Confirming the function of a Final Bronze Age wine processing site in the Nuraghe Genna Maria in Villanovaforru (South Sardinia)

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Summary

The stone artefact in the hut γ of the Nuraghe Genna Maria, object of this study, is part of a compound still unpublished today and dated to the Nuragic period. It was found during a 1991 excavation, revealing a situation unchanged since the collapse occurred between the 10th and 9th century B.C., thus preserving the situation at the time of the collapse to this day.

The presence of tartaric acid - the marker considered to determine the presence of wines or products deriving from grapes - has been determined using HPLC-DAD and UHPLC-HQOMS. So the findings under examination, together with the overall evaluation of the archaeological aspects examined, suggests to positively consider the stone artifact as a "laccus" (the Latin word for wine presses, still used in the Sardinian language today) for grape crushing. The internal slope of the floor of the "laccus" allowed the extraction of juice with rapid separation of juice from berry skins.

The presence in Sardinia of a large number of "stone wine presses" ("palmenti" in Italian) such as that of the Nuraghe Genna Maria studied in this article, brings a contribution to their dating and confirm the existence of an oenological industry on the island in the Archaic period (9th-10th century B.C.).

Key words: stone wine press; wine processing; Bronze Age; Sardinia; Nuragic civilization.

Introduction

Nuragic civilization and the Genna Maria Nuraghe: The nuragic civilization developed during the Sardinian Bronze Age, and it reflects in the landscape with the outlines of the megalithic structures of its towers (the nuraghes), its tombs (traditionally called "giants' tombs"), its villages, and its ceremonial sites (PERRA 2013, VANZETTI et al. 2014). The peak moment of its development occurred between the Middle Late Bronze, the Recent Bronze, and the Final Bronze (about 14th-11th century B.C.).

Nuraghe Genna Maria in Villanovaforru (Fig. 1) is located on top of the hill with the same name, Genna Maria, from
where it dominates the surrounding landscape of Marmilla and beyond, as far as the Gulf of Oristano. On the top of the hill (about 408 m above sea level), the ongoing archaeological investigations have revealed a site of settlement which, from its distant nuragic origins (about the 16th-15th century B.C.), continued, through alternate events, until the early Middle Ages (7th century A.D.) (Fig. 2).

Fig. 2: Plan of the nuragic settlement of Genna Maria, Villanovaforru, Sardinia, Italy. Hut γ is highlighted by red circle

The huts examined have brought to light a village marked by the presence of houses consisting of several rooms aggregated around a probably uncovered central courtyard, inside of which lithic and metal findings, ceramic, bone, and animal remains (remains of meals), as well as carbonized plant remains have been recovered, testifying moments of the daily life of a 10th-9th century B.C. community of farmers and breeders.

The intense phase of life of this nuragic community was affected by a dramatic event, as evidenced by the traces of fire on the wooden roofs and by the reddened walls of the houses. The fire, due to the strong heat released, has severely altered some of the findings and caused the collapse of the roofs. This event took place around the middle of the 9th century B.C.

Especially, the hut γ, subject of this study, and its artefacts have been protected thanks to the collapse in the 9th century B.C. and have not been exposed to sunlight (and to a possible and further use) until the excavation campaign of the second half of the 20th century: they therefore provide a picture of the situation created at the time of the collapse.

Wine trade within and from ancient Sardinia: The presence of wild grapevines naturally leads to the hypothesis that the evidence relating to local wine growing in the same territory is fairly old.

The wild grapevine (Vitis sylvestris) is in all respect a European grapevine (Vitis vinifera L.) and the ancestor of modern cultivated grapevine varieties. Some studies highlight the importance of secondary centres of domestication in the rest of the Mediterranean basin for the spreading of grapevine cultivation, as the presence of colonies of wild grapevine is well documented (Grassi et al. 2003).

Observations carried out in more recent years highlight the presence of cultivated types of grapes in Sardinia since the Middle Bronze Age. The varietal framework traceable from the grape seeds found in the 1400 B.C. nuragic well of "Sa Osa", near Oristano (central western Sardinia, about 30 kilometers north west far from Nuraghe Genna Maria) (Orrù et al. 2013), can be traced back to a viticulture which is advanced from a varietal point of view, composed of pips attributable to cultivated grapevines. This is also confirmed by the examination of the "nuragic" grape of Villanovatulo (central Sardinia, about 30 km north east far from Nuraghe Genna Maria), pips and berry belong to a cultivated type (Campus et al. 2014).

Under this point of view, a new light is shed on Iron Age pips, belonging to cultivated types, from Nuraghe Genna Maria (Bakels 2002), as these cultivated forms have been found in archaeological layers that precede by centuries commercial contacts with the Phoenicians.

The presence of an oenological industry in archaic age Sardinia needs to be confirmed by the discovery of artefacts or devices required for the production of wine starting from grapes. While the presence of wild grapevine and the finding of grape pips and berries in the archaeological layers of the excavations, as well as the historical information and documentary sources confirm the antiquity of the island's wine industry, not much is known much about wine production artefacts and processes. It must be said that throughout the island, several stone artefacts were found. They are sometimes characteristic elements of the landscape and have been traditionally used by the local population for the production of wine. These stone artefacts can be dug into the ground or built outside. In both cases these elements are characterized by a larger "tank" placed at a higher elevation (and having a sloping floor), and a smaller tank placed immediately below the first. There are no doubts about the use of these artefacts in recent times Sardinia: white winemaking process, grape juice is immediately separated from skins by the outflow.

This preliminary investigation aims at assessing whether the marl artefacts adjacent to the right side of the wall structure of the hut γ - never reused by man after the fire and collapse of the 9th century B.C. and opened only during the recent excavations - may have been used up to 900 years B.C. to produce wine. To achieve this goal this research aims to find chemical compounds that could provide evidence that artefacts described above have been used for winemaking process.

Material and Methods

Hut γ (Fig. 3): The subject of this study, is part of a compound still unpublished; it is a quadrangular hut whose main wall, overlooking the entrance, also encloses hut β, forming a corridor with the outer wall of the west tower of the three-lobed structure and its west wall. Surveys carried out in this area in 1982 confirmed that the structure covers a layer of collapse of the three-lobed structure which was covered by layers of sterile soil rich in marly flakes.
The upper layer consisted of an ash-grey layer with animal bones and geometric ceramics, some of which had been heavily altered by the heat. Blocks of the recent collapse of west wall external curtain lay on the ceramics of this layer. The WSW oriented entrance extends from 88 cm outside to 130 cm inside.

The resumption of the excavation carried out in 1989 made it possible to exhume a trunk of charred *Ilex* 40 cm long and with a diameter of 15 cm, belonging to the beams of the roof burnt and then collapsed (fire of the 9th century B.C.), and the recovery of fragments of a bowl with a recessed rim, an askos-shaped jug decorated with geometric pattern, a truncated-cone vessel, a whetstone pierced at one end, and a complete mandible of an adult swine. As the information of the previous excavations was not available, the hut γ was interpreted as a place for preparation and consumption of meals (pork) and as a space dedicated to the consumption of fermented drinks (decorated jug). On the basis of the type of findings recovered, the period of the environment (not carbon-14 (¹⁴C) dated) is around the 10th-9th century B.C.

What could have been a hearth, bordered by reused basalt ashlars, is visible against the wall facing the entrance. In the incoherent soil contained in its structures the following were identified: (1) ash lenses and carbon rustle; (2) reddish and yellowish baked clay perhaps used as hearth cladding; (3) pottery fragments probably used as fireproof material; (4) fragments of basalt wine presses; (5) an earthen andiron.

Sample collections and analytical methods: In recent decades different methods have been proposed for the identification of tartaric acid, such as the Feigl spot test and the DRIFTS spectrometry (Feigl et al. 1983, Michel et al. 1993). These methods are non-specific, do not allow definitive and unequivocal identification of the compound and may expose to the risk of wrong interpretations and false positives (Stern et al. 2008, Garnier et al. 2016). More recently, the application of liquid chromatographic or gaseous techniques coupled to a mass detector (GC-MS, LC-MS) has allowed a safe identification of the compound (Guasch-Jané et al. 2004 and 2006, Pecci et al. 2013, Garnier et al. 2016), although its extraction from archaeological finds (potsherd, jar or other artefacts) is influenced by the balance between the soluble free form and the little soluble tartrates (Michel et al. 1993).

Three samples were collected by abrading the surface of the upper basin (sample 1 in Fig. 4), the paved surface (sample 2), and the lower tank (sample 3 in Fig. 5) with a scraper and taken to the laboratory for analysis in contamination-free containers.
Homogeneous rates and weights of powder (500 mg) have been extracted with KOH 1M on the basis of the procedure specified by Pecci et al. 2013. The organic and aqueous fractions obtained were subsequently analysed to detect the presence of tartaric acid in the samples under examination. The ethyl acetate solutions derivatized with BSTFA (N,O-bis(trimethylsilyl)trifluoroacetamide, Sigma-Aldrich) were tested by GC-MS using an Agilent 7980A gas chromatograph (Agilent Technologies, Waldbronn, Germany), equipped with an Agilent 19091S-433HP 5MS column (30 m x 250 µm x 0.25 µm) and an Agilent 5975C mass spectrometer, with an electron impact ionization system and mass range of m/z 40-650. The following programmed temperature was applied: 50°C for 1 min, temperature increase of 3°C min⁻¹ up to 280°C, and isothermal for 10 min. The aqueous fractions (three per sample, corresponding to three subsequent extraction steps), separated from the ethyl acetate during the extraction process, were analysed with an HPLC Waters liquid chromatograph equipped with 600 Controller pump system, 717plus autosampler, and 996 Photodiode Array Detector (Waters Corporation, Milford MA, USA). A mobile phase consisting of H₂PO₄ 0.005 M operating in isocratic mode at a flow rate of 0.5 mL·min⁻¹ was used. The solutions under examination, previously filtered with 0.45µm membranes, were injected (injection volume: 20 µL) both as it is and after partial removal of the solvent, into a Restek Allure Organic Acids column (300 mm x 4.6 mm i.d. x 5 µm), thermostated at a temperature of 30°C. The chromatograms were set at 210 nm.

The same aqueous fractions were tested with a UHPLC ThermoUltimate™ 3000 RS equipped with DGP 3600 RS pump and WPS 3000 RS autosampler, combined with a high-resolution hybrid quadrupole orbitrap mass spectrometer (HQOMS; Q Exactive™) with heated electrospray source (HESI II; Thermo Scientific, Sunnyvale, CA, USA). A Raptor Biphenyl column (3 mm x 150 mm, 2.7 µm, Restek, Bellefonte, PA, USA) thermostated at a temperature of 40°C, was used for chromatographic separation using a ternary mobile phase composed of 2% formic acid (A), acetonitrile (B) and water (C). Initially, the elution gradient was set at 1% for A, 1% for B and 98% for C with a flow rate of 0.3 mL·min⁻¹ and kept constant for the first 4 min. In the following 4 min the percentage of A and B rose linearly to 5% and 95%, respectively, and remained constant for the next 3 min. The gradient returned to the initial phase in 0.1 min, and the column was conditioned for a further 4 min. The tartaric acid standard (≥ 99.5%, Sigma, St. Louis, MO, USA) was prepared in aqueous solution at a concentration of 1 mg·L⁻¹ and injected at a volume of 10 µL. Sample 1 was diluted with water three times while samples 2 and 3 were injected undiluted (10 µL). Ionization was performed with HESI II source by setting the parameters as follows: spray voltage, 2.5 kV; sheath gas flow, 40 arbitrary units; auxiliary gas flow, 20 arbitrary units; capillary temperature, 330°C; auxiliary gas temperature, 280°C. The mass spectra were acquired in negative ion mode with a full mass/data dependent-MS² experiment (Full MS/dd-MS²), at a resolution of 140,000 FWHM (full width at half-maximum; calculated for m/z 200, 1.5 Hz), automatic gain control(AGC) of 3 × 10⁶ and an injection time(IT) of 100 ms for the full MS spectra, and a resolution of 17,500 FWHM (12 Hz), 1× 10⁵ AGC and 50 ms IT for the dd-MS² spectra. The precursor ion of tartaric acid was identified in the deprotonated molecule [M-H]+/m/z 149.0092 (acid tartrate ion), while the fragments m/z 87.0088 and 72.9931, obtained with a collision energy (NCE) of 35 arbitrary units, were used as confirmation.

Results

The area of great interest is highlighted on the right side of the entrance of hut γ. Next to the wall structure there is a semicircular counter consisting of three blocks of marl and sandstone. A marl basin (Fig. 4) rests at the centre, on a pavement slightly sloping towards a quadrangular-shaped marl collecting vat sunken into the ground (Fig. 5). On the left-hand side of the entrance, just at the corner, another area is delimited by orthostatic blocks of sandstone. Shape and arrangement allow us to hypothesize a use for grape processing: after berry crushing juice was conveyed into the lower collecting vat through the sloping pavement for the next phase of fermentation.

Main biomarkers indicating the presence of wine or grape derived products are tartaric acid and its salts (Michel et al. 1993, Guasch-Jané et al. 2004, Barnard et al. 2011) and syringic acid. The latter is a degradation product of malvidin-3-glucoside and is considered a specific marker for the presence of red wine. For the considerations set out above (white wine making) we focused on tartaric acid. This acid, found in the pulp of berries, is a fundamental component of must, wine and their residues. Research and identification of tartaric acid would confirm the use of grape to produce must or wine: in the Mediterranean area, although tartaric acid is present in different types of plants and fruits that are less important for food and drink production (Barnard et al. 2011), is largely abundant in grape.

Normally in wine, tartaric precipitations (wine stone) mainly consists of potassium tartrate: potassium is available in high concentrations in grape juice. Furthermore, marl and sandstone are moderately porous calcareous rocks and therefore it is possible to imagine that tartaric acid could precipitate as calcium tartrate (McGovern et al. 2013) and it could be identified in the elements of the rocks composing the stone artefact.

Since the GC-MS analysis of the derivatized ethyl acetate solutions did not show the presence of peaks due to tartaric acid, the three residual aqueous fractions from the extraction process have been tested with HPLC-DAD. The sample extraction solutions taken from the upper basin (sample 1) shows the presence of a peak with RT and a spectrum similar to that of tartaric acid (Fig. 6a). The peak is even more evident in the chromatograms obtained following the removal of part of the solvent from the solutions (Fig. 6b). The fact that the peak RT 5.19 mins belongs to tartaric acid has been confirmed by the increase in the area following the addition of growing concentrations of tartaric acid. Similar results were obtained for the solutions traceable to the samples taken from the pavement (sample 2, Fig. 7) and from the lower collecting vat (sample 3, Fig. 8). Results obtained with the HPLC-DAD analysis lead to search for
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Fig. 6: (a) Chromatograms of Sample 1 extraction solutions: 1st extraction (black), 2nd extraction (blue), 3rd extraction (green). (b) Chromatograms of the 1st extraction solution of sample 1: as it is (red), and concentrated (black).

Fig. 7: Chromatograms of sample 3 extraction solutions: 1st extraction (black), 2nd extraction (blue), 3rd extraction (green) compared to chromatogram of sample 1 first extraction solution (red).

Fig. 8: Chromatograms of sample 2 extraction solutions: 1st extraction (blue), 2nd extraction (black), 3rd extraction (green) compared to chromatogram of sample 1 first extraction solution (red).
an analytical test to unequivocally reveal the identity of the peak identified at RT 5.19. So the same extracts (aqueous part) were analysed with high resolution mass spectrometer (UHPLC-HQOMS). Results confirmed what was detected by HPLC-DAD: all three samples showed the presence of a peak with RT (2.20 min, ∆RT = 0.05 min) compatible with that of the tartaric acid standard and presenting exactly an accurate mass (m/z 149.0095, ∆ m/z = 2 ppm), an isotopic pattern (Fig. 9), and a fragmentation spectrum (Fig. 10) corresponding to those of that same acid standard.

**Discussion**

The presence of archaeobotanical remains of *Vitis vinifera* in many sites in Sardinia, dating back to the Bronze Age or the Iron Age, reveal the existence of well-established wine making activities. Until now, however, not much has been known about the facilities used for wine production. In recent years, this gap has been filled by Loi’s studies (2017), which showed the presence of different types of wine basins in some areas of Sardinia, traditionally used up to the middle of the 20th century to produce particular varieties of white wine. The artefact of Genna Maria shows the morphological typology of the wine basin described by Loi (2017).

The evidence of tartaric acid in the findings under examination, together with an overall assessment of the archaeological aspects investigated, suggest that these artefacts should be attributed the function of wine presses.

Although tartaric acid is also contained in other fruits (McGovern et al. 2015) such as hawthorn (*Crataegus monogyna* Jacq., 1775), pomegranate (*Punica granatum*, *L.*) and carambola (*Averrhoa carambola*, *L*.), it seems very unlikely that the origin of the findings from the site under examination can be traced back to them: it is in fact impossible that pomegranate and hawthorn could be used to obtain juices in the artefact examined, and carambola is an exotic species the evidence of which can be found in Sardinia only in recent times (second half of the 20th century, due to the commercial interest in tropical and subtropical cultivations).

In accordance with the classification proposed by Loi (2017), the wine press appears to be a middle way between type 2 (bounded by orthostatic stone slabs) and type 3
could such a wine press be used? We can only make some hypotheses. In the case of daily use at least twice a day for about 45 d, the activity of crushing in the wine press could range from 180 to 250 L of still wine per day, depending on the characteristics of the grapes (Lovicu et al. 2017); this sums up to about 8,000-11,000 litres of wine per season. This quantity could double if the processing capacity of the laccus had been increased by filling it up to the top.

And what type of wine could be produced? The observations carried out on the wine press as it is today have shown an inclination of about 10 % on the paved bottom of the collection area, which allowed the must obtained by crushing the grapes to flow directly, more or less quickly, towards the collecting vat. This implies that must was gathered separately from the skins and therefore the alcoholic fermentation took place without skins. This would thus avoid the transfer of anthocyanins (responsible for the colour of red wines) to the hydro-alcoholic solution. The wine obtained was thus white or at most, in the case of red skin grapevine varieties, rosé. We could additionally assume that the described barrier could also be effective to produce mash for further use, including, for instance, red wine production, with the final shovelling of the mash to another collection vat. Another use of the grape mash could be assumed with the addition of water, sometimes with honey or fruit juice or fruit mash – from figs, for example, and this could explain the significant amount of achenes of figs found together with the grape seeds in the nuragic well of Sa Osa (Orku et al. 2013) – to obtain alcoholic beverages, as it is well documented in modern times in Sardinia up to the second half of the 20th century (Murgia 2008).

Conclusions

The several "laccus" distributed over some areas of Sardinia confirmed the island’s vocation (also supported by a population of wild grapevines – Vitis vinifera L. ssp. sylvestris - numerous and in excellent health) for the production of grapes.

The findings and reports in important archaeological contexts (for example, the Roman age "laccus" found in the Nuraghe Arrubiu in Orroli) give us information about the time of their presence, but due to the material with which they were made, no information is available about the age and therefore the time in which these artefacts began to be used for wine production. Since stone has a potentially infinite duration, it is only possible to refer to the presence of a wine press in a precise time (2nd-3rd century A.D.), as in the case of the nuraghe Arrubiu, but nothing is known about its date of building.

Presence of tartaric acid in the various elements of the stone artefact support that it was used as a "laccus", used for pressing and crushing of berries for production of must that was promptly removed and fermented in other containers. The stone artefact must therefore be understood exclusively as an equipment used for the release of the must and not for the fermentation of the same.

Moreover, according to the large number of "laccus" that nowadays characterize the Sardinian landscape, it can be deduced that grape cultivation and wine production were
certainly extended since the most ancient times and that the grape crushing tank has been the same for about 3,000 years: use of "laccus" to produce some kinds of white wine is well documented till the second half of the 20th century.

This article contributes to the dating of the stone wine presses, confirming that the production of wine on a large scale (for the time) was already active in the archaic era (10th–9th century B.C.) using equipment which will undergo only minor adjustments over the millennia. In this respect, the presence of a large number of stone wine presses in Sardinia, such as the one found in the nuraghe Genna Maria described in this article, confirms the existence of a wine industry in very ancient times and that Sardinia was already the source of trades with the rest of the Mediterranean, transporting wine as far as the eastern part of the "Mare Nostrum" (Sironi 2014).

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References


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Corrigendum

On page 93 (Vitis 59, 3/2020) of the manuscript:

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an error in the affiliations has occurred. The correct address of co-author M. Perra is:

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The editors apologise for this error.