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# The Missing Step of Pottery *chaîne opératoire*: Considering Post-firing Treatments on Ceramic Vessels Using Macro- and Microscopic Observation and Molecular Analysis

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## Abstract

Post-firing treatments, produced by the interaction of an organic material with the hot surface of a ceramic, are frequently described in ethnographic literature, but have rarely been identified in archaeological ceramic assemblages. In order to address this question, this paper describes a methodology that combines macro- and microscopic observation and molecular analysis. The study of experimental ceramic vessels provided diagnostic tools to identify the type of substances, their liquid or solid state, and their mode of application and attested that the post-firing treatments do not completely waterproof the ceramics. The difficulty to observe macro- and microscopic evidence of post-firing treatments when pots are fired in reducing atmosphere suggests that these processes are probably underestimated in archaeological assemblages. Furthermore, the identification of molecular thermal transformation markers, such as ketones, calls into question their classical interpretation as markers for the cooking of fatty content. This pioneering work highlights the complexity of studying post-firing treatments, which leave small traces that are easily missed or misinterpreted. In order to address this issue, we propose a multi-analytical approach, which can serve as a basis for future studies to explore the full diversity of post-firing treatments mentioned in ethnoarchaeological literature.

**Keywords** Post-firing treatments · Ceramic *chaîne opératoire* · Surface and edges aspects · Organic residue analysis · Ketones · Waterproofing

## Introduction

Reconstructing manufacturing techniques offers a way to determine the cultural and technical choices made by ancient craftsmen. Such work is therefore an important step

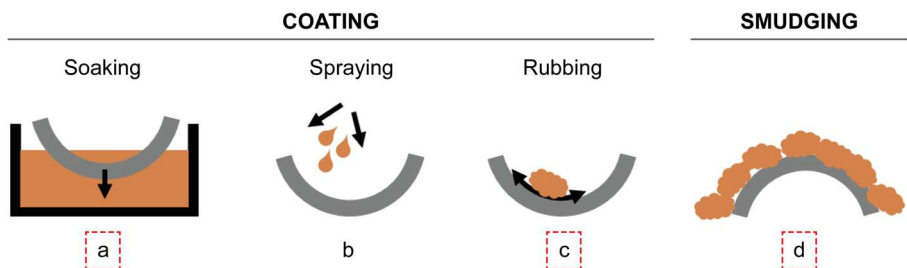
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towards understanding prehistoric human behaviour and cognition. In hand-built ceramic productions, *chaîne opératoire* studies are the main and most suited approaches to investigate technical processes (Arnold 2005; Arnold 1985; Gosselain 2002; Huysecom 1994; Pétrequin and Pétrequin 1999; Roux 2016). The main steps of the *chaîne opératoire*, such as supply of raw materials (e.g. Livingstone Smith 2000a; Spataro 2017), as well as hand-built ceramic production (e.g. Gomart et al. 2015, 2017; Livingstone Smith 2000b; Martineau 2010) and firing processes (Livingstone Smith 2000b; Martineau and Pétrequin 2000), have been largely studied but surface treatments have been much less addressed (Lepère 2009; Livingstone Smith 2010). Ethnoarchaeological literature attests to the great diversity of surface treatments involving organic products. These can be applied before the firing of the vessels, immediately after the removal from the fire, or after the cooling of the vessels. In this paper, we focus, among the so-called post-firing treatments, on those that are created by the contact between an organic product and the hot surface of a ceramic vessel at the end of the firing or immediately after the removal of the pottery from the fire or the oven. These processes generally generate a blackening of the surfaces.

Post-firing treatments have been mainly investigated from an ethnographic perspective and the ethnological models provide numerous examples (Arnold 1985; De Crits 1994; Gosselain 2002; Orton et al. 1993; Rice 1987; Shepard 1956; Sinapoli 1991). Two main techniques of post-firing treatments are traditionally distinguished, coating and smudging. Coating techniques imply the use of a natural or manufactured organic coating applied on the hot surfaces of the pottery. When the organic products are liquid (e.g. milk, blood, sap, decoction or infusion of roots, barks, leaves or fruits), they are applied by soaking, spraying or rubbing (Fig. 1a–c; Diallo et al. 1995; Gosselain 2002; Gosselain 1992a, 1992b; Harry et al. 2009). In solid form (e.g. moss, straw, resin, animal adipose fats), the products are directly rubbed on the surface, possibly causing the organic material to melt (DeBoer and Lathrap 1979; Gosselain 2002; Skibo 2013; Skibo et al. 1997). For smudging (Fig. 1d), the hot just-fired pots are covered with solid organic products (generally of vegetal origin, e.g. moss, chaff, bark, leaves or dung; Arthur 2002; Echallier 1984; Gosselain 2002; Longacre et al. 2000; Mahias 1994; Rice 1987; Rye 1987; Skibo et al. 1997).

These processes cut off the flow of oxygen at the surface of the pots and the blackening is probably induced by the burning of organic substances in the reduced atmosphere (Echallier 1984; Rice 1987; Rye 1981; Skibo et al. 1997). However, the exact mechanisms involved in post-firing treatments are still very poorly understood:



**Fig. 1** Simplified schema of the main techniques of post-firing treatments described in the literature. (a) Soaking, (b) spraying, (c) rubbing, (d) smudging. The various organic products involved in these processes are represented in orange and the ceramic in grey. The techniques studied during the experiments presented in this paper are surrounded in red

what is the degree of degradation of the organic substances? Is there production of new molecular compounds? How deep does the organic substance penetrate into the pottery walls? What is the impact of the surface treatment on ceramic properties (change in waterproofing properties, porosity, hardness, *etc.*), depending on the type of organic substances? Furthermore, the proxies to distinguish between the different types of post-firing treatments (type of organic product, state of this product, mode of application, temperature involved, *etc.*) on archaeological ceramic vessels are still lacking.

Observations on archaeological pottery suggest that the high diversity of post-firing treatments described in the course of ethnographic studies may date back to prehistoric times. Black surfaces possibly related to post-firing treatments have been identified on pottery from the Early Neolithic in the Balkans (Vinča and Danilo cultures; McClure et al. 2014; Spataro 2014), Middle Neolithic in south of France (southern Chassey culture; Lepère 2009; Martineau and Pétrequin 2000) and Middle and Late Neolithic in Macedonia and Greece (Schneider et al. 1991; Yiouni 2001). Identification of post-firing treatments is mainly based on ethnographic interpretative models and generally relies on the observation of the surfaces and the edges of the sherds. Only the extreme cases are usually identified: after an oxidising firing, such treatments produce black surfaces while the edge is totally pale (Martineau and Pétrequin 2000; Schneider et al. 1991). In a reducing atmosphere, it is generally accepted that the core and surfaces of the pot are dark in colour while the margins are oxidised (Gosselain 2002; Rye 1981). This suggests that when the oxygen input is brief, the very thin oxidised margins can be erased by the soaking of the organic treatment, making the identification of post-firing treatments more challenging. Furthermore, the distinction between coating and smudging remains poorly documented, even in the ethnographic record.

In brief, studies based on ethnographic materials shed light on some aspects of post-firing treatments, but a genuine and global method for reconstructing them in archaeological studies (type of organic product, mode of application, *etc.*) is still needed (Livingstone Smith 2010) and analytical tools must be developed to explore this step of the *chaîne opératoire*.

A complementary approach for studying post-firing treatments could be organic residue analysis. While such methods have been carried out on archaeological ceramic series for decades, most of the studies focused on the use of the vessels (*e.g.* for storage, cooking and serving; Evershed 2008a; Regert 2011). The only exception is non-edible organic products which, when identified in archaeological ceramics, are generally interpreted as evidence of cold surface treatment or of mending with organic substances (Heron and Evershed 1993; Bosquet et al. 2001; Rageot et al. 2016). Conifer resins have been highly investigated (*e.g.* Colombini et al. 2005a; McGovern et al. 1996; Reber and Hart 2008; Romanus et al. 2009), and it has been suggested that some other substances, such as beeswax (Charters et al. 1995; Garnier et al. 2002; Heron et al. 1994; Regert et al. 2001) or birch bark tar (Rageot et al. 2016; Regert et al. 2003; Urem-Kotsou et al. 2002), were used to waterproof pottery. The potential use of organic products for post-firing treatments involving the hot surfaces of the vessels has only been mentioned in biomolecular archaeology literature, without any experimental demonstration (Charters et al. 1993; Copley et al. 2005; Craig et al. 2005b; Heron and Evershed 1993). To the best of our knowledge, post-firing treatments have never been chemically studied, except by Diallo and co-workers, during a single experiment based on ethnographic observations in Cameroon and involving the coating of ceramics with bark decoctions (Diallo et al. 1995).

This paper presents two sets of complementary experiments of post-firing treatments, developed to understand the mechanisms that occur during this step of the manufacturing process (i) through macroscopic and microscopic observation and (ii) molecular analysis. The purpose of this study is to start building an analytical and interpretative model to (i) identify post-firing treatments on archaeological potsherds and (ii) determine the techniques of post-firing treatments that were used by ancient potters (application mode, temperature of the pots, type of organic product, *etc.*).

A first set of experiments was carried out to provide comparative pottery replicas for identifying various post-firing treatments by observing their surfaces and edges. Several processes and organic products were tested based on available ethnographic data, to evaluate how efficiently they covered the surface of the ceramic and to assess the percolation of organic product through the ceramic walls.

Based on these first results, a second series of experiments was set up to chemically investigate one of the post-firing treatments that leaves the strongest macroscopic traces and the more likely to generate molecular markers stable enough to be detected in archaeological potsherds. This second step of analysis is a critical investigation to understand (i) whether post-firing treatments can alter the lipid signal absorbed during the subsequent use in the pottery, by preventing the absorption of lipids related to use, or by combining to it, and (ii) if these two kinds of lipid inputs can be distinguished from each other.

## **Experimental Overview of Various Post-firing Treatments by Macroscopic and Microscopic Observation**

In order to reproduce the diversity of post-firing patterns observed in archaeological ceramic assemblages, three post-firing processes (soaking, rubbing and smudging) and four organic products (sheep fat, goat milk, moss and oak leaves) were tested (Table 1) in this first set of experiments. The replicas were studied by macro- and microscopic observation to evaluate the pattern variability on surfaces and edges and to determine whether the type of organic product and its way of application on the surface could be distinguished.

## **Materials and Methods**

### **Experimental Samples Manufacture**

In this first approach, various organic products (in terms of texture, chemical composition, possible application methods, *etc.*) were chosen in the hope of creating highly discriminatory patterns. They were chosen among the products available in abundance in the Neolithic contexts of the North-Western Mediterranean, where ceramic surfaces often suggest post-firing treatments. Sheep breast fat was obtained at the local slaughterhouse (Mandelieu-la-Napoule, France), and fresh goat milk in a local farm (Chèvrerie du bois d'Amon, Saint-Cézaire-sur-Siane, France). Moss and oak leaves were gathered in the surrounding landscape.

Experimental pots were handcrafted with cave clay (cave of la Baume Robert; Le Rouret, Alpes-Maritimes, France) tempered with calcite, using pinching and coiling techniques. Surfaces were scraped and then burnished. The pots were fired in oxidising

**Table 1** Experimental conditions for the macroscopic and microscopic observation of post-firing treatments

Experiment	Firing			Post-firing treatments		Replicas
	Structure	Temperature	Atmosphere	Organic product	Application mode	
A	Shallow pit	550–650	Oxidising	Sheep fat	Soaking	6
	Shallow pit	550–650	Oxidising	Goat milk	Soaking	6
	Shallow pit	550–650	Oxidising	Moss	Smudging	6
	Shallow pit	550–650	Oxidising	Oak leaves	Smudging	6
	Shallow pit	550–650	Oxidising	None	None	6
	Muffle furnace	700	Oxidising	Sheep fat	Soaking	1
	Muffle furnace	650	Oxidising	Goat milk	Soaking	1
	Muffle furnace	700	Oxidising	Moss	Smudging	1
	Muffle furnace	700	Oxidising	Oak leaves	Smudging	1
	Muffle furnace	700	Oxidising	None	None	1
B	Deep pit	550–650	Reducing	Sheep fat	Soaking	6
	Deep pit	550–650	Reducing	Moss	Rubbing	6
	Deep pit	550–650	Reducing	None	None	3
C	Shallow pit	580–700	Oxidising	Sheep fat	Rubbing	6
	Shallow pit	580–700	Oxidising	Moss	Rubbing	6
	Shallow pit	580–700	Oxidising	None	None	3
	Muffle furnace	650	Oxidising	Sheep fat	Rubbing	2
	Muffle furnace	650	Oxidising	Moss	Rubbing	2
	Muffle furnace	650	Oxidising	None	None	2

atmosphere in shallow pits and or in a muffle furnace for total control of the temperature parameter (Fig. 2a, c; Table 1, experiments A and C) and in deep pits in reducing atmosphere (Fig. 2b; Table 1, experiment B) for 1 h. Temperatures in the pits were recorded with thermocouple sensors located on the rim, the body and the base of the pots.

Immediately after firing, some pots were completely immersed in sheep fat or goat milk until completely chilled. Some others were covered with moss or oak leaves (both internal and external surfaces) for smudging (Table 1 experiments A and B; Fig. 2d, e). For the last set of replicas, the outer surface was rubbed with sheep fat, or moss to compare the impact of the organic product on the same way of application (Table 1, experiment C; Fig. 2f).

### Descriptive Criteria for Macro- and Microscopic Observation

Both ocular and stereomicroscopic observations (magnifications of  $\times 10$  to  $\times 60$ ) were carried out, mainly with oblique light. The descriptive method was systematised using several criteria, observed on the surface:

- Colour of the surface;
- Covering of the striations that result from the burnishing process;
- Covering of the non-plastic inclusions.





**Fig. 2** Firing and post-firing treatments. (a) Shallow pit for oxidising firing; (b) deep pit for reducing firing; (c) muffle furnace; (d) soaking in sheep fat; (e) smudging with moss; (f) rubbing with moss

And on the polished edges:

- Width of the external and internal margins (short, medium, large);
- Morphology of the external and internal margins (rectilinear, undulating or very undulating).

## Results and Discussion

The systematic observation of experimental pots reveals distinctive features between smudging and soaking when pots are fired in oxidising conditions (experiment A). The examination of sheep fat and goat milk-soaked surfaces shows that internal and external surfaces are black, even if irregular spills and colourations may occur (Fig. 3a). Furthermore, thin burnishing striations and small non-plastic particles are completely obliterated, and deep burnishing striations are partly covered (Fig. 3b). The colouring

and covering effects are stronger on sheep fat-soaked pottery than on the pots soaked in goat milk, suggesting that the lipid concentration may have an influence on the surface treatment efficiency. The total immersion of the vessels leaves almost identical traces on both surfaces of the vase, without discontinuity. As expected, when only one surface has been treated (experiment C, containers rubbed only on the outer surface), there is a clear separation on the rim between the two surfaces. Spills on the inner part of the vase have sometimes been observed on containers with the outer surface rubbed with sheep fat.

On smudged pottery, “black surfaces” are more superficial, with more colour variations, especially around the rim (Fig. 3c). The obliteration of burnishing striations and the non-plastic inclusions is much thinner.

Clearer distinctive patterns between the two techniques are observed on the edges. Soaking is characterised by black and grey margins, of large or medium width, with an undulating morphology (Fig. 4a). We suggest that organic matter is combusted as the liquid seeps through the wall, until a temperature too low to allow combustion is reached. On moss-smudged vases, the infiltration remains superficial, even if it can be locally deeper around the weaker parts of the vessel, such as coil junction (Fig. 4b). Comparing penetration through internal and external surfaces can also provide some information: soaking allows a regular penetration of the organic product into both surfaces while penetration in smudged pots is more variable.

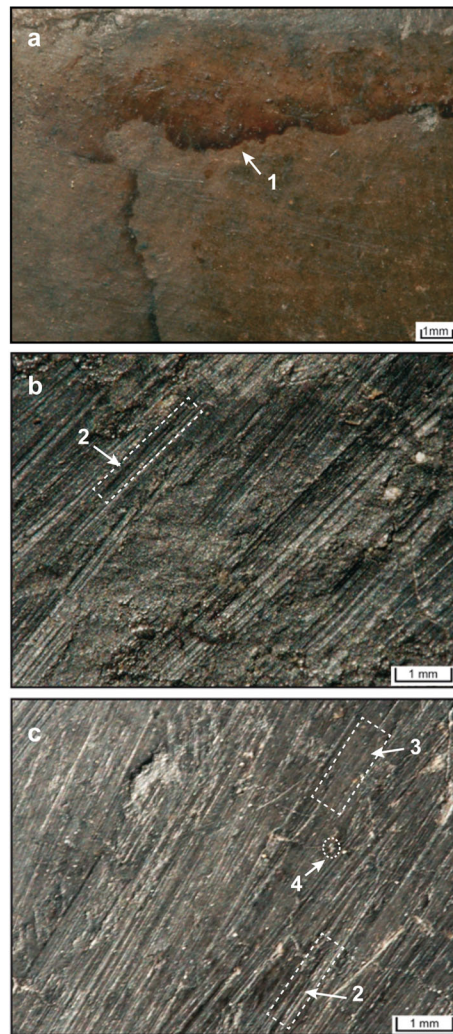
After reducing firings (experiment B), these distinctions remain: large dark margins are observed on soaked pots while the treatment seems more superficial for smudged replicas (Fig. 4c to f). The thick margins of the soaked vases are sometimes preceded by a red edging (Fig. 4c, d), but this pattern is not systematic (Fig. 4e, f). The absence of red margin is probably related to the quick application of the organic product (soaking or smudging) directly after the removal of the pots from the fire, preventing their oxidation (Gosselain 2002).

These patterns are also observed for pots rubbed with different organic products (experiment C). Rubbing with sheep fat causes obliteration of the burnishing striations and non-plastic inclusions and creates large dark margins on the edge, just like pots soaked in sheep fat. Replicas rubbed with moss present lighter obliteration of the burnishing striations and non-plastic inclusions and absence of penetration into the thickness of the wall, like the moss-smudged pots.

Based on this observation, we suggest that the variability of these traces is related to the type of products (type of molecular compounds) and/or to the state of the product (liquid or solid) rather than to the application mode (Table 2).

It is noteworthy that when several vessels are successively soaked in the same fatty material, the treatment efficiency is considerably reduced: the first vessel is entirely black, while the two following are only mottled with black spots and the colour of the last three remains unchanged. It therefore appears that the organic product used for post-firing treatment is modified by this process. It is very likely that the organic product is almost entirely consumed (due to absorption and carbonisation mechanisms) during a single operation. Differences in the temperature of the organic matter bath or of the walls of the vessels may also influence the phenomenon. New experiments could be conducted to discuss these mechanisms, by analysing the molecular composition of the organic matter bath before and after soaking the hot vessel.

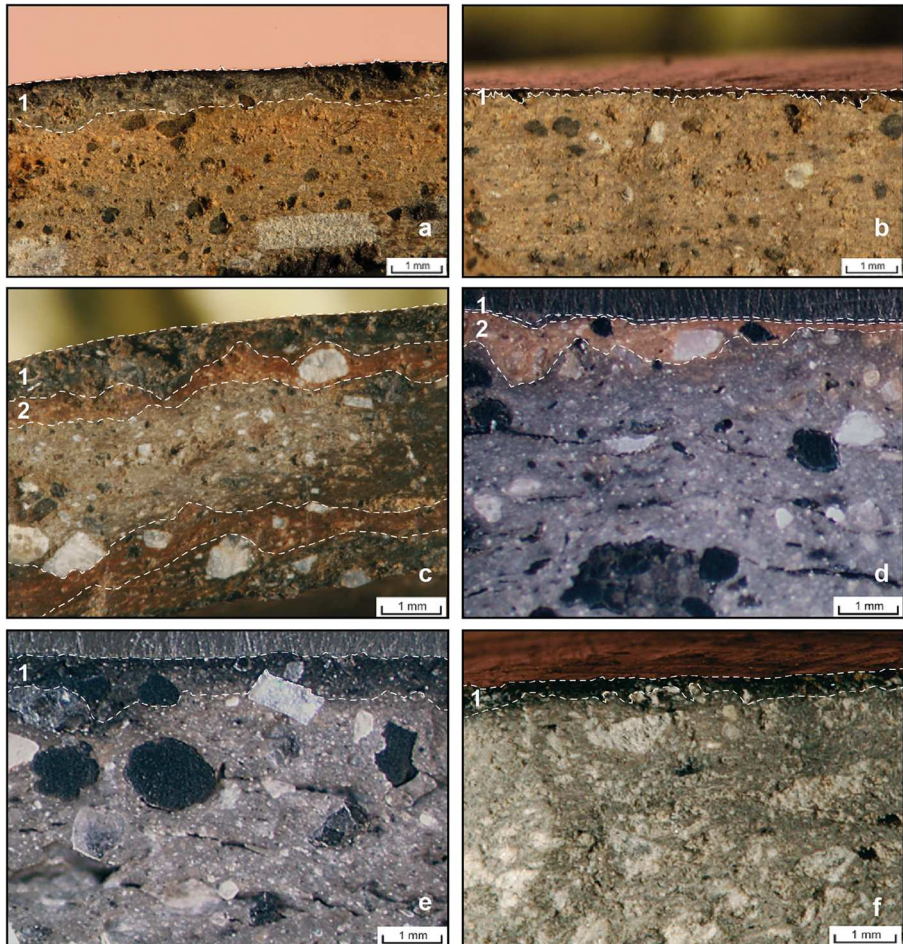




**Fig. 3** Comparison of surfaces after soaking and smudging processes (experiment A). (a) Resulting spills of fat after soaking in sheep fat; (b) partly covered burnishing striations after soaking in sheep fat; (c) very thin covering of burnishing striations after smudging with moss. 1: spills; 2: partly covered deep burnishing striations; 3: partly covered thin burnishing striations; 4: partly covered small non-plastic inclusions

## Controlled Laboratory Experiments for Molecular Investigation

These first data, together with some experiments in the literature, suggest a potential penetration of organic products into pottery walls during post-firing treatments (Martineau and Pétrequin 2000), but also the degradation of the molecular compounds due to the high temperature involved in such processes (400 to 600 °C; Gosselain 2002). This raises the question of the degradation degree of the organic product: is the degradation complete? If incomplete, could the molecular signal be used to identify the organic products used for surface treatment? Could this signal alter the one resulting from the subsequent use of the



**Fig. 4** Comparison of edges after soaking and smudging processes: (a) large dark margins (1) resulting from soaking in sheep fat on pots fired in oxidising conditions (experiment A); (b) thin dark margins (1) resulting from smudging with moss on pots fired in oxidising conditions (experiment A); (c) large dark margins (1) resulting from soaking in sheep fat on pots fired in reducing conditions with red margin (2) (experiment B); (d) thin dark margins resulting from smudging with moss on pots fired in reducing conditions with red margin (2) (experiment B); (e) large dark margins (1) resulting from soaking in sheep fat on pots fired in reducing conditions without red margin (experiment B); (f) thin dark margins (1) resulting from smudging with moss on pots fired in reducing conditions without red margin (experiment B)

pottery? To address these questions, a new set of experiments was built up with more controlled conditions, in order to create a model to evaluate the impact of post-firing treatments on the molecular content of pottery walls. The protocol was set up to limit the parameters that influence the absorption and degradation of organic compounds. A single organic product (lard) and a single way of application (rubbing) were selected. Firing was carried out in a muffle furnace for better control of the time and temperature. Lard was chosen because, as shown by our previous experiments, animal fats seem to be able to penetrate the pottery walls well, and because it is a product of well-known and rather simple molecular composition (*i.e.* only lipids, Dudd 1999). Furthermore, it is easy to purchase in

**Table 2** Summary of the results obtained from macroscopic and microscopic observation

	Surfaces		Dark margins on the edges
	Colouring	Non-plastic inclusion and burnishing striations	
Soaking in sheep fat	Very dark	Completely covered	Medium to large Regular
Soaking in goat milk			
Rubbing with sheep fat			
Smudging with moss	Superficial	Lightly obliterated	Thin Irregular
Smudging with oak leaves	Variable colour		
Rubbing with moss			

large quantities, which allows multiplication of the experiments to assess their reproducibility. Some non-treated pots were simply used to cook lard, to provide a comparison (i) of the penetration of organic products into pottery walls and (ii) of molecular composition resulting from cooking and post-firing treatments.

A second process was tested, involving the same way of application (rubbing) but pots were left to cool in the lard that melted during the operation. This experiment was set up to determine whether lipids are also absorbed during cooling and if this process (rubbing + cooling into organic product), frequently mentioned in ethnographic literature (Gosselain 2002), could be chemically distinguished from a simple rubbing.

To address the issue of a possible mixing with organic compounds originating from the subsequent use of the pottery, a third experiment was carried out by using post-firing treated pots to cook olive oil. Olive oil was chosen because its molecular profile is different from lard, with specific biomarkers easily identifiable (*e.g.* phytosterols).

## Materials and Methods

### Experimental Samples Manufacture

For this experiment, 15 ceramic cup replicas were manufactured in cave clay (cave of la Baume Robert, Le Rouret, Alpes-Maritimes, France), tempered with crushed quartz. After burnishing the whole surface, they were fired in a muffle furnace during 45 min at 650 °C (Table 3). Cups were removed from the furnace and six of them were allowed to cool down. The nine others, removed one by one, were rubbed with lard, using a metal clamp. During the operation, the lard melted and ignited in some samples; others only produced smoke. The cups were then allowed to cool, three of them still in direct contact with the lard that melted during the operation.

Three cups without post-firing treatments were used to simulate lard cooking on a sand bath heated to 100 °C for 1 h. Three cups coated after firing with lard were used to simulate olive oil cooking on a sand bath heated to 100 °C for 1 h. Lard (Saindoux Lardina, pure pork) and olive oil (Carrefour Bio, organic extra virgin olive oil, cold extracted) were purchased at the local supermarket.

**Table 3** Experimental conditions for the chemical analysis of post-firing treatments

Firing		Post-firing treatments		Use of the vessel	Replicas
Structure	Temperature (°C)	Organic product	Application mode		
Muffle furnace	650	Lard	Rubbing	—	3
Muffle furnace	650	—	—	Cooking lard	3
Muffle furnace	650	Lard	Rubbing	Cooking olive oil	3
Muffle furnace	650	Lard	Rubbing and cooling into melted lard	—	3
Muffle furnace	650	—	—	—	3

### Evaluation of the Waterproofing Properties

To assess the permeability of some of the experimental vessels (rubbed with lard after firing, used to cook lard, and not treated), one example of each was taken and filled with 40 mL of distilled water. After 1 h, the volume of water contained in each of the vessels was measured and then emptied. The vessels were weighed immediately after emptying ( $m_1$ ) and then after drying overnight ( $m_2$ ). The percentage of water absorbed was then calculated using the following formula (Bronitsky 1986):

$$\% \text{ of absorbed water} = \frac{m_1 - m_2}{m_2} \times 100$$

### Chemical Analysis

Sample treatment and analysis were carried out following Evershed et al. (1990) with slight modifications. A differential sampling protocol for internal and external surfaces and core has been implemented for most samples to compare the depth of penetration of organic matter into the wall during post-firing treatments and use. Few millimetres of the inner surface were ground using a modelling drill to obtain approximately 2 g of powder, the procedure was then repeated on the external surface. The exposed core of the vessel wall (few mm of thickness, around 2 g) was then sampled and crushed using a clean mortar and pestle. For cups coated and cooled in lard and the blank cups, the entire thickness of the wall was sampled and crushed using mortar and pestle, as these were only intended to evaluate differences in molecular composition, and not to study the penetration of the organic matter into the wall.

Tetratriacontane ( $n\text{-C}_{34}$ , 20  $\mu\text{L}$  of a 1  $\mu\text{g}/\mu\text{L}$  solution) was added to the ceramic powders as internal standard for quantification of the lipid extracts. The powders were solvent extracted with 10 mL of dichloromethane/methanol (2:1, v/v) by sonication ( $2 \times 15$  min) and centrifuged. The clear supernatants were evaporated under a gentle stream of nitrogen and the Total Lipid Extracts (TLE) were recovered in 500  $\mu\text{L}$  of dichloromethane/methanol (2:1, v/v).



An aliquot of the TLE (20  $\mu\text{L}$ ) was derivatised with *N,O*-bis(trimethylsilyl)trifluoroacetamide containing 1% trimethylchlorosilane (BSTFA; 20  $\mu\text{L}$ ) for 1 h at 70  $^{\circ}\text{C}$ . The excess BSTFA was evaporated under nitrogen and the sample dissolved in cyclohexane (2 mL) prior analyses by gas chromatography (GC) and gas chromatography–mass spectrometry (GC/MS). Few micrograms of lard and olive oil were also treated with BSTFA to provide reference samples for analysis.

GC analyses were performed using a gas chromatograph (Agilent Technologies 7890A) fitted with a high temperature non-polar column (DB5-MS, 15 m  $\times$  0.32 mm i.d., 0.1- $\mu\text{m}$  film thickness). The temperature of the oven was programmed as follows: initial temperature was 50  $^{\circ}\text{C}$  and increased to 100  $^{\circ}\text{C}$  at a rate of 15  $^{\circ}\text{C min}^{-1}$ , then from 100 to 375  $^{\circ}\text{C}$  at 10  $^{\circ}\text{C min}^{-1}$ .

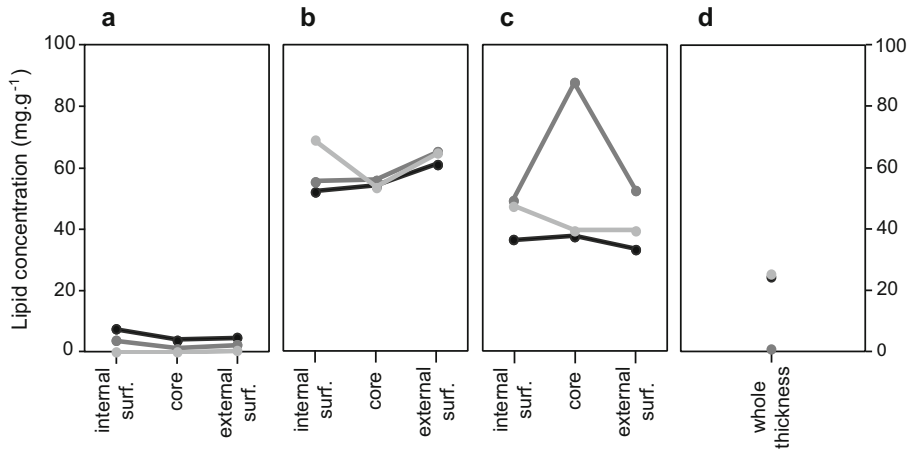
For GC/MS analysis, 1  $\mu\text{L}$  of sample was injected in splitless mode into a non-polar fused silica capillary column (DB-5HT column with a 0.1- $\mu\text{m}$  film thickness; 50 m  $\times$  0.32 mm i.d.). The analyses were performed on a Shimadzu GC 2010 PLUS gas chromatograph and the temperature programming was the following: after a 1 min isothermal hold at 50  $^{\circ}\text{C}$ , the temperature increased to 100  $^{\circ}\text{C}$  at 15  $^{\circ}\text{C min}^{-1}$ , then to 320  $^{\circ}\text{C}$  at 10  $^{\circ}\text{C min}^{-1}$ , then to 380  $^{\circ}\text{C}$  at 20  $^{\circ}\text{C min}^{-1}$  and was held at 380  $^{\circ}\text{C}$  for 7 min. The mass spectrometer was a Shimadzu QP 2010 ULTRA quadrupole run in EI mode (70 eV) and the spectra were recorded over the range  $m/z$  50–950.

## Results and Discussion

### Chemical Transformation During Post-firing Treatments

All the cups that have undergone post-firing treatments by rubbing with lard proved to have absorbed lipids (Fig. 5a, c). The amount of lipids in cups with simple lard rubbing ranges from 0.004 to 7.35  $\text{mg g}^{-1}$  (Fig. 5a). Inner and external surfaces yield more lipids than the core, a pattern that is consistent with the application of lard on surfaces during this process, though the difference is small. Vessels used to cook lard contain much more lipids (between 52 and 70  $\text{mg g}^{-1}$ ; Fig. 5b). Although patterns of absorption differ from one replica to another, it is noteworthy that liquid lard permeated the entire thickness of the walls during cooking, with no decreasing of concentration from internal to external surface. This suggests, at least for this type of cooking that does not involve water, that lipids continuously migrate through the pottery wall during the cooking process and accumulate on the external surface. The smaller amount of lipids (10 times less) absorbed during post-firing treatments compared to the cooking of lard is certainly due to the carbonisation of most of the lipid material when rubbing the very hot surface of the pottery. The contact duration with organic matter may also influence the amount of lipids absorbed. The blank replicas yield no lipids, confirming that the molecular signal from experimental vessels results only from the absorption of lard during post-firing treatments or cooking.

Typical chromatograms obtained for each experiment are presented in Fig. 6 and the relative distributions of triacylglycerols (TAGs) in Fig. 7. When sampling was differentiated between core, internal and external surfaces, no clear variation in the molecular profiles has been observed.



**Fig. 5** Lipid concentrations in (a) cups with post-firing treatments with lard; (b) cups used to cook lard; (c) cups with post-firing treatments with lard, used to cook olive oil; (d) cups with post-firing treatments with lard, cooled in the melted lard. The three curves correspond to the three replicates

In cups used to cook lard (Figs. 6b and 7b), the molecular composition of the lipid extract is very close to fresh lard, with large quantity of TAGs (85 to 91% of the TLE) displaying profiles largely dominated by  $T_{52}$  (Regert et al. 2005) and with a majority of  $C_{18:1}$  among the fatty acids (Dudd 1999). In cups with post-firing treatment,  $C_{16:0}$  is the major fatty acid and the TAGs are clearly degraded (0 to 22% of the TLE; Fig. 6a). Their profile, although still dominated by  $T_{52}$ , is more similar to that of ruminant adipose fats (Dudd 1999; Fig. 7a).

The clear difference of molecular composition absorbed in vessels rubbed with lard and in vessels used to cook lard is probably due to the difference of temperature involved in both processes (respectively around 650 °C and 100 °C).

The TAGs are hydrolysed in cups used to cook lard (some fatty acids are detected), but the mechanism left their distribution unaltered, as already observed in the literature (Evershed 2008b).

The degradation of lard during the post-firing process, with the heavier TAGs and fatty acids preferentially degraded over lighter ones, could be due to cracking processes (Kubátová et al. 2011; Schwab et al. 1988; Shimoyama et al. 1993), rather than hydrolysis and oxidation. This is also supported by the presence, in cups rubbed with lard after firing, of odd- and even-numbered short-chain fatty acids ( $C_{6:0}$  to  $C_{13:0}$ , maximum between  $C_{8:0}$  and  $C_{12:0}$ ), probably resulting from this mechanism. Indeed, even-numbered short-chain fatty acids ( $C_{4:0}$ – $C_{12:0}$ ) are present in fresh dairy products (Dudd 1999; Dudd et al. 1998; Evershed 1993) but this particular distribution of short-chain fatty acids including also odd-numbered ones has only been identified in experimental pyrolysis of lipid material (Raven et al. 1997; Schwab et al. 1988; Shimoyama et al. 1993). The variability in short-chain fatty acids profiles between replicates could be related to the combination of various cracking mechanisms (Shimoyama et al. 1993), due to the heterogeneity of the natural ceramic paste.

In all cups that underwent rubbing with lard, long mid-chain ketones, including symmetric (hentriacontan-16-one,  $K_{31}$  and pentatriacontan-18-one,  $K_{35}$ ) and



asymmetric (tritriacontan-16-one,  $K_{33}$ ) ones, are identified in small amounts. Symmetrical mid-chain ketones are common constituents of higher plant leaf waxes but the asymmetrical ketone ( $K_{33}$ ) is unlikely to be a component of a plant material (Kolattukudy 1970). These ketones are known to be formed by condensation of fatty acids, through decarboxylation and dehydration mechanisms occurring at more than 300 °C (Evershed et al. 1995; Raven et al. 1997), a temperature largely reached during the post-firing treatments that was tested. In cups simply used for lard cooking, the low temperature of the experiments, around 100 °C, did not allow their formation. In archaeological samples, it is noteworthy that the formation of ketones during repeated use of the same container on the fire cannot be excluded.

Cholesterol, a marker of animal fats, is detected in cups used to cook lard but it seems to be entirely degraded during post-firing treatment, probably due to the higher sensitivity of sterols to autoxidation when exposed to heat (Colombini et al. 2005b; Evershed et al. 1991; Evershed 1993).

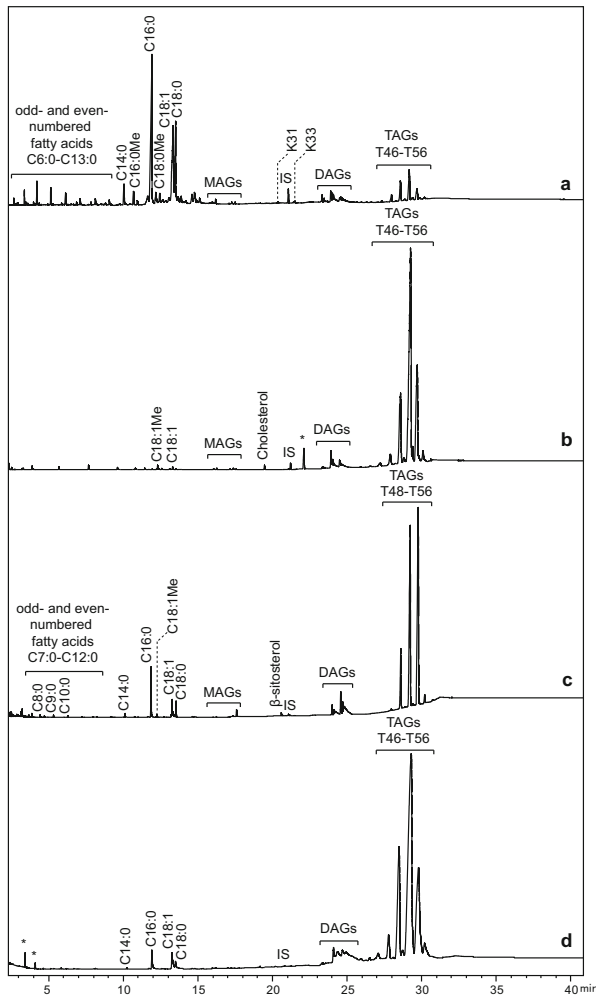
Methylated palmitic, oleic and stearic acids are identified in almost all the experimental cups, sometimes in higher amounts than the TMS fatty acids. Methylated fatty acids have been reported in experimental pyrolysis of lipids in the presence of inorganic matrices and is thought to be formed under vigorous pyrolysis (800 °C) by radical mechanisms (Raven et al. 1997). They are identified in post-firing treated cups but also in untreated cups, when lard was heated at 100 °C. These molecules were sometimes observed by one of us during cooking experiments of vegetable oils in vessels made of the same clay paste; the mechanism involved in their formation is still unclear but may be catalysed by metal salts from this natural clay matrix, even at low temperature. Methyl fatty acids are therefore unlikely to be adequate anthropogenic transformation markers of post-firing treatments.

### Sealing Effect of Post-firing Treatment

In cups rubbed with lard after firing and used to cook olive oil, a high quantity of lipids (30 to 80 mg g<sup>-1</sup>) were recovered, with variable profiles inside the thickness of the walls (Fig. 5c). These cups display typical molecular profiles of fresh olive oil (Fig. 6c): the TAG distribution is preserved (Fig. 7c, f) and  $\beta$ -sitosterol is also attested. A molecular signal from lard rubbing is also observed: odd- and even-numbered short-chain fatty acids are detected, as well as long-chain ketones in some samples. This demonstrates the penetration of olive oil into the cups rubbed with lard after firing, though generally in smaller quantity than the penetration of lard during simple cooking.

The test of water absorption revealed similar results. The post-firing treatment seems to have limited the absorption properties of the vessel, without fully neutralising them since 3% of the water was absorbed in 1 h. In the absence of post-firing treatment or use, the amount of water absorbed by the ceramic matrix is significant (+ 10% water). Cooking lard results in complete waterproofing of the vessel since 0% water is absorbed when the vase is reused to contain water. This result is certainly due to the hydrophobic properties of fresh/slightly degraded lard. The practice of initial cooking in the vessel as a waterproofing technique is commonly observed in ethnoarchaeology (Gosselain 2002; Harry et al. 2009; Henrickson and McDonald 1983; Rye 1981).

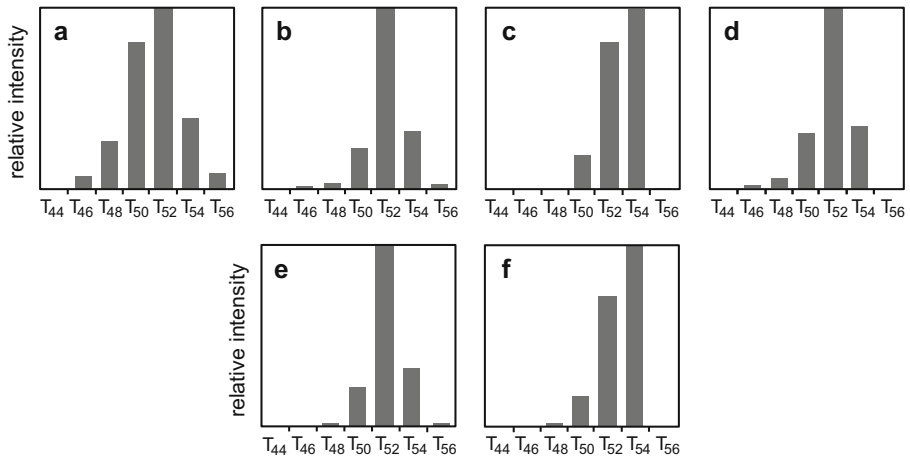
Our analyses highlight the only incomplete sealing effect of post-firing treatment, both for water and fatty products, already noted during other experiments on ethnographic material (Gosselain 2002; Longacre et al. 2000; Skibo and Deal 1995).



**Fig. 6** Characteristic gas chromatograms of experimental cups obtained by GC, (a) cups with post-firing treatments with lard; (b) cups used to cook lard; (c) cups with post-firing treatments with lard, used to cook olive oil; (d) cups with post-firing treatments with lard, cooled in the melted lard. Peaks were identified by GC-MS: Cx:y represents fatty acids of carbon chain length x and with y unsaturations, and Kx, ketones of carbon chain length x; MAGs: monoacylglycerols; DAGs: diacylglycerols; TAGs: triacylglycerols; \*: plasticiser contaminants; IS: internal standard (*n*-C34). Fatty acids and sterols are trimethylsilylated except fatty acid methyl esters labelled "Me"

### Cold Input Following Post-firing Treatment

An additional absorption of lipids seems to result from the cooling of the vessel in the melted lard after post-firing treatments. Between 0.78 and 26 mg g<sup>-1</sup> of lipids were extracted from pots of this experiment, which is a smaller quantity than the amount of olive oil absorbed in the previous experiment. This is probably due to the progressive solidification of lard during cooling. The extracted lipids are very similar to those obtained from fresh and slightly cooked lard (Fig. 7d): the TAG distributions are



**Fig. 7** Typical TAG distributions in (a) cups with post-firing treatments with lard; (b) cups used to cook lard; (c) cups with post-firing treatments with lard, used to cook olive oil; (d) cups with post-firing treatments with lard, cooled in the melted lard; (e) fresh lard; (f) fresh olive oil.  $T_X$  is the number of acyl carbon atoms in each TAG

equivalent, and cholesterol is attested in both types of cups. This molecular signal is probably due to a second input of lipids, during the cooling of the vessel inside the melted lard. This hides most of the signal created at high temperature, and therefore cold input of organic products during post-firing treatments would be difficult to distinguish from a simple use of the vessel in an archaeological pottery.

## Synthesis: Significance and Impact for Future Research

### Understanding Processes Involved During Post-firing Treatment

Macro- and microscopic observations on experimental pots confirmed that all types of post-firing treatments tested in this study result in the formation of a layer on the surfaces and revealed that the covering power depends on the type of organic product, but more importantly on its liquid or solid state.

As expected, considering the temperature of the pottery surface during the process, post-firing treatments involve combustion of large quantity of organic products. This is noticed both at a macroscopic level (blackening of the surfaces, loss of efficiency of the organic product after the treatment on one first vessel) and at a molecular level (lower quantity absorbed when lard is rubbed on the surfaces after firing than when lard is simply cooked). This suggests that the covering caused by post-firing treatments is partly made of mineral carbon. However, our study revealed that part of the organic products can persist, despite the high temperature involved during post-firing treatments and that organic compounds permeate deeply through the wall thickness. The high temperature involved in post-firing treatments causes significant transformations of the organic molecules: when using animal fats, TAGs and fatty acids are degraded by cracking and generate odd- and even-numbered short-chain fatty acids; long chain ketones are formed through condensation processes; and sterols are lost due to their

sensitivity to high temperature. Diallo et al. (1995) obtained similar results from pots soaked in bark decoctions immediately after firing: the authors describe partial preservation of organic substances and identified molecular compounds produced at high temperature (pyrolysis products of procyanidins).

### Effect of the Post-firing Treatments on the Pottery Properties: the Issue of Sealing

Post-firing treatments are generally believed to be applied on the ceramic walls to waterproof them (Charters et al. 1995; DeBoer and Lathrap 1979; Diallo et al. 1995; Echallier 1984; Evershed et al. 1991; Gosselain 2002; Harry et al. 2009; Henrickson and McDonald 1983; Martineau and Pétrequin 2000; Rice 1987; Schiffer 1990; Skibo et al. 1997). Ethnoarchaeological studies report examples of vessels that change function when the post-firing treatment has lost its waterproofing properties through use, as boiling is no longer obtained quickly enough for use as a cooking vessel (Skibo 2013). Our analyses confirm that post-firing treatments seal the surface, but only partially. Based on these results, we propose that several mechanisms generate this partial waterproofing effect: (i) formation of a layer on the surface and filling of the pores (physical barrier, macro- and microscopically observed) and (ii) hydrophobic behaviour of the preserved organic molecular compounds (chemical barrier, observed through organic residue analysis). More importantly, this study revealed that this process limits but does not prevent subsequent absorption of organic products processed in the vessels after post-firing treatments, as already suggested in the literature (Gosselain 2002; Longacre et al. 2000; Schiffer 1990).

This partial sealing effect may have been deliberately sought, for example to avoid an excessive rise in temperature when using the container (e.g. simmering cooking). It should also be noted that such treatments may also have been used by prehistoric potters for other reasons than sealing: improving the mechanical strength of the pots (Gosselain 1992a), limiting abrasion of the surfaces during use (Skibo et al. 1997), colouring the surfaces (Gosselain 2002; Longacre et al. 2000) or preventing the breaking down of calcite-tempered pots fired at temperatures higher than 700 °C (Lepère 2009). A comprehensive analysis of ceramic vessels including, *inter alia*, the study of the shape and type of paste, could contribute to enrich the discussion on the role of post-firing treatments, in particular by providing elements relating to the physical performance of the vessels (Skibo 2013).

### Identifying Post-firing Treatments on Archaeological Pottery to Discuss *chaînes opératoires*

The experiments carried out in this study show that both macro- and microscopic observation and organic residue analysis provide complementary information about the *chaîne opératoire* of post-firing treatments.

At macro- and microscopic scales, the degree of penetration of the product inside the walls is a criterion to distinguish processes of post-firing treatments in archaeological series, in particular for identifying the state (liquid or solid) of the product. Differences of aspect (e.g. colour) between internal and external surfaces and potential coverage irregularities around the rim may provide information on how the product was applied.

However, identifying post-firing treatments applied after reducing firing can be challenging. When oxidised margins are either poorly or not developed, the identification of post-firing treatments is virtually impossible, especially after smudging. In addition, smudging can be accidental and affect part of the vase during firing. The quantity of archaeological pots treated with smudging processes after firing in reducing atmosphere is therefore probably underestimated.

This study reveals that post-firing treatments can result in the absorption of organic matter, and the formation of molecular markers related to the high temperatures involved in the process. Organic residue analysis may therefore provide information to discuss the organic products involved in post-firing treatments. The use of fatty products (animal fats, but probably plant oils too) leads to the formation of mid-chain ketones and/or short-chain fatty acids when applied on the hot surfaces after firing. However, these molecules are not optimal markers of these processes. First, due to the solubility of short-chain fatty acids in water, they are likely to be lost during burial of archaeological samples through groundwater leaching (Evershed 1993). Secondly, these molecules, in particular mid-chain ketones, can also be formed during repeated heating of fatty commodities, as they are often interpreted in the literature (Carrer et al. 2016; Craig et al. 2005a; Evershed et al. 2008; Kherbouche et al. 2016; Nieuwenhuysen et al. 2015; Salque et al. 2013; Šoberl et al. 2014).

These experiments also demonstrated that post-firing treatments do not prevent absorption of other products during use. Complex mixed molecular signals, resulting from both post-firing treatments and use of the vessel, can therefore be detected in archaeological sherds.

Furthermore, it is important to highlight that lipids absorbed during post-firing treatments may be incorrectly attributed to the use of the pots, especially when detecting low abundances of lipids trapped in the porous clay matrix of the ceramic vessels.

The combination of different approaches is therefore essential when post-firing treatments are suspected on archaeological ceramic vessels because of the limitations related to each analytical method and the complementary information they provide (Fig. 8).

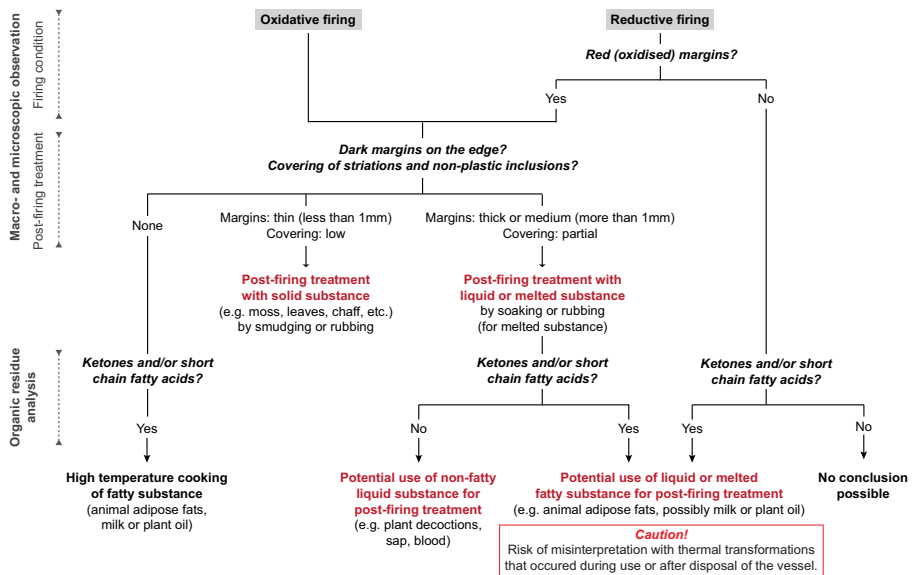
Potsherds fired in oxidising conditions (or in reducing conditions with large oxidised margins) remain the easiest case to interpret. The careful observation of the colour of the surface, the covering of the burnishing striations and non-plastic inclusions, and the width and morphology of the dark margins on the edges provide evidence about the state of the organic product applied on the surface. This informs about the type of application method: soaking and rubbing can be suggested for liquid or melted products, while smudging or rubbing are likely to be used for solid products. Organic residue analysis can then be performed to detect molecular compounds formed at high temperature. The identification of mid-chain ketones and/or short-chain fatty acids may indicate the use of fatty product for post-firing treatment, while pyrolysis products of tannins may reveal the use of plant materials, such as bark, leaves or steams (Diallo et al. 1995). However, interpretative precautions must be observed, since these molecular markers may also be formed during subsequent exposure to high temperatures (*e.g.* during use or accidental heating after discard of the pot).

Because of the difficulty in identifying post-firing treatments carried out using solid product on pots fired in reducing atmosphere by macro- and microscopic observation,

the detection of molecules formed at high temperatures can provide arguments in favour of potential post-firing treatments, especially when macro and micro traces of such treatments are observed on vessels fired under oxidising conditions within the same ceramic assemblage.

On the basis of these pioneering results, new experiments should be conducted to deepen the interpretation of the molecular signal related to surface treatments. For example, macro- and microscopic traces resulting from spraying on the surface are poorly studied. Furthermore, the chemical biomarkers produced during the application of fatty substances such as milk or plant oil (probably short-chain fatty acids and mid-chain ketones) must be confirmed, and other biomarkers, resulting from the use of blood, dung or plant product (fruits, leaves, bark, moss, *etc.*) should be investigated. The first experiments on applying organic matter to raw surfaces before firing (Admiraal et al. [accepted](#)) seem to indicate a total disappearance of the organic signal. New experiments should determine whether this complete degradation is also observed for short firing or after pit-firing. In addition, new experiments will be required to determine whether the conditions of use (atmosphere, location of the pot in relation to the fire, repetitious uses, *etc.*) have an impact on the macro and micro and molecular traces of post-firing treatments and whether sooting during use can be confused with the effect of smudging. Artificial ageing should also be performed to evaluate the preservation of the macro- and microscopic traces and preservation of the molecular profile during burial.

In addition, acidified methanol extraction (Correa-Ascencio and Evershed [2014](#); Craig et al. [2013](#)), which provides access to molecules chemically bound to the ceramic matrix, should be tested. The comparison between the two extraction methods could



**Fig. 8** Partial interpretation grid, based on macro- and microscopic observation of surfaces and edges and organic residue analysis, to study some of the post-firing treatments that were carried out on ceramic vessels over time



provide new criteria to distinguish between post-firing treatments and the use of ceramics, as post-firing treatments may generate by-products that can bind to the ceramic matrix (e.g. diacids, hydroxy acids).

### Studying Pottery Function by Organic Residue Analysis and Potential Pollution by the Manufacturing Process

The present study stresses the need for a careful observation of archaeological potsherds (both surface and edges) before any extraction for organic residue analysis, to check for evidence of the use of the vessel as cooking pot or aspects of post-firing treatment. For example, when no foodcrust or external traces of sooting are identified on potsherds that have yield long chain ketones (Craig et al. 2005a; Fanti et al. 2018) but uniform darkening of the surface and the edges are observed, thermal transformation markers could be related to post-firing treatments with fatty materials, rather than cooking. Similarly, the detection of thermal transformation markers in pottery with properties that make their use on fire unlikely suggests post-firing treatments. More generally, lipid extracts from pots bearing macro and micro traces of post-firing treatments need to be cautiously interpreted.

These experiments also reveal that the molecular profile of fatty products can be modified by the application on hot surfaces.

### Conclusion

Post-firing treatments are often mentioned in the literature but this step of the *chaîne opératoire* is rarely studied. This paper proposes a multi-scale and multi-proxy methodological approach to detect and identify some of the surface treatments described in the literature, but also to investigate the kind of organic substances involved in the treatments, their solid or liquid state and the application modes.

In particular, this study showed that the results of organic residue analysis must be interpreted very cautiously, since there is nothing to distinguish, at this stage of our knowledge, between molecular signals resulting from post-firing treatments and those related to the use of pottery. Organic residue analyses must therefore systematically be carried out in tandem with an in-depth ceramological study in order to avoid misinterpretations of the origin of the signal. When macro and microscopic traces of post-firing treatment are identified on surfaces and edges, the presence of molecular markers of thermal transformation could be used to initiate a discussion on the type of substance involved in the process. The development of experiments such as those presented in this paper could eventually make it possible to be more precise on the origin of molecules preserved in archaeological ceramics.

In a long-term perspective, the study of post-firing treatments on large sets of archaeological samples (e.g. from the southern Chassey culture; Lepère 2009) using both macro- and microscopic observation and organic residue analysis could provide new data to discuss the ceramic *chaîne opératoire* and the diversity of cultural practices over space and time.

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