

Wine before Greeks: the contribution of the organic chemistry analysis

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Abstract – In this occasion we'd like to point out the value of the results obtained by chemical analysis combined to bioarchaeological and traditional archaeological methods in order to determine the organic content of vessels and their implication in funerary ritual. Furthermore, through identification and contextualization of food and drink remains trapped in funerary sets belonging to four tombs of the indigenous necropolis of Cuma (Napoli) dated to the Iron Age, the research has led to the recognition of functional categories of proto-historical pottery.

I. INTRODUCTION

In the 2006 thanks to the archaeological campaign conducted by the team of the Centre Jean Bérard of Naples, the most ancient *strata* of the first Greek settlement in South Italy, Cuma, have been investigated leading to the discovery of a pre-Hellenic necropolis which gave back twenty-six burials (among which one *enchytrismos*) and a cremation. The discovery of such necropolis belonging to the natives living in Cuma before Greeks arrival has increased evidences about this population that hasn't returned written sources, known only by unearthed material culture [1-2]. An opportunity to go into funerary ritual of the Cuma's inhabitants, through the characterization of organic substances involved together with specific ceramics forms, has been provided by the research project named MAGI "Eating, drinking and offering for eternity in Gaul and pre-Roman Italy". Directed by Dominique Frère in collaboration with the Centre Jean Bérard of Naples (USR 3133 CNRS - EFR), the École Française de Rome, the AOROC (Archéologie d'Orient et d'Occident et text anciens - UMR 8546), the UMR 5140 (Archéologie des sociétés méditerranéennes) and the chemist Nicolas Garnier (Laboratoire Nicolas Garnier). Funded by the Agence Nationale de la Recherche (ANR) this program focused on the identification and contextualization of remains of food and drinks trapped in the porous walls of pottery

belonging to different archaeological excavations and museum collections by adopting chemistry analysis to cross with archaeobotanical and traditional methods (of which the anthropological one was entrusted to Henri Duday, Laboratoire d'Anthropologie des Populations du Passé UMR 5199 - PACEA, CNRS Univ. Bordeaux 1). In the case of Cuma a sample of four tombs and their corresponding sets have been chosen for the contents analysis.

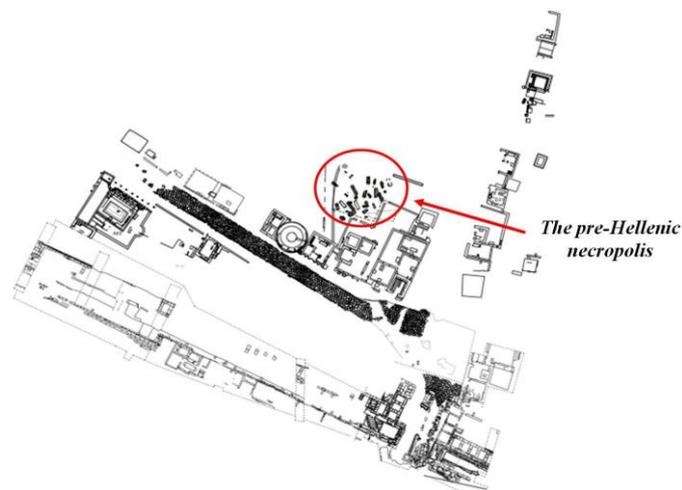


Fig. 1. Plant of the necropolis (drawings Centre Jean Bérard USR 3133 CNRS - EFR).

II. ANALYSIS OF ARCHAEOLOGICAL CONTEXTS

The pre-Hellenic necropolis located on the southern side of the lake of Licola (this one no longer existing) and the Monte Grillo, a hill that closes the necropolis to the east, consists of twenty six tombs related to both sexes and to all age groups, in specific immature, infants, children, young adults, generic adults, adults, mature adults, elderly people. Those tombs are representative of a widespread way to inhumate topologically named "a

fossa" which approaches Campania's populations to the contemporary people of Abruzzi, Southern Latium and Northern Calabria from the end of Tenth to the half of Eighth century BC. Individuals are buried in wooden coffins let down in rectangular shaped pits excavated directly in the silt, covered with heap of tuff stones and found at -5 m from current level of trampling. Almost all burials are enriched by ornaments and ceramic sets involved in dismissal ceremony. Furthermore, in some cases the distinction between genres is guaranteed by the presence of weapons for males and fusaroles for woman ones. The vessel have been found between the upper and the lower quarters of burials [1-2]. Funerary sets chosen for the content analysis belong to three male tombs namely SP700678, SP700743, SP700653 and one female, SP700633. Here follows a short description of each tombs and the interior dispositions of pottery:

A. Tomb SP700633

Primary burial oriented north-est/south-west discovered in the southern part of the survey. The tomb is characterized by five layers where the first one is the covering system made up of an heap of tuff, immediately below a layer of lapillus covered the skeleton and the associated set, while the last one corresponds to the cut of pit (2,47 m of lenght, 1,10 m of width). The body belonged to an adult female laying on the back with her head oriented south-west. The set consists in seven objects found between the upper and lower quarters of the tomb (Figure 2), specifically: a pyxis closed to the right side of the skull; a bronze *fibula* at the right side of the chest togheter with an amber pearl; sequentially next to the feet a shallow bowl; an upside down amphora with a cup within; and an *askos* for last [3].



Fig. 2. tomb SP700633 with set diposition (Photo Centre Jean Bérard USR 3133 CNRS - EFR).

B. Tomb SP700678

Primary burial oriented north-est/south-west found in the southeast part of the survey. The tomb is characterized by five layers, the first of which

corresponds to the covering system made up of an heap of tuff, immediately below a layer of lapillus covered the skeleton and the associated set, while the last one corrisponds to the cut of pit (2,37 m of lenght, 1,60 m of width). The body belonged to a generic male adult, laying on the back with his head oriented southward and facing east. The set consists in six objects found exclusively in the upper quarter of the tomb (Figure 3), specifically: an *askos*; an amphore to the South of the skull which contained a cup; two bowls and a bronze *fibula* [3] on the western part of the tomb.



Fig. 3. tomb SP700678 with set disposition (Photo Centre Jean Bérard USR 3133 CNRS - EFR).

C. Tomb SP700743

Primary burial with north-west/south-east orientation discovered in the eastern part of survey. The tomb is characterized by five layers of which the first is the covering system made up of an heap of tuff, immediately below a layer of lapillus covered the skeleton and the associated set, while the last one corrisponds to the cut of pit (2,36 m of lenght, 1,98 m of width). The body belonged to a young male adult (aged between 18/22 years) laying on backbone *decubitus* with his head oriented to the South. The set consists in six objects found exclusively in the upper quarter of the tomb (Figure 4), specifically: an *askos*; an amphore to the South of the skull which has contained a cup; to the west two bowls and a bronze *fibula* [3].

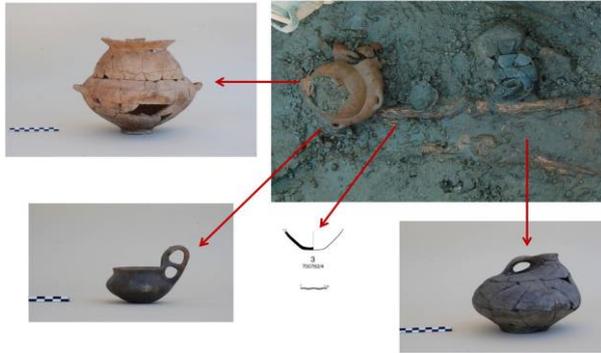


Fig. 4. tomb SP700743 with set disposition (Photo Centre Jean Bérard USR3133 CNRS - Efr)

D. Tomb SP700753

Primary burial oriented North/South found in the eastern part of the survey. The tomb is characterized by five layers of where the first one is the covering system made up of an heap of tuff, immediately below a layer of lapillus covered the skeleton and the associated set, while the last one corresponds to the cut of pit (2,36 m of length, 1,98 m of width). The body belonged to a generic male adult laying on the back with his head oriented southward, facing North. The set consists in five objects found between the upper and lower quarters of the tomb (Figure 5), specifically: a biconical jug close to the right side of the skull; a bronze fibula to the left side of the chest; sequentially next to the feet a shallow bowl containing an *askos*; and beside the right foot a bronze spear cusp [3].

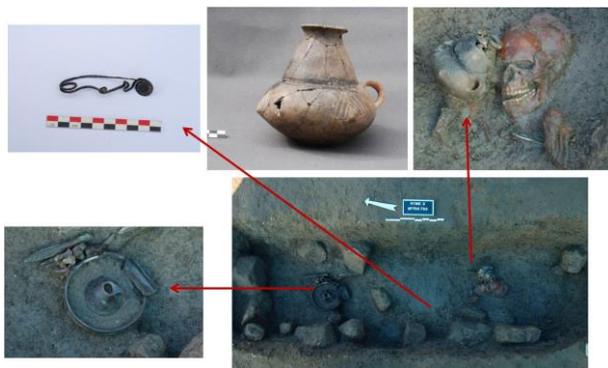


Fig. 5. tomb SP700753 with set disposition (Photo Centre Jean Bérard USR 3133 CNRS - EFR)

III. ARCHAEOBOTANICAL ANALYSIS

The sampling of intern sediment of the tombs along with those filling pottery was entirely sifted in order to collect seeds belonging to plants involved in the funerary ritual, and also to gain information about sustistence productive system and enviroment. The study of the

archaeobotanical remains is still at a preliminary stage. Among the available *data* there's the discovery of some grape pips belonging to *Vitis vinifera sp.* within some ceramics and internal sediments of the burials (certainly in tomb SP300146). Cereal consumption affects cultivated wheat species (*Triticum monococcum/dicocum*), millet (*Panicum miliaceum*), barley (*Hordeum vulgare*); even legumes are attested by the broad bean (*Vicia faba*).

IV. ORGANIC CHEMISTRY

The conference constitutes an opportunity to point out the value of the results obtained by chemical analysis which through the sampling methods and the two-step extraction methodology has allowed to identify molecular markers of the organic substances contained in archaeological pottery clarifying also their function and associations in funerary ritual.

An amount of seventeen vascular forms belonging to the sets of the tombs illustrated before has been submitted to the contents analysis, in specifics: four askoi, three amphorae, one biconical jug, a pyxis, three cups, three bowls and two basins (Table 1). In order to identify contents the inner sides of ceramics were sampled whit a drill or a scalpel. The outer side of ceramics wasn't sampled because vases were restored.

As the ceramics did not present any visible traces on their inner sides, the organic analysis carried out by Nicolas Garnier focused on the identification of chemical markers absorbed in the collected porous ceramic powder. The characterization of such organic materials, preserved as tiny traces, and consisting in degraded and often mixed materials, needs the implementation of an adopted protocol for the extraction of soluble and insoluble markers, their purification, and their analysis by separative methods, i.e. by gas chromatography-mass spectrometry (GC-MS). In this way, each preserved biomarker is clearly identified by its mass *spectrum*. Then the interpretation of chemical data consists on several successive steps:

- The identified biomarkers are classified into different associations;
- Each association, according to the identity of biomarkers (qualitative aspect) and their relative concentration in a same chemical family (semiquantitative aspect), allows to identify one or more natural products. Some complementary *data* can be obtained and permits to document the state of preservation-conservation of the materials, determining whether it has been heated, cooked, mixed ..., details that inform about the transormation of commodities;
- In case of plants identification a confront is possible with the archaeobotanical knowledge, permitting to validate or to precise the chemical interpretation;
- Chemical interpretations are confronted to other analysis conducted on the site, and all the data are recontextualized, permitting to propose answers/ the

proposal of answers to the original problematic.

The analytical methodology implemented in this study was recently developed and validated with reference to modern materials and archaeological ones. Briefly, the ceramic powder is extracted according to two complementary methods: the first one, consists in using a mixture of dichloromethane/methanol under sonication, that allows the extraction of soluble markers such as fatty acids, sterols, terpenoids, aromatics, hydrocarbons, sugars... The second one was developed for extracting insoluble and/or bound matter from the clay, giving access to polar compounds and aldaric acids permitting the identification of fruit derivatives. Both extracts are analyzed separately by GC-MS. The improved method allows the detection of grape and wine in traces reaching an extreme sensibility of 10 ng of tartaric acid / g sherd, corresponding to 2 nL of impregnated wine ($2 \cdot 10^{-9}$ L) / g sherd. In addition, this method allows the identification of a wide range of phenolic and aldaric acids: if tartaric acid allows the identification of grape, the presence of syringic issued from the degradation of malvidine (a typical purple-coloured anthocyanin present in the dark and teinturier grapes) permits to discriminate white grape extracts from dark grape products. In the end, a series of short chain acids (succinic, maleic, fumaric, pyruvic, lactic acids) allows the must to be distinguished from the fermented juice e.g. wine [4]. The corpus of studied pottery showed that organic matter was present in each ceramic even if no residues were visible to the naked eyes. Even if chemical pollutions have been detected, the efficient separation by chromatography allows the characterization of all the organic markers:

- Fatty acids and cholesterol allows to determine animal fats. Ruminant sources are recognized when even odd-numbered chain, branched and linear, fatty acids actedre detected, in association with phytanic acid;

- Odd ket-16/18-ones (C_{29} - C_{35}) formed from the thermal decay of triacylglycerols indicate an important heating of fats (at temperature $> 250 - 280$ °C).

- Fatty acids even odd-numbered chain (5:0 -18:0), branched and linear and cholesterol one are representative of dairy products founded in the pyxis (SP700633/01) and a bowl (SP700633/03) both belonging to the female tomb SP700633.

- Medium-chain fatty acids (C_{16} - C_{18}) associated to phytosterols (maily sisterol) indicate plant oil or a fatty material derived from plants;

- Among diterpenic acids, dehydroabietic acid reveals materials from *Pinaceae*, and specifically the methylated dehydroabietic acid and polyaromatic hydrocarbons attest the presence of pitch.

- Traces of fatty acids (14:0 -18:0) and benzoic acid presence in two cases (*askoi* SP700678/01, SP700753/04) may correspond to a flowers essence.

- Sisterol and *migliacina* in two cases (bowls SP700633/03 and SP700753/03) indicate the presence of

millet.

- No sugars were detected.

The second analytical protocol allowed the extraction of high-concentrated polar compounds:

- Tartaric and malic acids are present in sixteen samples on seventeen and in fourteen cases is associated to the syringic one, indicating the large use of dark grape derivatives. Succinic acid allows to precise that in ten vases the beverage was fermented (e.g. red wine).

- In one case (pyxis SP700633/01) aldaric acids associated to tartaric and malic ones have been detected allowing to hypothesize a white grape juice.

As the analysis were conducted in a series of ceramics issuing from the same context, the comparison of qualitative and quantitative data can be cautiously considered. For example, tartaric acid is present in very variuos proportion. Three vases belonging to the same set, specifically the bowl (SP700743/04), the *amphora* (SP700743/05) and the cup contained in it (SP700743/06), have revealed a high tartaric acid concentration in a way we can deduce they were filled with wine at moment of deposition.



Fig. 6 sets for beverage consumption from tomb SP700633 (Photo Centre Jean Bérard USR 3133, CNRS-EFR).

V. CONCLUSION

Firstly it has to be underlined how methods imported by "hard" science combined with traditional archaeology can assume an historical and anthropological value, especially in characterizing ancient societies that have not returned written or iconographic sources. Crossing chemical results with the archaeobotanical and

anthropological *data* has made possible to prove the production and the consumption of wine among indigenous people who occupied *Cumae* between the end of Tenth and the half of Eighth century BC, a population that literature depicts like it had been emancipated by allogenic contribution. In this way, the use of such alcoholic beverage (that should be understood rather as vinegar) in funerary ceremonial before the arrival of the Greeks in Southern Italy requires a review about their cultural contribution. The grape pips membership to the *Vitis vinifera* species found in other tombs of the same necropolis fits with the evidence available for Poggiomarino [3]. This one is a settlement built on piles located in the southeast of Campania dated to Bronze Age which gave back the rests of must and wooden elements probably belonging to a wine press [6]. Furthermore, through this multidisciplinary work it has been possible for the first time to reinforce functional study of protohistorical pottery available hitherto on morpho-typological basis [5] on one side reinforcing the archaeological evidence and on the other side recognizing vascular forms associations for beverages consumption involved in funerary ritual. The "beverage sets" (Figure 6) recognized is generally composed by vases like cups, askoi, amphorae, olla/biconical jug and biconical jug the last three of which are interchangeable. In specific, the amphora should have been used to storage and mix the beverage; the cup used to draw the beverage from storage forms; and the *askos* used to pour and also to sprinkle the tomb before the final closure [3]. Cups which have been found within storage vases are mentioned in literature evidence proving the increase of beverage consumption (them were probably fermented) in Italy from Late Bronze Age [7]. Not last the pyxis. This one, found in the upper part of the only one female tomb analyzed, where the beverage set was laying at her feet, has revealed from chemical analysis to contain white grape juice, fats and dairy products. Such compound thought being a cosmetic product represents a data that combined with the presence of dairy products from the bowl belonging to the same burial suggests the possibility for milk to be associated to the female sphere. Furthermore it has been observed that pitch it's the most common substance

present in the analyzed sets, in which it can be used where it had three functions as coating, to correct wine acidity and as aroma [3].

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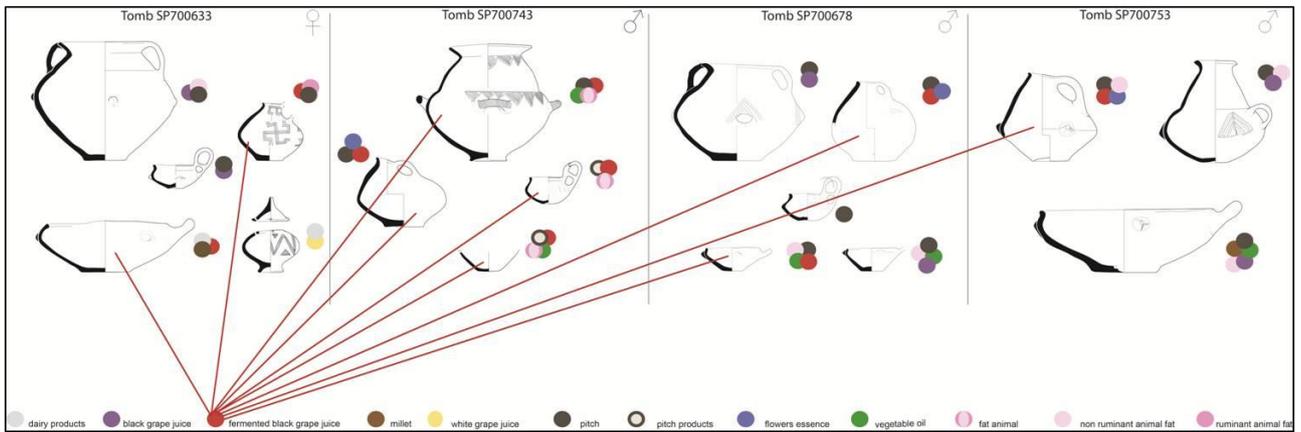


Table 1 - organic residues in the ceramics vessel