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1 Chemical evidence for the persistence of wine production and trade

2 in Early Medieval Islamic Sicily

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19

20 Keywords

Transport amphorae, wine, organic residue analysis, Late Antiquity and Early Middle Ages Sicily,
 provenance and trade

23

24 Abstract

25 Although wine was unquestionably one of the most important commodities traded in the 26 Mediterranean during the Roman Empire, less is known about wine commerce after its fall, and 27 whether the trade continued in regions under Islamic control. To investigate, here we undertook 28 systematic analysis of grapevine products in archaeological ceramics, encompassing the chemical 29 analysis of 109 transport amphorae from the 5th to the 11th centuries, as well as numerous control 30 samples. By quantifying tartaric acid in relation to malic acid, for the first time, we were able to 31 distinguish grapevine from other fruit-based products with a high degree of confidence. Using these 32 new quantitative criteria, we show beyond doubt that wine continued to be traded through Sicily 33 during the Islamic period. Wine was supplied locally within Sicily but also exported from Palermo to 34 ports under Christian control. Such direct evidence supports the notion that Sicilian merchants 35 continued to capitalise on profitable Mediterranean trade networks during the Islamic period, 36 including the trade in products prohibited by the Islamic hadiths, and that the relationship between 37 wine and the rise of Islam was far from straightforward.

38

39 Significance statement

40 As a high-value luxury commodity, wine has been transported across the Mediterranean since the 41 Bronze-Age. The wine trade was potentially disrupted during political and religious change brought 42 about by Islamisation in the Early Medieval period; wine consumption is prohibited in Islamic 43 scripture. Utilising a novel quantitative criterion based on the relative amounts of two fruit acids in 44 transport amphorae, we show that wine was exported from Sicily beyond the arrival of Islam in the 45 9th century, including to Christian regions of the Central Mediterranean. This finding is significant for 46 understanding how regime change affected trade in the Middle Ages. We also outline a robust 47 analytical approach for detecting wine in archaeological ceramics that will be useful elucidating 48 viniculture more broadly.

49

50 Introduction

51 Sicily was described by the 10th century Palestinian geographer al-Muqaddasī as 'the profitable island' 52 and new archaeological research is enhancing the evidence for its commercial prosperity, especially 53 in the 10th-11th century (1–3). There is increasing evidence that trade remained active in the centuries 54 following the fall of the western Roman empire, as Sicily emerged as a key commercial centre. 55 Transport amphorae produced in Sicily during the Islamic period are found throughout the Central 56 Mediterranean (e.g., refs 4–6) and a wide variety of goods were likely to have been traded with Sicilian 57 merchants at this time, including edible commodities, such as salted fish, vegetable oils, dairy 58 products, fruits, spices and sugar (4, 7–9). But it is not clear whether the major political and economic 59 upheaval during the Byzantine-Islamic transition had an impact on the traded commodities 60 themselves.

61 Wine was certainly one of the major high value goods traded in the Roman and Byzantine periods (10–

62 12). Some scholars consider that its production and trade dramatically decreased after the Islamic

63 conquest of the island due to hadithic prohibitions (13, 14). The well-documented existence of

- viticulture during the Islamic period (13, 15) may instead have been oriented towards table grapes,
- raisins and vinegar, which are widely used in Islamic cuisine (e.g., refs 16, 17). In contrast, the

66 continuation of wine production in Islamic Sicily is also suggested by some sources (15), although the 67 extent of production is hard to determine. A tax on wine is reported when the island was under the

Fatimid rule (18), which suggests that it continued to be traded and of economic significance, but the

69 volume and destination of this commerce is largely undetermined.

70 Indeed, the equation between the transportation of wine and the rise of Islam is likely to be far from simple and most likely fluctuated between the 7th and the 13th century. Perhaps our best source of 71 evidence comes from transport amphorae which can often be provenanced by their form and 72 73 composition to specific origins to reveal potential trade routes (2). In the 6th and 7th centuries 74 commodities carried in Late Roman type 5-7 amphorae, produced in the Eastern Mediterranean, were 75 reaching destinations in the Aegean, Adriatic and Tyrrhenian seas. Some of these are thought to have 76 carried wine (2). At the beginning of the 8th century the Emir of the Theban region was ordering wine 77 from Apollonopolis to supply other destinations in Egypt, including Fustat, and his cook was receiving 78 a consignment of wine according to a document in the Christian monastery of Baouît (2). In the 10th 79 and 11th centuries, an important new amphora production centre rose at Palermo, whilst at the height 80 of Islamic control, supplying commerce to North Africa and the Tyrrhenian Sea area, notably Sardinia 81 (6). The Norman conquest of Sicily in 1061 AD is thought to mark a revival of viniculture (14) and wine 82 is again considered a major Sicilian export after this date (4). In the 12th and 13th centuries, new types 83 of amphorae handled bulk supply in the Aegean (e.g. Calchis) but Sicily loses its primacy as an exporter 84 and becomes a net importer, in the face of diverse and rising centres of production on the Italian 85 peninsula (2).

86 Deciphering the wine trade from the distribution of amphorae and the few documents available is 87 however far from straightforward without knowing their contents. In the absence of visible residues, 88 marks or labels, chemical analysis of organic compounds absorbed into the walls of amphorae offers 89 the only direct approach for assessing changes in the commodities traded during this period. Although 90 some studies have begun to explore the contents of amphorae exchanged in Sicily in the Early Middle 91 Ages (19–21), no large-scale investigation has been carried out to date. Furthermore, the identification 92 of wine through chemical analysis remains controversial (e.g., ref 22) and particularly prone to false 93 positive identification (23). In the absence of other archaeological or historical data to confirm 94 interpretations, application of a robust methodology including quantification of target molecules and 95 the use of appropriate controls is essential, particularly to distinguish wine from other fruit-based 96 products. In the context of Islamic Sicily, this is especially pertinent, as a range of fruits, their juices 97 and syrups, are known to have been exported (9, 15, 19). For this reason, previous reports of wine in 98 Islamic amphorae (19–21) need to be interpreted cautiously. In one of the largest studies of its kind, 99 here we present the analysis of more than 100 amphorae produced or imported in Sicily between the 100 5th and the 11th century AD. We propose a novel quantitative criterion for the identification of 101 grapevine products using the relative concentration of tartaric acid to malic acid as a proxy, validated 102 on more than 80 control samples.

103 Results and Discussion

One hundred and nine amphorae produced or imported in Sicily from the Late Roman period to the Early Middle Ages were selected from the assemblages of 17 Italian and North African sites (Table 1, Fig. 1, and SI Appendix, Fig. S1). Knowledge of provenance (i.e. place of production), identified based on the typological characteristics and the petrographic composition of ceramic pastes (4, 6, 24) (SI Appendix, Table S1 and Fig. S1) and place of discard allowed us to distinguish four groups (Table 1).

109 These are i) amphorae that were found close to the centre of production (local trade), ii) those

produced in Sicily and exported within the island (Sicilian trade), iii) those produced in Sicily and exported outside the island (overseas export), and iv) those produced elsewhere and imported into the island (import). To facilitate comparison over time, the samples were divided into three chronological groups: the Late Roman and Byzantine periods (5th to 7th century), the transition from the Byzantine to the Islamic period (8th to 9th century), and the Islamic period (10th to 11th century). Notably, only a limited number of samples were available from the 8th to 9th centuries, reflecting the scarcity of ceramic assemblages in this period (4, 25).

Of the entire sample set, only two containers show visible residues on the inner surfaces (SI Appendix, 117 118 Table S1) that indicate sealing with plant exudates (resin, pitch, etc.), a feature commonly used to 119 putatively identify wine amphorae in classical antiquity (e.g., ref 26). To facilitate the robust 120 identification of wine, we undertook comparative analysis of control samples from similar contexts 121 that would not have been expected to have come into contact with grapevine products, satisfying the 122 stringent criteria outlined by Drieu et al. (23). In this case, we used cooking pots from the same 123 contexts and, where available, wall and floor tiles and sediments (Table 1). The results were compared 124 with control samples from replica potsherds impregnated with wine and degraded for one year 125 through burial under controlled conditions, and samples of archaeological pottery with known 126 contents (SI Appendix, Table S2).

127 Criteria for the identification of wine

Sixty-nine amphorae (63%) yielded tartaric acid (TA), in varying amounts (Fig. 2, SI Appendix, Fig. S2 and Table S3). Additional small organic acids were identified in most of the amphorae and controls, including malic (82% of samples), succinic (54%), fumaric (15%), maleic (10%), malonic (7%) and oxalic (5%) acids. TA was also detected in many control samples (cooking pots, sediments, and tiles) but only at low concentration (< 0.7 μ g g⁻¹) in all but two domestic cooking vessels (3.2 and 1.4 μ g g⁻¹; Fig. 2 and SI Appendix, Fig. S2). Overall, the transport amphorae had significantly higher TA concentrations than

the control sample set (Mann-Whitney test: W = 5602; p < 0.01), implying a difference in use (Fig. 2).

However, the detection of TA alone is insufficient to provide definitive evidence for the presence of 135 136 wine, as this compound is present in many other fruits (23, 27, 28). In grapes, the proportion of TA 137 increases with ripening while the proportion of malic acid decreases correspondingly (29, 30). 138 Although the absolute amounts of both acids are dependent on the growing conditions (temperature, 139 hydrological state, exposure to sunlight, etc.; 30-32), we are able to exploit their relative 140 concentrations to distinguish grapevine products. A comparison of TA and MA for the identification of 141 wine and other fruit products in an archaeological context has been noted before (33, 34), but neither 142 quantitative data nor interpretative ranges have been reported. Consideration of authentic reference 143 products from the literature shows that the median % tartaric acid (%TA), expressed as the amount of 144 TA divided by the sum of TA and malic acid, is significantly higher in ripe grape and grape-products 145 compared to other fruits (Mann-Whitney U test; W = 136452, p-value < 0.01), with the exception of tamarind (Fig. 3A and SI Appendix, Table S4). Fruits other than grape and tamarind have a median %TA 146 of 7% compared to 63% for ripe grape products. The lower limit (5th percentile) of the %TA range for 147 148 ripe grape products is 35%, and over 90% of the published data for fruits and berries (N = 163; 149 excluding unripe grape, pomegranate and tamarind) have %TA below this value.

To test the robustness of this criterion, 18th and 20th century Georgian *qvevri*, traditionally used for wine production, were analysed. These vessels yielded %TA within the range of grapevine products (i.e. %TA > 35%; Fig. 3C and SI Appendix, Table S2). Similarly, the %TA obtained from experimental pots soaked in wine and buried for one year under different environmental conditions also remains

154 within the range of grapevine products, despite some alteration in the ratio when compared to the

non-degraded control (Fig. 3B). It cannot be excluded that degradation of fruit products, other than
grapes, may lead to an increase in %TA. However, foodcrusts containing Viburnum berries found on
the surface of Russian hunter-gatherer pottery (23, 36), show a %TA below the range for grapevine
products (Fig. 3C), giving confidence to the use of this criterion on archaeological samples of unknown
content.

160 Among all the transport amphorae studied, twenty-one show %TA > 35%, which corresponds to the range of grapevine products (Fig. 3C). Interestingly, all of them yielded > 0.3 μ g g⁻¹ of tartaric acid, i.e. 161 greater than all the tiles and the majority (79%) of cooking pots. The use of these amphorae to 162 163 transport wine is therefore highly likely given the context and prior historical knowledge, although the 164 storage or transport of vinegar, grape syrup, pomegranate or tamarind cannot be excluded. Indeed, 165 many of these products are mentioned in the cuisine and pharmacopoeia of the Late Antique and 166 Early Medieval Mediterranean (e.g., refs 13, 16, 17, 36, 37) but are overwhelmingly considered less 167 likely to be commercial commodity transported in amphorae. Hereafter, we therefore consider 168 transport amphorae with %TA > 35% to have contained wine. It is important to note, that the same 169 rationale cannot be applied to cooking pots or amphorae produced and discarded locally (i.e. potential 170 storage amphorae), as we cannot be sure that wine rather than other grapevine products (vinegar, 171 grape syrup, etc.) were processed in these vessels.

172 Almost all of the cooking pots and 88 amphorae show %TA \leq 35 %, with varying yields of TA (Fig. 3C). 173 The TA in these samples may be derived from unripe grape products or other fruits (e.g. black currants, 174 blackberries, mulberries, raspberries, cherries, some types of pomegranate). It is important to note 175 that for amphorae with %TA \leq 35%, we are not able to exclude wine if it were mixed with other 176 products containing malic acid (e.g. honey, other fruits, etc.) as was common in the Roman period 177 (e.g. addition of honey to sweeten wine; 38). Similarly, the reuse of amphorae (e.g. for transporting 178 wine and then other fruit juices) would reduce the %TA value leading to false negative identifications. 179 However, subsequent re-use for transporting olive oil would not be expected to substantially alter the 180 %TA value. The use of fruits likely explains the presence of tartaric and malic acids, sometimes in 181 substantial amounts, in Sicilian cooking pots, in keeping with Islamic recipes available from this period 182 (e.g., refs 17, 39). Small amounts of TA and malic acid (respectively around 0.1 and 1 µg g⁻¹) are present in both wall and floor ceramic tiles, always with %TA < 25% (Fig. 3C), most likely indicating 183 184 contamination from the burial environment. Amphorae and cooking pots that yielded less TA and 185 malic acid than found in these control samples therefore cannot reasonably be interpreted as 186 containers of wine or fruit products.

187 The Sicilian wine trade through time

Having established this robust criterion for the identification of wine in amphorae, we now turn to 188 189 comparison of their use through time (Fig. 4A). First, wine was identified in all periods regardless of 190 the political regime in power. The low number of samples available from the 8th and 9th centuries 191 precludes identification of a specific pattern, but even during this turbulent period, it is clear that wine 192 was also traded within Sicily. By far the most surprising result is that wine was also used in the 10th 193 and 11th centuries, when Sicily was under full Islamic control. A group of Sicilian-made amphorae, 194 representing 15% of the total analysed from this period is clearly distinguished with a %TA > 35% (Fig. 195 4A).

During the Islamic period, petrographic analysis shows that Palermo was the main production centre
 for amphorae found in Sicily and Palermitan amphorae are also found throughout the Central
 Mediterranean (e.g., refs 5, 6, 24). Five of the amphorae that contained grapevine products during the
 Islamic period were produced and discarded in Palermo (Fig. 4B). This finding is interesting since

200 Palermo was under full Islamic control and our results may indicate that these vessels were used for 201 local transport or storage of wine vinegar or grape syrup rather than wine; the former were widely 202 used in medieval Islamic cuisine, as a preservative, or for medicinal purposes (e.g., refs 17, 36, 37, 40). 203 However, wine cannot be excluded and equally may have been produced for consumption by the 204 Jewish and Christian communities still present in Sicily at this time (13, 41, 42), or by some members 205 of the Muslim community, as discernible from Islamic medieval poems (13, 41). No traces of wine 206 were found in amphorae exported to inland Sicily, but, surprisingly, grapevine products were 207 identified in several Palermitan amphorae exported overseas to Christian mainland Italy and Sardinia 208 (Fig. 4B). Therefore, by using a combination of analytical approaches aimed at provenance and use on 209 a large corpus of amphorae, we can begin to reveal the extent of a Sicilian wine trade network that 210 appears to encompass the city of Palermo itself, and also the Central Mediterranean. Of course, it is 211 difficult to estimate the volumes of wine trade, not least as wine and grapevine products may also 212 have been stored or transported in perishable organic containers, such as barrels or skins, which do 213 not survive in the archaeological record (43).

It is important to note that wine was not the only product transported in the amphorae manufactured 214 215 and imported into Sicily between the 5th and 11th centuries. Degraded lipids from various fats and oils were identified in 75% of the amphorae analysed, including the majority of that also contained wine, 216 217 suggesting extensive reuse of these containers, as has been previously suggested (e.g., ref 44). 218 Significant lipid degradation, and the potential for extensive mixing, precludes further identification 219 in the majority of cases, with profiles dominated by saturated fatty acids. Two amphorae from the 5th to 7th centuries and three from the 10th to 11th centuries contained more distinctive fatty acid profiles 220 221 with a high relative abundance of oleic acid (C_{18:1}) and palmitic acid (C_{16:0}) compared to stearic acid 222 $(C_{18:0}; C_{18:1}/C_{18:0} \ge 1.5 \text{ and } C_{16:0}/C_{18:0} \ge 2; \text{ SI Appendix, Table S1} \text{ and are broadly attributed to vegetable}$ 223 oils (45). We undertook individual carbon stable isotope measurements of fatty acids of all of the 224 amphorae and based on this evidence we were able to exclude marine products, which have fatty acid 225 δ^{13} C greater than -27‰ (46), in all but one amphora from the 5th century and two amphorae from the 226 10th to 11th centuries (SI Appendix, Fig. S3 and Table S3). Therefore, fermented fish sauces and pastes, 227 such as garum, liquamen or salsamenta, do not seem to have been a major trade commodity during 228 this period.

229 Finally, the presence of diterpenes and their degradation products derived from Pinaceae resin and 230 pitch (47) were far less abundant in Islamic amphorae (5% of samples) compared to Late Roman and 231 Byzantine periods (60%). Resin linings and sealants are thought to aid waterproofing or help preserve 232 the contents and were frequently applied to Mediterranean amphorae during the Classical and Late 233 Roman periods (e.g., refs 48-50). The presence of undetermined fats or oils in the majority of 234 amphorae could be due to an alternative waterproofing method, as has previously been suggested for 235 amphorae of the same period (19, 21). It is not clear whether this change in practice is unique to the 236 Islamic period or whether it is specific to Sicilian production.

237 Conclusion

Using a novel quantitative approach for distinguishing ripe grape products from other fruits, here we provide compelling evidence that the production and trade in Sicilian wine continued into the Islamic period and therefore were not substantially affected by the political and religious changes in Sicily between Late Antiquity and the Early Middle Ages. These results do not necessarily imply that Islamic prohibitions (51) were not strictly observed on the island, as wine may have been produced and traded for the benefit of non-Muslim communities in Sicily and elsewhere. We found evidence that wine was exported from Palermo under Kalbid rule to the Christian regions of the Mediterranean, 245 demonstrating continuity of the wine trade, at least, since the Byzantine period when the great Sicilian 246 estates supplied Rome with wine via the port of Palermo (52). The volumes of wine traded are difficult 247 to discern using this approach as a range of other commodities were also transported to and from Sicily at this time in similar containers, including vegetable oils, and the organic residue analysis shows 248 249 evidence of re-use. Nevertheless, there is little direct evidence to suggest that the Mediterranean 250 wine trade decreased under Islamic control as has often been assumed, rather Islamic merchants 251 benefited from new markets satisfying the Christian demand for Sicilian wine, a trade that must have 252 been approved by the Kalbid emir. Finally, we note that only by using our more robust quantitative 253 criterion we can distinguish grapevine products and other fruits. Indeed, 69% of Sicilian amphorae and 254 70% of the cooking pots we tested contained tartaric acid but only a small fraction of these could be 255 accurately assigned to wine, avoiding false positive identifications. We recommend that this new 256 quantitative criterion should now be used to identify the presence of grapevine products in 257 archaeological pottery, particularly in contexts where wine production is disputed (e.g. to study the 258 origins of viniculture).

259 Material and Methods

260 Degradation of authentic wine in pottery

Three replica pots were filled with different wine obtained from commercial producers for two days 261 (SI Appendix, Table S2). One potsherd from each pot was directly analysed after being emptied and 262 dried. Other potsherds were buried for 12 months in different environments in order to evaluate the 263 264 degradation of wine molecules in different climatic conditions and soil pH: the archaeological site of Casale San Pietro in Castronovo di Sicilia (Lat 37.68, Long 13.63; September 2018 – September 2019), 265 266 a field in the south of France (Eze, Alpes-Maritimes; Lat 43.73, Long 7.36; November 2018 – November 267 2019), and at the YEAR Centre at the University of York (United Kingdom; Lat 53.94, Long -1.06; 268 November 2018 – November 2019).

269 Experimental approach

270 Following the most recent publications in terms of identification of grapevine products (23, 53), two 271 successive extractions were used. Approximately 2 g of ceramics were drilled into the inner walls of 272 the potsherds, after removal of the outer surface (1-2 mm) to remove contamination from the 273 surrounding sediments and from the handling. Ten μg of an internal standard (*n*-C₃₄) was added to 1 274 g of the powder, which was then extracted 3 times with DCM/MeOH (2:1, v/v) in an ultrasonic bath. 275 The successive extracts, that contained lipids and resin acids (terpenes), were combined and 276 evaporated under a nitrogen flow. The powder remaining after extraction with DCM/MeOH was 277 treated with a boron trifluoride-butanol/hexane mixture (1:2, v/v) for 2 hours at 80°C to extract and 278 butylate small organic acids, in particular malic and tartaric acids. The samples were centrifuged, and 279 the supernatants were neutralised with a saturated sodium carbonate solution. The samples were 280 then extracted 3 times with DCM and washed twice with distilled water before being evaporated 281 under a stream of nitrogen. All samples were derivatized with BSTFA (*N,O*-282 Bis(trimethylsilyl)trifluoroacetamide, 1% trimethylchlorosilane). After evaporation under nitrogen 283 flow, 10 μ g of an internal standard (*n*-C₃₆) was added and the samples were dissolved in hexane before 284 injection in gas chromatography-mass spectrometry (GC/MS). The untreated powder (about 1 g) was 285 sonicated for 15 min in 4 mL of methanol, before adding 80 µL of sulphuric acid and heating at 70°C 286 for 4h (54). The methylated lipids were extracted three times in hexane before analysis in GC/MS. Samples with sufficient lipids (> 10 μ g g⁻¹) were injected in gas chromatography-combustion-isotope 287 288 ratio mass spectrometry (GC-C-IRMS), to study the stable carbon isotope composition of palmitic and 289 stearic acids and to verify the presence of marine fats.

290 Instrumentation

291 The analyses were performed on an Agilent 7890A chromatograph, equipped with a DB5-HT column 292 (30 m x 0.25 mm i.d., 0.1 µm film thickness, Agilent J&W), via splitless injection. The temperature 293 program was as follows: the oven was maintained at 50°C for 2 min, then the temperature was raised 294 to 325°C at 10°C min⁻¹, and held for 15 min. The mass spectrometer used was an Agilent 5977B, used 295 in electron ionization mode (EI, 70 eV), with mass spectra acquisition between m/z 50 and 1000. The 296 presence of tartaric acid was identified from the mass spectrum of trimethylsilylated tartaric acid 297 dibutyl ester (m/z 147, 276 and 391) (53). In some samples, a peak of trimethylsilylated tartaric acid 298 methyl butyl ester (m/z 147, 234, 276 and 349), resulting from the reaction with residual methanol 299 from the DCM/MeOH extraction, was also considered for quantification. Other small acids were also 300 identified from the mass spectrum of their trimethylsilylated dibutyl ester: malic (m/z 145, 161, 173, 301 217 and 303), succinic (*m/z* 101, 157), fumaric and maleic (*m/z* 99, 117, 155, 173), malonic (*m/z* 87, 302 105, 143) and oxalic (m/z 57, 87, 130) acids. GC-C-IRMS analyses were performed using a Hewlett 303 Packard 7890B series gas chromatograph (Agilent Technologies) with an Isoprime GC5 interface 304 coupled to an Isoprime 100 isotope ratio mass spectrometer. The carrier gas (helium) was used at a 305 constant flow rate of 3 mL/min. The samples were analysed in a DB-5MS fused silica column (60m× 306 0.25 mm× 0.25 µm; J&W Scientific), after injection of 1 µL of sample via a splitless injector at 300°C. The eluted compounds were ionized by electronic impact (70°C). The ${}^{13}C/{}^{12}C$ ratio of each peak was 307 308 calculated from measurements of the ion intensities of m/z 44, 45 and 46. The calculations were 309 carried out by comparison with measurements of a standard reference gas (CO_2), and the results are 310 expressed compared to the international standard Vienna Pee Dee belemnite (VPDB), in m/z (‰).

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- 472 Figure legends
- Table 1: Overview of the archaeological samples examined in this study. * The origin of the pots,
 identified based on typological characteristics and the composition of ceramic pastes, is indicated in
 parentheses. More detailed information on amphora type and dates is available in Supplementary
 Information (SI Appendix, Table S1 and Fig. S1).

Fig. 1: Map of all the sites studied and details on the Sicilian trade routes during the Islamic period. 477 478 The sites are shown by period: 5th to 7th century (blue circles); 8th to 9th century (green circles), and 479 10th to 11th century (orange circles): Castello Brina (1), Via Cavalca (2), Via Sapienza (3), Largo delle 480 Monache Cappuccine (4), Stazione Universita', Piazza Bovio (5), Santa Maria degli Angeli, detta della 481 Gancia (6), Castello San Pietro (7), Palazzo Bonagia (8), San Miceli (9), Mazara del Vallo (10), Casale 482 San Pietro (11), Valle dei Templi, Quartiere Ellenistico (12), Piazza Armerina, Islamic village (13), 483 Piazza Armerina, Excavation Gentili (14), Rocchicella di Mineo-Paliké (15), Catacombe di Siracusa 484 (16), Althiburos (17). Black diamonds indicate the main towns and ports in the central Mediterranean between the 10th and 11th centuries, and the lines show the main direct (solid) and 485 486 indirect (dashed) Sicilian maritime trade routes, according to the distribution of Palermo's pottery

- 487 production and historical documents (6, 8).
- 488 Fig. 2: Extraction yields of tartaric acid in transport amphorae and control samples. a) Transport
- amphorae; b) Cooking pots; c) Tiles; d) Sediments. The number of samples analysed is shown in

491 Fig. 3: Results of tartaric (TA) and malic (MA) acids analysis in Early Medieval amphorae and

- 492 control samples. (A) Box plots of %TA, expressed as the % contribution of TA to the sum of TA and
- 493 MA, in various fruits and fruit products (data from the literature, detailed in SI Appendix, Table S4).
- The number of samples considered is shown in italics. (B) %TA in experimental pots used to contain
- 495 wine (filled circles) and degraded in different environmental contexts for 1 year (open circles). (C)
- 496 %TA in archaeological samples, plotted versus the amount of tartaric acid extracted (μg g⁻¹,
 497 logarithmic scale) in amphorae (blue filled circles), cooking pots (blue open circles), tiles (black
- 498 circles), Georgian *qvevri* (pink circles), and Viburnum foodcrusts (Zamostje, Russia; Bondetti et al.,
- 499 2020; yellow circles). The vertical dashed line indicates the %TA value of 35%. Archaeological
- samples yielding < 0.05 μ g g⁻¹ of TA are not shown in this figure but are reported in SI Appendix,
- 501 Table S3.

502 Fig. 4: Results of tartaric (TA) and malic (MA) acids analysis in amphorae by chronological period.

- 503 (A) %TA plotted against the amount of TA extracted (µg g⁻¹, logarithmic scale) in transport amphorae
- from the 5th-7th century, 8th-9th century, and 10th-11th century. (B) Examples of typical Palermitan
- amphora forms (from Sacco, 2018). (C) %TA plotted against the amount of TA extracted ($\mu g g^{-1}$,
- 506 logarithmic scale) in Palermitan amphorae from the 10th-11th centuries found in Palermo (green),
- 507 Castronovo di Sicilia (orange), Mazara (light blue), Sardinia (yellow), Tuscany (pink), and Tunisia (dark
- 508 blue). The type of trade is derived from the place where the amphorae were made, the location
- 509 where they were found and their date. Samples yielding < 0.05 μ g g⁻¹ of TA are not shown in this
- 510 figure but are reported in SI Appendix, Table S3. The number of samples yielding both malic and
- 511 tartaric acids in relation to the total number of samples analysed is indicated in italics. The dotted
- 512 grey line indicates the %TA value of 35%.

Table 1: Overview of the archaeological samples examined in this study.

Site	Region	Period group	Transport amphorae	Provenance group*	Control samples
Excavation Gentili (Piazza Armerina)	Sicily	5 th -7 th	3	nd	
Valle dei Templi, Quartiere Ellenistico (Agrigento)	Sicily	5 th -7 th	8	Imports (<i>Tunisia</i>) and Sicilian trade (<i>nd</i>)	
San Miceli (Salemi)	Sicily	5 th -7 th	13	Imports (<i>Tunisia</i>)	
Mazara del Vallo	Sicily	5 th -7 th	3	Imports (<i>Tunisia</i>)	
		10 th -11 th	22	Imports (<i>Tunisia</i>), Sicilian trade (<i>Palermo</i>) and local trade	
Rocchicella di Mineo- Paliké (Mineo)	Sicily	8 th -9 th	3	Imports (<i>Aegean</i>) and Local trade	
Catacombe di Siracusa	Sicily	8 th -9 th	1	Imports (Aegean)	
Casale San Pietro (Castronovo di Sicilia)	Sicily	8 th -9 th	2	Sicilian trade (<i>nd</i>)	23 cooking pots 7 tiles 4 sediments
		10 th -11 th	7	Sicilian trade (Palermo)	
Santa Maria degli Angeli, detta della Gancia (Palermo)	Sicily	10 th -11 th	5	Imports (<i>nd</i>) and local trade	18 cooking pots
Castello San Pietro (Palermo)	Sicily	10 th -11 th	5	Local trade	18 cooking pots
Palazzo Bonagia (Palermo)	Sicily	10 th -11 th	10	Local trade	15 cooking pots
Piazza Armerina, Islamic village	Sicily	10 th -11 th	1	Sicilian trade (<i>nd</i>)	
Althiburos	Tunisia	10^{th} - 11^{th}	1	Oversea export (Palermo)	
Castello Brina (Sarzana)	Northern Italy	10 th -11 th	2	Oversea export (Palermo)	
Stazione Universita', Piazza Bovio (Naples)	Southern Italy	10 th -11 th	1	Oversea export (Palermo)	
Via Cavalca (Pisa)	Northern Italy	10 th -11 th	4	Oversea export (Palermo)	
Via Sapienza (Pisa)	Northern Italy	10 th -11 th	4	Oversea export (Palermo)	
Largo delle Monache Cappuccine (Sassari)	Sardinia	10 th -11 th	13	Oversea export (Palermo)	

* The origin of the pots, identified based on the typological characteristics and the composition of ceramic pastes, is indicated in parentheses. More detailed information on amphora type and dates is available in Supplementary Information (Table S1 and Figure S1).



Figure 1







Figure 3



Figure 4