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## Birch-bark tar at Neolithic Makriyalos, Greece

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*The authors discuss the first evidence for the use of birch-bark tar on Late Neolithic pottery from Greece. This appears to have been used for two different purposes, to seal a fracture and to line the interior walls. The authors also discuss other possible uses.*

*Key-words:* Makriyalos, Greece, Late Neolithic, birch-bark tar, gas chromatography-mass spectrometry

### Introduction

The potential for organic analysis of Neolithic pottery from Greece is largely unexplored. The results of a pilot study conducted on vessels from the Late Neolithic settlement at Makriyalos, northern Greece are reported in part here. Gas chromatography-mass spectrometry (GC-MS) is used to study the lipid composition of 19 vessels representing the range of main vessel types. The lipids from visible residue and ceramic extracts of three of these vessels show the presence of molecular markers consistent with birch-bark tar. These results are the first evidence in Greece both for its use and for the use of natural products to affect the performance characteristics of pottery vessels.

### The site

The site at Makriyalos is situated in the coastal

area of Pieria, Northern Greece (FIGURE 1), less than 2 km from the sea. Fifteen km to the west lie the Pieria Mountains with Mt Olympus, the highest mountain in Greece, on the southern side. The settlement is located on the gentle slopes of a natural low hill. Two ravines pass near the site to the northeast and southwest. The prehistoric settlement covers about 50 ha and is one of the largest non-tell sites in prehistoric Macedonia. Two main phases of occupation, Makriyalos I and II, both dated to the Late Neolithic period, are clearly distinguished (Pappa & Besios 1999).

### Samples

All 19 vessels analysed for organic residues come from Makriyalos I which is dated to the beginning of the Late Neolithic period (c. 5400–4900 BC; Pappa & Besios 1999). Samples of three of

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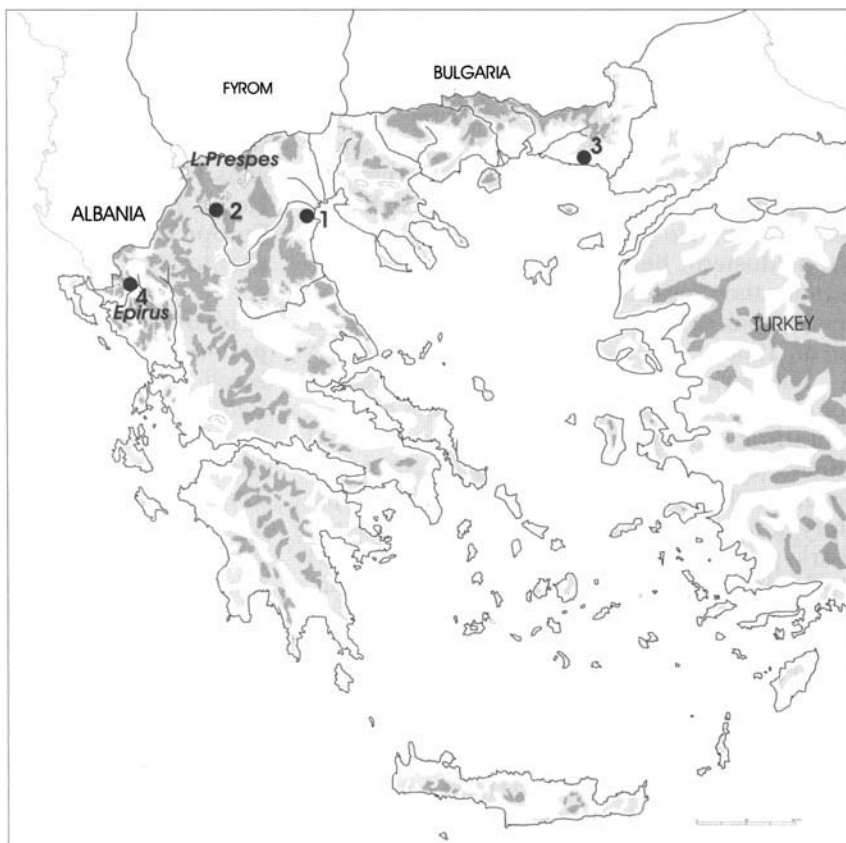


FIGURE 1. Map showing location of Makriyalos and the sites mentioned in the text.

1. Makriyalos    2. Dispilio    3. Makri    4. Boila

these vessels are discussed here. A black-topped carinated vessel has a visible black residue on the interior surface in the form of a narrow strip along a fracture. It is likely that the vessel was broken and subsequently repaired in antiquity at the point where two coils joined. A small sample (6.2 mg) of the residue was removed with a scalpel and dissolved in dichloromethane.

Two sherds from bases of 4-handled jugs have traces of black residues deposited on the bottom and lower part of the inner vessel walls. Two grams of the powdered potsherd with trace residue were taken from the interior and exterior surface of the sherds up to a depth of 2 mm using a Dremel drill fitted with an abrasive bit. The resulting sherd powders were then extracted with 10 ml of chloroform:methanol 2:1 (v/v) with ultrasonication for 5 minutes. After centrifugation, the solvent was transferred to a clean vial. A portion of each extract was decanted and evaporated under a stream of

nitrogen. These were then derivatized with a few drops of BSTFA, with 1% TMCS. Combined gas chromatography-mass spectrometry (GC-MS) was carried out. The splitless injector and interface were maintained at 300°C and 340°C respectively. The temperature of the oven was programmed from 50°C (2 minutes) to 340°C (12 minutes) at 10°C/min. The GC was fitted with a CP-SIL 5 CB low bleed/MS (*Chrompack*) coated (0.1 µm) fused silica column (15 m x 0.25 mm I.D.). The column was directly inserted into the ion source where electron ionization (EI) spectra were obtained at 70 eV with full scan from  $m/z$  50 to 700.

**The molecular identification of birch-bark tar**  
Partial reconstructed ion chromatograms of the visible residue and the sherd extracts are shown in FIGURE 2. The identified components are shown in TABLE 1, with references to an extensive body of published mass spectra. The GC

elution orders were the same as reported in these published works. The presence of components 3 (*lupa-2,20(29)-diene-28-ol*), 5 (*lupenone*), 6 (*lupeol*) and 9 (*betulin*) identify all three residues as birch-bark tar. Components 1 ( $C_{30}H_{48}$ ) and 2 ( $C_{30}H_{46}$ ) are degradation products of triterpenoids resulting from the heating of birch bark (Regert *et al.* 1998). No peaks such as  $\alpha$ - or  $\beta$ -amyrin, or  $\beta$ -sitosterol have been identified. This excludes the presence of other plant tars such as beech, oak or alder (Hayek *et al.* 1990; Regert *et al.* 1998).

The bark of *Betula* spp. contains a variety of triterpenoid compounds including betulin, betulinic aldehyde, betulone, lupenone and lupeol (Ekman 1983; O'Connell *et al.* 1988; Cole *et al.* 1991). Although not identified in prehistory, a process of destructive heating of birch bark, probably in a sealed container, is thought to be involved in the production of the tar. Archaeological birch-bark tars have been identified using these biomarkers by a variety of workers (Hayek *et al.* 1990; Binder *et al.* 1990; Regert 1997; Regert *et al.* 1998; Aveling & Heron 1998; 1999; Charters *et al.* 1993; Reunanen *et al.* 1993). The mixing of birch bark tar with animal fat (Regert *et al.* 1998; Dudd & Evershed 1999) and other plant tars (Hayek *et al.* 1990; Regert *et al.* 1998) has also been reported.

Birch-bark tar has been reported from the Middle Palaeolithic onwards in Europe (Grünberg *et al.* 1999). Most of the finds re-

ported to date are from northern Europe, although finds from Italy and Slovenia have also been confirmed. The uses are wide-ranging, including hafting, waterproofing, caulking and repairing. Birch-bark tar was also chewed; reasons for this have been explored (Aveling & Heron 1999). A review of finds in prehistoric Europe is included in Pollard & Heron (1996: chapter 7).

### Evidence of modern and ancient birch from pollen and charcoal analysis

Birch is represented in Greece by the species *Betula pendula* Roth. Today, its geographical distribution is restricted to mountainous areas near and along the northern borders of Greece. The only low-altitude region, where a few birch trees are found, is around Lake Prespes in North-western Greece (Gerasimidis 1996). Birch contributes very little to the forest vegetation, except in one range in the Rhodopes where it forms woodland. The competitiveness of birch and therefore its potential for a wider distribution in the country is minimized by geographical position, climatic conditions and the relatively high proportion of calcareous soils in Greece (Gerasimidis 1996; Gerassimidis & Athanasiadis 1995).

Information about past and present vegetation in Greece comes from 35 pollen diagrams derived from cores taken at 32 locations in various parts of the country, particularly from ar-

peak no.	identity	mass spectra comparable to published data
1	$C_{30}H_{48}$ (dehydration product of lupeol)	Regert <i>et al.</i> 1998; Binder <i>et al.</i> 1990; Aveling & Heron 1998
2	$C_{30}H_{46}$ (dehydration product of betulin)	Regert <i>et al.</i> 1998
3	<i>lupa-2,20(29)-diene-28-ol</i> (TMS)	Regert 1997; Aveling & Heron 1998
4	allobetul-2-ene	Binder <i>et al.</i> 1990; Charters <i>et al.</i> 1993; Regert 1997
5	lupenone	Budzikiewicz <i>et al.</i> 1963; Charters <i>et al.</i> 1993; Regert 1997; Aveling & Heron 1998
6	lupeol (TMS)	Charters <i>et al.</i> 1993; Regert 1997; Aveling & Heron 1998; §
7	betulone (TMS)	Aveling & Heron 1998
8	betulinic aldehyde (TMS)	Regert 1997; Aveling & Heron 1998
9	betulin ( <i>bis</i> -TMS)	Charters <i>et al.</i> 1993; Regert 1997; Aveling & Heron 1998
10	allobetulinol (TMS)	Aveling & Heron 1998
*	unknown contamination	

§ = comparison to authentic standard

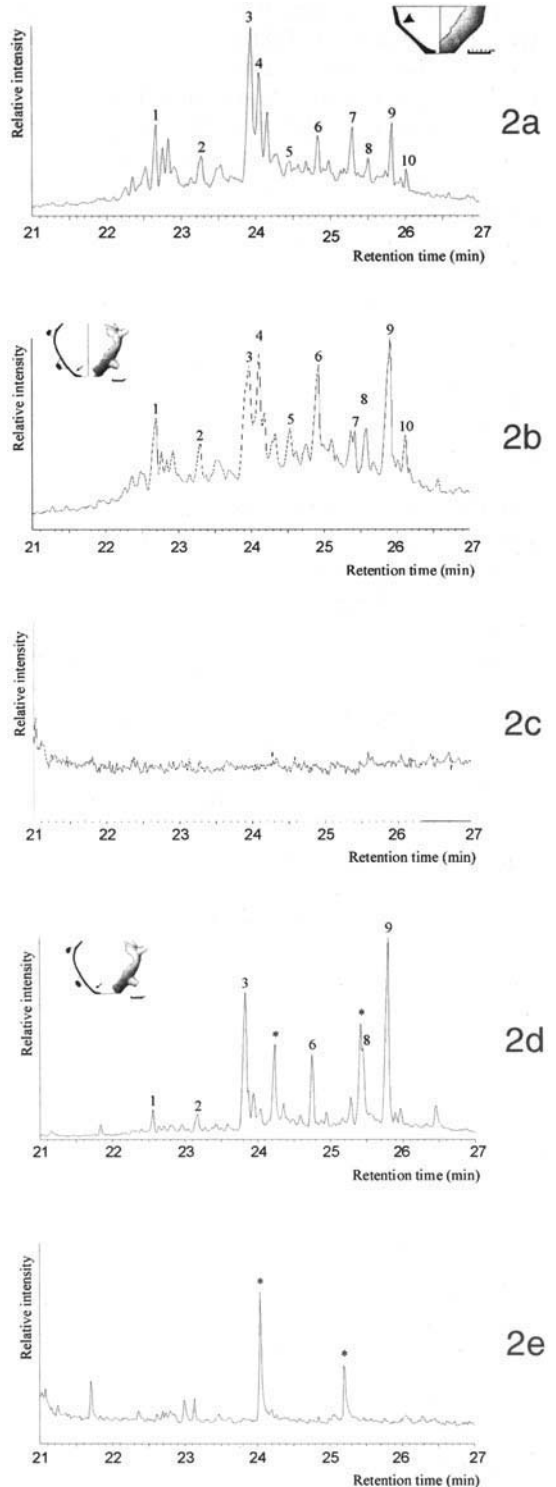
TABLE 1. Peak numbers, identified extracted components and references to comparable published mass spectra.

eas of low and intermediate altitude (up to 1000 m) with a few from higher altitude (e.g. Rezina pollen diagram in Epirus from 1800 m). In most cases they provide information only for the last few millennia. Thus, evidence for the more distant past is fairly limited. Judging from the pollen diagrams, the geographical distribution of birch in prehistory was quite broad. However, the contribution of the species to forest vegetation was never significant. Indeed, in many pollen diagrams birch does not appear at all or its appearance is very limited (Gerasimidis 1995; Gerasimidis & Athanasiadis 1995; Gerasimidis 2000; Ntinou & Kotjabopoulou *in press*). On the basis of a few pollen diagrams, which contain levels belonging to the Pleistocene, birch was a constant, although not significant, forest element in Northern and Central Greece including Thessaly.

Information about birch in the early Holocene (8500–6500 BC) comes from a few diagrams including those in Central Macedonia and Epirus. It seems that the presence of birch in these two regions at that time was not stable and constant. In the middle Holocene (6500–2000 BC), birch is a stable although not significant element in many areas of Central and Northern Greece. In the late Holocene (2000 BC until recent times), there is variability and interruptions in the appearance of birch in Central and Northern Greece. Gradually it disappears from many areas (e.g. Thessaly). The elimination of birch from some areas of Greece has been attributed partially to the effects of human activities on forest vegetation (Gerasimidis 1996; Ntinou & Kotjabopoulou *in press*).

In the region of Makriyalos, two pollen diagrams from the Pieria Mountains give information about the vegetation, although only for the last 3000 years. They show birch was a constant component of the forest vegetation in the past, but that it disappeared, perhaps due to intensive human activities in the region (Gerasimidis 1995, 1996; Gerasimidis & Athanasiadis 1995).

FIGURE 2. *Partial reconstructed ion chromatograms: a Internal wall of the black topped carinated bowl; b internal wall of medium sized 4-handled jug; c external wall of medium sized 4-handled jug; d internal wall of small sized 4-handled jug; e external wall of small sized 4-handled jug.*



There are two sites in Northern Greece contemporaneous with Makriyalos where charcoal analyses have been undertaken: Dispilio in northeast Greece and Makri in Thrace (northeast Greece), both dated to the Late Neolithic (second half of the 6th millennium). They do not provide any evidence of birch (Ntinou & Badal 2000). However, there is considerable evidence of birch from the Late Glacial rock-shelter site of Boila in the Pindus mountain range, Epirus (dated approximately 15,000 BP to early Holocene). Here, much of the stratigraphical sequence is dominated by birch. The picture changed after 10,000 BP when birch for the first time is clearly underrepresented (Ntinou & Kotjabopoulou in press).

### Archaeological considerations

This study provides the first evidence for the use of birch-bark tar in Greece. To date, it has been identified in three of the 19 pots examined. Birch-bark tar was used for at least two different purposes. In the case of the black-topped carinated vessel, it was used to seal a fracture in the vessel. The results represent the first firm evidence for the use of birch-bark tar as an adhesive in the prehistory of Greece. The use of adhesive, most probably of resinous or tarry origin, for repairing broken Neolithic vessels has already been recorded in the past (Sampson 1987: 83), but no analysis has been conducted of its composition.

In the case of the two 4-handled jugs, birch-bark tar was found only as a visible residue coating the interior surface. The exterior surface yielded no such biomarkers (FIGURE 2). It may have been used to seal the interior walls of the vessels, by reducing the permeability of the jugs. The two jugs are small (c. 2 litres) to

medium (c. 5 litres) in terms of capacity. It should also be noted that both have low porosity, as indicated by the visual estimation of ceramic thin sections. This raises a question as to whether waterproofing of these jugs was the sole reason for the application of birch-bark tar.

Water storage needs may have been served by lining permeable ceramic containers. Conversely, there is abundant ethnographic evidence in hotter climates for storing water in permeable containers, as water percolates through the fabric and evaporates from the exterior surface of the vessel, taking heat with it and keeping the water in the container cool (Rice 1987: 231).

Although it is difficult to speculate about the kinds of liquids stored in vessels coated with birch-bark tar, it should be noted that this substance has additional properties beyond waterproofing. Birch bark itself is highly resistant to fungal attack (Aveling & Heron 1999; Heron *et al.* 1991) and the disinfectant properties of the tar have been used to facilitate the storage of fermented beverages (Rajewski 1970).

Although there is no direct evidence for the presence of birch in the wider area of Makriyalos during the period of its occupation, it is quite possible that birch existed in the area in the 6th millennium BC. There is no reason to suggest that the bark or the tar itself was imported from elsewhere.

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## Archaeology and ‘QAA subject review’: what did we learn?

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*The authors recount their personal experience of the recent assessment of archaeology teaching in the United Kingdom.*

*Key-words:* teaching, assessment, QAA, United Kingdom

In the middle of March 2002, with the last review of a Department of Archaeology in England, the process of assessing the quality of academic courses by Subject Specialist Reviewers (SSRs) appointed by the Quality Assurance Agency (QAA) came to a temporary halt. The programme of reviews has been in existence since 1991 and, as it happens, archaeology was one of the last subjects to be reviewed — though it was assessed in Welsh universities as long ago as 1995–96, and in Scotland the process is continuing, with archaeology yet to be done.

The editors of *ANTIQUITY* have already drawn attention to the process in an editorial (Malone 2000: 741).

The process in England and Northern Ireland started in September 2000 with Cambridge and concluded in March 2002 with Southampton. All archaeology staff in English universities and in Queen’s University Belfast have been living with the ‘subject review’, formerly ‘teaching quality assessment’ or TQA, for the last 18 months, as have those in other subject areas since 1991. In this article, we want to cast an

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