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Looking for ancient wine as gift for the Principe of Lavau (5th c. BC)

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Abstract – **The excavations in Lavau brought in light a large monumental necropolis with a burial mound in its center overlying the inviolate chieftain's grave from the end of the 1st Iron Age or beginning of the 2nd one. In the funerary chamber a rich furniture accompanies the dead: a bronze cauldron containing serving and drinking vessels in ceramic, silver, and bronze, two bronze plates, and a cist. As the inner surface of the cauldron presents visible deposits, a series of samples was taken off from different parts of the cauldron and the local oenochoe. Using a double-step methodology of extraction and structural analysis by GC-MS, main biomarkers have been identified. The high sensitive and selective method and its efficiency for dissolving particularly insoluble markers from fruits, all owed the identification of coniferous pitch and fermented dark grape juice (red juice). For the first time, the interdisciplinary research of archaeologists and chemists highlight the content of rich vessel used for the funerary banquet.**

I. INTRODUCTION

In 2014-2015, the rich tomb of the *Prince of Lavau* has been discovered during an excavation conducted by Bastien Dubuis, INRAP [1]. The monumental necropolis occupied from the end of the Bronze Age to the Galloroman period, has revealed monumental elevation protected by a thick layer of dark earth from Middle-Age. The central burial mound was hiding a rich chieftain's grave from the 5th c. BC. The exceptional discovery establishes one of the paroxystic demonstrations of the "princely phenomenon", following the example of the grave of Vix situated in some 60 km upstream on the Seine. Inside the tomb, the death Prince was lying in a car accompanied by deposited vessel in an angle, consisting on a dozen of pieces, mainly imported. A large cauldron in bronze was found over a cist and contained pieces used for serving or drinking: An Attic black-figure oenochoe, a golden silver sieve, a silver drilled spoon, the foot of a golden silver cup, a bronze olpé, rests of a composite object in animal matter and iron (maybe a drinking horn). These vessels have been probably let on a woody shelf and fell into the cauldron following the decomposition of the perishable support. Beside the cauldron two bronze plates have been placed on the floor of the grave with a regional fluted bottle in ceramic with a bronze lid. The morphology of the platform where the funerary ceremony took place involves the assembly was sitting on the west part of the tomb partially carved in the chalk hill, between the monumental gate and the grave. Thus, the cortege had a look on the death and the deposited vessel, traducing a staged ceremony.

In this article, we focused our research on the cauldron and the regional ceramic. The cauldron, with a unique and huge dimension (c. 1 m of diameter, 80 cm of opening mouth, and more than 60 cm high), presents an exceptional decoration of four ties presenting the Greek River-God Achelous (Figure 1). Its capacity was around 200 – 350 L, one the most important capacities after the cauldron of Hochdorf [2]. As a foot, the cauldron was placed on a bronze cista or placed on a perishable support overlying the cista, covered by a plate in vegetal fibres. Among the ceramics deposited in the cauldron, a regional jug was discovered in horizontal position, only its foot was taken its original vertical position. The ceramic, typical from the elitists at the end of the 6th and 5th c., is the first entire artefact discovered of this type.

One of the more frequent and unresolved question deals with the deposit of offerings for the death, specially beverages. Unfortunately, in the past, when the crater of Vix has been excavated in 1953 relationships between archaeology and analytic sciences did not exist and the knowledge in chemistry did not allow the characterization of ancient residues. Subsequently, the bronze case has been restored and protected by synthetic varnishes, banning any future organic analysis. As the crater if Lavau has been discovered and before any intervention or excavation, the archaeologist team asked if any analysis if the content would be possible and able to determine the content. Under the ANR programme MAGI (Eating, Drinking, and Offering of the Eternity in pre-Roman Gaul and Italy) directed by Dominique Frère, a series of samples has been taken off from the inner sides of the vase, still remained. Indeed, a thin and continuous yellow-brownish deposit was observed on the total area of the inner side of the crater. This deposit was 1 to 10-mm thick, thicker on the base of the container, and ended clearly under the rim of the vase, practically as far as the edge of the opening.

Analysing such samples represents a particular challenge because the greatest part of the organic matter preserved on the walls of the container consist on pitch. Until now, many chemists have been blocked because no known protocol allow the detection of markers present as traces and mixed with diterpenic markers of pitch or resin. In order to detect traces of wine, we develop a new methodology including the extraction of soluble lipidic markers (fatty acids, terpenic acids and hydrocarbons) and the extraction of insoluble materials, among which acids of grape and fermentation.

II. MATERIALS AND METHODS

A. Archaeological samples

Seven samples of the deposit visible on the inner (#7, #8, #9, #13, #15) and outer walls (#12, #16) of the crater have been taken off, at different altitudes, from the bottom to the rim, and conditioned in an aluminium foil in order to prevent for any supplementary modern contamination. Four samples (#17 - #20) come from the local ceramic

B. Method

Samples have been crushed and treated according a double-step methodology of extraction and analysis by gas chromatography coupled to mass spectrometry (GC-MS). The first extraction is conducted in the presence of organic solvents (dichloromethane / methanol 1:1 v/v) under ultrasonication for 20 min. The mixture is centrifugated (2 000 rpm, 20 min) and the upper organic layer is collected [3]. The extraction is repeated 2 or 3 times, until the disappearance of the brown colour of pitch. The organic layers are mixed together and consist on the "first lipid extract" (noted 1LE). The solid residue is then extracted by a mixture of boron trifluoride : *n*-butanol : cyclohexane (1:2:4 v/v/v) for 12h at 80°C. The mixture is then neutralized and extracted by dichloromethane. The organic layers are washed with water, dried, filtered on a silica cartridge, and then evaporated to dryness under a flow of nitrogen consisting on the second lipid extract noted 2LE [4]. The first and second extracts are submitted to silylation with a mixture of pyridine and *N,O*-bis(trimethylsilyl)trifluoroacetamide (1:10 v/v) at 80°C for 20 min. The mixture is evaporated to dryness. An aliquot of a solution of internal standard (100 µL of *n*-triacontane *n*-C30) was added and the residue is dissolved in dichloromethane (100 to 1000 µL).

An aliquot (1 µL) is injected splitless at 280°C onto a 20 m × 0.18 mm internal diameter × 0.1 µm film thickness Phenomenex Zebron-5MSi of a Thermo GC Trace coupled with a DSQ II mass spectrometer. The oven temperature is held at 50°C for 8 min, then programmed to increase at 10 °C/min to 350°C and then hold for 7 min, for a total run time of 45 min. The transfer line to the mass spectrometer is maintained at 300°C, and the source of the spectrometer heated at 200°C. The range 50-800 amu is scanned at 7500 amu/s. The compounds are identified according to their mass spectrum recorded in electronic impact mode (70 eV) by comparison with the NIST and Wiley libraries and by studying the fragmentation mechanisms for transesterified compounds.

III. RESULTS

All the samples from the crater reveal a common first lipid extract with a chromatographic profile characterized by major diterpenic acids present as free and methylated acids. This association is characteristic of pitch obtained by pyrogenation of resinous wood. Polyaromatic hydrocarbons, mainly reten and 4-methyl reten, confirm the pitch. The resinous material is identified in great amounts in all samples except #12 and #16, that come from the outer side of the cauldron (the first one corresponds to a wood fragment deposited on the rim of the cauldron, the second one a wood fragment preserved under the foot of the vase). Fatty acids and sterols indicate the presence of fatty material coming for non-ruminant animal and from vegetal oil. In the case of #8, a yellowish bloc preserved at the bottom of the crater, the association of palmitic, stearic, oleic acids associated with long chain even fatty acids and 15-hydroxy palmitic acid, odd *n*-alkanes dominated by the C_{27}, even *n*-alkanols (24-ol to 32-ol), indicate beeswax.

The second extraction protocol reveals very interesting results. Although the major part of the resinous markers is extracted during the first extraction process, insoluble molecules remain protected and preserved even if the first extraction process is repeated 3 to 5 times, as the analysis by GC-MS of each successive extract confirms their absence. The acido-catalyzed extraction allows the dissolution of the particularly insoluble calcium tartarate. Indeed, the acid of Lewis boron trifluoride acts for displacing the equilibrium of solubility towards the solubilisation of the acid under the esterified form. Cyclohexane helps for the continuous extraction of the butylated acids and then the progressive conversion of tartare salts into extractible butylated esters. In the case of resinous markers still abundant, the second lipid extract is purified by flash chromatography. The elution on an aminopropyl cartridge of the 2LE allows to separate neutral and acidic compounds. The analysis of the neutral fraction clearly highlights the presence of tartaric, malic, and citric acids, interpreted as grape markers. The syringic acids is released by malvidine and its derivatives (glycosylated or esterified forms), an anthocyanin specific of dark and teinturier grape. Shorter aldaric acids such as succinic, maleic, fumaric, and pyruvic acids come from the alcoholic fermentation. The association of grape markers, dark colour markers, and fermentation markers represents the minimum combination for the correct identification of red wine. More often, fermentation markers are not detected, either they never have been present in the vase, or they have disappeared since the deposition in the tomb.

The analysis clearly highlights the presence of a grape derivative in the crater in all samples taken off on the inner wall of the container, from the bottom to the rim. The sample #16 allows to control that no tartaric acid is present outside the vase. However, traces of grape are identified on the rim (#12). The presence of tartaric, malic, syringic, succinic acids allows to conclude of the presence of red wine. As the series of samples, representative of all the height of the crater, shows the continuous presence of tartaric acid, the more insoluble and more representative biomarker of grape, we can conclude that the crater was deposited full of red wine in the tomb. The observed upper limit of deposit and corrosion correspond to limit of the beverage when it was let for the defunct.

The sample #8, corresponding to a yellow block found at the bottom of the container, shows the interesting presence of beeswax. As the material was preserved as a block, it would have been added in the wine either as a block of beeswax, or as honeycomb. In the first case, only the flavouring molecules of beeswax (mainly aldehydes, [5]) dissolved in the alcoholic beverage. In the case of honeycomb, all the saccharidic constituents of honey have dissolved in the wine giving a honeyed wine such as the *mulsum* from Roman times. As honey seems to be a better candidate than beeswax for obtaining a flavoring wine, the preservation of the block of wax at the bottom of the crater could evidence the preparation of a honeyed red wine in the tomb.

The local jug in ceramic shows the global presence of tartaric acid (#17 - #20). Two samples (17 and #20) allow to precise the red color of grape. As the crater besides, the presence of grape biomarkers at the bottom of the vase and at the upper limit of the liquid allows to conclude the jug has been placed in the tomb, full of red wine.

IV. RED WINE AS OFFERING FOR THE DEATH PRINCE OF LAVAU

Punctually documented by the discovery of shards of vinary amphorae (as in the Mount Lassois in Vix for example), the consumption of wine by the Celtic elites of the 5th century is highlighted for the first time, in association with a deposit of imported ceramic, in a leading grave. The origin of this drink must be looked for in Marseille, otherwise farther in the Mediterranean Sea, in the Italic territory for example. The presence of a sieve in the deposit is most probably understandable by the necessity of filtering the wine. This filtering can turn out to be necessary by the presence of the pitch. The entire cauldron was entirely coated by pitch. As the metal is not porous, the resinous internal coat can only be explained by the total filling of the container; if not, the inner walls of the cauldron would not have been cleaned? The presence of the upper limit of the liquid, the preservation of grape biomarker on all the height of the walls, support the hypothesis the cauldron was placed in the tomb and then completely filled with wine. Although chemistry does not allow the direct identification of honey because of its high solubility in water and its loss since the deposition, the combination of the presence of the sieve at the bottom of the cauldron and the chemical identification of beeswax, probably coming from honeycomb used for flavouring and sweeten the wine, would testify, for the first time, of the consumption of wine flavoured by the addition of various spices or additives, almost honeycomb for honey, that will be named *mulsum* later.

It is a mattering point to discuss forms of the banquet and the degree of imitation operated by the local Celtic aristocracy, towards this Mediterranean practice.

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Fig. 1. General view of the deposit.

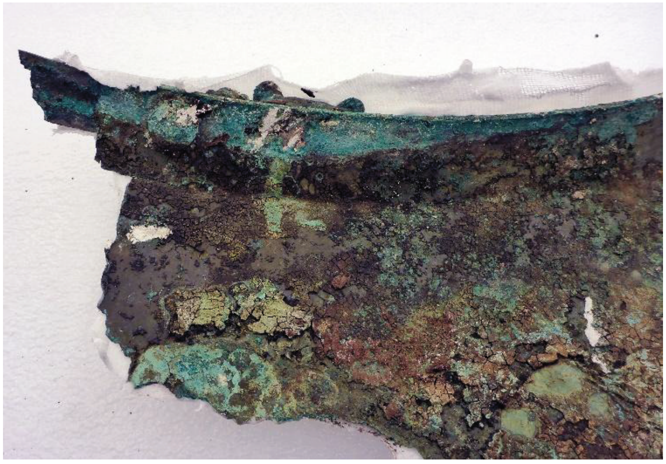

Fig. 2. Upper limit of the deposit and pitch residues preserved on the inner wall of the crater.

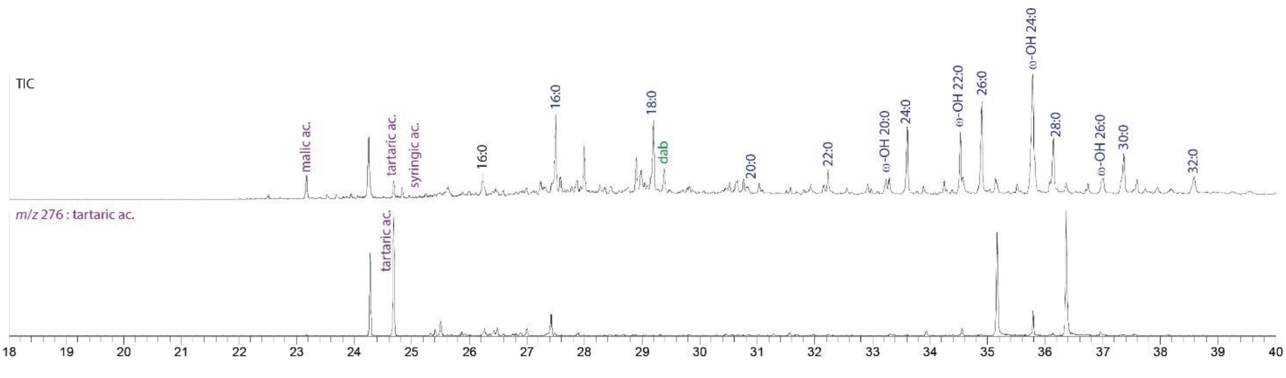

Fig. 3. Chromatogram of the second lipid extract (2LE) obtained from the residues preserved at the bottom of the jug (#17). Markers of dark grape are clearly visible.

Sample	Object	Description	Identified materials
#7	crater	Inner side, yellowish deposit	Pitch, grape
#8	crater	Inner side, yellow block found at the bottom of the vase	(non-ruminant) animal fat, vegetal oil, pitch, beeswax
#9	crater	Inner side, browinsh deposit on the upper wall	Pitch, grape (traces)
#12	Crater iso 100	Outer side, fragment of wood found on the rim	Wood of deciduous tree (triterpenoids), heated vegetal oil, fermented grape juice
#13	crater	Inner side, fragment of wood in contact with the bottom of the crater	Heated vegetal oil, pitch, wood from deciduous tree (triterpenoids), fermented dark grape juice
#15	crater	Inner side, yellowish matter at the bottom of the crater	Pitch, grape
#17	Jug iso 147	Inner side, organic deposit at the bottom	deciduous tree (triterpenoids), dark grape
#18	jug	Inner side, organic deposit at the distal part of the body	Pitch, grape
#19	jug	Inner side, linear limit of the deposit observed on the rim	Pitch, grape
#20	jug	Inner side, linear limit of the deposit observed on the rim	Pitch, dark grape, woody material (suberin)

Table 1. Results of the analysis of the content of the crater and the local jug.