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## Management systems of adhesive materials throughout the Neolithic in the North-West Mediterranean

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### Abstract

Plant resins, tars and organic fossil substances provide valuable insights into the ecological, environmental and cultural contexts of ancient societies. Their study offers evidence of past know-how, production systems, socio-economic networks and mobility. In this paper, we present new data from 16 sites located in the North-West Mediterranean that provide new insights into the exploitation of these substances for their adhesive and hydrophobic properties throughout the Neolithic (6000-2500 cal BCE). The substances investigated are discussed in the light of their molecular composition, their uses and manufacturing processes. Spatial analyses were also performed to elucidate raw material procurement strategies.

This study considerably increases the body of data available from the Mediterranean and tells a diachronic story of adhesive production and use throughout the Neolithic, highlighting the variability and complexity of production systems and supply networks at different spatial scales. While most adhesive and hydrophobic substances were probably collected locally, birch bark tar was very likely transported across long distances to reach Mediterranean coastal sites. Birch bark tar exploitation intensified in South-Eastern France during the Middle Neolithic, while the Late Neolithic is characterised by a diversification of the substances employed and their range of uses: bitumen, birch bark tar (pure or mixed with Pinaceae resin, beeswax and possibly fat/oil) were important materials that were used for a variety of purposes. Pure Pinaceae exudates were exclusively employed for waterproofing pottery. We also highlight the standardisation of birch bark tar production for adhesive manufacture observed in Provence during the first part of the 4<sup>th</sup> millennium cal. BCE.

### Keywords

Adhesives, Neolithic, Western Mediterranean, Organic residue analysis, Birch bark tar, Pinaceae resins, Bitumen, Production systems, GIS analysis and modelling

## 1. Introduction

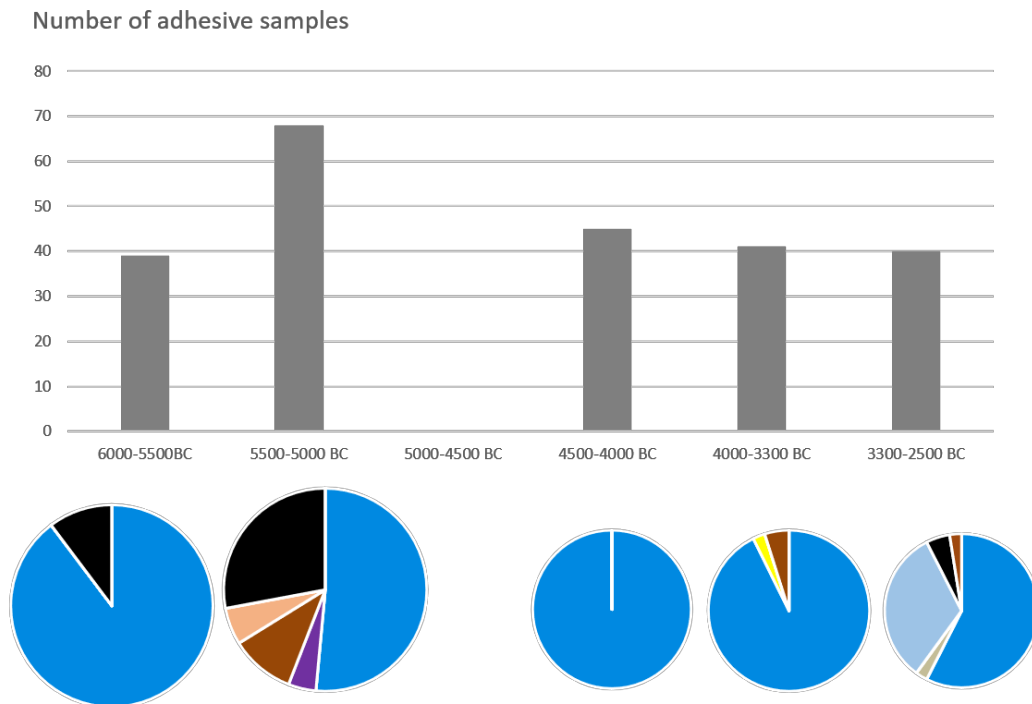
Plant resins, tars and organic fossil substances (e.g. bitumen) have been exploited since the Middle Palaeolithic (Boëda et al., 2008; Boëda et al., 1996; Grünberg et al., 1999; Hauck et al., 2013; Mazza et al., 2006; Nardella et al., 2019; Niekus et al., 2019). Their role as a hallmark of cognitive sophistication remains a matter of debate (Schmidt et al., 2019). Very recently, it was demonstrated that birch bark tar can represent a new source of ancient DNA that reveals the genetic characteristics of those who chewed it (Jensen et al., 2019; Kashuba et al., 2019).

These substances are multifunctional materials that were used since Prehistory for their adhesive and hydrophobic properties, among other things (Table S1). In the archaeological record, they are usually discovered as elements used to haft tools or to mend ceramic vessels, as waterproofing agents (Aveling and Heron, 1998a; Bonfield et al., 1997; Connan, 1999; Connan and Van de Velde, 2010; Evans and Heron, 1993; Langlois et al., 2005; Mitkidou et al., 2008; Regert, 2001; Regert, 2004; Regert et al., 1998), or even as aesthetic components of various objects (including for colour) (Bosquet et al., 2001; Connan et al., 2004; Rageot et al., 2016; Regert et al., 2019; Sauter et al., 2002; Urem-Kotsou et al., 2018). Plant exudates and tars may also have been employed in medicinal practices, such as dental care (Aveling and Heron, 1999; Evans and Heron, 1993; Stern et al., 2006), or used for their odoriferous properties (Lucquin et al., 2007; Marangou and Stern, 2009; Mathe et al., 2004; Stern et al., 2003).

Although plant exudates and tars provide valuable insight into the ecological, environmental and cultural contexts of ancient societies, their informational potential is generally underestimated and not fully tapped. In large part, this can be explained by the fact that organic residues are prone to degradation, they do not present any characteristic morphology in archaeological contexts, and the chemical analyses applied to these substances are not always appropriate (for a more detailed state of the art, see S1).

Adhesive materials from Palaeolithic contexts are particularly scarce. In Europe, only 15 analyses based on the reliable molecular characterisation of adhesive substances are available. Birch bark tar (from Central Italy to the Netherlands) (Grünberg et al., 1999; Mazza et al., 2006; Niekus et al., 2019) and Pinaceae resin (in Southern Italy) (Degano, et al., 2019) have been identified as hafting adhesives. In the Levant, bitumen was commonly used for the same purpose (8 analyses) (Boëda et al., 2008; Boëda et al., 1996; Hauck et al., 2013). During the Palaeolithic, in most cases, adhesives were made from raw materials that were locally available in significant quantities (birch/Pinaceae forests or bitumen sources).

More evidence is available in Europe from the 6th millennium cal. BCE onwards. In total, 234 samples from 37 sites dated to 6000-2500 cal. BCE have been analysed at the molecular scale using GC-MS or LC-MS/MS methods (Fig. 1; for a detailed list of sites, see Table S1). The relative abundance of samples from the Holocene can be ascribed to better preservation of organic matter from more recent periods and/or more favourable preservation contexts, particularly at Northern European wetland Mesolithic sites (Aveling and Heron, 1998b, 1999; Stern et al., 2006). Favourable conditions are also observed at 10 Neolithic sites (mostly wetland sites from central Europe), which represent 63 % of all Neolithic sites analysed and 87 % of all samples analysed from North of the Alps and in the alpine regions (Aveling and Heron, 1998b; Bleicher et al., 2015; Evans and Heron, 1993; Hayek et al., 1990; Heron et al., 1991; Mirabaud et al., 2009; Regert et al., 1998; Regert et al., 2000; Sauter et al., 2000)(Table S1). The emergence of ceramic technology may also have contributed to the increase in the amount of material that have been studied. Although bitumen, birch bark tar, Pinaceae resins and beeswax can be preserved as free lumps in the soil (S1) (Rageot et al., 2016; Rageot et al., 2019b), other lipidic additives (e.g. fats and oils) are more prone to degradation due to bacterial activity, unless trapped in the clay matrix of ceramics. Notably, pottery could also have provided a wider range of uses/applications for adhesive and hydrophobic materials (Drieu et al., 2018; Rageot et al., 2019a; Rageot et al., 2016), whereas their function cannot be inferred when they were associated with a perishable support material.



**Fig. 1:** Adhesive materials in Europe (6000–2500 BC). Information solely based on published works which involved GC-MS analyses (Table S1). Black= bitumen, blue= birch bark tar, brown = Pinaceae resin, pink = cedar resin/oil, yellow= birch bark tar – beeswax, purple= Pinaceae - birch bark, light blue= other plant tar(s), grey= animal glue (hide).

To date, research on adhesives north of the Alps and in the alpine regions (99 samples from 20 sites) seems to show an interesting continuity of the use of pure birch bark tar up until the first part of the 4<sup>th</sup> millennium cal. BCE (Table S1, Fig. 1). Birch bark tar was mostly used for its adhesive properties, especially for hafting tools and repairing ceramics, but it was also employed for decorative purposes and chewed (possibly as a form of dental care). In the early 4<sup>th</sup> millennium cal. BCE, several other substances began to be used for their adhesive properties in addition to pure birch bark tar, namely bitumen, animal glue and a multicomponent material including birch bark tar and Pinaceae resin, as well as other plant tars. Currently, data from regions South of the Alps (135 samples from 17 sites) are mostly restricted to South-Eastern Europe and the Adriatic, from 15 sites dated to the 6<sup>th</sup> millennium. Bitumen was used in Abruzzo and Apulia (Nardella et al., 2019) for its adhesive properties (stone tool hafting). In the Balkans and the Northern Aegean different adhesive substances and functions are observed, as illustrated by the use of birch bark tar and Pinaceae tar / resins for ceramic reparation, coating and decoration, and possibly for their odoriferous properties (Marangou and Stern, 2009; Mitkidou et al., 2008; Urem-Kotsou et al., 2018). In sum, considering the European Neolithic on the whole, our knowledge of use of adhesives has been limited to specific and isolated chronocultural contexts. Indeed, prior to this study, only two Neolithic sites (Nice-Giribaldi and La Rouvière) South-West of the Alps had been investigated. These sites date to between the end of the 6<sup>th</sup> millennium and the 2<sup>nd</sup> millennium cal. BCE, and published data indicate the use of pure birch bark tar (Binder et al., 1990; Perthuisson et al., 2019; Rageot et al., 2019b; Regert et al., 2000).

Given the significant gaps in our knowledge regarding adhesive use in the North-West Mediterranean, our goal is to gain a more comprehensive and diachronic understanding of the exploitation of adhesive and hydrophobic materials in the region. Thus far, only a small number of publications have addressed adhesive management, with most of these focusing on procurement strategies of bitumen (Buckley et

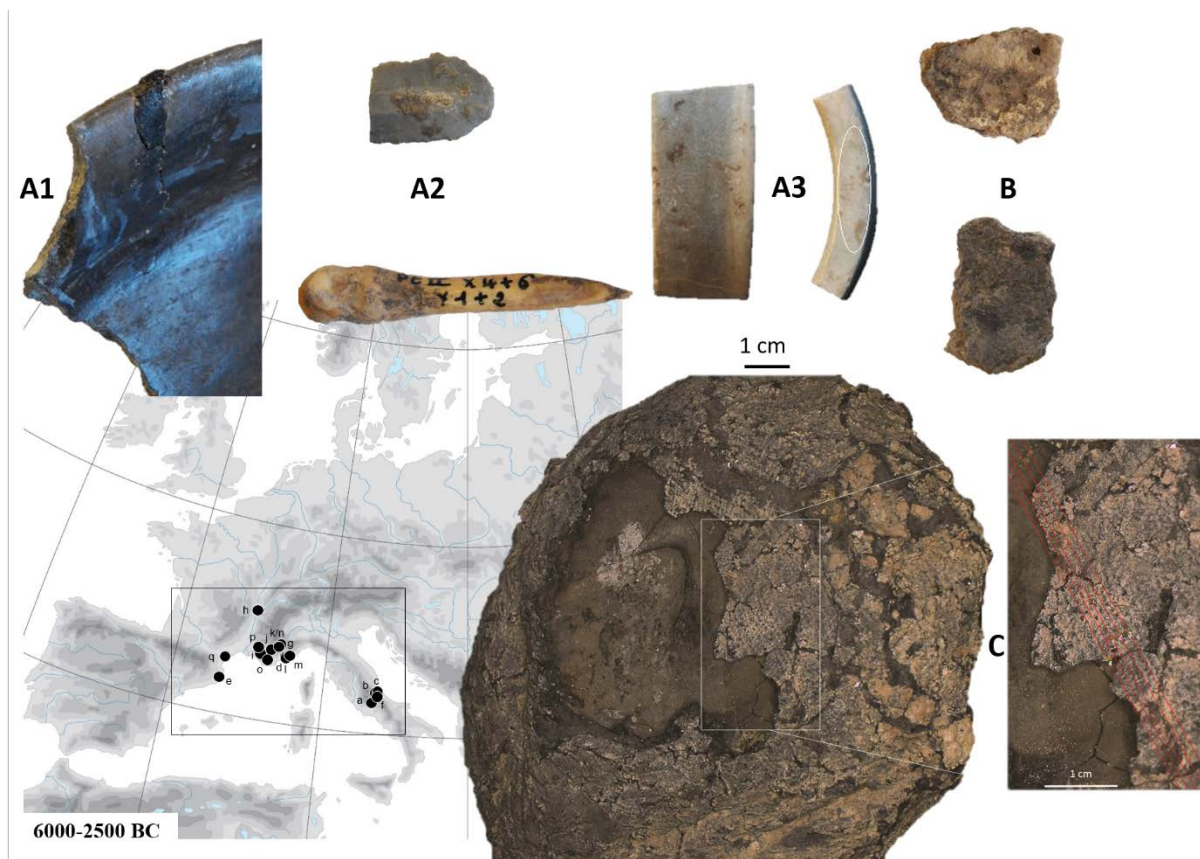
al., 2004; Connan, 1999; Nardella et al., 2019) and birch bark tar (Rageot et al., 2016; Rageot et al., 2019b; Urem-Kotsou et al., 2018). One study also deals with decisive steps in the *chaîne opératoire* of tar production in archaeological contexts (Rageot et al., 2019b).

In this study, organic residues were analysed from 16 archaeological sites (23 archaeological layers) located between North-Eastern Iberia and Abruzzo and occupied between the Early and the Late Neolithic (6000-2500 cal. BCE), with a particular focus on Middle and Late Neolithic contexts from Southern France as these have yielded a particularly large quantity of adhesive materials. An integrated approach employing biomolecular archaeology, spatial analysis, experimental archaeology and botany was developed to (i) characterise the organic substances, (ii) investigate procurement strategies and systems of production of adhesive and hydrophobic materials, and (iii) determine the spheres of activity areas in which adhesives were used. Specific practices and mobility patterns linked to the exploitation and circulation of these biomaterials are also examined yielding new insights into technical and territorial systems of the Neolithic.

## 2. Materials and methods

### 2.1. Archaeological sites and samples investigated in the North-Western Mediterranean Neolithic

A total of 85 visible organic residues adhering to ceramic vessels, lithic or bone tools or recovered as free lumps from 16 sites were chemically analysed (for a detailed list of the sites and sampling contexts, see Table S2). The investigation was focused on organic residues from sites in southern France (76 samples). A large inventory of archaeological materials from Provence was studied including, free lumps recovered directly from the sediment or following flotation (together with macrobotanical remains). Nine samples from North-Eastern Iberia (Spain) and Abruzzo (Italy) were also examined (Fig. 2).



**Fig. 2:** Illustration of the different functional classes of samples and location of sites from which samples were analysed.

Functional classes: A1= adhesive used to repair pottery (MR6547, Pertus II), A2= hafting adhesive associated with flint and bone tools (MR6521 and MR6541, Pertus II), A3= decoration / assembling adhesive applied to a marble bracelet (MR2731, La Draga, © La Draga team), B= layers covering the interiors of ceramic - probably coating residue (MR2864 and MR2867, Pertus II), C= free lumps (MR2824, Montpezat-Grotte Murée= large balls with cloth negatives, © Didier Binder).

Archaeological sites: a= Colle Santo Stefano; b= Catignano; c= Colle Cera; d= Giribaldi (layer 6); e= La Draga; f= Grotta dei Piccioni; g= Grotte Saint-Benoit II; h= Lyon-Favorite; i= Vernègues-Cazan-l'Heritière; j= Grotte Murée; k= Pertus II (I-D); l= Nice-Fodéré; m= Pendimoun (Phase 2A, upper); n= Pertus II (A-C); o= Chemin de Barjols; p= Bonnieux-Les Fabrys; q= Bringairet.

Samples were classified into functional categories according to the position of the organic residues on lithic/bone tools or ceramic vessels (Table S2; Fig. 2). 59 samples were used for their adhesive properties (Fig. 2A). Within this category, adhesives were used to repair ceramic vessels (residue on the edge of the sherd or close to a reparation hole: n=48), to haft stone tools (n=8) and possibly in decorative processes (n=3). 21 samples were taken from layers of residue covering the interior of

ceramic vessels or pits (Fig. 2B). Although the possibility that these residues derived from the contents of the vessels cannot be excluded, they were most likely applied as a hydrophobic coating (n=16). Similarly, the thick black layers deposited at the base of several pits at Bonnieux-Les Fabrys likely were used to waterproof these structures (n=5). Finally, 5 free lumps recovered from the sediment were also analysed. The dark brown residues from Nice-Giribaldi are uncharacteristic fragments. However, the two large black balls (100 g and 8 g) from Montpezat-Grotte Murée display the negative imprints of textiles, suggesting the transport and storage of a sticky malleable substance wrapped in cloth (Fig. 2C).

## 2.2. Sample extraction, GC and GC-MS analyses

GC and GC-MS analyses were carried out to determine the molecular composition of the samples and to assess their degree of anthropogenic transformation and/or natural alteration. Sample preparation was performed using the same method already described elsewhere (Rageot et al., 2016; Rageot et al., 2019b).

The samples were first ground and extracted for 30 min by ultrasonication in HPLC grade dichloromethane ( $1\text{mg}\cdot\text{mL}^{-1}$  for experimental tars and  $4\text{mg}\cdot\text{mL}^{-1}$  for archaeological samples). Each extract was derivatised by adding 50  $\mu\text{L}$  of BSTFA and 4  $\mu\text{L}$  of pyridine. An aliquot of this solution (1  $\mu\text{L}$ ) was directly analysed by gas chromatography (GC) and GC-Mass Spectrometry (GC-MS).

GC analyses were performed on an Agilent 7890A gas chromatograph equipped with an on-column injector and GC-MS analyses were carried out using a Shimadzu QP2010 ultra with a S/SL injection system used in splitless injection mode (purge flow of 2.0 mL/min and split ratio of 3.0). To detect the presence of high molecular weight compounds (especially wax fatty esters), samples were analysed by using an Agilent J&W DB5 HT column (15 m  $\times$  0.32 mm i.d.; 0.1  $\mu\text{m}$  film thickness). The inlet temperature was set at 350°C. The oven temperature was ramped from 50°C (held isothermally for 2 min) to 150 °C at 10 °C/min, and then increased to 320 °C at 20 °C/min (held isothermally for 15 min). To focus on terpenes molecular markers, samples were analysed by using an Agilent J&W DB-5MS column (30 m  $\times$  0.25 mm i.d.; 0.25  $\mu\text{m}$  film thickness); the inlet temperature set at 300 °C. The oven temperature was ramped from 50 °C (held isothermal for 2 min) to 150 °C at 10 °C/min, then increased to 320 °C at 4 °C/min (held isothermal for 15 min). The GC analysis was carried out using hydrogen as carrier gas with a constant column head pressure of 16 psi and the temperature of the flame ionization detector (FID) at 340°C. GC-MS analyses were carried out using helium as carrier gas and mass spectra were acquired using electron ionization at 70 eV. The mass range was scanned from m/z 50–950 in 0.6 s. The ion source temperature was set at 200 °C and the transfer line at 250 °C. Mass spectra were matched against those of authentic standards (betulin, betulinic acid, lupeol, lupenone, oleanolic acid and  $\beta$ -amyrin), by using data previously published by several authors (Aveling and Heron, 1998a; Charters et al., 1993; Courel et al., 2018; Hayek et al., 1990; Perthuison et al., 2019; Rageot, 2015; Regert et al., 1998), and the NIST library 2008 edition.

## 2.3. Modelling potential acquisition areas of raw materials used for adhesive production

In order to explore procurement strategies and the circulation of plant and fossil resources, spatial analysis was performed using Geographical Information Systems. A cost-distance model was used to evaluate the distance between sites and potential areas of raw material acquisition. As the aim was to evaluate the distances to source of bitumen, but also birch bark, a preliminary attractiveness model of areas favourable to the birch tree (*Betula pendula* L.) was also built.

### 2.3.1. Plant resources as raw materials

The objective of assessing the spatial distribution of plant resources was to investigate raw material exploitation strategies in terms of effort-yield and wider networks of procurement and exchange. However, raw material acquisition strategies are difficult to elucidate in the case of ubiquitous plant resources such as pines. Indeed, though palaeobotany is able to distinguish at least two types of pines (usually Mediterranean vs. Scots pine type), the characterisation of biomolecular markers from archaeological samples is generally not precise enough to distinguish between species. Thus, there is currently no way of knowing if the exploitation of pine followed a local pattern or a more regional one with exchanges occurring over longer distances. Within the chrono-geographical context considered in this study, pine was the most common taxon and other Pinaceae taxa, such as fir, were expanding in certain areas (Andrieu-Ponel et al., 2000; Battentier et al., 2018; Battentier et al., 2015; Battentier et al., 2019; Nicol-Pichard and Dubar, 1998; Revelles et al., 2018; Thiébault, 1999; Thiébault, 2001). In contrast, at the time the sites studied were occupied birch was not common—even extremely rare—around the Mediterranean. While it was still well represented during the Preboreal - Boreal, its sporadic and very discreet presence in the pollen records from the Atlantic period onwards suggests that, much as today, birch was not well-adapted to the Mediterranean climate. Hence, throughout the Neolithic at sites located at lower altitudes within the mesomediterranean vegetation belt, birch bark was most likely not exploited locally. However, the fact that birch resources probably were available in the relatively close alpine foothills made it interesting to evaluate the minimal acquisition radiuses for this tree at different sites. Indeed, birch resources were potentially accessible from sites such as Pendimoun (690 m a.s.l.), as suggested by one piece of birch charcoal found in the Cardial levels that has been considered proof that Neolithic groups frequented the montane vegetation belt (Battentier et al., 2015). We also took into account the fact that isolated birch trees would not have provided a sustainable source of bark capable of meeting the needs of a community. According to previous observations and experiments, only an acquisition area rich in birch (i.e. birch forests) would have provided enough raw material for the sustainable production of tar (Rageot et al., 2019b). We built a predictive model of the distribution of birch in South-East France in order to evaluate the minimum distances between the sites and the nearest potential birch forests. Our working hypothesis was that even though the vegetation around the Mediterranean changed significantly over the past eight millennia, the autecology of birch did not change radically and thus, that birch forests were more likely to be found in the upper mountain and subalpine vegetation belts (Rameau et al., 1993, 2008).

### 2.3.2. Current distribution of birch (*Betula pendula*) and predictive model

Indeed, birch is a eurosiberian drought intolerant and relatively heat intolerant species, not well adapted to the Mediterranean climate (Rameau et al., 1989). In Southern France, its current distribution is therefore mainly altitude-dependant: under Mediterranean climatic influences, the development of *Betula* tree species mainly occurs between 800 and 1500 m a.s.l. and requires the presence of moist soils (Rameau et al., 2008). *Betula pendula* is the main tree species from which it is possible to harvest bark, while *B. pubescens* is extremely rare and was thus not taken into account for the model.

A GIS was created to assess the current distribution of birch in order to understand which areas are suitable for these trees to thrive. A potential distribution map of areas favourable to birch was then created. We were able to draw information from two sources: the CNRS potential vegetation maps (created at a 1/200,000 scale by various botanists for the French Scientific Research Centre (CNRS) in



the second half of the 20<sup>th</sup> century), and the Sophy-database containing hundreds of thousands of punctual vegetation surveys (Garbolino et al., 2012). We compiled the series of printed maps for Southern France (Barbero, 1991; Carles, 1951; Dupias, 1965, 1966; Dupias, 1973; Dupias, 1982; Dupias and Molinier, 1968; Gaussen, 1947, 1964a, b, 1972; Gobert, 1966; Izard, 1970; Jovet, 1969; Lascombes, 1955; Lavergne, 1963, 1968; Molinier, 1976; Ozenda, 1961, 1970; Rey, 1959). These were scanned, mosaicked, and georeferenced in ArcMap 10.5. (ESRI Inc.). We then digitalized all the birch stands in the maps within a polygonal vector layer in ArcGis (2800 polygons). The vegetation surveys from the Sophy database in which birch was present were entered into a digital database in Excel (e.g. geographic coordinates, characterization, coding) and exported to a vector layer of ArcGIS. In addition, the type of vegetation which birch trees or stands were associated with was read from the vegetation maps and manually entered as an attribute of each dot (vegetation survey) or polygon (area dominated by birch). Other attributes—altitude, exposure, rainfall, mean annual temperatures and slopes—were calculated automatically by creating/importing different kinds of maps/layers (Fig. 3).

The main results of the spatial analysis show that birch behaves very differently in South-West and South-East France. In South-East France under Mediterranean climatic influences, the distribution of birch is mainly altitude-dependent, with 85% of the stands growing at altitudes between 1000 and 1750 m a.s.l. and a minimum of 900 mm rain per year. The rest of the attributes are a result of this distribution in the Alps and its foothills: birch stands grow on rather steep slopes up to 40 degrees and around 80% of the stands grow on slopes steeper than 15 degrees. Probably because of the high insolation, birch seems to prefer northern slopes (60% of the effective), where they may also benefit from fewer competitors. The great majority of the stands (77%) grow under mean annual temperature conditions between 3 and 7 degrees Celsius. In the South-West, under Atlantic climate influences, birch is able to grow at lower altitudes (optimum: 750 m a.s.l.) and under higher annual temperatures (optimum: 9-11 °C) as it benefits from overall moister conditions, with annual precipitation between 700 and 1000 mm being optimal. These results show that the potential distribution of birch in South-East France is particularly suitable for predictive modelling, as it is in fact conditioned by altitude and overall negatively correlated with Mediterranean climate conditions. The predictive model was based on these results. Attribute values were grouped into classes, to which we allocated ordinal attractiveness values from 0 to 3. The map obtained shows the potential distribution of the birch tree in Eastern Provence, which was used to evaluate the cost-distances from the sites to areas where birch bark could have been harvested (Fig. 3).

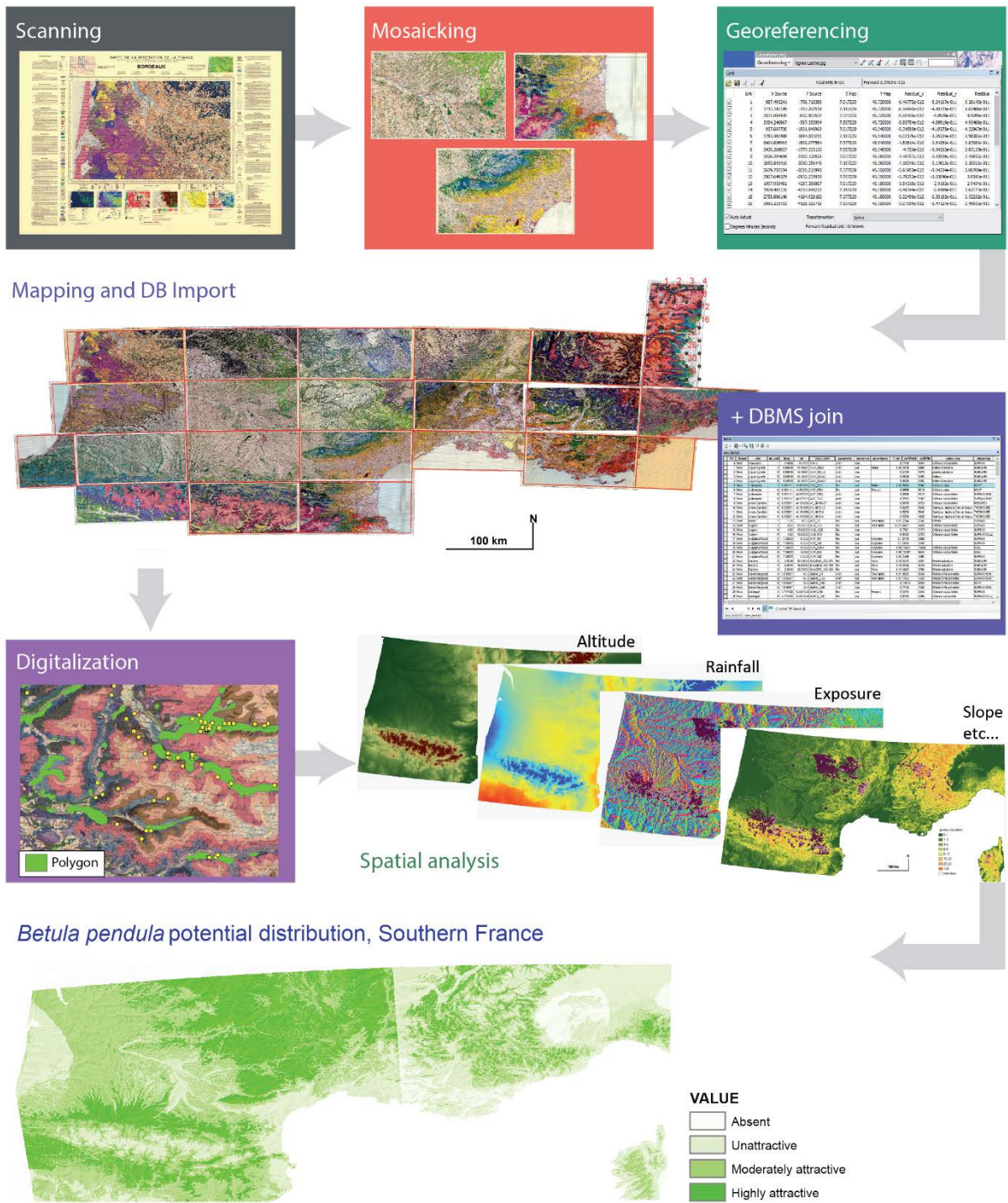


Fig. 3: Predictive attractiveness model: *Betula pendula* potential distribution, southern France

### 2.3.3. From the sites to the procurement areas: cost-distance calculations

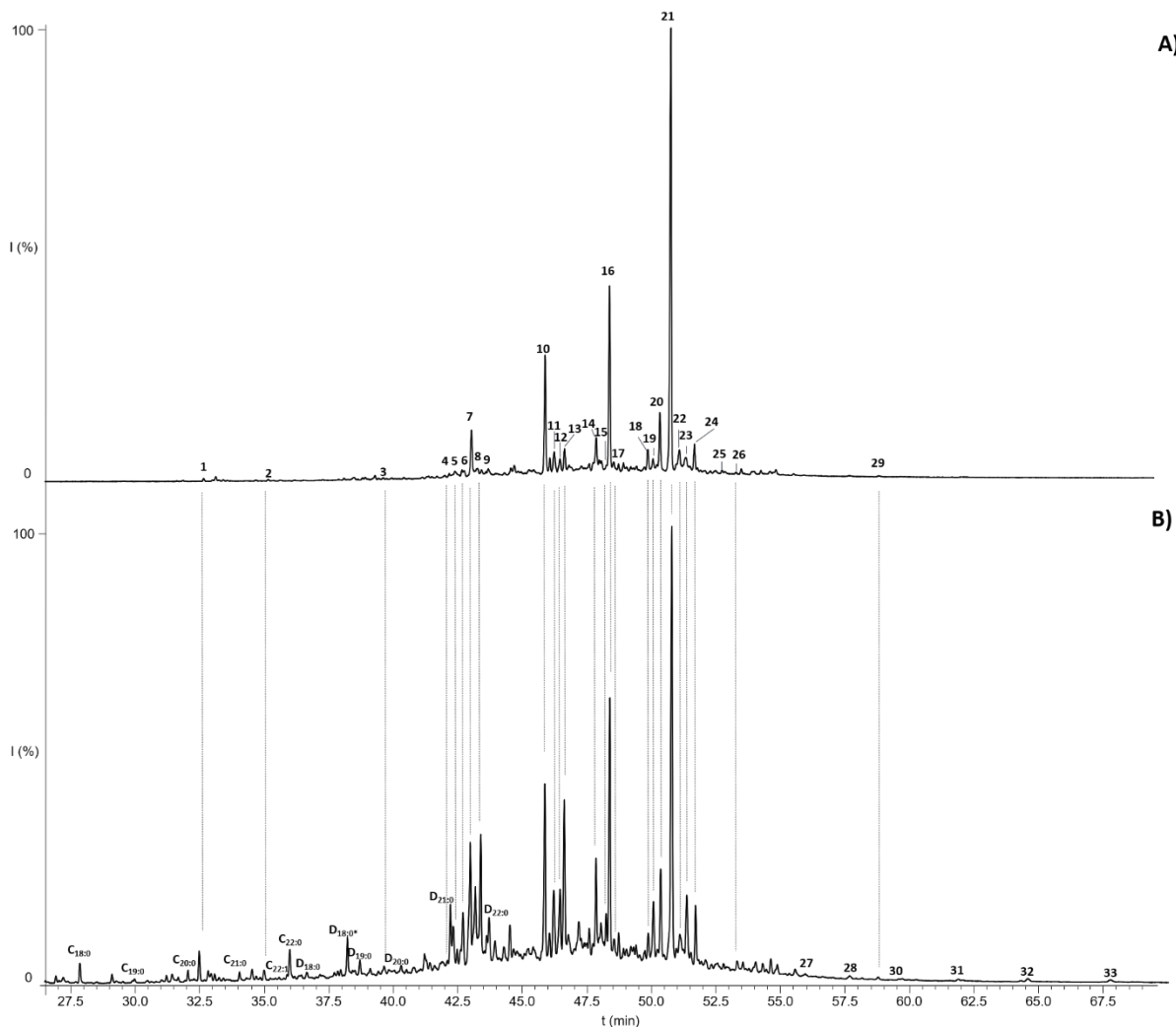
A geographic information system (GIS) was set up to spatialize and categorize natural archaeological substances according to their attributes (especially type of material, chronology and function). The analytical tools used to spatialize the data included (i) the creation of a digital elevation model (DEM) with 50 m accuracy for Provence and 100 m for the wider North-Western Mediterranean, (ii) the calculation of a friction map from the slope map ( $C = 0.031 * p^2 - 0.025 * p + 1$ , with  $C$  = stress for a field unit and  $p$  = slope in degrees) (Eastman et al., 1993) and (iii) the creation of a cost-distance map in kilometres from each archaeological site, which excludes inaccessible areas (steep reliefs and maritime areas). The costs/distance were calculated in walking hours (average of 5 km/h on a flat surface) from sites where plant tars, resins and fossil organic materials have been identified. Walking time was calculated by considering the degree of slope of the landscape. Without being perfectly precise (travel time will obviously vary depending on a number of factors, e.g. the density of forested areas), walking distances thus incorporate the topography so as to provide a better representation of the spaces to be covered than would radial distances. The threshold for the local sphere was set at 2 hours of walking (rather than 5 km) in regions with steep terrain. Areas beyond this local sphere are considered to be too far from the site for both a round trip and the acquisition of the resource to be completed in one day. Unless the products were obtained through contact with other people at the perimeter of this area, such trips would entail a longer journey with different organizational parameters. To delimit the neighbouring sphere, the 6-hour walking distance proposed by D. Binder (Binder, 1998) was maintained. The border between the far and very far spheres corresponds to about 20 hours.

### 3. Results

Extractable organic residues were detected in 64 of the 85 samples tested. At least six different organic substances were identified based on their molecular composition. They were detected pure or as mixtures, sometimes at different stages of transformation or degradation: birch bark tar, fat/oil, beeswax, bitumen and two different profiles of Pinaceae resin. Most of the samples from which organic could not be extracted were carbonised residues from the cave of Pertus II (17/21). Their carbonised state could be explained by their proximity to particular layers associated with episodes of fire, which recur throughout the occupation of the cave.

#### *3.1. Molecular profiles of birch bark tar*

Pentacyclic triterpenes from lupane and oleanane families were identified in 49 samples (58 %) from 13 of the 16 sites investigated (Table S3, Fig. 4), providing evidence for the widespread use of birch bark tar. Betulin and lupeol, the main biomarkers of birch bark (Krasutsky, 2006), were present in most of the samples (n=43). Erythrodiol and betulinic acid, two other biomarkers less abundant in birch bark, were also often detected. These biomarkers were associated with other pentacyclic triterpenes. They result from oxidation (e.g. betulone), dehydration (e.g. lupa-2,20(29)-dien-28-ol) and/or cycloisomerization (e.g. allobetul-2-ene) of the native molecules. These degradation markers are formed during tar production. Some of them are also the result of natural decay that occurs post deposition (Aveling and Heron, 1998a; Binder et al., 1990; Hayek et al., 1990; Regert et al., 1998). Odd and even numbered saturated fatty acids (C16 to C22) and diacids (C18 to C22) are sometimes associated with triterpenes (33 samples). They can arise from the degradation of suberin (Ekman, 1983; Ukkonen and Erä, 1979), even if several of them (in particular palmitic and stearic acids) are also present in many other natural substances.



**Fig. 4:** Chromatogram of birch bark tars. A): Large ball from Montpezat-Grotte Murée (category E). B): repair adhesive from Pertus II (category D).

1= C24 Pentacyclic terpenes; 2= C25 Pentacyclic terpene; 3= C27 Pentacyclic terpene (trisorlupene); 4= norlupa-2,20(29)-diene; 5= norlupa-2-ene; 6= norlupa-2-ene, isomer; 7= lupa-2,20(29)-diene; 8= lupa-2-ene; 9=  $\alpha$ -betulin I; 10= lupa-2,20(29)-dien-28-ol; 11= lupa-2,20(29)-dien-28-oic acid; 12= lupa-20(29)-en-28-ol; 13= allobetul-2-ene; 14= lupenone; 15= dehydrolupenone; 16= lupeol; 17= dehydrolupeol; 18= erythrodiol; 19= 28-oxoallobetul-2-ene; 20= betulone; 21= betuline; 22= betulinic acid; 23= 3-oxoallobetulanone; 24= allobetulin; 25= dihydrobetuline; 26= acetate, betulinic acid; 27=  $\Delta^2$ -betulin, heptanoate ester; 28=  $\Delta^2$ -betulin, octanoate ester; 29= betulin, caffeate; 30=  $\Delta^2$ -betulin, nonanoate ester; 31= betulin, heptanoate ester; 32= betulin, octanoate ester; 33= betulin, nonanoate ester

Furthermore, the in-depth examination of the distribution of the various categories of molecular markers points to the diversity of manufacturing processes involved in birch bark tar production (Rageot et al., 2019b) (Table 1). The distribution of triterpenes (biomarkers and markers of strong heating), fatty acids (C19, C21 and C22) and diacids (C18 to C22) can be used to distinguish between different production systems and/or specific heat treatments (see details in S2) (Rageot et al., 2019b).

**Table 1:** Summary and description of tar production systems

The identification of birch bark tar in a significant number of samples enabled a comparative study of their molecular profiles across the Neolithic period in the North-Western Mediterranean. Six different profiles of birch bark tar were detected (S2, Fig. 4) and compared with previously published experimental birch bark tars and 19 birch bark tars from the Middle Neolithic layers of the site of Nice-Giribaldi (Rageot et al., 2019b) (Table 2). Profile A (La Draga) is characterised by a molecular signature

typical of a tar produced by an autothermic process (e.g. condensation method (Schmidt et al., 2019)) while profiles B (Pertus II), C (Grotta dei Piccioni) and D (Nice-Giribaldi layers B-C and base 6B; Pertus II; Vernègues-Cazan-l'Heritière; Nice-Fodéré; Pendimoun-2A/upper) are known to be formed via allothermic production—more specifically, a *per descensum* system. Profile B suggests a short heating time or a low-heat treatment (e.g. first exudation) and profile D reflects a longer heating time and/or higher intensity of heat treatment (e.g. double-pot system). Profile E (Montpezat-Grotte Murée) shows a molecular signature that was not identified in the experimental tars tested, possibly the result of allothermic production using an unknown system. Finally, profile F (Saint-Benoit - Grotte II and Nice-Giribaldi C, already discussed in (Rageot et al., 2019b)) could be associated with allothermic production without separation (e.g. single-pot). These molecular profiles are thus related to different systems of production across the Neolithic sites investigated. Furthermore, the molecular signature of a sample from the Final Neolithic site of La Rouvière (Perthuison et al., 2019) that includes triterpenoid esters, markers of intense heating, and a low quantity of biomarkers suggests another strong thermal process of birch bark tar preparation, possibly using an additional system/heat treatment.

**Table 2:** molecular profiles of Neolithic (ID<2, n= 45) and experimental birch bark tars.  
BM= biomarkers; PT= pentacyclic triterpenes; HPT= hydrocarbon pentacyclic triterpenes; DPT= compounds mainly resulting from cycloisomerisation on cycle E and alcohol degradation on cycle A of betulin and betulinic acid.

### 3.2. Detection of fat and beeswax combined with birch bark tar

In two samples from the sites of La Draga and Vernègues-Cazan-l'Heritière, triterpenoid markers of birch bark tar were associated with very high proportions of palmitic (52-56 %) and stearic (14-39 %) acids. Such quantities of fatty acids are about 5 times higher than those observed in different experimental *per descensum* tars (Rageot et al., 2019b), suggesting that birch bark tar was mixed with a fatty substance. In the sample of La Draga, cholesterol and its derivative cholesta-3,5-dien, formed following heating and/or natural degradation (Evershed et al., 2004), were also detected.

In 3 samples adhering to ceramic vessels from the site of Vernègues-Cazan-l'Heritière, beeswax occurs in a mixture with birch bark tar. The presence of beehive-product is demonstrated by characteristic assemblages of palmitic esters (40 to 48 carbon atoms), *n*-alcohol (C24), and other fatty acids with even carbon numbers (C24-C28) (Evershed, et al., 1997, Regert, et al., 2001). In addition, *n*-alkanes (C25, C27 and C29; C27 major) were detected in two of these samples, which could indicate the absence of an intense heating treatment (Regert et al., 2001). Adhesive materials composed of birch bark tar and beeswax have already been documented in one Neolithic sample (Mirabaud et al., 2009) and in several samples from the Iron Age (Rageot et al., 2016; Regert et al., 2003). Beeswax could have been added as a plasticizer to modify the properties of the material (Rageot et al., 2016). However, the possibility that the beeswax derived from the contents of the vessel rather than a deliberate mixture cannot be excluded.

### 3.3. Molecular profiles of bitumen

Stigmastane, gammacerane, tetracyclic terpane and hopane derivatives (from 26 to 33 carbon atoms) were identified in samples from the sites of Colle Santo Stefano (n=2), Grotta dei Piccioni (n=1) and Bonnieux -Les Fabrys (n=2) (Fig. S1). This assemblage of hydrocarbons is typical of bitumen (Connan, 1999; Connan and Deschesne, 1992; Connan and Ourisson, 1993; Nardella et al., 2019). Only hopane derivatives (C27 to C32) were detected for the less concentrated samples from Grotta dei Piccioni (n=2), Colle Cera (n=1) and Catignano (n=1) and Bonnieux -Les Fabrys (n=3). The most intense signals (12 hopane derivatives) came from two samples from Colle Santo Stefano and one from Grotta dei

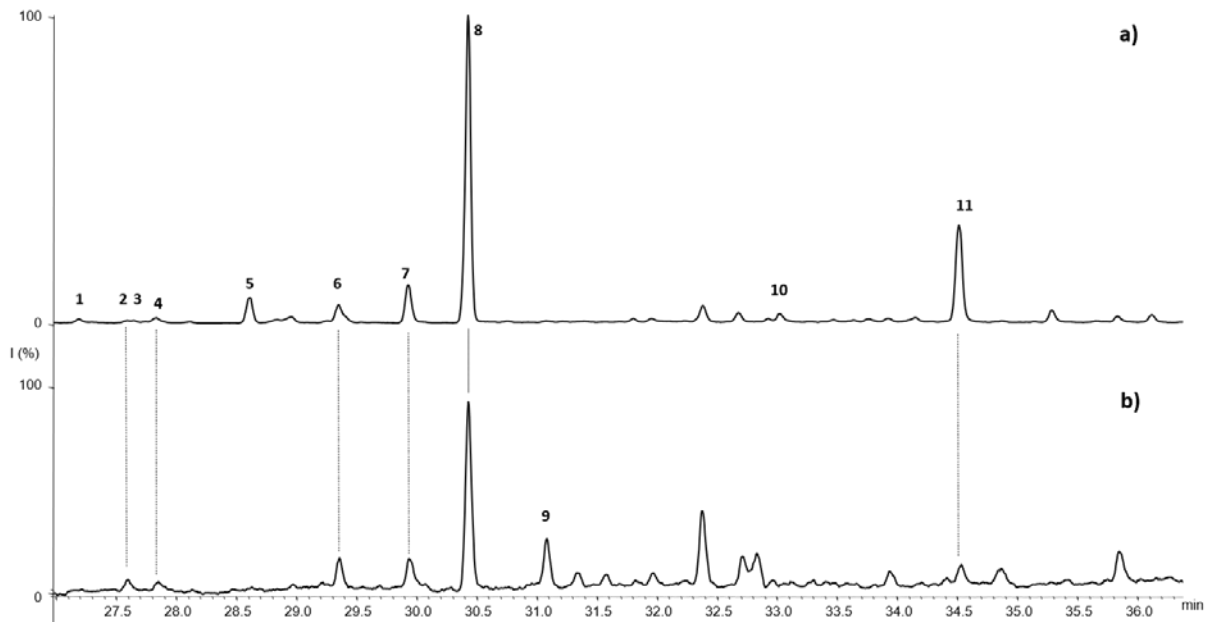
Piccioni. Among hopanes, 17 $\alpha$ (H),21 $\beta$ (H)-norhopane (C29) is the main marker (24 to 35%) followed by 17 $\alpha$ (H),21 $\beta$ (H)-hopane (C30, 15%) and 17 $\alpha$ (H), 22,29,30-trisnorhopane (C28, 10%) for the sample from Grotta dei Piccioni and those from Colle Santo Stefano, respectively. These molecular signatures (norhopane >> gammacerane; presence of bisnorhopane) are similar to geological bitumen and to bitumen used in the Early Neolithic in the Abruzzo region (Nardella et al., 2019).

Markers of bitumen were associated with a very high proportion of palmitic and stearic acids (15% of the molecular mixture) in both samples from the site of Colle Santo Stefano suggesting the addition of a fatty substance. In one of these two samples, triterpenoid markers from a highly degraded birch bark tar (absence of betulin) were also identified indicating the manufacture of a composite material (Fig. S2).

### *3.4. Molecular profiles of Pinaceae resins*

The presence of diterpenes from the abietane and sometimes pimarane families were identified in 10 samples from the site of Pertus II. Dehydroabiatic acid is the most abundant compound and is often associated with other biomarkers (sandaracopimaric acid and isomers of isopimaric acids). Degradation markers, generally formed by oxidation (7-hydroxydehydroabiatic, 7-oxodehydroabiatic, and 15-hydroxy-7-oxodehydroabiatic acids) complete the molecular assemblage. These markers are characteristic of a Pinaceae origin (Cartoni et al., 2004; Helwig et al., 2008; Steigenberger and Herm, 2011; van den Berg et al., 2000). The absence of heating markers (hydrocarbon or methylated diterpenes) suggests the exploitation of a resin rather than a tar (Hjulström et al., 2006).

In two samples from the site of Pertus II, the presence of pimaric acid as the main pimarane as well as  $\alpha$  and  $\beta$  seco-dehydroabiatic acids indicates a pine origin (Helwig et al., 2008) (Fig. 5). In two other samples from Pertus II, a biomarker assemblage including abiatic, dehydroabiatic, and isopimaric acids was identified. This suggests that another Pinaceae resin could have been used. Indeed, pimaric and seco-dehydroabiatic acids are not observed while the presence of a less stable biomarker, abiatic acid (in both samples), points to a high degree of preservation (Fig. 5). This molecular signature could correspond to larch, spruce, or fir resin. Although, no characteristic markers were detected that could distinguish between fir (such as abienol and norambrenolide) spruce or larch (Epimanool) (Cartoni et al., 2004; Helwig et al., 2008; Mills, 1973; van den Berg et al., 2000), the absence of epi-torulol and especially larixol, which is less sensitive to natural degradation (van den Berg et al., 2000), excludes larch resin.



**Fig. 5:** Chromatogram of a pine resin (a = MR2892) and another Pinaceae resin (b = MR2877), identified in the layer G of the sites of Pertus II.

1= seco-dehydroabietic acid,  $\beta$  isomer; 2= isopimaric acid, isomer; 3= seco-dehydroabietic acid,  $\alpha$  isomer; 4= sandaracopimaric acid; 5: pimaric acid; 6: isopimaric acid; 7= abieta-6,8,11,13-tetraen-18-oic acid; 8= dehydroabietic acid; 9= abietic acid; 10= 7-hydroxy dehydroabietic acid; 11= 7-oxodehydroabietic acid.



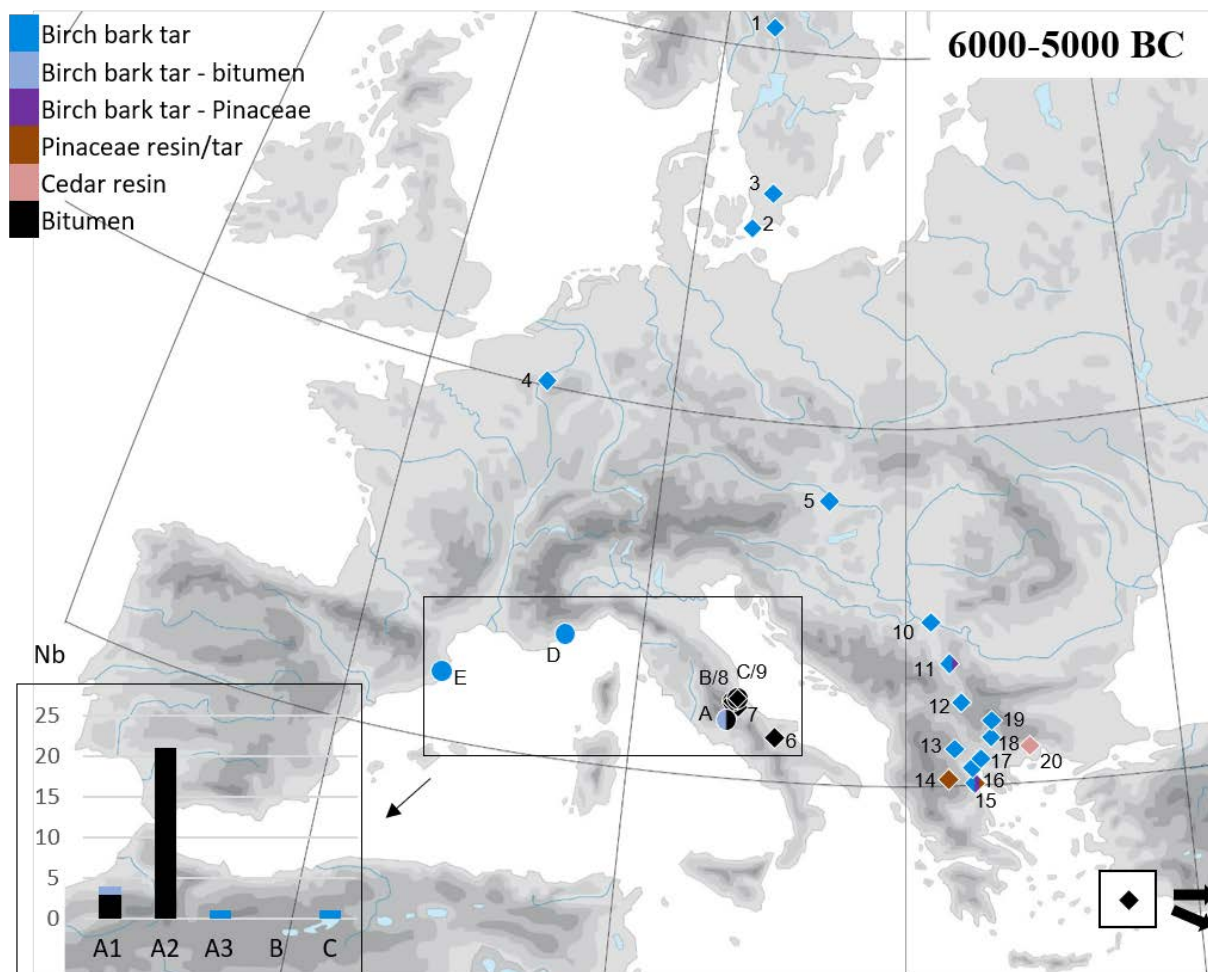
## 4. Discussion

With this study, the number of samples and of archaeological contexts associated with adhesive materials from the Mediterranean Neolithic have both substantially increased (from 135 to 198 and from 17 to 32, respectively) (Table S3 and Table S4). Maps of Figs. 6 to 9 combine the data based on molecular analyses obtained in this work with those already published. Although this study is not exhaustive, the expanded body of data nevertheless enables discussion of the evolution of adhesive management practices throughout the Neolithic, from the 6<sup>th</sup> to the 3<sup>rd</sup> millennium cal. BCE. These initial observations will have to be refined and completed by further study, which would benefit from greater recognition and standardized collection of adhesive materials in the field (e.g. free lumps obtained by flotation) and more consistent application of suitable chemical analyses.

Neolithic communities of the North-Western Mediterranean made significant use of birch bark tar (identified in 57 % of the 85 samples investigated). Although this tar is known to have been extensively exploited in Europe during the Neolithic, its abundance in southern latitudes raises the question of supply networks involved in the procurement of the bark or tar. Despite the low number of samples dated to the 6<sup>th</sup> millennium cal. BCE, the identification of distinct materials on either sides of the Apennines, birch bark tar to the West and bitumen to the East, sheds light on different economic but also cultural practices (Fig. 6). The extensive exploitation of birch bark tar at the sites dated to 4500 - 3300 cal. BCE (Late Ripoli, Early and Late Chassey cultures) enables the investigation of tar production systems over time and space. In particular, the high number of samples from the site of Pertus II (n=51; 59 %) dated between the Late Chassey and the Final Neolithic (3800 – 2900 cal. BCE), cover a long stratigraphic sequence that highlights a diachronic story of adhesive production and use.

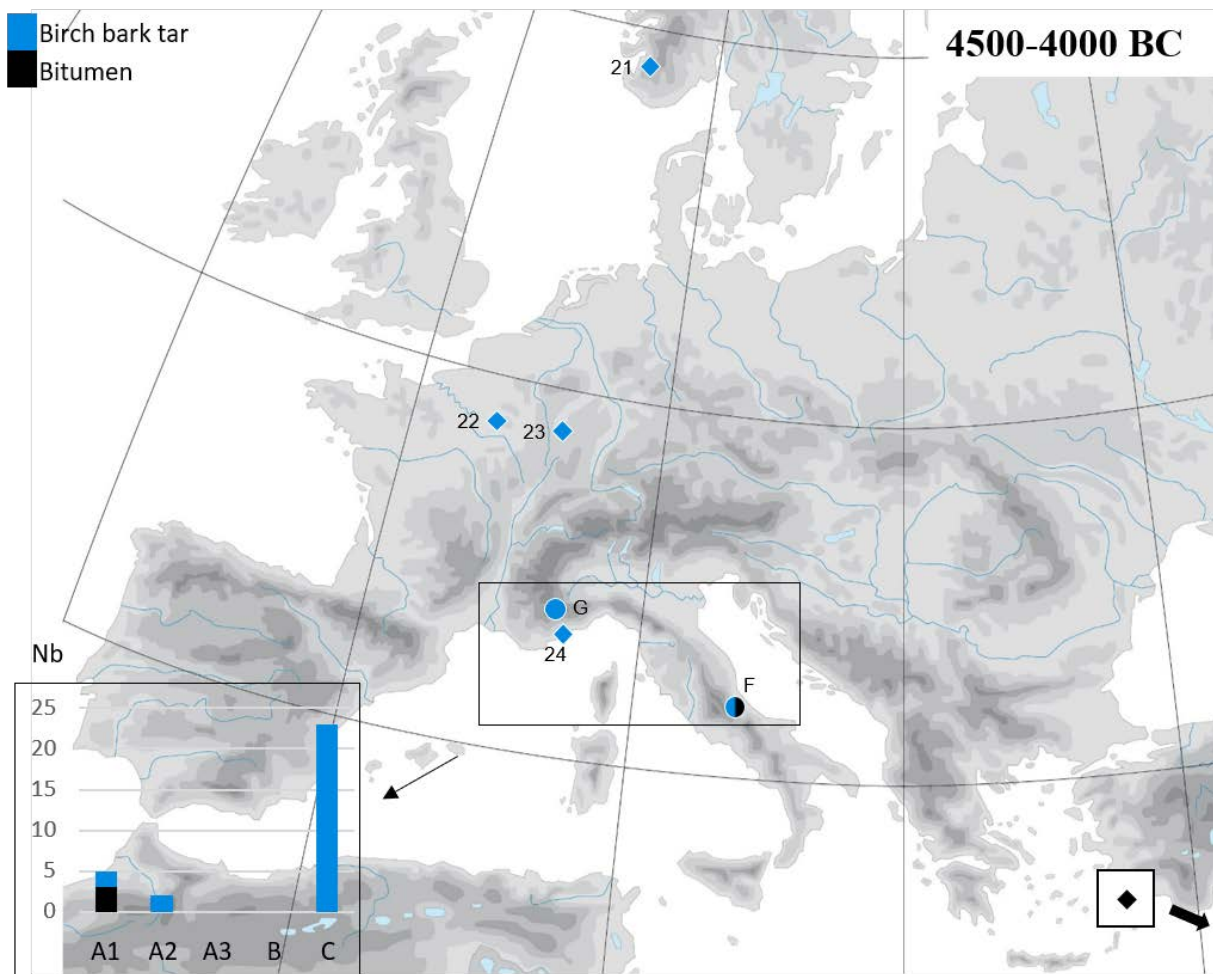
### *4.1. Evolution of exploited materials throughout the Neolithic*

Birch bark tar is attested as early as the beginning of the Neolithic at the sites of La Draga (Spain) and Nice-Giribaldi (France) (Fig. 6). At La Draga, it is associated with a fatty substance which could suggest the making of a composite glue applied to a marble bracelet as part of a decorative element. Although bitumen is the main material used in Abruzzo, birch bark tar was also used in this region (see section on the results in Abruzzo below). Up to now, birch bark tar was mainly known to be used during the 6<sup>th</sup> millennium cal. BCE near areas rich in birch forests (Table S1; Fig. 6) which could suggest opportunistic management/acquisition strategies. These new results show that it was also used along the Northern Mediterranean including in coastal areas which are not favourable to the growth of birch tree. During the same period (6<sup>th</sup> millennium cal. BCE), the north Aegean presents a specific pattern, with pure Pinaceae resins being used for their hydrophobic and odoriferous properties, or mixed with birch bark tar and used for their adhesive properties (Marangou and Stern, 2009; Mitkidou et al., 2008; Urem-Kotsou et al., 2018).



**Fig. 6:** Distribution of plant tars, resin and bitumen in Europe during the 6<sup>th</sup> Millennium BC combining published data (numbers) and present results (letters). Map base © S. Sorin, CNRS, CEPAM.  
 Published works (diamond): 1= Ringsjöholm; 2= Segebro; 3= Bokeberg; 4= Podrí l'Cortri; 5= Brunn am Gebirge; 6= Ripatetta; 7= Grotta dei Piccioni; 8= Catignano; 9= Colle Cera; 10= Starčevo; 11= Drenovac; 12= Pavlovac-Gumnište; 13= Apsalos; 14= Toumba Kremastis Koiladas; 15= Makriyalos; 16= Paliambela; 17= Stavroupoli; 18= Promahonas; 19= Ilindentsi; 20= Dikili Tash.  
 Present work (circle): A= Colle Santo Stefano; B= Catignano; C= Colle Cera; D= Giribaldi (layer 6); E= La Draga.  
 Material function (left frame): A1= reparation adhesive, A2= hafting adhesive, A3= decoration/assembly, B= coating/content residue, C= uncharacteristic free lump

The relatively large quantities of bark tar identified in the Middle Neolithic layers of Nice-Giribaldi compared to a residual presence or even absence in the Early Neolithic layers (Nice-Giribaldi-Layer 6 and Pendimoun) suggests, based on the current state of research, the intensification of the exploitation of this material in Provence during the 5<sup>th</sup> millennium cal. BCE. Birch bark tar was used to repair vessels at the Saint-Benoit-Grotte II and at the Grotta dei Piccioni. This tar was also recovered as uncharacteristic free lumps and was employed to haft bone spear blades at Nice-Giribaldi, within a Mediterranean vegetation context (Rageot et al., 2019b). This confirms the widespread use of pure birch bark tar in Western Europe, independently of the local availability of birch bark (Table S1; Fig. 7). This could be linked to specific (especially adhesive) properties of birch bark tar, which may have been required for various activities at the Provençal sites, and/or result from the many social interactions of the Chassey period characterized by dense exchange networks.



**Fig. 7:** Distribution of plant tars, resin and bitumen in Europe during the second part of the 5<sup>th</sup> Millennium BC combining published data (numbers) and present results (letters). Map base © S. Sorin, CNRS, CEPAM.

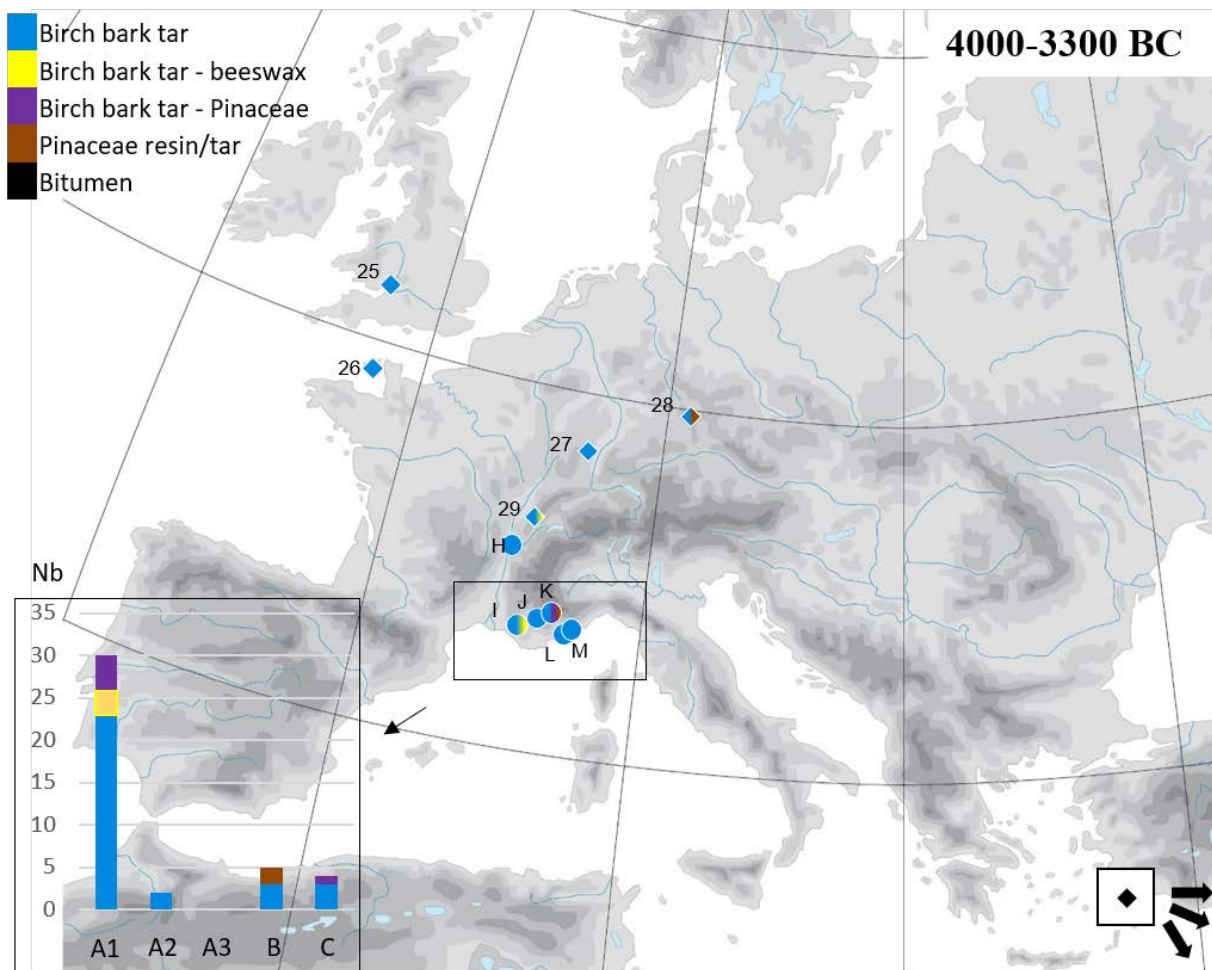
Published work (diamond): 21= Øvre Storvatnet; 22= Beaurieux; 23= Waldbillig Karelské; 24= Nice-Giribaldi.

Present work (circle): F= Grotta dei Piccioni; G= Grotte Saint-Benoit II.

Material function (left frame): A1= repair adhesive, A2= hafting adhesive, A3= decoration/assembly, B= coating/content residue, C= uncharacteristic free lump.

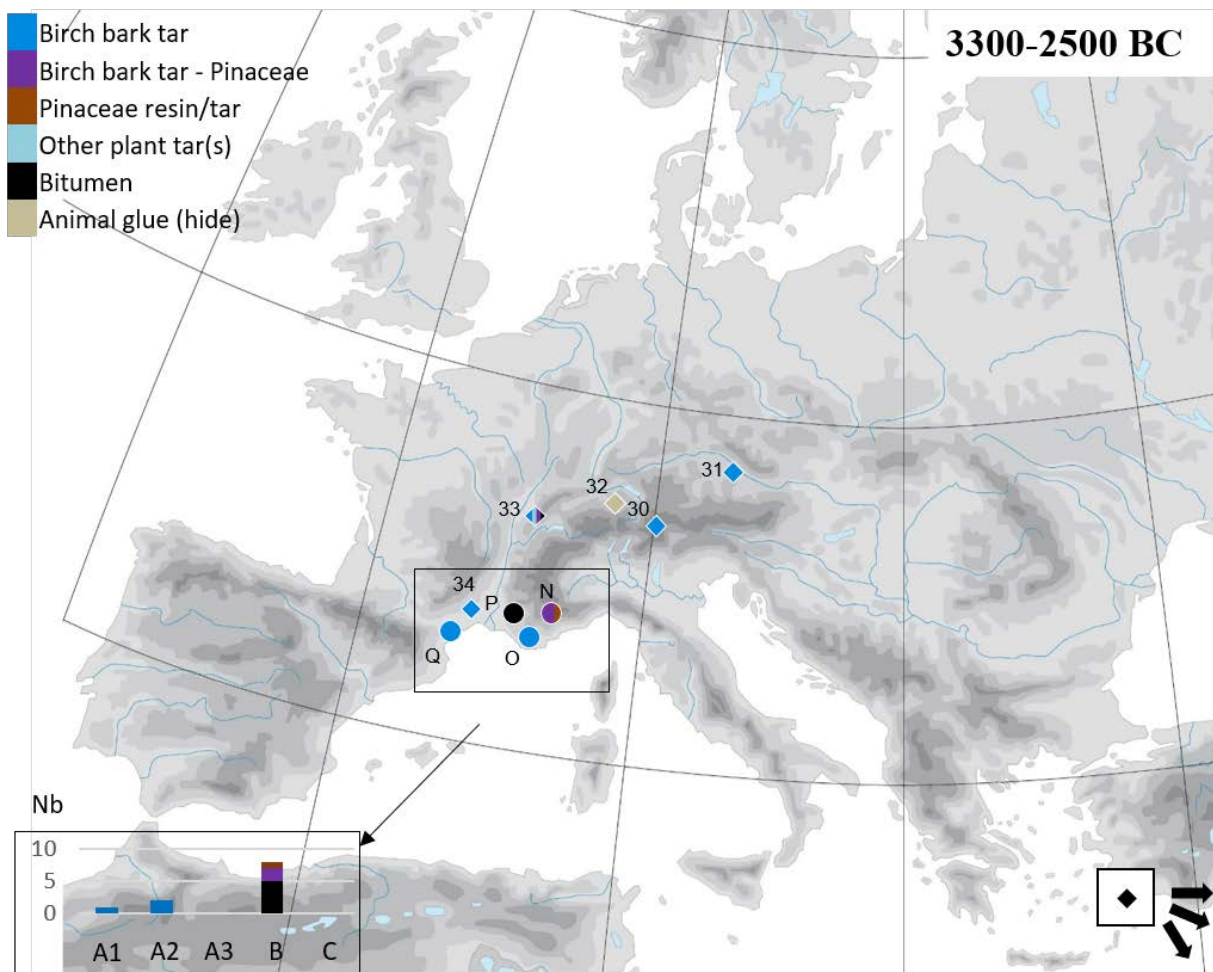
The new data from Provence dating to the beginning of the 4<sup>th</sup> millennium cal. BCE mirror previous findings from Central and Western Europe during the same period: it appears that birch bark tar production/exploitation intensified and the number of organic substances employed diversified, as did their range of uses (Table 1, Fig. 8). Birch bark tar still represents the main substance exploited for its adhesive properties (ceramic repair and hafting tools), but it also begins to be used for its hydrophobic properties (ceramic coating) at the site of Pertus II. The identification of big balls of birch bark tar (more than 100 g, Fig. 2C) wrapped in a cloth at the site of Montpezat - Grotte Murée represents evidence for the exploitation of tar in large quantities. The impression of textiles on their surfaces implies that it was necessary to protect the adhesive in its sticky malleable form from external contamination and to avoid too much direct handling/contact during transport (e.g. from the production site to the cave) and storage. Multicomponent materials were also detected: a mixture of birch bark tar with Pinaceae resins was identified at Pertus II, while birch bark tar was mixed with beeswax at Vernègues-Cazan-l'Heritière. It is important to note that pure Pinaceae resin(s) were only identified inside the pots and were thus connected to the coating of ceramic vessels. The presence of Scots pine type (*Pinus sylvestris* type) and fir (*Abies alba*) near Pertus II is corroborated by charcoal data, while spruce/larch seem to have been absent from the local vegetation (Battentier et al., 2016).

Thus, the second type of Pinaceae resin identified at the site could correspond to fir, which would suggest local procurement strategies.



**Fig. 8:** Distribution of plant tars, resin and bitumen in Europe during the first part of the 4<sup>th</sup> Millennium BC combining published data (numbers) and present results (letters). Map base © S. Sorin, CNRS, CEPAM.  
 Published work (diamond): 25= Sweet Track; 26= La Hougue Bie; 27= Rosheim; 28= Ergolding Fischergasse; 29= Clairvaux VII and XIV.  
 Present works (circle): H= Lyon-Favorite; I= Vernègues-Cazan-l'Heritière; J= Grotte Murée; K= Pertus II (I-D); L= Nice-Fodéré; M= Pendimoun (Phase 2A, upper).  
 Material function (left frame): A1= reparation adhesive, A2= hafting adhesive, A3= decoration/assembling, B= coating/content residue, C= uncharacteristic free lump.

From the end of the 4<sup>th</sup> millennium to the beginning of the 3<sup>rd</sup> millennium cal. BCE, the use of birch bark tar seems to decrease in the North-Western Mediterranean (6 samples from 5 sites, Fig. 9) as illustrated by the diachronic study of Pertus II: this substance was only identified in two samples from the Final Neolithic layers of the site. When present, it is always combined with Pinaceae resin. However, the diversification of organic substances employed continued, as previously described in the Alps region (Table S1, Fig. 9). Indeed, the first evidence of bitumen exploitation in Southern France (pit coating) was identified at Bonnieux-Les Fabrys. Despite the scarce data, plant tar/resin and bitumen seem to have been used for their hydrophobic properties more than their adhesive properties in Provence.



**Fig. 9:** Distribution of plant tars, resin and bitumen in Europe between the end of the 4<sup>th</sup> Millennium BC and the beginning of the 3<sup>rd</sup> Millennium BC combining published data (numbers) and present results (letters). Map base © S. Sorin, CNRS, CEPAM. Published work (diamond): 30= Ötzi; 31= Mondsee; 32= Zurich-Parkaus-Opéra; 33= Chalain 2, 3 and 4; 34= La Rouvière. Present works (circle): N= Pertus II (A-C); O= Chemin de Barjols; P= Bonnieux-Les Fabrys; Q= Bringairet. Material function (left frame): A1= repairation adhesive, A2= hafting adhesive, A3= decoration/assembling, B= coating/content residue, C= uncharacteristic free lump.

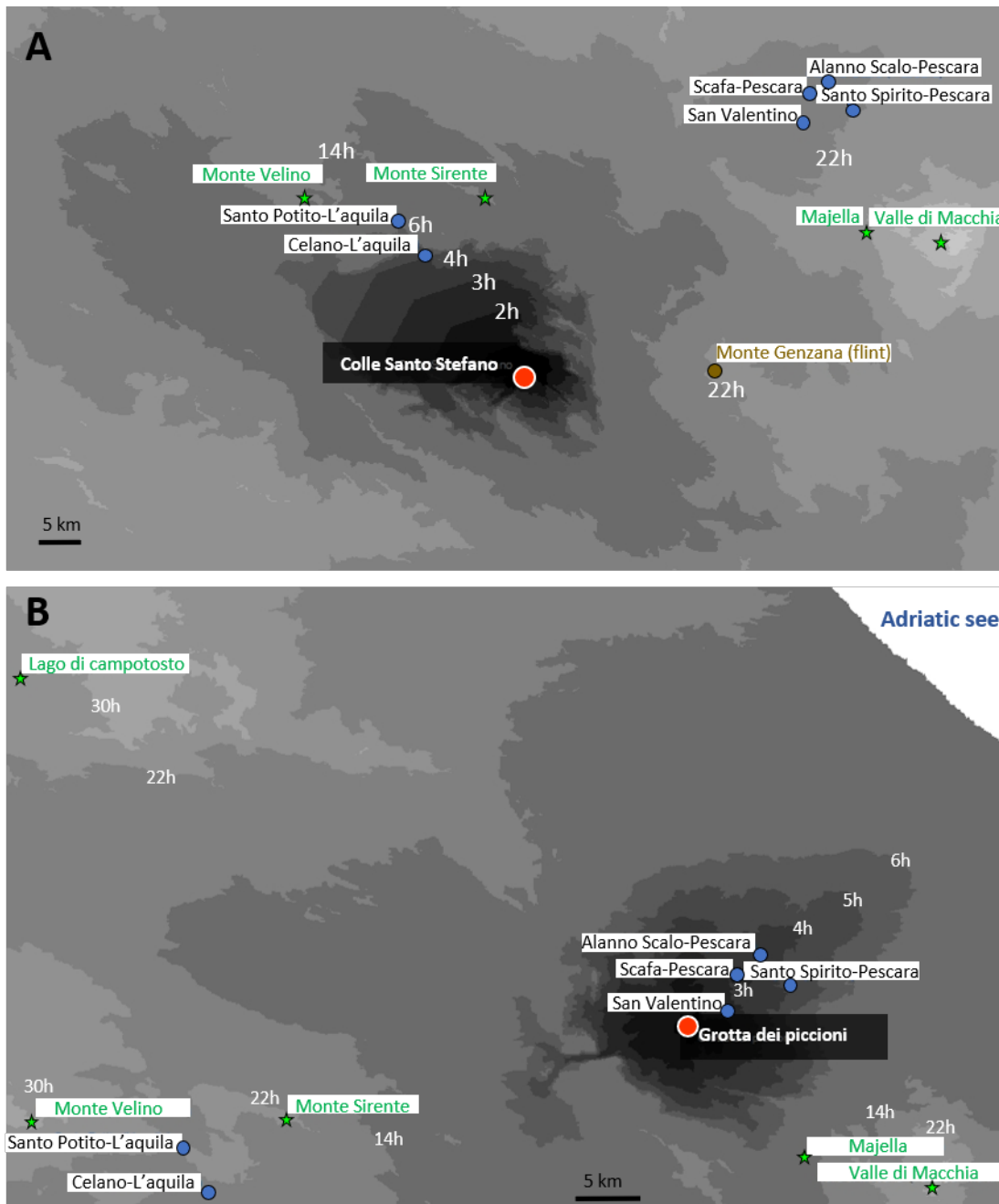
#### 4.2. The case of the Abruzzo sites (6<sup>th</sup> and 5<sup>th</sup> millennium): procurement of local bitumen and imported birch bark tar?

During the 6<sup>th</sup> millennium cal. BCE, the materials used for their adhesive properties (n=6) differ between samples from the Abruzzo (Colle Santo Stefano, Colle Cera and Catignano) and those from the North-Western Mediterranean (La Draga and Nice-Giribaldi). In the region located between the Adriatic Sea and the Apennine Mountains, bitumen was used to repair vessels. This represents further evidence for the significant exploitation of this fossil substance for its adhesive properties, as pure bitumen was previously identified as a hafting adhesive within similar chrono-cultural contexts (Nardella et al., 2019). Bitumen is also widely documented in the Levant where it had a more diverse range of applications (Connan et al., 2004; Connan and Van de Velde, 2010). The presence of a mixture of bitumen with birch bark tar in one sample from Colle Santo Stefano indicates the use of a multicomponent glue for pottery repairation, nuancing the picture of bitumen as the only adhesive used in the Apennine Mountains. This mixture, possibly representing from the intentional creation of a material with novel properties, is very surprising. To our knowledge, it would be the first evidence of the production of a composite glue made of bitumen and birch bark tar. Indeed, these substances are usually known to be used pure for the same function. Although they could be difficult to differentiate

by their appearance (depending on the manufacturing process), birch bark tar has a specific smell of "Russian leather" (e.g. Rageot et al., 2019b) that persists for several years. Therefore, we consider it unlikely that birch bark tar would have been confused for bitumen by Neolithic populations. The fat mixed with bitumen and/or birch bark tar from Colle Santo Stefano could also be the result of the intentional addition of a third substance to manufacture a composite material (e.g. mixture with animal glue) with different properties, such as increased plasticity (Urem-Kotsou et al., 2018). However, the possibility that the fat was unintentionally mixed with the adhesive components during the lifetime of the artefact cannot be ruled out. Indeed, the presence of fat could also derive from the contents of the pottery itself (Salque et al., 2012).

During the end of the 5<sup>th</sup> millennium (Late Ripoli culture layers), an interesting change is observed at the site of Grotta dei Piccioni. Bitumen was still used to repair *figulina* vessels recovered from a worship context (circular spaces delimited by pebbles or rock fragments) and a connected area associated with a workshop for pottery repair. However, pure birch bark tar was also employed to mend contemporaneous black vessels in the same workshop. G. Cremonesi has suggested a link between the workshop and worship contexts in the cave because of the ceramist's role in the community: these artisans had specific skills (mastery of fire and earth) and were capable of giving new life to broken pottery using adhesives (Cremonesi, 1976). This could suggest different symbolic meanings or properties ascribed to each substance.

The molecular profile of bitumen identified in the archaeological sites of Abruzzo during the 6<sup>th</sup> and 5<sup>th</sup> millennia is similar to that of the geological bitumen available in the region (Nardella et al., 2019) (Colombo and Sironi, 1961), suggesting procurement at local scales (<3 hours of walking for Catignano and Grotta dei Piccioni) or from neighbouring area (4-6 hours of walking for Colle Cera and Colle Santo Stefano) (Fig. 10).



**Fig. 10:** Cost-distance map from A/ Colle Santo Stefano (Abruzzo, Early Neolithic) and B/ Grotta dei Piccioni (Abruzzo, Middle Neolithic). Grey scale refers to the walking time, blue points to bitumen sources (from Colombo and Sironi, 1961) and green stars to potential birch forest according to current data.

Birch bark tar was identified in the Apennines, at the sites of Colle Santo Stefano (mixed with bitumen) and at Grotta dei Piccioni (pure) in contrast to the lowland sites on the Adriatic side (Colle Cera and Catignano). This may be explained by the residual presence of birch trees in the Apennines (still observed nowadays), even if they are extra-local (more than 10 hours of walking distance) (Fig. 10). This resource, possibly obtained within the management of a relatively large territory, may have been sufficient for the occasional production of tar. For larger-scale tar production, the raw material could have been sought among the birch forests located further north of the Italian peninsula. A birch by-product would not be the only exogenous material from more distant regions found at Colle Santo Stefano (e.g. flint from Monte Genzana, shells and *Myliobatis* tail from Adriatic coast, obsidian from Palmarola and Lipari (Angeli et al., 2019; Radi and Tozzi, 2009)). At the end of the 5<sup>th</sup> millennium, the

procurement of birch by-products at Grotta dei Piccioni could have been integrated into already existing exchange networks, which have been documented for geomaterials from Northern Italy and Southern France (Southern Chassey and Lagozza contexts (Cremonesi, 1976)). Although only 4 samples were analysed, the use of an exogenous substance (birch bark tar) alongside a locally available alternative (bitumen) could also reflect different symbolic meanings of these materials used in the workshop and/ or worship contexts at the site.

#### 4.3. Southern France and North-Eastern Iberia during the Neolithic: supply networks and birch bark tar production systems

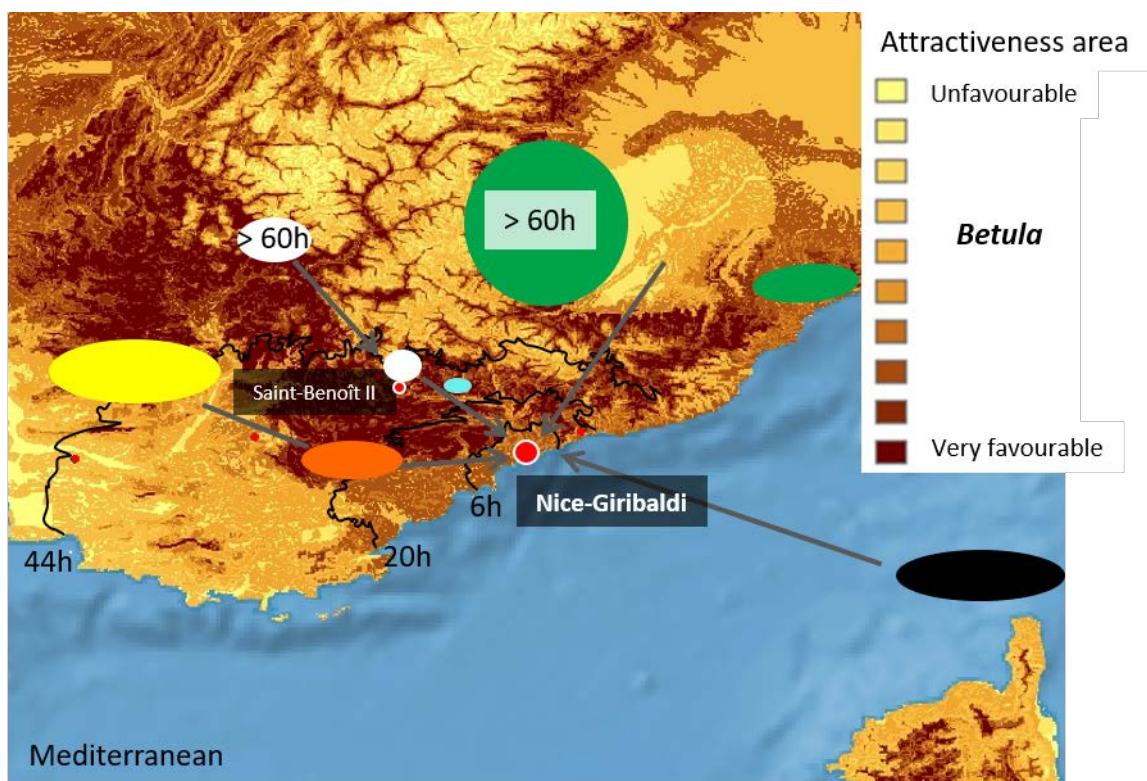
The means of procurement of a raw material can be investigated by modelling a raw material's distribution and considering the procurement networks demonstrated for other archaeomaterials. Pinaceae and beehive products were most probably harvested in the vicinity of the sites. The bitumen used to coat pits at Bonnieux-Les Fabrys in Western Provence was also locally available: the deposits of Apt-Manosque-Forcalquier (Debrand-Passard et al., 1984)(Fig. S3) are located at about a three-hour walk from the site. Areas very favourable to birch forests (or potential areas with concentrations of birch stands) can be observed in the Southern Alps and around the Pyrenees, but are absent on the Mediterranean coast. In a geographic area where birch trees are scarce, birch bark and/or its sub-products were probably obtained from extra local areas and stored for regular use. Indeed, access to birch forests is essential for the regular and sustainable production of birch bark tar (Rageot et al., 2019b). Furthermore, tar yields can be increased by selecting quality raw materials while careful, seasonal harvesting helps to preserve the trees (Burri, 2012; Rageot et al., 2019b). These practices suggest the anticipation of future needs through an annual procurement strategy. Birch was likely available in the local/neighbouring areas of both sites in Upper Provence (Pertus II and Saint-Benoit-Grotte II) and birch by-product procurement could have been linked to the acquisition and management of other local resources, such as clay. However, birch forests were located further away from the sites of South-Eastern Provence (Nice-Giribaldi, Nice-Fodéré and Pendimoun), Western/Central Provence (Vernègues-Cazan-l'Heritière, Montpezat-Grotte Murée and Chemin de Barjols), Southern Languedoc (Bringairret) and North-Eastern Iberia (La Draga) (Fig. 11 and Fig. S3) (Battentier et al., 2015; Binder et al., 1993; Caruso and Piqué, 2014; Thiébault, 2001). Favourable areas may have been present at the edge of the neighbouring sphere for the sites of South-Eastern Provence and La Draga, or even more distant for the other sites (> 10 hours of walking). The use of birch bark tar as an adhesive material at Vernègues-Cazan-l'Heritière and at Chemin de Barjols was very likely a non-opportunistic choice (Fig. S3). Indeed, other resources like pine or geological bitumen (Apt-Manosque-Forcalquier (Debrand-Passard et al., 1984)) are located closer to the site (9 hours of walking) and on the way to the closest birch forests to Vernègues-Cazan-l'Heritière.

The study of birch bark tar production systems during the 6<sup>th</sup> millennium still suffers from a lack of data, with only two samples having been investigated (from La Draga and Nice - Giribaldi). Birch by-products were transferred from areas very favourable to birch forests located in or on the way to the Pyrenees or Alpine regions and could have been integrated in long-distance exchange networks previously documented for geomaterials at both sites, and for woody material at La Draga (Binder, 1998; Terradas et al., 2012). The adhesive materials from the two sites indicate the application of different heating processes. The molecular profile of the birch bark tar adhered to the La Draga bracelet and mixed with fat is rather similar to tar produced by the condensation method, while that of the free lump discovered at Nice-Giribaldi corresponds instead to a *per descensum* process.



From the mid-5<sup>th</sup> to the mid-4<sup>th</sup> millennium cal. BCE, a dense exchange network entailing many social relationships could also have contributed to the expansion of the use of birch bark tar. Bark or tar could have been integrated into exchange networks of geomaterials coming from more distant areas. An intensification of exchanges and craft specializations has been documented during the formation of the Chassey complex. The Southern Chassey is part of this general development, as particularly evidenced by the circulation of lithic raw materials: Bedoulian flint, eclogites and jadeitites (Binder, 1998; Borrell et al., 2019; Pétrequin et al., 2003), hyaline quartz (Brisotto, 1999; Rostan, 2005, 2007), and obsidian (Binder et al., 2012; Vaquer, 2006). The study of the lithic industries found at Giribaldi during these periods also testifies to the importation of quartz and green rocks (eclogites, jadeites) from the Alps (Binder, 2016)(Fig. 11). Axes made of alpine green rocks have also been identified at the site of Montpezat-Grotte Murée (Lepère, 2009). In order to reach the most distant sites of Provence, birch by-products could have been transferred through alpine / peri-alpine sites like Pertus II. Three models for the diffusion of birch bark or tar can be proposed:

- (i) integrated within the management of a relatively large territory as evidenced by other activities such as pastoralism;
- (ii) integrated within systems of exchange of other goods (especially minerals);
- (iii) independent production and circulation linked to craft specialization comparable to that of lithic or ceramic productions, which may involve relay sites.



**Fig. 11:** Cost-distance map from Nice-Giribaldi (Provence, protchassey / Early Chassey), including *Betula* attractiveness area and source of mineral materials found at Nice-Garibaldi (from Binder et al., 2008). Yellow= bedoulian and oligocene flint; orange= bauxite; green= greenstones; white= quartz; azure =azurite; black= obsidian from Lipari.

The large number of samples discovered in Provence from the mid-5<sup>th</sup> to the mid-4<sup>th</sup> millennium cal. BCE allowed a comparative study of birch bark tar production systems. During the end of the 5<sup>th</sup> millennium, at least two methods of tar production were identified at Nice-Giribaldi (Rageot et al., 2019b) and Saint-Benoit-Grotte II. A *per descensum* system (profile D) was used in the Proto-

Chassey/SMP2 layers (Nice -Giribaldi, Phase B) and during the early Chassey (Phase C). However, this system was also associated in the latter period with another allothermic production technique without separation (profile F at Nice -Garibaldi, Phase C and Saint-Benoit-Grotte II). At Nice-Giribaldi, this was interpreted as reflecting the acquisition of new know-how and/or the diversification of procurement networks for birch bark tar. During the first part of the 4<sup>th</sup> millennium in Provence, a standardisation of birch bark tar production in order to manufacture adhesive materials seems to have occurred. Indeed, a similar molecular signature (profile D including triterpenic esters) was identified among a large number of samples from Pertus II, Vernègues-Cazan-l'Heritière, Nice-Fodéré and Pendimoun (latest or post Chassey layer) (Fig. 12). This profile is similar to that of *per descensum* production, specifically double pot system. Birch bark tar was used pure, mixed with beeswax (Vernègues-Cazan-l'Heritière, later phases) or Pinaceae resin (Pertus II). Mixtures could have been produced to obtain other materials with particular properties that were desired or to compensate for the lack of birch bark tar. They could also be the fingerprints of recipes from local traditions. Another molecular profile of birch bark tar (profile B), with very low quantities of degradation markers, suggesting a *per descensum* process with low heat treatment such as the first exudation, was identified in two samples from Pertus II. Interestingly, they correspond to the two birch bark tars covering the internal part of ceramics, probably to coat the vessels. Pure Pinaceae resin was also used for the same function. Finally, the two large imported balls of birch bark tar from Montpezat-Grotte Murée are characterised by a distinctive molecular profile (profile E, Table 2, Fig. 4), which could result from a different production system.



Fig. 12: Late Chassey in Provence (4000-3300 BC): Production of adhesive / hydrophobic materials and cultural dynamics (in black and grey, adapted from Lepère, 2012).

## 5. Conclusion

This work provides the most extensive view to date of the exploitation of adhesive and hydrophobic materials in the North-West Mediterranean Neolithic. Despite the continuous use of birch bark tar throughout this period, current results indicate that substances used for their adhesive and hydrophobic properties became more diversified from the 4<sup>th</sup> millennium BCE onwards (Fig. S4). Overall, pure Pinaceae exudates were only identified as waterproofing agents of ceramic vessels, while bitumen and birch bark tar in its pure form, or mixed with Pinaceae resin, beeswax and possibly fat were multifunctional materials that were used in a range of daily activities. The fact that products were manufactured and not merely harvested implies different forms of know-how, spatial organisation and investments of time. The manufacture of tar and composite materials requires some control of the process (especially during heat treatment) and is not necessarily restricted to the season for harvesting resins/bark.

The diversity of local organic substances exploited at different sites (Pinaceae products, beeswax, bitumen) testifies, as in the case of mineral resources, to Neolithic populations' comprehensive knowledge of the resources available in the immediate environment of the sites investigated, whether plant, fossil or mineral. Birch bark tar was identified at sites along the coast of Eastern Provence, in Western Provence, in Languedoc, and in North-Eastern Iberia—all areas unfavourable to the natural growth of birch forests. Several models of procurement can be proposed according to the chrono-cultural contexts and the location of the sites.

From a diachronic viewpoint, the rare occurrence of birch bark tar in the Early Neolithic (3 samples found at Colle Santo Stefano, La Draga and Nice-Giribaldi) suggests that its use was uncommon, and possibly that it was an exogenous product. From the mid-5<sup>th</sup> to the mid-4<sup>th</sup> millennium cal. BCE, birch bark tar is found in larger quantities in Provence. The procurement of the raw material as well as that of finished products (tar, mixtures) could have been integrated within the management of a relatively large territory. These products could also have circulated within exchange networks of other goods and been part of the Neolithic package transferred through long-distance exchanges. The different manufacturing processes of birch bark tar identified in Provence at the end of the 5<sup>th</sup> millennium could be explained by different origins of the product. The first part of the 4<sup>th</sup> millennium sees the standardisation of birch bark tar production in the region. This could be linked to craft specialisation and/or indicate expanded exchange networks, which is observed for several other spheres of activities during this period. However, other materials could also have been manufactured in order to obtain different properties, such as hydrophobic properties to coat the vessels, or possibly to compensate for the lack of birch resources available (mixtures). The more restricted exploitation of birch bark tar during the Final Neolithic in Southern France could correspond to the dismantling of previously established networks and to more spatially restricted systems of exchange.

By combining the chemical characterisation of organic substances with broader considerations surrounding their manufacture and use as well as spatial analysis and comparison with the procurement networks of mineral resources, it is possible to provide compelling evidence for the management of adhesives over time.

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## Supplement information texts

### S1: Methods and limitations for the study of adhesive materials

Plant resins, tars and organic fossil substances (e.g. bitumen) are not consistently integrated into archaeological studies, nor are they systematically analysed using appropriate methods. As they do not present any characteristic morphology in archaeological contexts, they can only be securely identified by chemical analyses and the characterization of their molecular composition. Another important factor limiting the study of these materials is their organic constitution, since they generally undergo more significant degradation processes than do inorganic artefacts, and the rate of degradation can vary according to the burial context. Thus, the study of such substances does not have the same resolution as that of inorganic materials. Furthermore, adhesive and hydrophobic materials are often discovered as surface residues (associated with ceramic vessels, lithic and bone tools, etc. or as free lumps within the sedimentary matrix) and therefore they are less well protected from exogenous contamination than organic residues that have been trapped in an inorganic matrix (ceramic, bones or dental calculus). Among organic materials, bitumen, plant tars and resins are relatively well preserved due to the higher stability of their di- and triterpenes markers. Other substances such as protein glues made from terrestrial animals or fish (Allain and Rigaud, 1989; Bleicher et al., 2015; Solazzo et al., 2016) and gums (Buckley et al., 2004) could also have been used for their adhesive and hydrophobic properties. However, proteins and saccharides generally degrade rapidly outside of contexts beneficial for their preservation (such as arid or waterlogged contexts), significantly reducing the potential for the study of their exploitation. Historically, different analytical methods have been applied to characterise dark visible residues that could have been used for their adhesive, hydrophobic or odoriferous properties. During the 19th century, visual observation, burning and smelling were used to categorise residues as organic or odoriferous materials (e.g. (de Cussé and Galles, 1866)). From the 1960s on, Fourier transform infrared spectroscopy was used to identify these substances, in particular to confirm their organic origin and, in cases of good preservation, to identify resinous or tarry materials (Langer and Koško, 1992; Sandermann, 1965; Sauter, 1967) (Cristiani et al., 2009; Daher et al., 2010; Sulgostowska, 1997; Vahur et al., 2011). SEM-EDX was also used to provide evidence of the potential organic origin of materials (Dinnis et al., 2009; Pawlik and Thissen, 2008, 2009). The development of chromatographic methods in the 1980s has contributed to improving scientific understanding of the molecular families which make up such materials. First, the TLC method (thin layer chromatography) was applied to distinguish triterpenic substances (often associated with birch bark in Europe) from diterpenic substances (associated with conifer resins/tars). Indeed, the studies conducted at Zulawka Mala in Poland or at the waterlogged alpine lake sites of Hornstaad-Hörnle I, Zürich Seefeld and Portalban-Montilier dating to the Late and Final Neolithic (Langer and Rola, 1997; Rottländer, 1981; Schoch, 1992) likely indicate the presence of tar produced from birch (a hypothesis supported by the environmental context). However, the use of GC-MS can further refine the molecular signatures of organic residues by providing more precise structural information on their different molecular components (earliest: (Binder et al., 1990; Evershed et al., 1985; Hayek et al., 1990; Heron et al., 1991)). In particular, this technique was used to detect and distinguish between different bark tars composed of similar molecular families (Regert et al., 1998) and mixtures of resins/tars and/or other organic substances (Buckley et al., 2004; Clark et al., 2013; Mirabaud et al., 2009; Rageot et al., 2016; Regert et al., 1998; Regert et al., 2000; Regert et al., 2003).

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## **S2: Molecular profiles of birch bark tar and systems of tar production (detailed information) identified in the North-Western Mediterranean during the Neolithic**

Previous research has shown that the differential degradation of molecular markers of birch bark tar can be related to the anthropological history of these materials, especially the manufacturing process (Rageot et al., 2019).

Different molecular profiles and degrees of degradation were observed among the 48 samples, indicating a variety of thermal and/or decay processes. We first classified the different tars according to the ratio of triterpenic biomarkers to triterpenic markers which are known to be formed by natural decay within the sedimentary matrix (e.g. lupa-2,20(29)-dien-28-ol and betulone) (Aveling and Heron 1998; Garnier 1999). An indicator of natural degradation (ID) was calculated with the ratio  $[\text{lupa-2,20(29)-dien-28-ol} + \text{betulone}]/\text{betulin}$ . Since betulin can be degraded by oxidation and dehydration following heating, the ID calculated for experimental tars ( $\text{ID} < 1$ ) was used as a reference value (Rageot et al. 2019). Different degradation patterns identified according to the ID and the percentage of biomarkers (BM%) are presented in the table above (S2 table 1). Categories 1 ( $\text{ID} < 1.1$ ;  $n = 19$ ) and 2 ( $2 > \text{ID} > 1.1$ ;  $n = 7$ ) indicate a lower degree of degradation while categories 3 ( $8 > \text{ID} > 2$ ;  $n = 5$ ) and 4 ( $\text{ID} > 8$ ;  $n = 17$ ) display relatively high degrees of degradation. To investigate the underlying systems of tar production, we chiefly considered the least degraded samples (categories 1 and 2) as categories 3 and 4 were more difficult to interpret due to their complex life histories (partial carbonisation, repeated reheating, long use-life and/or recycling) (Rageot et al. 2019). This does not exclude the possibility that the tars classified in categories 3 and 4 could derive from a production system resulting in a high degradation profile. Biomarkers and markers of strong heating (triterpenes), fatty acids (C19, C21 and C22) and diacids (C18 to C22) were used as indicators to distinguish the different tars. Triterpenic markers of intense heating have been previously defined in Rageot et al. 2019 and can be formed during specific thermal treatments, especially single-pot and double-pot processes. The main markers identified in this category are the hydrocarbon pentacyclic triterpenes (HPT) from lupanes,  $\alpha$ -lupanes or norlupanes (except for lupa2,20(29)-diene), and compounds mainly resulting from cycloisomerisation on ring-E and alcohol degradation on cycle A of betulin and betulonic acid (DPT: 3-oxo-allobetulane; 28-oxoallobetul-2ene;  $\alpha$ -olean-28-al; allobetul-2-ene;  $\alpha$ -allobetulin I). These hardly ever occur in nature, especially triterpenic markers resulting from intramolecular rearrangement of ring-E which only form during heating under acidic conditions (Green et al., 2007; Li et al., 1998).

Among the least degraded samples classified in categories 1 and 2, six birch bark tar profiles were distinguished with reference to previously published birch bark tars produced experimentally using allothermic systems such as double-pot or single-pot processes (Rageot et al. 2019) or an autothermic system (condensation method; Schmidt et al. 2019).

-Profile A (cat. 1-A= 1)

The tar is characterised by a very high quantity of biomarkers (BM = 53%) and the very low presence of intense heating markers (HPT or DPT <2%). This suggests a short heating time or a low-heat treatment. Fatty acids/diacids (C19, C21 and C22) and triterpenic acid biomarkers (betulonic and/or oleanolic acids = BM acids) were not detected.

-Profile B (cat. 1-B =2)

These tars are also characterised by a very high quantity of biomarkers (BM > 40%) and the very low presence of heating markers (HPT and DPT <5%). However, in contrast with profile A, fatty acids (C19, C21, C22), diacids and betulonic acid were detected in the mixture.

-Profile C (cat. 2-C)

The tar is characterised by a high quantity of biomarkers (BM= 28%) and the very low presence of HPT (2%) but an important quantity of DPT (14%). Fatty acids (C19, C21 and C22), diacids and betulinic acid were also detected.

-Profile D (cat. 1-D =23 and cat. 2-D =8).

The tars in cat. 1-D are characterised by a high quantity of biomarkers (BM= 25-45%) and a relatively larger quantity of triterpenic markers of intense heating (HPT and DPT =6-18%). Fatty acids (C19, C21 and C22), diacids and betulinic acid were also identified. Small quantities of triterpenic esters ( $\Delta^2$ -betulin and betulin esters) were also identified, except in the sample from Nice-Giribaldi. The tars in the 2-D category show a slightly more degraded profile (BM= 17-19%, HPT= 13-25% and DPT=7-24%).

-Profile E (cat. 1-E =2)

These tars are characterised by a very high quantity of biomarkers (BM= 32-45%) and the low presence of heating markers (HPT and DPT =5-10%). They are also characterised by the absence of fatty acids/diacids (C19, C21 and C22) combined with the presence of betulinic acid.

-Profile F (cat. 1-F = 4 and 2-F = 4)

These tar samples are characterised by the presence of intense heating markers, the absence of triterpenic acids, fatty acids, and diacids, despite a significant quantity of biomarkers (cat. 1-F: BM= 28-45 %, HPT= 10-19% and DPT =6-14%; cat. 2-F: BM= 18-22 %, HPT= 8-16% and DPT =17-28%).

**S2 table 1:** Molecular profiles of Neolithic and experimental birch bark tars.

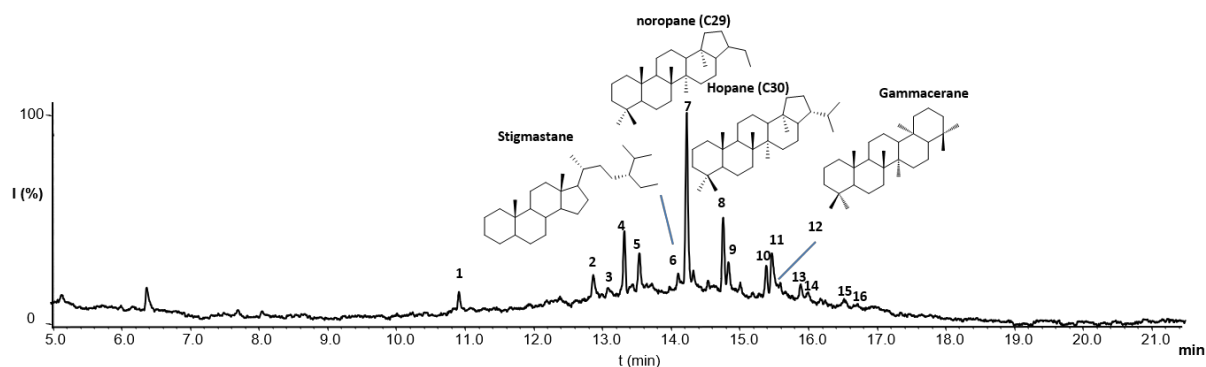
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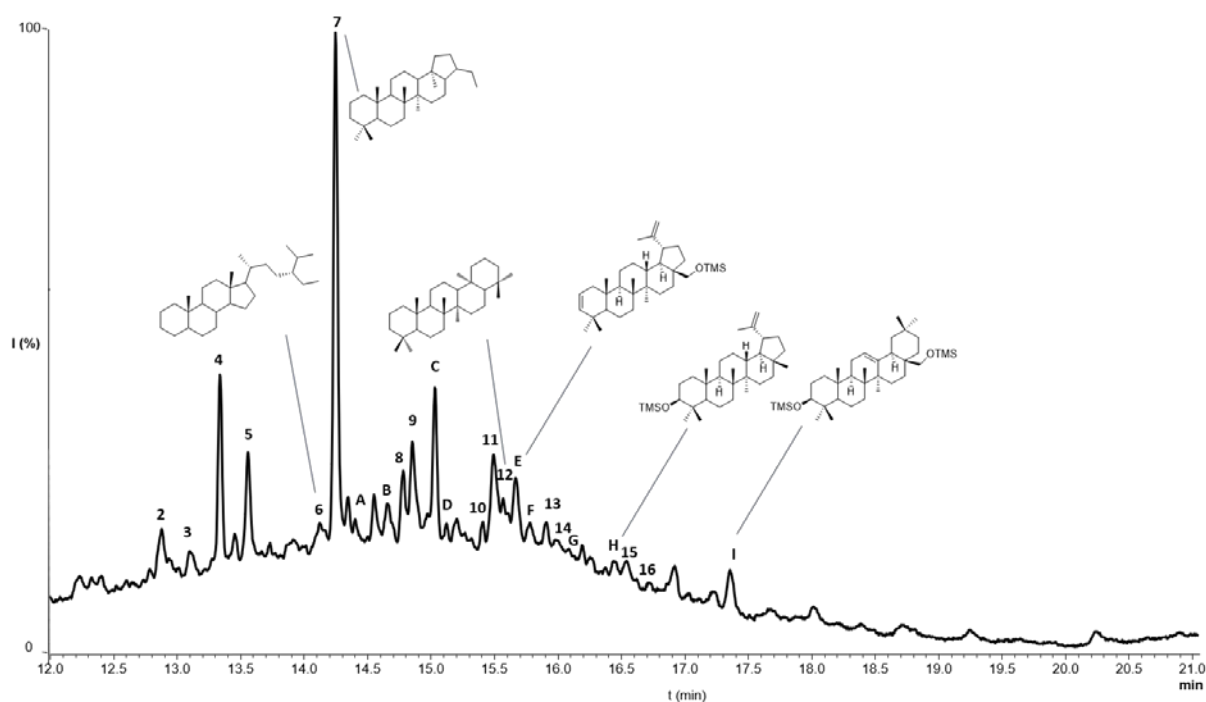
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## Supplement information figures

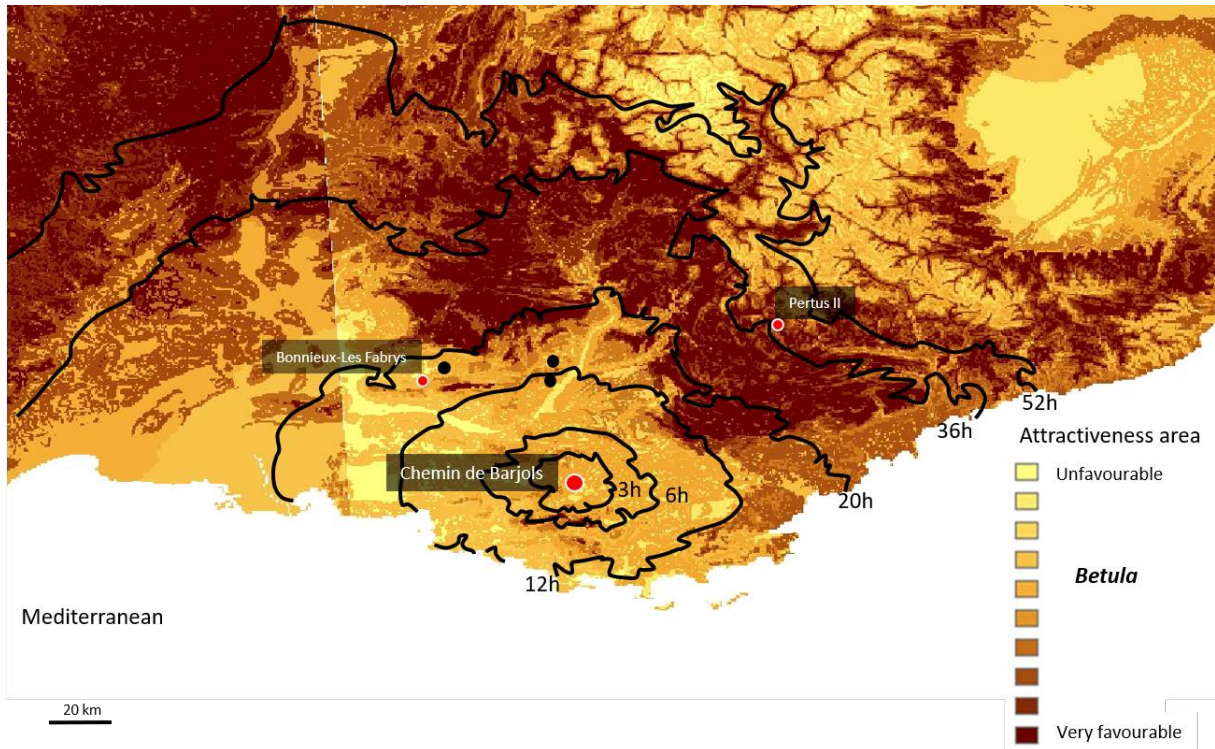


**Fig. S1:** Chromatogram of bitumen used to repair ceramic vessels in the sites of Grotta dei Piccioni (MR4104). 1= C24 Tetracyclic terpane; 2= 8,14-secohopane; 3= 18 $\alpha$ (H), 22,29,30- trisnorneohopane (Ts); 4= 17 $\alpha$ (H), 22,29,30-trisnorhopane (Tm); 5= 17 $\alpha$ (H), 22,29,30-bisnorhopane; 6= Stigmastane; 7= 17 $\alpha$ (H),21 $\beta$ (H)-norhopane; 8= 17 $\alpha$ (H),21 $\beta$ (H)-hopane; 9= 17  $\beta$  (H),21 $\alpha$ (H)-Hopane; 10= 22S-30-Homohopane; 11= 22R-30-Homohopane; 12= Gammacerane; 13= 22S-30,31-Bishomohopane; 14= 22R-30,31-Bishomohopane; 15=22S-30,31,32-Trishomohopane; 16= 22R-30,31,32-Trishomohopane.



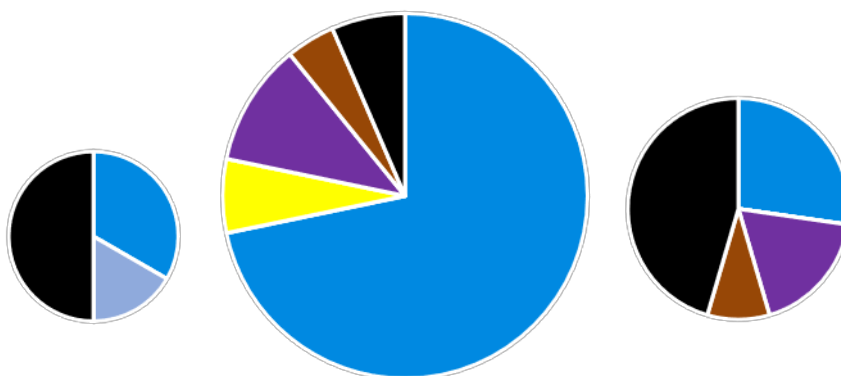
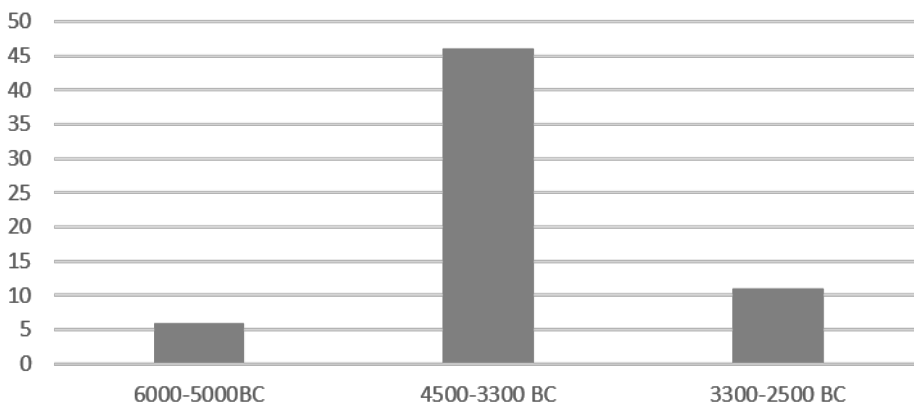
**Fig. S2:** Chromatogram of bitumen and birch bark tar used to repair ceramic vessels in the sites of Colle Santo Stefano, (MR4101). 2= 8,14-secohopane ; 3= 18 $\alpha$ (H), 22,29,30- trisnorneohopane (Ts) ; 4= 17 $\alpha$ (H), 22,29,30-trisnorhopane (Tm) ; 5= 17 $\alpha$ (H), 22,29,30-bisnorhopane ; 6= Stigmastane ; 7= 17 $\alpha$ (H),21 $\beta$ (H)-norhopane ; 8= 17 $\alpha$ (H),21 $\beta$ (H)-hopane ; 9= 17  $\beta$  (H),21 $\alpha$ (H)-Hopane; 10= 22S-30-Homohopane ; 11= 22R-30-Homohopane; 12= Gammacerane ; 13= 22S-30,31-Bishomohopane ; 14= 22R-30,31-Bishomohopane; 15=22S-30,31,32-Trishomohopane; 16= 22R-30,31,32-Trishomohopane. A= lupa-2,20(29)-dien ; B, C, D = lupa-2,20(29)-dien derivatives ; E= lupa-2,20(29)-dien-28-ol ; F= lupa-2,20(29)-dien-28-oic acid ; G= lupenone ; H= lupenol; I= erythrodiol





**Fig. S3:** Cost-distance map from the site of Chemin de Barjols (Provence, Final Neolithic), including *Betula* attractiveness area and source bitumen sources (black point= Apt-Manosque-Forcalquier sources, from Debrand-Passard et al., 1984)

### Number of adhesive samples



**Fig. S4:** Adhesive materials identified in the present work in the North-Western Mediterranean region (6000–2500 BC). Black= bitumen, blue= birch bark tar, light blue= birch bark tar – bitumen, brown = Pinaceae resin, yellow= birch bark tar – beeswax, purple= Pinaceae - birch bark.

## Supplement information tables

**Table S1:** Uses and functions of plant tars, resin and bitumen in Europe (6000–2500 BC). Information is based solely on published works which involved GC-MS analyses. Black= bitumen, blue= birch bark tar, brown = Pinaceae resin, pink = cedar resin/oil yellow= beeswax, grey= animal glue (hide).

**Table S2:** List of the archaeological samples investigated. (1) This aggregate, directly dated by AMS, is considered as inherited from the Layer 6 (where a few Cardial sherds were found) which was cut by pit 6B.

### Table S2 References

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**Table S3:** Complete results of the Neolithic samples studied in the North-Western Mediterranean.

**Table S4:** Summary of results obtained for samples from the sites in the Western Mediterranean area (6000–2500 BC). Black= bitumen, blue= birch bark tar, brown = Pinaceae resin, yellow= beeswax.