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1 INFLUENCE OF POROSITY ON LIPID PRESERVATION INTO THE WALL OF ARCHAEOLOGICAL POTTERY

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19 20 21 ABSTRACT

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24 Porosity of archaeological pottery is a key parameter to assess its ability to trap lipids during the use
25 of the pot and to preserve them overtime. Mercury intrusion porosimetry and gas chromatography
26 were used to study the distribution of porosity and the preservation of lipids in different chrono-
27 cultural contexts. The data obtained show that the porosity pattern, related to the raw materials and
28 the *savoir-faire* of the potters, influences the amount of lipids accumulated in the pottery. A
29 significant overall porosity together with high level of small pores is generally favourable to the
30 preservation of lipids, but variations related to the environmental context are observed.

31 32 33 KEYWORDS

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36 Organic residue analysis; Mercury intrusion porosimetry; Organic matter degradation; Pottery use

37 38 39 INTRODUCTION

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42 Organic molecules have proven to be absorbed inside the walls of unglazed pottery during their use
43 and to be preserved over millennia in archaeological vessels (Charters et al., 1997; Evershed, 2008;
44 Evershed et al., 1995; Regert, 2011). Thanks to the development of analytical techniques such as gas
45 chromatography, mass spectrometry and isotopic ratio mass spectrometry, a wide diversity of

46 natural substances was detected in archaeological pottery. The study of these organic residues
47 provided valuable data to understand past communities and their changes over time by investigating
48 pottery function (Drieu et al., 2018; Fanti et al., 2018; Salque et al., 2013) and the exploitation of
49 natural resources (e.g. Craig et al., 2011; Debono Spiteri et al., 2016; Evershed et al., 2008b).

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52 The porous nature of unglazed ceramics is known to be one of the key parameters allowing both
53 absorption and preservation of organic products inside pottery walls (Evershed et al., 2008a;
54 Shepard, 1956, p. 126). The absorption of liquid or semi-liquid substances inside the pores of
55 unglazed pottery is easily understood, and the analysis of non-porous vessels generally yields poor
56 results (Evershed, 2008), except if micro-cracks exist on pottery surface (Pecci et al., 2015, 2016). The
57 absorption of organic molecules inside the porous ceramic matrix is thought to be an essential factor
58 of their preservation over time (Eglinton et al., 1991; Heron and Evershed, 1993). Indeed, when
59 trapped into the pores, the organic molecules are protected from the surrounding sediment, in an
60 environment generally less favourable to the growth of microorganisms (pH conditions, availability of
61 oxygen, water, and nutrients; Aillaud, 2001, pp. 4–5; Evershed, 1993, 2008). Furthermore, part of
62 the organic compounds is located in small-size pores that strongly limit their access for fungi and
63 microorganisms (Evershed, 1993, 2008; Heron et al., 1991; Heron and Evershed, 1993). Thus,
64 porosity characteristics are thought to play an important role in both the absorption and
65 preservation of organic molecules within the pottery walls.

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68 Porosity of ceramic vessels has been investigated for studying pottery manufacture and firing
69 (Carvalho et al., 2006; Gomart et al., 2017; Maniatis and Tsirtsoni, 2002; Morariu et al., 1977;
70 Sanders, 1973; Sobott et al., 2014; Thér, 2016; Volzone and Zagorodny, 2014), physical properties
71 related to pottery function (Lapp, 2012; Moraru and Szendrei, 2010; Rice, 1987, pp. 350–354), and
72 resistance to degradation during burial (Bronitsky, 1986, pp. 225–231). However, although several
73 authors mention relationships between porosity and organic products trapped into pottery walls,
74 only few have investigated porosity in this view (Correa-Ascencio and Evershed, 2013; Matlova et al.,
75 2017; Namdar et al., 2009) and none have specifically studied the properties of absorption and
76 preservation of organic molecules detected in archaeological pottery using porosity analysis.
77 From a methodological perspective, porosity of archaeological pottery has been studied by producing
78 2D images using Scanning Electron Microscope (SEM; Carvalho et al., 2006; Correa-Ascencio and
79 Evershed, 2013; Maniatis and Tsirtsoni, 2002; Moraru and Szendrei, 2010) or 3D images by micro
80 tomography (Gomart et al., 2017; Kulkova and Kulkov, 2016; Sobott et al., 2014). Both techniques
81 have the advantage of being non-destructive, but quantitative study of the distribution of porosity
82 requires specific data processing (image analysing software or mathematical treatments of the
83 tomography data; Adrian De la Fuente and Vera, 2015; Aprile et al., 2014; Reedy et al., 2014, Thér,
84 2016). Mercury Intrusion Porosimetry (MIP), a technique specifically adapted to the quantitation of
85 the porosity that allows both the measurement of the total volume of pores and an estimation of the
86 pores distribution depending on their diameter (Giesche, 2006; Sobott et al., 2014), was used to
87 study the porosity of archaeological ceramics (Matlova et al., 2017; Morariu et al., 1977; Namdar et
88 al., 2009; Sanders, 1973; Sobott et al., 2014; Volzone and Zagorodny, 2014), but up to now, the
89 question of the influence of porosity on the preservation of organic molecules has not yet been
90 considered in this way

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With mercury intrusion porosimetry, the present study investigates the relationship between the amount of lipids preserved in archaeological potsherds and the porosity of the ceramic matrix (quantity of pores and distribution). This issue is addressed by studying the porosity of potsherds taken from three different chrono-cultural contexts and having preserved various quantities of lipids as determined by gas chromatography analysis. By improving our understanding of the impact of porosity on the amount of lipids extracted from archaeological sherds, this work aims, in the long term, to (i) determine if it is possible to build a selection grid for optimising sampling of archaeological pottery for lipid analysis; and (ii) better understand lipid absorption and preservation in pottery walls for in-depth interpretation of pottery use.

MATERIALS AND METHODS

Archaeological potsherds

Three archaeological sites, having different chronological and geographical locations, were chosen to represent different contexts of preservation which were either more, or less favourable to biochemical (anoxic vs. oxic conditions, basic vs. acid sediment) and physical degradation (various degrees of waterflow, wetlands).

The Pendimoun rock shelter was chosen to represent a context favourable to biochemical degradation processes, with oxic conditions of burial and basic sediments related to the calcareous geological environment. In this settlement, archaeological artefacts were also exposed to intensive leaching, due to the location of the site at a stratification joint between Jurassic limestones and Cretaceous marl-limestone (Binder et al., 1993). This site, situated in the south-east of France near the Italian border (Castellar, France), revealed archaeological remains from the Epipaleolithic to the Middle Ages (Binder et al., 1993). Thirteen samples dating from the Early Neolithic period (*Impressa* ware, 5720 to 5470 BCE; Binder et al., 2017) were selected for analysis. Pottery from this period was recovered in high amounts and is made of three main fabrics: granitoid, glauconitic and mixed granitoid and glauconitic earths (Binder & Sénépart, 2010; Gabriele, 2014, pp. 223–225). Due to the heterogeneity and complexity of mixed earths, only granitoids and glauconitic potsherds were sampled for the present study.

The site of Cuciurpula was selected because of its acidic sediment, unfavourable to microorganism activity (DeLaune et al., 1981; Drieu et al., 2018; Moucawi et al., 1981). Twelve potsherds were sampled from this open-air site dating from the end of the Bronze Age to the first half of the Iron Age and situated in the mountainous region of central south Corsica (Serra-di-Scopamena and Sorbollano, France; Peche-Quilichini et al., 2015). In-depth analysis of the ceramic fabric has not yet been carried out but most of the pottery seems to be made of local granitic earth with high quantity of non-plastic inclusions of variable grain size (Peche-Quilichini, 2010).

Clairvaux XIV was selected for its wet and anoxic environment, very unfavourable to biochemical degradation of lipids (Den Dooren De Jong et al., 1961; Eglinton et al., 1991). This site is one of a number of settlements surrounding the Lake of Clairvaux (Jura, France) ranging from the Neolithic to

136 the Bronze Age (Pétrequin and Pétrequin, 2016a) and is dated to the first half of the 4th millennium
137 BC (Pétrequin, 2016). For the present study, we selected thirteen potsherds, made of marl clay
138 tempered with ground limestone or calcite (Pétrequin and Pétrequin, 2016b).

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141 To limit excessive destruction of archaeological artefacts, a single fragment of pottery (between 2.5
142 and 4 g) was sampled on each ceramic vessel investigated. Unspecific samples (non-refitting sherds,
143 absence of decoration or chrono-cultural markers) were preferentially selected. Each sample was
144 then divided into two subsamples for lipid and mercury intrusion porosimetry analyses.

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147 Lipids extraction and analysis

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150 Sample treatment and analysis were carried out following Evershed et al. (1990) with slight
151 modifications. When visible residues existed on the surface of potsherds, they were sampled using a
152 clean scalpel blade. Following the vast majority of the literature on lipid residue analysis, the surface
153 of the potsherds (around 1 mm) was then removed using a clean scalpel blade to eliminate any
154 exogenous lipid. Around 2 g of ceramic sherd and between 20 and 100 µg of visible residue were
155 then crushed with a mortar and pestle and 20 µL of internal standard was added for quantitation (*n*-
156 tetratriacontane, 1 mg/mL in *n*-hexane). Lipids were extracted with 10 mL of
157 dichloromethane/methanol (DCM:MeOH; 2:1, v/v) by sonication (2 × 15 min). After centrifugation,
158 the supernatant was evaporated to dryness under a gentle stream of nitrogen and dissolved in
159 500 µL of DCM/MeOH to obtain the total lipid extract (TLE). An aliquot of the TLE (100 µL) was
160 evaporated to dryness and treated with 50 µL of *N,O*-bis(trimethylsilyl)trifluoroacetamide containing
161 1% trimethylchlorosilane (BSTFA; 70°C, 1h). The excess BSTFA was evaporated under nitrogen and
162 the sample recovered in 25 to 2000 µL of cyclohexane (depending on the amount of lipid matter
163 preserved) for high temperature gas chromatography analysis (HT GC).

164 1 µL of sample was introduced into an Agilent Technologies 7890A gas chromatograph, via an on-
165 column injector. The analysis was performed using a 15 m x 0.32 mm i.d. fused silica capillary column
166 (DB5-MS, 0.1 µL film thickness, Agilent J&W), and helium as carrier gas. The temperature programme
167 consisted of an increase from 50°C to 100°C at 15°C.min⁻¹, and then from 100°C to 375°C at
168 10°C.min⁻¹.

169 Gas-chromatography mass-spectrometry was used to determine the structure of the molecular
170 compounds, in particular to distinguish between molecules originating from the pottery use and
171 modern contaminants. These analyses were performed on a Shimadzu GC 2010 PLUS chromatograph
172 coupled to a Shimadzu QP 2010 ULTRA mass spectrometer. An aliquot of sample (1 µL) was injected
173 on a high temperature non-polar column (DB5-HT, 15 m x 0.322 mm i.d., 0.1 µm film thickness,
174 Agilent J&W) via a splitless injector. The GC temperature programme was as follows: 1 min
175 isothermal hold at 50°C followed by an increase to 100°C at 15°C.min⁻¹, then to 240°C at 10°C.min⁻¹
176 and to 380°C.min⁻¹ and a final isothermal hold for 7 min. The GC-MS interface temperature was
177 maintained at 300°C. The mass spectrometer was used in electron ionization mode (EI, 70 eV) and
178 mass spectra were acquired over the range *m/z* 50–950.

179 The lipid concentration was calculated by summing the area of all the peaks and comparing it with
180 the area of the internal standard peak. Modern contaminants, such as phthalates (easily identified by
181 the characteristic m/z 149 fragment), were excluded from the overall calculation.

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184 This study is part of a wider project of lipid analysis, in which large sets of samples were analysed for
185 each site (Drieu et al., 2018, submitted). For the present study a subset of samples was selected from
186 each of these assemblages to represent the complete range of lipid preservation inside the ceramic
187 walls at each site: the samples with the best preservation of lipids of each site were selected and
188 compared with samples with medium and very low preservation (Table 1). Potsherds from Clairvaux
189 XIV and Cuciurpula originate from a large diversity of ceramic types: cooking pots, serving and storing
190 vessels. The functional study of the pots, based on their content, shape and traces of use have been
191 published elsewhere (Drieu et al., 2018, submitted). Most of the samples from the site of Pendimoun
192 originate from pots of unknown function, especially because it was not possible to reconstruct the
193 form, and they did not display any traces of use (carbonised residues, traces of soot, etc.).

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196 Table 1: List of samples analysed during the study and lipid yield. * two distinct residues removed
197 from the internal and external surfaces of the pot.

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200 Mercury Intrusion Porosimetry

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203 Mercury intrusion porosimetry analyses were performed using microporosimeter Autopore IV
204 (Micromeritics). The pressure range of the technique was from sub ambient up to 400 MPa, in order
205 to cover a pore diameter range from approximately 360 μm to 3 nm. Archaeological samples were
206 broken into fragments having a small volume between 0.5 and 1 cm^3 (0.30 to 1.75 g), dried overnight
207 in an oven at 45 °C and introduced alone or in pairs in the analysis cell. A contact angle of 130° was
208 used for the calculation of the entrance diameter of pores, a value already used for mercury intrusion
209 porosimetry on archaeological samples (Sanders, 1973).

210 Considering equation (1) where P is the apply pressure; γ is the surface tension of the liquid
211 (mercury); θ is the contact angle between the liquid and the substrate; we can determine r , which is
212 the radius of the pores.

$$213 r = (-2 \gamma \cos \theta) / P \quad (1)$$

214 This method of characterisation is often used to study the porosity of different types of materials.
215 However, some assumptions need to be considered before discussing the results, such as the aging
216 of the samples, the presence of mineral post-deposits, but also the influences of the pressure on the
217 microstructure, the presence of residual air or humidity into the pores, the use of a cylindrical pore
218 model, etc. (as well explained by A.J. Klemm [2009]). In this study, the preparation of the samples
219 was designed to remove most of the remaining humidity without inducing any damage in the
220 microstructure, by gently drying the samples. The analytical conditions were tested on modern
221 pieces of ceramics in order to rule out the risk of damages due to the pressure. The presence of
222 visible carbonated deposits on some sherds from the site of Pendimoun is not correlated with a
223 reduced porosity, suggesting that they have limited impact on the post-depositional evolution of the

224 porosity, contrarily to what was stated in the literature (Bronitsky, 1986, pp. 228; Rice, 1987, pp. 353).
225 Finally, these analyses are semi-quantitative due to the use of the cylindrical pore model and the
226 presence of potential residual air or humidity. However, they provide useful comparative results
227 because they were carried out on similar ceramic materials and in the exact same analytical
228 conditions.

229 It is noteworthy to emphasize that this protocol does not specifically measure the porosity of the
230 internal surface of the pot. This is because mercury not only enters the samples through the pores of
231 the internal and external surface of the pot, but also enters through the fractured edges. The effect
232 of surface treatments, such as burnishing and the application of a slip is thus not measured. As
233 these treatments heterogeneously affect the surface properties of the pottery, we think that a
234 specific research project should be entirely dedicated to the study of the influence of the surface
235 properties of the samples. Consequently, as a first approach of the topic, we decided to restrict the
236 scope of this paper to the study of the influence of the core properties (microstructure) of the
237 ceramics.

238 To evaluate the ability of microorganisms to penetrate the pottery walls, the data of Total Intrusion
239 Volume were subdivided for each sample. Two types of pores were distinguished based on their
240 diameter: pores of diameter larger than 1 μm , accessible to microorganisms and pores with smaller
241 diameters («small pores»), where microorganisms cannot penetrate due to their size (generally in
242 the range of the micrometer; Davis et al., 1990, p. 21).

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245 RESULTS

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248 Porosity analysis

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251 Figure 1 details the results obtained on the pore distributions of the samples. The percentage of
252 overall porosity ranges from 14 to 36% of the volume of the sherd, and the percentage of the total
253 intrusion volume relative to «small pores» (diameters < 1 μm) ranges from 23 to 78% of the overall
254 porosity (Table 2).

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257 The samples from Pendimoun are distributed in three different porosity groups (Table 2). Samples
258 from the first group (AP1; LD10700a, LD10702a, LD10703a, LD10716a, LD10718a, LD10720a and
259 LD10723) are characterised by:

- 260 - an overall porosity between 22 and 25%,
- 261 - between 48 and 67% of pores having a diameter < 1 μm («small pores»),
- 262 - three main types of pores having a diameter around 10 μm , around 4 μm and between 0.03
263 and 0.15 μm (Figure 1a),
- 264 - less than 7 $\mu\text{g.g}^{-1}$ of lipids preserved.

265 A second group (AP2; LD10711, LD10724, and LD10731) which included three samples made of
266 granitoid paste with:

- 267 - much smaller overall porosity, between 16 and 19%,

- 268 - a smaller quantity of «small pores» having a diameter < 1 µm (44 to 45%),
269 - one main pore type with a diameter between 0.5 and 4 µm (Figure 1b),
270 - between 1.2 and 34.1 µg.g⁻¹ of lipids preserved.

271 The third group (AP3; LD10710, LD10713, and LD10714; Figure 1c) comprised samples with:

- 272 - a small percentage of overall porosity (14 to 20%),
273 - between 23 to 40% of «small pores» having a diameter < 1 µm,
274 - two main types of pores having a diameter around 4 µm and around 10 µm,
275 - less than 6.6 µg.g⁻¹ of lipids preserved.

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278 Figure 1: Differential distribution curves measured by mercury intrusion porosimetry for the
279 archaeological potsherds. a) Group AP1; b) Group AP2; c) Group AP3; d) Group Cuci1; e) Group Cuci2;
280 f) Group Cuci3; g) Group Cl1; h) Group Cl2. Dotted lines indicate the main types of pores discussed in
281 the text.

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284 The percentage of overall porosity is more homogeneous for the samples from Cuciurpula (21.8 to
285 28.7%). Three groups of samples can nonetheless be distinguished based on the distribution of the
286 pore diameters (Figure 1d, e, f). The first group (Cuci1; LD10659, LD10665, and MR2707) is defined
287 by samples having:

- 288 - between 49 and 45% of «small pores» with diameters < 1 µm
289 - two main types of pores with diameter of around 10 µm and 4 µm, and a smaller number of
290 pores between 0.1 and 1 µm (Figure 1d)
291 - low preservation of lipids (0.94 to 15.1 µg.g⁻¹ of lipids).

292 The second group (Cuci2; MR2696, MR2698, MR2711, and MR2717) is characterised by:

- 293 - a percentage of «small pores» higher than the group Cuci1 (55 to 57%)
294 - three main types of pores with diameters close to 10 µm, 4 µm and between 0.01 and 0.1 µm
295 (Figure 1e).
296 - overall low preservation of lipids except one sample that yielded 316.4 µg.g⁻¹ of lipids.

297 A third group (Cuci3; LD10656, LD10667, LD10676, MR2699 and MR2701) includes samples
298 characterised by:

- 299 - between 46 and 51% of «small pores» with diameters < 1 µm
300 - homogeneous porosity profile without clear peaks (Figure 1f)
301 - diverse preservation of lipids: two samples yielded respectively 0.2 and 25.0 µg.g⁻¹ while the
302 remaining three preserved between 153.3 and 856.2 µg.g⁻¹ of lipids.

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305 Samples from Clairvaux XIV were divided in two groups, mainly defined by their percentage of
306 porosity (Figure 1g, h). The first group (Cl1; LD10100, LD10101, LD10103, LD10114, LD10126, and
307 LD10133) comprised samples having:

- 308 - overall porosity between 25 and 36%
309 - less than 65% of «small pores»
310 - two main types of pores with diameters between 6 and 200 µm and between 0.02 and 1 µm
311 (Figure 1g).
312 - less than 22 µg.g⁻¹ of lipids preserved.

313 The second group is composed of the seven samples (Cl2; LD10104, LD10113, LD10117, LD10125,
314 LD10129, LD10130, and LD10131) displaying:
315 - overall porosity between 23 and 30%
316 - large quantity of «small pores» (more than 65%).
317 - one main type of pores with a diameter between 0.02 and 1 μm (Figure 1h)
318 - excellent preservation of lipids (between 95.1 and 901.9 $\mu\text{g.g}^{-1}$, except for LD10104, yielding
319 3.5 $\mu\text{g.g}^{-1}$ of lipids.

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322 Table 2: Table summarising the results obtained by lipid and mercury intrusion porosimetry analyses
323 for all groups analysed.

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326 Comparison between lipids preservation and porosity

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329 Figure 2: Lipid concentration (TLE, $\mu\text{g.g}^{-1}$) versus overall porosity (a) and «small pores» (diameters < 1
330 μm) (b).

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333 All the samples preserving lipids have specific porosity values (between 18 and 30% of overall
334 porosity and 43 and 78% of «small pores» of diameters < 1 μm ; Figure 2), potentially suggesting a
335 range of % overall porosity and % of pores of «small pores» (diameters < 1 μm) that favours the
336 preservation of the lipids absorbed into the ceramic matrix.

337 Particularly, the quantity of «small pores» (diameters < 1 μm) seems to be related to lipid
338 preservation (Figure 3). This relationship is notably seen for extreme cases: for example only one of
339 the eight samples displaying less than 45% of «small pores» with diameters < 1 μm yielded more
340 than 20 $\mu\text{g.g}^{-1}$ of lipids (Figure 2b). On the contrary, among the six samples with more than 70% of
341 «small pores» of diameter < 1 μm , five preserved lipids (Figure 2b). The samples having significant
342 percentage of overall porosity (more than 26%; LD10100, LD10103, LD10114, LD10133, LD10659,
343 MR2707, LD10665, LD10126), seem to better preserve lipids when their porosity is mostly made up
344 of «small pores» (more than 65% of pores of diameter < 1 μm).

345 The near absence of lipids in some samples which have a large quantity of «small pores» (LD10104,
346 LD10700, LD10702, LD10703, LD10716, LD10718, LD10720, LD10723, MR2698, MR2699, MR2711,
347 MR2717) could be related to other parameters such as chemical degradation or specific use of the
348 vessels for non-fatty substances. This latter hypothesis is confirmed for 4 samples from Cuciurpula
349 (MR2698, MR2699, MR2711, and MR2717) bearing visible surface residues that yielded very low
350 amounts of lipids (between 3 and 84 $\mu\text{g.g}^{-1}$, when other visible residues at the site contain several
351 hundred $\mu\text{g.g}^{-1}$; Table 1 and Drieu et al., 2018).

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354 Figure 3: Degree of preservation of lipids depending on «small pores» < 1 μm . Samples with TLE > 20
355 $\mu\text{g.g}^{-1}$ are considered as well preserved and those with TLE < 20 $\mu\text{g.g}^{-1}$ are considered as badly
356 preserved. The percentage indicated corresponds to the % of well-preserved samples for each
357 category of size distribution of «small pores» < 1 μm .

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The impact of «small pores» is mainly seen in potsherds from Pendimoun and Clairvaux XIV (Figure 2b), as they display extreme cases of porosity: a very low quantity of «small pores» in Pendimoun and a very high quantity in Clairvaux XIV. At Pendimoun, samples with less than 40% of «small pores» (LD10713 and LD10714) did not preserved any lipids, while the only sample yielding more than 20 $\mu\text{g.g}^{-1}$ of lipids displays such pores, even in small quantities (LD10731, 44% of pores < 1 μm). Samples from Clairvaux XIV with both a high quantity of «small pores» and absence of pores of large diameter (more than 10 μm ; Group Cl2) seem to preserve the highest quantity of lipids: 85% of samples yielding more than 20 $\mu\text{g.g}^{-1}$ are also characterised by more than 65% of «small pores» with diameters smaller than 1 μm . At Cuciurpula, the porosity range seems to have a lesser impact on the preservation of lipids into pottery walls, as lipids are better preserved inside samples with a very homogenous distribution of pores (Group Cuci3).

DISCUSSION

Diversity of the porosity pattern and making of the pottery

Pottery from the three sites investigated presents various patterns of porosity (Figure 4): sherds from Clairvaux XIV are the most porous (mean value of overall porosity of 28%) with the highest level of «small pores» < 1 μm (mean value of «small pores» of 66.%) while the opposite is observed for the site of Pendimoun (mean value of overall porosity of 25%; mean value of «small pores» of 50.%). The site of Cuciurpula presents intermediate values (mean value of overall porosity of 21%; mean value of «small pores» of 66%). This diversity reflects different manufacturing *chaînes opératoires* between sites: differences in terms of the nature of the clay, quantity, nature and granulometry of non-plastic inclusions, intensity of handling, and firing conditions (Bronitsky, 1986, p. 226; Rice, 1987, p. 351; Rye, 1981, pp. 40 and 122; Shepard, 1956, p. 126; Skibo, 2013, p. 40). For example, at Pendimoun, the small percentage of overall porosity of some samples (groups AP2 and AP3) and the absence of very small pores (less than 0.1 μm) are to be compared with petrographic information. Sherds investigated are all made of granitoid earth and comprised very large quantities of non-plastic inclusions and a very small amount of clay matrix (Binder & Sénépart, 2010). This specificity of the ceramic paste could explain the absence of very small pores, that are probably related to clay structures and cannot exist if no clay fine fraction is present. At Clairvaux, the porosity seems to be related to the level of *savoir-faire* (Pétrequin and Pétrequin, 2016b): the best made ceramics generally have low overall porosity and high amount of «small pores».

Figure 4: Overall porosity versus «small pores» (diameter < 1 μm) depending on the sites investigated.

Relationship between porosity and preservation of lipids

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405 Given the diversity of environmental contexts considered in this study, the diameter of the pores
406 appears to impact different types of lipids degradation processes.

407 First, our results confirm that the presence of «small pores» limits the degradation of lipids by
408 microorganisms, as supposed in the literature. Generally larger than 1 μm , (Davis et al. 1990, p. 21)
409 most of bacteria and fungi are not able to enter pores smaller than this size. Thus, the lipids within
410 the ceramic matrix are protected from microbial degradation (Evershed, 1993, 2008; Heron et al.,
411 1991; Heron and Evershed, 1993; Matlova et al., 2017; Saboyainsta and Maubois, 2000). This
412 property has been exploited in food science for microfiltration: porous ceramic fabrics with pore
413 diameters under 1.4 μm are used as effective milk microfiltration devices, removing up to 99.75% of
414 microorganisms responsible for the biochemical degradation of milk (Saboyainsta and Maubois,
415 2000; Trouvé et al., 1991). The impact of porosity on the degradation of lipids by biochemical
416 degradation was probably important at the site of Pendimoun, but limited at Clairvaux XIV and
417 Cuciurpula respectively due to the anoxic context of Clairvaux and the acidic sediments of Cuciurpula
418 (Drieu et al., 2018, submitted) considerably reducing microbial activity.

419 Other degradation processes therefore need to be considered to explain the impact of porosity on
420 the preservation of lipids at Clairvaux. In this wet environment, reduced transport of water through
421 porosity is more likely to explain good preservation of lipids in «small pores». Following Poiseuille
422 equation, for a laminar flow of water, the smaller the radius of the pore the slower the flow rates
423 through it. In «small pores», the slowing of the water flow probably limits the leaching of absorbed
424 lipids, and possibly reduces hydrolysis. A similar hypothesis has also been suggested to explain the
425 poor preservation of chlorine in Late Neolithic salt moulds (Ard and Weller, 2012). This type of
426 degradation process may have also occurred at Pendimoun. Indeed, despite the limited rainfalls of
427 the Mediterranean climate, this rock shelter is exposed to a significant water flow related to its
428 geological location, as evidenced by the substantial calcium carbonate deposits on the potsherds
429 from the site (Binder et al., 1993). At Cuciurpula, leaching is probably limited as the site is open-air,
430 without rock walls favouring water flow.

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433 The effect of other parameters on lipid degradation in archaeological samples should also be
434 examined in the future.

435 First, the impact of pottery surface treatment (slipping, burnishing) on the absorption and the
436 degradation of organic matter has never been studied in-depth, to the best of our knowledge (Reber,
437 2007). However, this type of treatment considerably modifies the surface of the pots by promoting
438 smaller pores at the surface of the walls, probably affecting both the preservation of lipids and the
439 amount absorbed during pottery use (Correa-Ascencio and Evershed, 2013; Reber, 2007). A protocol
440 for coating the edges of potsherds with polymer resin is under development to specifically measure
441 the porosity of the internal surface of the vessels. This investigation will be particularly useful to
442 better understand some samples from Pendimoun that display evidence of deep burnishing (Binder
443 et al., 1993; Binder & Maggi, 2001), not reflected in the core porosity measured in the present study.
444 Secondly, hydrolysis is not the only chemical reaction responsible for the degradation of lipids in
445 archaeological samples: radical oxidation, photo-oxidation, and reduction also affect the lipid content
446 (Aillaud, 2001; Heron and Evershed, 1993) and porosity has probably no impact on it.

447 Finally, the actual use of pottery is a key parameter influencing the amount of lipids absorbed and
448 preserved in archaeological potsherds. The absence of lipids in numerous samples from Pendimoun
449 may not be due to their degradation but to specific use of pottery in this early phase of the Neolithic
450 in the western Mediterranean, to transform cereals or to store water, for example, as suggested by
451 other researchers (Spiteri et al., 2017).

452

453

454 CONCLUSION

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457 This article has revealed that when potsherds are exposed to normal microbial activity (as at the site
458 of Pendimoun) or to water (at Clairvaux XIV, and to a lesser extent at Pendimoun), the range of
459 porosity inside the pottery walls is of importance for the preservation of lipids. When trapped in
460 «small pores» (less than 1 μm of diameter), lipids are protected from microorganisms, but also from
461 leaching. A high abundance of «small pores» of diameter $< 1 \mu\text{m}$ in pottery walls favours thus the
462 preservation of lipids in archaeological samples, by reducing biological (microorganism activity),
463 physical (leaching) and possibly chemical (hydrolysis) degradation.

464 In very specific environments when leaching is limited, and microorganism activity reduced, porosity
465 appears to have a limited impact on the preservation of lipids. The site of Cuciurpula considered in
466 this study meets these criteria, but other types of archaeological contexts, such as arid or frozen
467 environments, should be considered and studied in the future.

468 These first results need now to be confirmed with new analyses of larger sample sets from a range of
469 environmental contexts (acid and basic soils, arid, frozen and submerged environments). A better
470 understanding of the preservation of lipids in porous ceramic matrices could lead to more selective
471 sampling of pottery in the future, avoiding the destruction of archaeological potsherds unlikely to
472 have preserved lipids. Secondly, mercury intrusion porosimetry can be used as a new tool for
473 functional analysis allowing a better understanding of the process of penetration of organic
474 substances into the porous walls of ceramic vessels and the degradation likely to have occurred. In
475 particular, this technique can be used to understand the use of ceramic vessels yielding small
476 amounts of lipids, such as in the Mediterranean.

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478

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481

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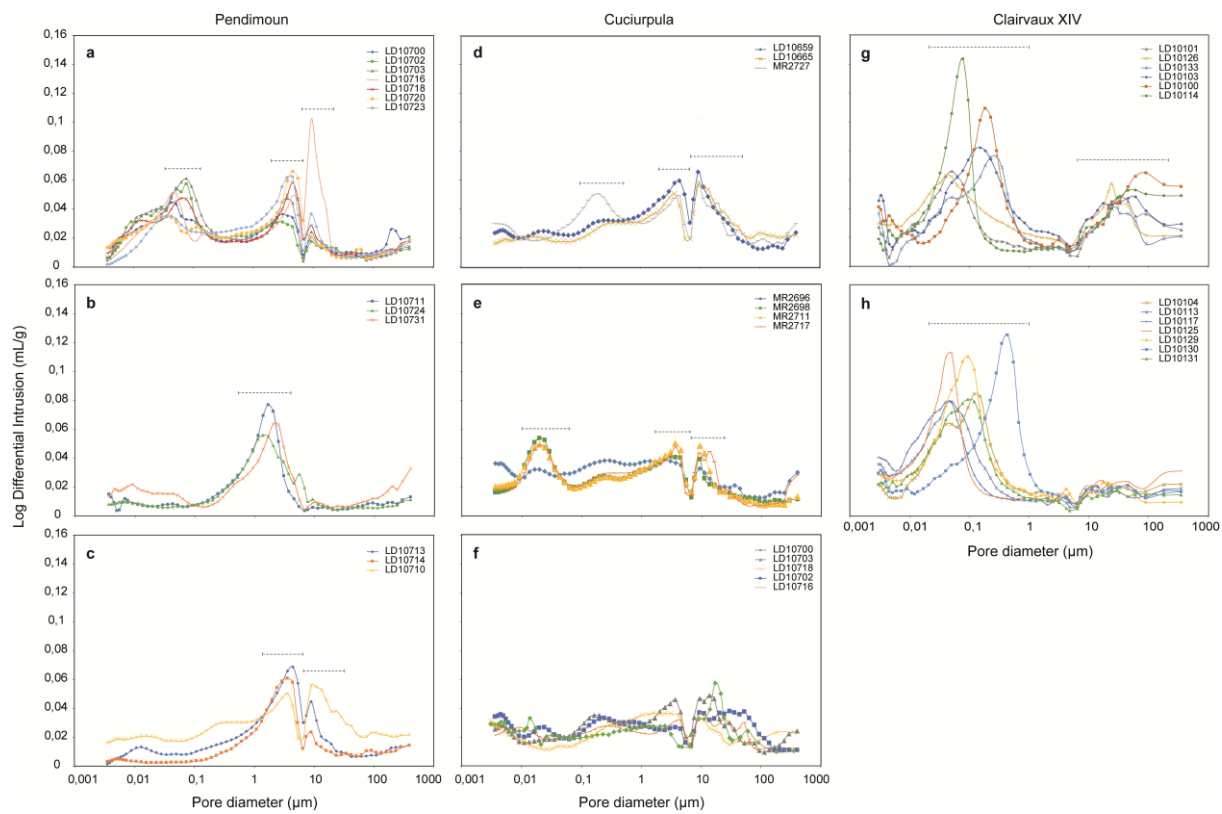
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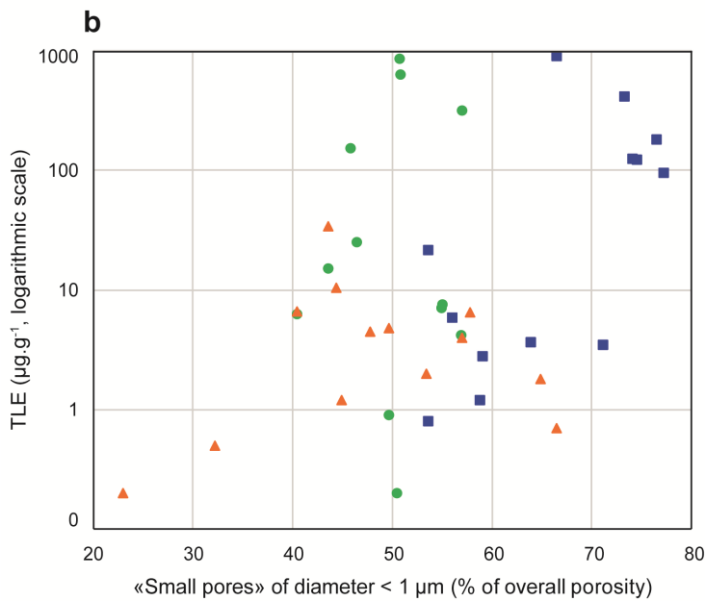
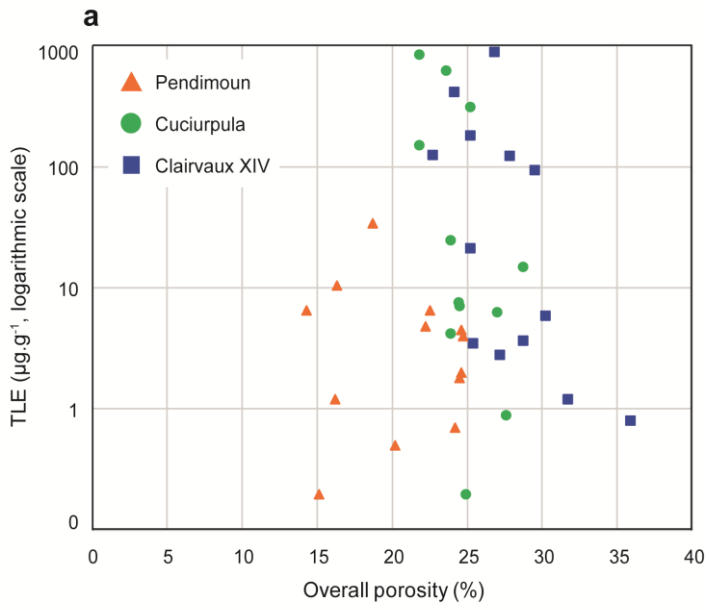
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799 FIGURES
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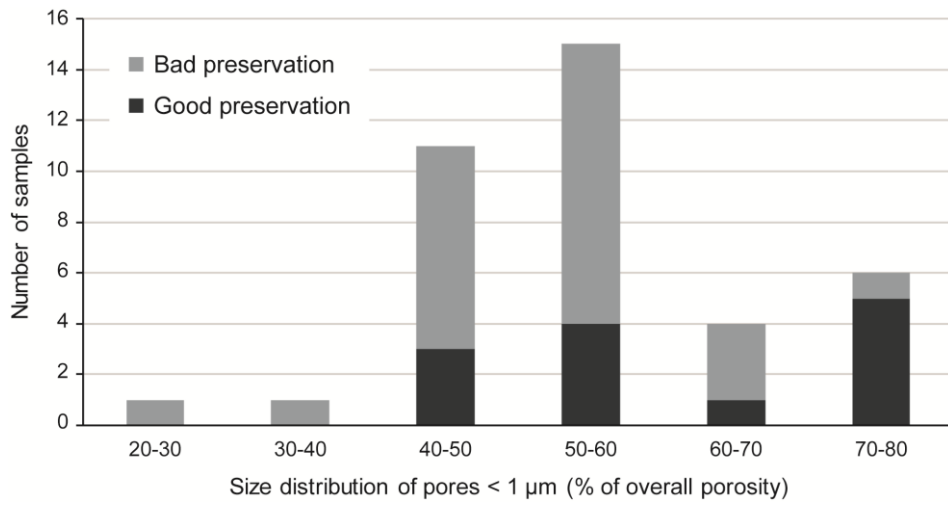


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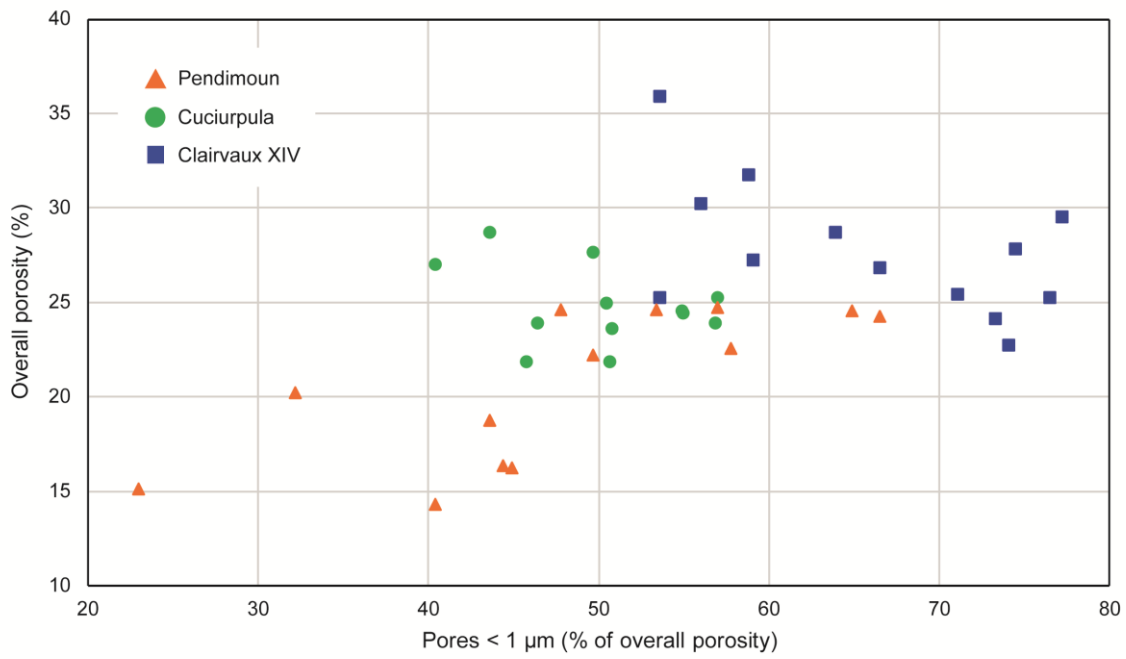
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Figure 2



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