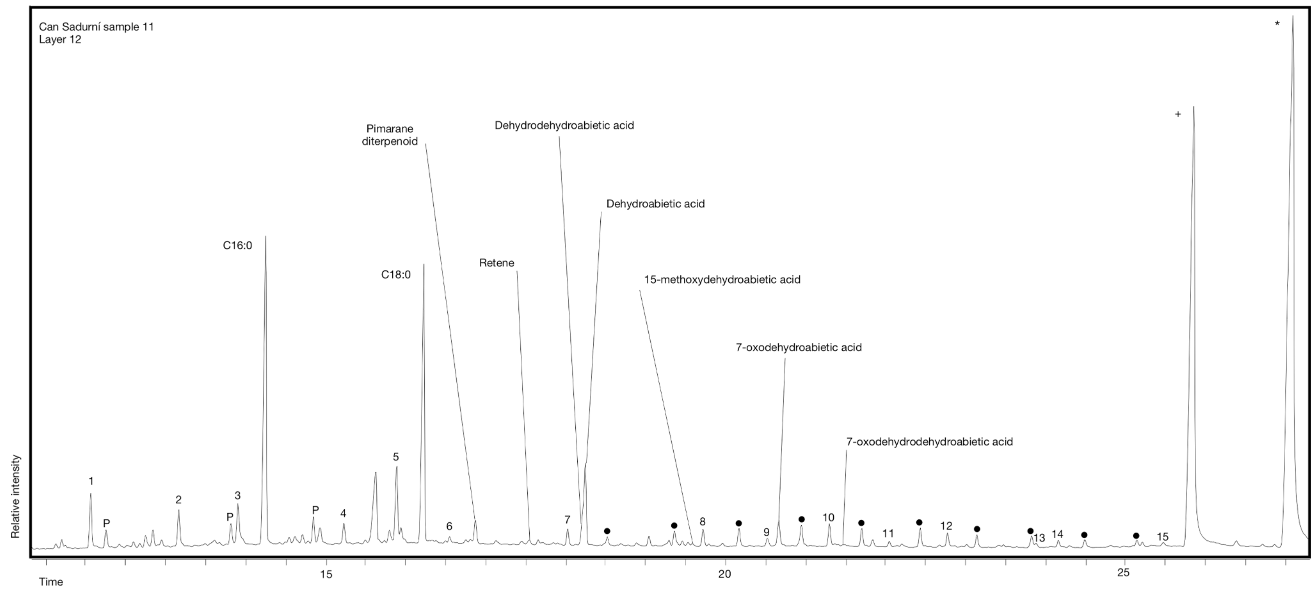

Fig. 2. Chromatogram of sample CS11 highlighting a range of diterpenoids originating from an aged Pinaceae resin. Numbers 1, 2, 4, 6–12, 14 and 15: saturated free fatty acids. 3 and 5 monounsaturated fatty acids. 13: Cholesterol methylether. ●: alkane series (C24-C33) +: tetatriacontane (internal standard 1), *: hexatriacontane (internal standard 2). See identification and mass spectra of numbered peaks in supplementary 4.

Table 4
Number and percentage of samples for each diterpenoid score over the total amount of GC–MS analyses and the GC-FID analyses with no evidence of lipids.

Diterpenoid Score	Number of samples	Percentage of the studied assemblage
≥1	97	70%
≥2	52	38%
≥3	31	22%
≥4	13	9%
5	4	3%

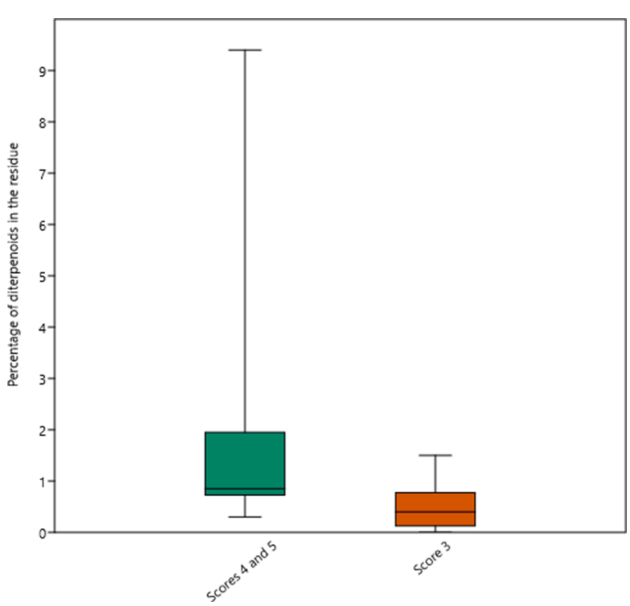

Fig. 3. Box-plot presenting the relation between diterpenoid scores (3 to 5) and the amount of resin as a percentage of the total residue.

samples with high diterpenoid scores was noticed between the Cardial (36%) and Epicardial period (8%) (X^2 = 8.54, df = 1, N = 138, p(no association): 6·10^{-5}), but this apparent change is difficult to assess given that 96% of the Epicardial assemblage from Carrer Reina Amàlia presented a score of 2 or less, which is one of lowest percentages of diterpenoid occurrence in this study.

4. Discussion

The study of the residues preserved in the ceramic matrix of Early Neolithic pottery in the northeast of the Iberian Peninsula has demonstrated the presence of multiple diterpenoids characteristic of aged Pinaceae resins in up to 31 ceramic vessels, representing 22% of the studied assemblage. This figure is in the range of the 30% of vases found at Pendimoun (Drieu et al., 2021), the 14% from studies in Greece and the Balkans (Garnier and Valamoti, 2016; Urem-Kotsou et al., 2018) and the 8% detected at Cueva del Toro (Tarifa-Mateo et al., 2019). Similar to the yields reported by Drieu et al (2021) and Hjulström et al. (2006), only small amounts of diterpenoids were recovered in the vessels, representing a maximum of 9% of the total lipid extract (CS11). Given their occurrence as mixtures and only in minor quantities, an archaeological interpretation of these results must carefully consider the possibility of soil contamination and the possible introduction of diterpenoids from softwood used in cooking fireplaces and kilns (Reber et al., 2018) given the availability of Pinaceae taxa in the Early Neolithic environment.

While diterpenoids can survive in soil for extended periods of time (Simoneit, 1977), its incorporation to the clay matrix would be expected to follow the same mechanisms demonstrated for other hydrophobic matter such as fats and waxes, notably a heating event mobilising the lipids (Charters et al., 1997, 1993; Evershed, 2008). Nonetheless, although this would be unlikely after vessel burial, the immediate inner surface (1–2 mm) of all the studied vessels was removed before sampling. Furthermore, soil contamination would be expected to similarly affect pottery remains from the same stratigraphic unit. Nevertheless, in this study, score values and diterpenoid percentages varied significantly between samples from the same archaeological context. As an example, silo 1 in Caserna de Sant Pau del Camp contained both a sample with one of the highest percentages of diterpenoids in this study (2.3%) and several samples where Pinaceae resins were completely absent (additional comparisons between samples originating from the same stratigraphic unit can be performed following the data in the supplementary materials, SI3). Significant disparities in the abundance and variety of diterpenoids between adjacent archaeological sites (Caserna de Sant Pau and Carrer Reina Amàlia) also suggests that environmental factors alone cannot explain the Pinaceae resin biomarkers present in the pottery matrix.

Recent experimental work by Reber et al. (2018) demonstrated the incorporation of diterpenoids from woodsmoke during the vessel's firing process. The reported compounds (18/19-norabieta-8,11,13-triene, 1,2,3,4-tetrahydroretene, retene, didehydroabietic acid, dehydroabietic acid and 7-oxodehydroabietic acid) were consistent with the thermal dehydrogenation and oxidation of diterpenoids and would partially match the data recovered in this study. Nevertheless, there is a significant lack of evidence supporting the use of Pinaceae wood as fuel in the Early Neolithic. Pinaceae charcoal represented only 1% of the assemblage recovered from layers 17 and 18 in Can Sadurní (Antolín et al., 2013), 0.81% of the charcoal recovered from El Cavet (Fontanals et al., 2008b), 3.9% of the assemblage from layer IIe in Cova de la Guineu (Allué et al., 2009) and, in the later Postcardial layers at Caserna de Sant Pau, only 5% of the recovered charcoal remains (Mensua and Piqué, 2008). While *Quercus* sp. was the main taxon used as fuel from the Mesolithic onwards across the territory (Piqué et al., 2018), Pinaceae twigs and branches could have been used as fire starters (Peña and Zapata, 2003) when pottery vases would have been most probably still away from the fire. Regional studies in the northeast of the Iberian Peninsula suggest pine would only be used as firewood in mountainous sites where oak forests were absent (Piqué et al., 2021). Yet, conifers such as *Pinus* sp. or *Juniperus* sp. were present in the Early Neolithic pollen records in non-negligible quantities (Ballesteros Ferrandis, 2009; Gassiot et al., 2012; Piqué et al., 2018; Revelles et al., 2018; Riera et al., 2016) and pine carpological remains including cones were recovered from several sites such as Can Sadurní and Coves del Fem (Antolín et al., 2013; Palomo et al., 2018), located in the highlands and the lowlands (Antolín et al., 2018; Gassiot et al., 2012). To summarise, while the carpological and pollen evidence supports the availability and exploitation of the Pinaceae taxa by Early Neolithic societies, anthracological studies indicate they were not used as fuel, thus implying that direct human activity would be the best candidate to explain the presence of degraded diterpenoids as residues in pottery from this study.

There is a range of possible reasons for the accumulation of resinous deposits in Early Neolithic vessels. Firstly, the vessels could have been used in the acquisition and transformation process of resin itself. They could have been placed below an open tree wound to gather exudates or used to heat and store the collected product. Alternatively, resins and their heated derivatives, could have been intentionally applied as a waterproofing agent used to repair broken or cracked vessels (Reber et al., 2018; Reber and Hart, 2008; Regert et al., 2003; Stacey et al., 2010). The co-occurrence of minor quantities of diterpenoids with significant amounts of fatty acids suggests that none of the aforementioned possibilities should be considered as the container's only or main purpose. Within the studied assemblage, there is no evidence to support the existence of vessels specialised in the management of resinous substances. Yet, all the archaeological sites analysed except for La Serreta and El Molló contained two or more vessels with a diterpenoid score of 3 or higher. The evidence is thus scarce, but ubiquitous.

The distribution of aged Pinaceae resin biomarkers in the studied assemblage suggests that only a limited quantity of resin-related vessels was needed for everyday life. This could mean that only some pottery was treated with resin or tar/pitch after firing. In this case, this could be the result of a technological choice by the potter or the result of a limited need for vessels requiring said post-firing treatment. The low quantity of diterpenoids across all the studied vessels and the consistent presence of retene in samples with a high diterpenoid score might support this interpretation. Alternatively, it could also mean that some ceramic vessels would have been sporadically used to gather, prepare, and store resinous substances for a limited period before the container was reused for other purposes. Experimental work exploring diterpenoid degradation, deposition pattern and distribution across the vessel walls will be necessary to obtain further information which allows the identification of distinct types of uses.

Regardless of the purpose for which Pinaceae resins came into contact with pottery vessels, the results clearly indicate that this product was part of the Early Neolithic subsistence practices in the northeast of the Iberian Peninsula. Nonetheless, a direct comparison with results obtained by Rageot et al (2021) should proceed with caution as their analyses were performed on visible adhesive deposits attached to either lithic or pottery artefacts. It is therefore possible that birch bark tar and Pinaceae resins were used for different purposes across the Mediterranean and that the absence of birch bark tar in the Early Neolithic of the Iberian Peninsula is the result of research biases rather than an effective substitution of exploited species. Nonetheless, the incidence of *Betula* sp. in this region is significantly limited. Pollen records from cores in northern Catalonia and the Pyrenees (Gassiot et al., 2012; Revelles et al., 2018) suggests only limited amounts of birch were present at the onset of the Neolithic. Furthermore, minimal amounts of *Betula* sp. charcoal remains have been found in a handful of Early Neolithic sites only, including Cova 120, Codella and Bauma del Serrat del Pont, which are all placed in the mountainous region of La Garrotxa (Revelles et al., 2018). When looking at other pollen cores and charcoal evidence closer to the areas where the studied sites are located, birch is completely absent. There are no traces of *Betula* sp. in the pollen records from Barcelona (Riera et al., 2016), the Font Major cave (Ballesteros Ferrandis, 2009), or in anthracological studies from any of the sites included in this research.

5. Conclusion

This study has integrated biomolecular data from pottery vessels with anthracological, carpological and pollen studies to show that Pinaceae resins were the most commonly used adhesive by Early Neolithic groups in the northeast of the Iberian Peninsula. This presents a notable change from birch bark tar, which dominates the results reported by Rageot et al. (2021) for northern Italy and the south of France, and Urem-Kotsou et al. (2018) in Greece and the Balkans. The results support an exploitation pattern where Pinaceae resins sporadically but ubiquitously came into contact with pottery vessels either as contents or as post-firing treatments. Further research is necessary to assess whether the detected resin practices were an innovation expanding the diversity of Neolithic technologies or an adaptation from the persistence of hunter-gatherer knowledge.

CRediT authorship contribution statement

A. Breu: Conceptualization, Formal analysis, Investigation, Visualization, Writing – original draft. **A. Rosell-Melé:** Supervision, Methodology, Resources, Writing – original draft. **C. Heron:** Writing – review & editing, Resources. **F. Antolín:** Writing – review & editing, Resources. **F. Borrell:** Resources. **M. Edo:** Resources. **M. Fontanals:** Writing – review & editing, Resources. **M. Molist:** Writing – review & editing, Resources, Project administration. **N. Moraleda:** Methodology, Validation, Resources. **F.X. Oms:** Writing – review & editing, Resources. **C. Tornero:** Resources. **J.M. Vergès:** Writing – review & editing, Resources. **O. Vicente:** Resources. **A. Bach-Gómez:** Writing – review & editing, Resources, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

All data is available in the supplementary materials.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jasrep.2022.103744.

References

Allué, E., Vernet, J.L., Cebrià, A., 2009. Holocene vegetational landscapes of NE Iberia: Charcoal analysis from Cova de la Guineu, Barcelona, Spain. Holocene 19, 765–773. https://doi.org/10.1177/0959683609105301.

Antolín, F., Buxó, R., Piqué, R., Edo, M., 2013. L'aprofitament dels recursos vegetals silvestres al jaciment de la Cova de Can Sadurní. Des de l'Epipaleolític al Neolític Final. VI Monografies del Garraf i d'Olèrdola. 301201265, 151–172.

Antolín, F., Jacomet, S., Buxó, R., 2015. The hard knock life. Archaeobotanical data on farming practices during the Neolithic (5400–2300 cal BC) in the NE of the Iberian Peninsula. J. Archaeol. Sci. 61, 90–104. https://doi.org/10.1016/j.jas.2015.05.007.

Antolín, F., Navarrete, V., Saña, M., Gassiot, E., 2018. Herders in the mountains and farmers in the plains? A comparative evaluation of the archaeobiological record from Neolithic sites in the eastern Iberian Pyrenees and the southern lower lands. Quat. Int. 484, 75–93. https://doi.org/10.1016/j.quaint.2017.05.056.

Aveling, E., Heron, C.P., 1998. Identification of Birch Bark Tar at the Mesolithic Site of Star Carr. Anc. Biomol. 2, 69–80.

Ballesteros Ferrandis, A., 2009. Restitució paleoambiental de l'entorn de la cova de la Font Major (l'Espluga de Francolí) mitjançant la palinologia i els sistemes d'informació geogràfica. Aplec de treballs 71–80.

Bar-Yosef, O., 1987. Direct and Indirect evidence for hafting in the Epi-Palaeolithic and Neolithic of the Southern Levant. La Main et l'Outil. Manches et emmanchements préhistoriques.

Baumer, U., Dietemann, P., Koller, J., 2009. Identification of resinous materials on 16th and 17th century reverse-glass objects by gas chromatography/mass spectrometry. Int. J. Mass Spectrom. 284, 131–141. https://doi.org/10.1016/j.ijms.2008.09.010.

Binder, D., Clop, X., Convertini, F., Manen, C., Sénépart, I., 2010. Les productions céramiques entre Provence et Catalogne, in: Premières Sociétés Paysannes de Méditerranée Occidentale. Structures Des Productions Céramiques. pp. 115–129.

Blasco, A., Edo, M., Villalba, M.J., 2011. La cova de can Sadurní i la prehistòria de Garraf. Recull de 30 anys d'investigació. Actes de les Jornades internacionals de Prehistòria 'El Garraf, 30 anys d'investigació arqueològica.

Borrell, F., Gómez, A., Molist, M., Tornero, C., Vicente, O., 2014. Les ocupacions de la Cova de Sant Llorenç (Sitges, Garraf): Noves aportacions al coneixement de la prehistòria del Garraf. Tribuna d'Arqueologia 110–128.

Breu, A., Gómez-Bach, A., Heron, C., Rosell-Melé, A., Molist, M., 2021. Variation in pottery use across the Early Neolithic in the Barcelona plain. Archaeol. Anthropol. Sci. 13, 53. https://doi.org/10.1007/s12520-021-01296-2.

Breu, A., Rosell-Melé, A., Molist, M., Bach-Gómez, A., 2022. Bayesian mixing models as a tool to explore Bronze Age bitumen trade from Tell Lashkir (Erbil, Iraq). J. Archaeol. Sci. 145, 105643 https://doi.org/10.1016/j.jas.2022.105643.

Bondetti, M., Lucquin, A., Savel'ev, N.A., Weber, A.W., Craig, O.E., Jordan, P.D., 2020. Resource processing, early pottery and the emergence of Kitoi culture in Cis-Baikal: Insights from lipid residue analysis of an Early Neolithic ceramic assemblage from the Gorelyi Les habitation site, Eastern Siberia. Archaeol. Res. Asia 24, 100225. Doi: https://doi.org/10.1016/j.ara.2020.100225.

Cebrià, A., Fontanals, M., Martín, P., Morales, J.I., Oms, F.X., Rodríguez-Hidalgo, A., Soto, M., Vergès, J.M.[a], 2014. Nuevos datos para el Neolítico antiguo en el nordeste de la Península Ibérica procedentes de la Cova del Toll (Moià, Barcelona) y de la Cova de la Font Major (L'Espluga de Francolí, Tarragona). Trabajos de Prehistoria 71, 134–145. Doi: https://doi.org/10.3989/tp.2014.12128.

Charters, S., Evershed, R.P., Goad, L.J., Leyden, A., Blinkhorn, P.W., Denham, V., 1993. Quantification and distribution of lipid in archaeological ceramics: implications for sampling potsherds for organic residue analysis and the classification of vessel use. Archaeometry 35, 211–223. https://doi.org/10.1111/j.1475-4754.1993.tb01036.x.

Charters, S., Evershed, R.P., Quye, A., Blinkhorn, P.W., Reeves, V., 1997. Simulation Experiments for Determining the Use of Ancient Pootery Vessels: the Behaviour of Epicuticular Leaf Wax During Boiling of a Leafy Vegetable. J. Archaeol. Sci. 24, 1–7. https://doi.org/10.1006/jasc.1995.0091.

Chen, S., Vahur, S., Teearu, A., Juus, T., Zhilin, M., Savchenko, S., Oshibkina, S., Asheichyk, V., Vashanau, A., Lychagina, E., Kashina, E., German, K., Dubovtseva, E., Kriiska, A., Leito, I., Oras, E., 2022. Classification of archaeological adhesives from Eastern Europe and Urals by ATR-FT-IR spectroscopy and chemometric analysis. Archaeometry 64, 227–244. https://doi.org/10.1111/arcm.12686.

Clop, X., 2005. Las primeras producciones cerámicas del nordeste de la Península Ibérica: estudios de caracterización. Monografías del Instituto Internacional de Investigaciones Prehistóricas de Cantabria, 1.

Colombini, M.P., Modugno, F., Ribechini, E., 2005. Direct exposure electron ionization mass spectrometry and gas chromatography/mass spectrometry techniques to study organic coatings on archaeological amphorae. J. Mass Spectrom. 40, 675–687. https://doi.org/10.1002/jms.841.

Connan, J., van de Velde, T., 2010. An overview of bitumen trade in the Near East from the Neolithic (c.8000 BC) to the early Islamic period. Arab. Archaeol. Epigr. 21, 1–19. https://doi.org/10.1111/j.1600-0471.2009.00321.x.

Correa-Ascencio, M., Evershed, R.P., 2014. High throughput screening of organic residues in archaeological potsherds using direct acidified methanol extraction. Anal. Methods 6, 1330–1340. https://doi.org/10.1039/C3AY41678J.

Cubas, M., Lucquin, A., Robson, H.K., Colonese, A.C., Arias, P., Aubry, B., Billard, C., Jan, D., Diniz, M., Fernandes, R., Fábregas Valcarce, R., Germain-Vallée, C., Juhel, L., de Lombera-Hermida, A., Marcigny, C., Mazet, S., Marchand, G., Neves, C., Ontañón-Peredo, R., Rodríguez-Álvarez, X.P., Simões, T., Zilhão, J., Craig, O.E., 2020. Latitudinal gradient in dairy production with the introduction of farming in Atlantic Europe. Nat. Commun. 11, 2036. https://doi.org/10.1038/s41467-020-15907-4.

Degano, I., Soriano, S., Villa, P., Pollarolo, L., Lucejko, J.J., Jacobs, Z., Douka, K., Vitagliano, S., Tozzi, C., 2019. Hafting of Middle Paleolithic tools in Latium (central Italy): New data from Fossellone and Sant'Agostino caves. PLoS One 14, 1–29. https://doi.org/10.1371/journal.pone.0213473.

de Vareilles, A., Bouby, L., Jesus, A., Martin, L., Rottoli, M., vander Linden, M., Antolín, F., 2020. One sea but many routes to Sail. The early maritime dispersal of Neolithic crops from the Aegean to the western Mediterranean. Journal of Archaeological Science: Reports 29, 102140. Doi: https://doi.org/10.1016/j.jasrep.2019.102140.

Drieu, L., Lucquin, A., Cassard, L., Sorin, S., Craig, O.E., Binder, D., Regert, M., 2021. A Neolithic without dairy? Chemical evidence from the content of ceramics from the Pendimoun rock-shelter (Castellar, France, 5750–5150 BCE). J. Archaeol. Sci. Rep. 35 https://doi.org/10.1016/j.jasrep.2020.102682.

Evershed, R.P., 2008. Experimental approaches to the interpretation of absorbed organic residues in archaeological ceramics. World Archaeol. 40, 26–47. https://doi.org/10.1080/00438240801889373.

Evershed, R.P., Payne, S., Sherratt, A.G., Copley, M.S., Coolidge, J., Urem-Kotsu, D., Kotsakis, K., Özdoğan, M., Özdoğan, A.E., Nieuwenhuyse, O., Akkermans, P.M.M.G., Bailey, D., Andeescu, R.-R., Campbell, S., Farid, S., Hodder, I., Yalman, N., Özbaşaran, M., Bıçakcı, E., Garfinkel, Y., Levy, T., Burton, M.M., 2008. Earliest date for milk use in the Near East and southeastern Europe linked to cattle herding. Nature 455, 528–531. https://doi.org/10.1038/nature07180.

Fletcher, L., Milner, N., Taylor, M., Bamforth, M., Croft, S., Little, A., Pomstra, D., Robson, H.K., 2018. The Use of Birch Bark. Star Carr II, 419–435. https://doi.org/10.22599/book2.p.

Fontanals, M., Belén, A., Morales, J.I., Vergès, J.M., Itzaso, E., Oms, F.X., 2008a. L'assentament litoral a l'aire lliure del Cavet (Cambrils, Tarragona). Butlletí Arqueològic. Reial Societat Arqueològica Tarraconense 30, 5–28.

Fontanals, M., Euba, I., Morales, J.I., Oms, F.X., Vergés, J.M., 2008b. El asentamiento litoral al aire libre de El Cavet (Cambrils, Tarragona). In: Hernández, M.S., Soler, J. A., López, J.A. (Eds.), IV Congreso Del Neolítico Peninsular. Museo Arqueológico de Alicante, Alicante, pp. 168–175.

García, R., 2010. Contenidos inorgánicos y orgánicos de Ratinhos. Análisis mineralógicos y químicos, in: Berrocal-Rangel, L., Silva, A. (Eds.), O Castro Dos Ratinhos (Barragem Do Alqueva, Moura). Escavaçoes Num Povoado Proto Histórico Do Guadiana. 2004-2006. Museu Nacional de Arqueologia, Lisboa, pp. 402–408.

Garnier, N., Valamoti, S.M., 2016. Prehistoric wine-making at Dikili Tash (Northern Greece): Integrating residue analysis and archaeobotany. J. Archaeol. Sci. 74, 195–206. https://doi.org/10.1016/j.jas.2016.03.003.

Gassiot, E., Rodríguez-Antón, D., Burjachs, F., Antolín, F., Ballesteros, A., 2012. Poblamiento, explotación y entorno natural de los estadios alpinos y subalpinos del Pirineo central durante la primera mitad del Holoceno. Cuaternario y Geomorfología 26, 29–45.

Gibaja, F.J., Oms, F.X., Mestres, J., Mazzucco, N., Palomo, A., 2018. Primeros resultados sobre la función del utillaje lítico de las primeras comunidades neolíticas asentadas en Les Guixeres de Vilobí (Sant Martí Sarroca, Barcelona). SAGVNTVM-PLAV 50, 35–56.

Gómez, A., Guerrero, E., Clop, X., Bosch, J., Molist, M., 2008. Estudi de la ceràmica neolítica del jaciment de Caserna de Sant Pau. In: Molist Montaña, M. (Ed.), Estudi Del Jaciment Neolític de La Caserna de Sant Pau. QUARHIS, Barcelona, pp. 25–35.

Gómez, A., Molist, M., 2017. Caserna de Sant Pau del Camp (Barcelona): Noves dades per al Neolític Antic Cardial del Nord-Est peninsular. Cypsela 11–23.
González, J., Harzbecher, K., Molist, M., 2011. Un nou assentament del V mil· lenni a la costa de Barcelona. Quarhis: Quaderns d'Arqueologia i Història de la Ciutat de Barcelona 7, 86–100.
Hjulström, B., Isaksson, S., Hennius, A., 2006. Organic geochemical evidence for pine tar production in middle Eastern Sweden during the Roman Iron Age. J. Archaeol. Sci. 33, 283–294. https://doi.org/10.1016/j.jas.2005.06.017.
Izzo, F.C., Zendri, E., Bernardi, A., Balliana, E., Sgobbi, M., 2013. The study of pitch via gas chromatography–mass spectrometry and Fourier-transformed infrared spectroscopy: the case of the Roman amphoras from Monte Poro, Calabria (Italy). J. Archaeol. Sci. 40, 595–600. https://doi.org/10.1016/j.jas.2012.06.017.
Lough, A.K., 1964. The production of methoxy-substituted fatty acids as artifacts during the esterification of unsaturated fatty acids with methanol containing boron trifluoride. Biochem. J. 90, 4–5. https://doi.org/10.1042/bj0900004C.
Manzano, E., García, A., Alarcón, E., Cantarero, S., Contreras, F., Vílchez, J.L., 2015. An integrated multianalytical approach to the reconstruction of daily activities at the Bronze Age settlement in Peñalosa (Jaén, Spain). Microchem. J. 122, 127–136. https://doi.org/10.1016/j.microc.2015.04.021.
Mazza, P.P.A., Martini, F., Sala, B., Magi, M., Colombini, M.P., Giachi, G., Landucci, F., Lemorini, C., Modugno, F., Ribechini, E., 2006. A new Palaeolithic discovery: tar-hafted stone tools in a European Mid-Pleistocene bone-bearing bed. J. Archaeol. Sci. 33, 1310–1318. https://doi.org/10.1016/j.jas.2006.01.006.
Mensua, C., Piqué, R., 2008. L'aprofitament de l'entorn forestal per a l'obtenció de combustible. Quarhis: Quaderns d'Arqueologia i Història de la Ciutat de Barcelona 4, 52–53.
Mitkidou, S., Dimitrakoudi, E., Urem-Kotsou, D., Papadopoulou, D., Kotsakis, K., Stratis, J.A., Stephanidou-Stephanatou, I., 2008. Organic residue analysis of Neolithic pottery from North Greece. Microchim. Acta 160, 493–498. https://doi.org/10.1007/s00604-007-0811-2.
Molina, E., 2015. La producción cerámica en el sudeste de la península ibérica Durante el iii y ii milenio ane (2200-1550 cal ane): integración del análisis de residuos orgánicos en la caracterización funcional de los recipientes argáricos. Universitat Autònoma de Barcelona, Barcelona.
Molist, M., Gómez, A., Breu, A., González, J., Bordas, A., Harzbecher, K., Fernández, J., 2018. Buried structures in Barcelona plain's neolithic settlements: A general revision, morphological and morphometric analysis gaining a functional interpretation. Quat. Int. 472, 246–258. https://doi.org/10.1016/j.quaint.2017.05.048.
Morales, J.I., Oms, F.X., 2008. Cambrils al Neolític: implantació i desenvolupament de les economies de producció al Camp de Tarragona. Ajuntament de Cambrils, Cambrils.
Nardella, F., Landi, N., Degano, I., Colombo, M., Serradimigni, M., Tozzi, C., Ribechini, E., 2019. Chemical investigations of bitumen from Neolithic archaeological excavations in Italy by GC/MS combined with principal component analysis. Anal. Methods 11, 1449–1459. https://doi.org/10.1039/C8AY02429D.
Niekus, M.J.L.T., Kozowyk, P.R.B., Langejans, G.H.J., Ngan-Tillard, D., van Keulen, H., van der Plicht, J., Cohen, K.M., van Wingerden, W., van Os, B., Smit, B.I., Amkreutz, L.W.S.W., Johansen, L., Verbaas, A., Dusseldorp, G.L., 2019. Middle paleolithic complex technology and a Neandertal tar-backed tool from the Dutch North Sea. PNAS 116, 22081–22087. https://doi.org/10.1073/pnas.1907828116.
Oms, F., Mestres, J., Cebrià, A., Morales, J., Nadal, J., Pedro, M., Mendiela, S., Martín, P., Fullola, J., 2016. La cova de la Guineu (Font-Rubí , Barcelona) i les relacions plana-muntanya al Penedès durant el neolític inicial, in: Del Neolític a l'edat Del Bronze En El Mediterrani Occidental. Estudis En Homenatge a Bernat Martí Oliver. Valencia, pp. 97–107.
Oms, F.X., Esteve, X., Mestres, J., Martín, P., Martins, H., 2014. La neolitización del nordeste de la Península Ibérica: datos radiocarbónicos y culturales de los asentamientos al aire libre del Penedès. Trab. Prehist. 71, 42–55. https://doi.org/10.3989/tp.2014.12123.
Oras, E., Lucquin, A., Lõugas, L., Tõrv, M., Kriiska, A., Craig, O.E., 2017. The adoption of pottery by north-east European hunter-gatherers: Evidence from lipid residue analysis. J. Archaeol. Sci. 78, 112–119. https://doi.org/10.1016/j.jas.2016.11.010.
Palomo, A., Terradas, X., Piqué, R., Rosill, R., Bogdanovic, I., Bosch, À., Saña, M., Alcolea, M., Berihuete, M., Revelles, J., 2018. Les Coves del Fem (Ulldemolins, Catalunya). Tribuna d'arqueologia 88–103.
Papakosta, V., Smittenberg, R.H., Gibbs, K., Jordan, P., Isaksson, S., 2015. Extraction and derivatization of absorbed lipid residues from very small and very old samples of ceramic potsherds for molecular analysis by gas chromatography-mass spectrometry (GC-MS) and single compound stable carbon isotope analysis by gas chromatogra. Microchem. J. 123, 196–200. https://doi.org/10.1016/j.microc.2015.06.013.
Peña, L., Zapata, L., 2003. Uso y gestión del bosque en la Euskal Herria atlántica: aprovechamiento tradicional de los recursos forestales en Encartaciones y Gorbea. Zainak. Cuadernos de Antropología-Etnografía 155–169. https://doi.org/10.13039/501100003086.
Piera, M., Gómez, A., Molist, M., Ríos, P., Alàntara, R., Arnaiz, R., Montero, I., 2016. El tram baix de l'Ebre a les èpoques del Neolític i Bronze inicil: Aportacions al seu coneixement a partir de l'assentament del Molló (Móra la Nova), in: Balde, F., Pegueroles, N., Martínez, J., Diloli, J., Villalbí, M. del M., Ferré, R., Mulet, J., Poy, M. (Eds.), I Jornades d'Arqueologia de Les Terres de l'Ebre. Serveis Territorials de Cultura de les Terres de l'Ebre, Tortosa, España, pp. 91–104.
Piqué, R., Alcolea, M., Antolín, F., Berihuete-Azorín, M., Berrocal, A., Rodríguez-Antón, D., Herrero-Otal, M., López-Bultó, O., Obea, L., Revelles, J., 2021. Mid-holocene palaeoenvironment, plant resources and human interaction in northeast Iberia: An archaeobotanical approach. Applied Sciences (Switzerland) 11, 1–23. https://doi.org/10.3390/app11115056.
Piqué, R., Revelles, J., Burjachs, F., Caruso Fermé, L., Pérez-Obiol, R., 2018. Interdisciplinary approach to the landscape and firewood exploitation during the Holocene at La Garrotxa (Girona, NE Iberia). Quat. Int. 463, 401–413. https://doi.org/10.1016/j.quaint.2016.11.025.
Pollard, A.M., Heron, C., 2008. The Chemistry and Use of Resinous Substances, Archaeological Chemistry.
Prats, G., Antolín, F., Alonso, N., 2020. Household storage, surplus and supra-household storage in prehistoric and protohistoric societies of the Western Mediterranean. PLoS One 15, e0238237. https://doi.org/10.1371/journal.pone.0238237.
Rageot, M., Lepère, C., Henry, A., Binder, D., Davtian, G., Filippi, J.-J., Fernandez, X., Guilaine, J., Jallet, F., Radi, G., Thirault, E., Terradas, X., Regert, M., 2021. Management systems of adhesive materials throughout the Neolithic in the North-West Mediterranean. J. Archaeol. Sci. 126, 105309 https://doi.org/10.1016/j.jas.2020.105309.
Rageot, M., Pêche-Quilichini, K., Py, V., Filippi, J.J., Fernandez, X., Regert, M., 2016. Exploitation of Beehive Products, Plant Exudates and Tars in Corsica During the Early Iron Age. Archaeometry 58. https://doi.org/10.1111/arcm.12172.
Reber, E.A., Hart, J.P., 2008. Pine resins and pottery sealing: Analysis of absorbed and visible pottery residues from central new york state. Archaeometry 50, 999–1017. https://doi.org/10.1111/j.1475-4754.2008.00387.x.
Reber, E.A., Kerr, M.T., Whelton, H.L., Evershed, R.P., 2018. Lipid Residues from Low-Fired Pottery. Archaeometry 61, 131–144. https://doi.org/10.1111/arcm.12403.
Regert, M., Vacher, S., Moulherat, C., Decavallas, O., 2003. Adhesive Production and Pottery Function During the Iron Age at the Site of Grand Aunay (Sarthe, France)*. Archaeometry 45, 101–120. https://doi.org/10.1111/1475-4754.00098.
Revelles, J., Burjachs, F., Palomo, A., Piqué, R., Iriarte, E., Pérez-Obiol, R., Terradas, X., 2018. Human-environment interaction during the Mesolithic- Neolithic transition in the NE Iberian Peninsula. Vegetation history, climate change and human impact during the Early-Middle Holocene in the Eastern Pre-Pyrenees. Quat. Sci. Rev. 184, 183–200. https://doi.org/10.1016/j.quascirev.2017.08.025.
Riera, S., Julià, R., Picornell, L., 2016. Evolució del paleoambient de la plana barcelonina al Neolític, in: Gomez, A., Molist, M. (Eds.), La Prehistòria al Pla de Barcelona, MHUBA Documents, 11. Ajuntament de Barcelona, Barcelona, Spain, pp. 65–73.
Robinson, N., Evershed, R.P., James Higgs, W., Jerman, K., Eglinton, G., 1987. Proof of a pine wood origin for pitch from tudor (Mary Rose) and Etruscan shipwrecks: Application of analytical organic chemistry in archaeology. Analyst 112, 637–644. https://doi.org/10.1039/an9871200637.
Rosenberg, D., Chasan, R., 2021. Between Novelty and Variability: Natufian Hunter-Gatherers (c. 15-11.7 kyr) Proto-Agrotechnology and the Question of Morphometric Variations of the Earliest Sickles. Proceedings of the Prehistoric Society. Doi: 10.1017/ppr.2021.5.
Saña Seguí, M., Navarrete Belda, V., Ferratges Kwekel, E., 2021. Animal Resources, Foodways and Cooking Practices during the Neolithic in the Western Mediterranean. An Integrated Archaeozoological Approach. Food Hist. 19, 203–233. https://doi.org/10.1484/J.FOOD.5.126405.
Simoneit, B.R.T., 1977. Diterpenoid compounds and other lipids in deep-sea sediments and their geochemical significance. Geochim. Cosmochim. Acta 41, 463–476. https://doi.org/10.1016/0016-7037(77)90285-X.
Stacey, R., Cartwright, C., Tanimoto, S., Villing, A., 2010. Coatings and Contents: Investigations of Residues on Four Fragmentary Sixth-century BC Vessels from Naukratis (Egypt). The British Museum Technical Research Bulletin 4, 19–26.
Tarifa-Mateo, N., Clop-García, X., Rosell-Melé, A., Camalich-Massieu, M.D., Comes-Bordas, P., Martín-Socas, D., Nonza-Micaelli, A., Rodríguez-Santos, F.J., Tarifa, N., Clop, X., Rosell, A., Massieu, M.D., Comes, P., Martín, D., Nonza, A., Rodríguez, F., 2019. New insights from Neolithic pottery analyses reveal subsistence practices and pottery use in early farmers from Cueva de El Toro (Málaga, Spain). Archaeological and Anthropological Sciences. Doi: https://doi.org/10.1007/s12520-019-00874-9.
Tresserras, J., 2000. Les resines vegetals, in: Bosch, A., Chinchilla, J., Tarrús, J. (Eds.), El Poblat Lacustre Neolític de La Draga. Excavacions de 1990 a 1998. Monografies del CASC, 2. Museu d'Arqueologia de Catalunya, p. 149.
Urem-Kotsou, D., Mitkidou, S., Dimitrakoudi, E., Kokkinos, N., Ntinou, M., 2018. Following their tears: Production and use of plant exudates in the Neolithic of North Aegean and the Balkans. Quat. Int. 496, 68–79. https://doi.org/10.1016/j.quaint.2018.10.027.
Weser, U., Kaup, Y., Etspüler, H., Koller, J., Baumer, U., 1998. Peer Reviewed: Embalming In The Old Kingdom Of Pharaonic Egypt. Anal. Chem. 70, 511A–516A. https://doi.org/10.1021/ac981912a.