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LEFTOVERS: THE PRESENCE OF MANUFACTURE-DERIVED AQUATIC LIPIDS IN ALASKAN POTTERY*

M. ADMIRAAL† ⓘ

Arctic Centre, University of Groningen, Aweg 30 9718CW Groningen, the Netherlands and BioArCh Laboratory, University of York, Wentworth Way, Heslington, York YO10 5DD, United Kingdom

A. LUCQUIN ⓘ, L. DRIEU ⓘ

BioArCh Laboratory, University of York, Wentworth Way, Heslington, York YO10 5DD, United Kingdom

S. CASALE ⓘ

Department of Archaeology, Leiden University, Einsteinweg 2 2333CC Leiden, the Netherlands

P. D. JORDAN

Arctic Centre, University of Groningen, Aweg 30 9718CW Groningen, the Netherlands

and O. E. CRAIG ⓘ

BioArCh Laboratory, University of York, Wentworth Way, Heslington, York YO10 5DD, United Kingdom

Lipids preserved within the walls of ancient pottery vessels are routinely analysed to reveal their original contents. The provenience of aquatic lipids in pottery is generally connected to vessel function (e.g., for cooking or storing fish, shellfish and aquatic mammals). However, ethnographic reports from early historic Alaska mention the use of aquatic oils for waterproofing low-fired pottery. Results of lipid residue studies on Alaskan pottery reflect an exclusive function of pottery to process aquatic resources. However, can one be sure these residues are the product of vessel function and not a remnant of the manufacturing process? The study presents the results of an experiment where the preservation of aquatic lipids during the firing process at different temperatures was measured. It was found that nearly all lipids were removed at firing temperatures of ≥ 400°C. Petrographic analysis of Alaskan pottery samples indicates that firing temperatures were generally > 550°C but < 800°C. The contribution of pre-firing manufacture-derived lipids to samples fired at these temperatures may be regarded as negligible. While the possible presence of aquatic lipids from post-firing surface treatments cannot be excluded, such treatments appear unnecessary for well-fired pottery.

KEYWORDS: POTTERY, LIPID RESIDUE ANALYSIS, PETROGRAPHY, FIRING TEMPERATURE, AQUATIC LIPIDS, QUANTIFICATION, ALASKA

INTRODUCTION

The study of lipid residues in archaeological pottery has advanced significantly over the past decade and it has yielded new information about the prehistoric diet and cuisine (Craig *et al*. 2013; Lucquin *et al*. 2016b; Gibbs *et al*. 2017). Various lipid compounds, such as tars, resins and

waxes, have also been identified which were clearly used to repair pottery and to waterproof porous vessels, and had nothing to do with food preparation or cuisine (Regert *et al.* 2003; Regert 2004; Hjulström *et al.* 2006; Reber and Hart 2008; Stern *et al.* 2008; Rageot *et al.* 2019). Other substances identified through residue analysis are more ambiguous to interpret, and so far there has been little consideration about whether fats, oils and waxes used in the manufacture of pottery leave a significant residue signal following firing.

In Alaska, the use of organic materials in pottery manufacture is well documented. Materials such as grass, hair, feathers and even aquatic oils were used as tempering agents in the clay, or were applied to the surface of the pottery vessel (de Laguna 1940; Frink and Harry 2008; Anderson 2019; Admiraal and Knecht 2019). Recent lipid residue analysis has shown that prehistoric Alaskan pottery was used almost exclusively for processing freshwater or marine (aquatic) animal fats and oils (Solazzo and Erhardt 2007; Farrell *et al.* 2014; Anderson *et al.* 2017). The ubiquity of such aquatic oils is intriguing and has been interpreted to reflect the dominance of maritime and riverine subsistence economies. However, can we be sure these residues are the product of culinary practices and not a remnant of the manufacturing process?

A common assumption is that any organic molecules present in the ceramic paste are destroyed, or thermally altered beyond detection during the firing process, and therefore before use (Evershed 2008; Berstan *et al.* 2008). However, this depends on the firing temperature and the duration of firing, as well as other factors such as the thickness of the pottery and the extent of the organic inclusion. It is thought that relatively high temperatures (> 600°C) are needed to destroy most organic molecules in clay, reducing them to graphitic carbon or combusted to carbon dioxide. An experimental study by Johnson *et al.* (1988) showed that such leftover carbon, naturally occurring in clay, still remained in pottery fired at temperatures as high as 800–1000°C. While such carbon remnants likely have no influence on the lipid profiles discussed here, it complicates the radiocarbon dating of archaeological pottery. Most prehistoric firing temperatures would not have reached 800–1000°C. An open fire generally reaches between 600 and 900°C, but with great variability dependent on many circumstances. For instance, a gust of wind can decrease local firing temperatures by as much as 200°C (Rye 1981).

Interestingly, Reber *et al.* (2018) showed that naturally occurring alkyl lipids in clay are removed during firing at > 400°C for 4 h, and concluded, therefore, that any fatty acids identified are associated with pottery use or post-firing treatments. While this study greatly enhances our knowledge of the preservation and removal of lipids during firing, it does not consider the addition of (large amounts of) organic temper during manufacture. Large amounts of organics present in the clay may not be entirely removed under the same circumstances. The addition of organic materials as temper to clay is a well-known phenomenon in archaeological pottery worldwide (Chard 1958; Rye 1981; Arnold 1988), and is well recorded in ethnographic settings (including plant temper and hot surface coating). In general, studying these issues will allow one to interpret organic residues in archaeological ceramics more accurately and will also open up new perspectives for the study of pottery production by ancient societies through organic residue analysis.

In prehistoric Alaska ethnographic sources suggest that large amounts of oily substances may have been added to the clay, or were applied to vessel walls during manufacture (Frink and Harry 2008). In this study, we specifically aim to explore whether aquatic oils, mixed with clay at high concentration, and applied as surface treatment, are detectable following firing at various temperatures and firing durations. Subsequently, we determined the approximate firing temperature of archaeological pottery from the Southwest Alaskan Norton, Thule and Koniag traditions, through petrographic analysis. We then aimed to infer the probable contribution of manufacture-derived lipids in prehistoric Alaskan pottery.

BACKGROUND

The sudden appearance of pottery in the North American Arctic and Subarctic is unexpected and remains largely unexplained. Pottery is generally restrained to zones of temperate climate where it can properly dry before being fired at relatively high temperatures (> 800°C). Cold winters in Alaska constrain pottery production to the short, but warmer, summer season (June–August). However, even in summer, pottery production is highly influenced by climate, as temperatures are often unstable. Days can be overcast and rainy, and humidity is high (≤ 85%). This leads to several problems during the manufacturing process. Wet clays are difficult to work with and lengthy to dry, which can result in breakage of the vessel during firing due to steam build-up (Harry *et al*. 2009a, 2009b; Admiraal and Knecht 2019). Additionally, rainfall and wind during firing will significantly decrease the firing temperature and pose problems for atmosphere control (Frink and Harry 2008; Harry *et al*. 2009b). In contrast to the treeless northern coastal areas, where fuel in the form of wood was limited to the occasional finds of driftwood, in Southwest Alaska wood was much more widely available due to the presence of regions with forest cover.

Despite the many challenges facing early Alaskan potters, ceramic technology entered the New World *c*.2800 cal BP from Northeast Asia. It quickly spread with the Norton culture along coastal Alaska, ranging from the Arctic North to the Subarctic Alaska Peninsula in the Southwest (Fig. 1). Norton pottery actually appears to have been relatively well-fired (> 500°

Figure 1   *Alaska, including the Alaska Peninsula and Kodiak Island. [Colour figure can be viewed at wileyonlinelibrary.com]*

C). It was tempered with organic materials such as grass, hair and feathers (Oswalt 1955). While still relatively thick-walled, Norton pots have generally thinner walls (< 10 mm) than their later counterparts of the Thule tradition (> 10 mm), and appear more refined. Very little research has been done on Norton ceramic technologies (Oswalt 1955; Dumond 2000, 2016). No research has been published to date on the manufacturing techniques and function of Norton pottery. In the modern literature, it is often either overlooked or classified together with the later Thule pottery as 'Arctic' or 'Alaskan' pottery. Note that Norton and Thule are in fact two very different pottery technologies.

With the arrival of the Thule cultural tradition *c*.1000 cal BP, Norton pottery was replaced quickly by Thule pottery. Substantial amounts of crude mineral temper in the shape of small pebbles, gravel and crushed rock made the thick-walled Thule pots susceptible to breakage. This was a problem that was further enhanced by the apparently low temperatures at which Thule pots were fired (Duelks 2015). The transition from Norton to Thule pottery is an enigma, as it seems that the latter was inferior to the former. Harry *et al.* (2009a, 2009b) explained the seemingly poor quality of Thule pottery as technological choice, and the result of environmental circumstances and culinary preferences. While this may be the case, it does not explain why people in the same region were making far superior pottery for a period as long as 1500 years before Thule (Admiraal and Knecht 2019).

Pottery was only adopted on Kodiak Island some 500 years ago by the Koniag tradition. It was most likely an influence from the Alaska Peninsula, as is visible in similarities among other artefact groups. While tempered with vast amounts of gravel, crushed slate and other mineral materials, Koniag pottery differs from Thule pottery of the mainland in several ways. Koniag pots are much larger than their counterparts on the Alaska Peninsula, and also their shape differs. It also appears that Koniag pottery is well-fired (de Laguna 1939), while most Thule pottery from the Alaska Peninsula is described as poorly fired. Pottery was only adopted on the southern half of Kodiak Island. The reasons for this distribution remain unclear (Knecht 1995; Clark 1998; Admiraal and Knecht 2019).

Ethnographic information

The growing body of modern literature on Alaskan pottery technology and function is mainly focused on Thule pottery (Arnold and Stimmell 1983; Frink and Harry 2008; Harry and Frink 2009; Anderson *et al.* 2017). Furthermore, there is abundant ethnographic information on this early historic ceramic technology as people were still using ceramic pots during the early contact period in the area (for an extensive summary, see Anderson 2019).

Aquatic oil and blood as temper

In the ethnographic literature there is repeated mention of the addition of sea mammal oil (Bogoras 1904, 186; de Laguna 1939, 339; Oswalt 1952, 20; Fienup-Riordan *et al.* 1975, 14; Fienup-Riordan 2007, 48), and even sea mammal blood (Geist and Rainey 1936, 129; de Laguna 2000, 128) to the clay paste as a temper (Gordon 1906; de Laguna 1947; Spencer 1959; Fienup-Riordan *et al.* 1975). It is also described that aquatic oils and blood were applied to the pottery walls as a coating both before and after firing. Additionally, Osgood (1940) and de Laguna (1947) mention a pottery vessel was filled with oil and left to stand so that the oil could permeate the vessel walls. All these measures seem to have been aimed at waterproofing the porous and low-fired contact-period pottery.

Figure 2   *Alaskan pottery sherd. Photo: M. Admiraal; courtesy: University of Oregon Museum of Natural and Cultural History [Colour figure can be viewed at wileyonlinelibrary.com]*

Harry *et al.* (2009a, 2009b) investigated the manufacturing technologies of unfired pottery and found that boiling an oily broth in a very porous vessel would plug the pores and make the vessel waterproof. Additionally, by coating an unfired cooking pot with aquatic oil and blood, they managed to boil water in the vessel, proving that low-fired, or even unfired, pottery could still be used. In this experiment, it was also observed that coating leather-hard clay with blood produced a crusted layer identical to that found on the majority of archaeological sherds from Alaska (Fig. 2). Producing a charred surface deposit similar to those observed on archaeological pottery from other regions has proven difficult to achieve experimentally. De Laguna (2000, 119) described the formation of the charred black encrustation on the inner surface of the pottery as a result of repeated greasing of the pottery with fish grease, as was described to her by an elderly Native woman from Nulato (Yukon, Canada).

Drying and firing

Ethnographic accounts on the drying and firing of contact-period Thule pottery are limited and practices probably varied throughout time and space. De Laguna (2000, 119) describes how in the Yukon 'the vessel was set near the fire and slowly dried, being greased and turned as it dried'. Nelson (1900, 210) mentions that pottery from the Norton Sound 'was baked inside and out for an hour or two in an open fire'; it is also stated that near the Bering Strait more attention was paid

to firing. Here a fire was built in- and outside the pot which was kept burning as hot as possible for up to two days (228). Osgood (1940) describes the process of making pottery by the Ingalik of the Yukon–Kuskokwim River Delta in great detail:

> When the pot has been shaped it is moved on its plank about 3 or 4 feet from the fire and allowed to dry slowly. This takes about two days, the pot being turned from time to time and tested by tapping with a little stick in order to determine its condition of dryness by the sound. When the wall of the pot is dry, it is tipped over so the bottom also dries. After this, a little fire is made inside with shavings to burn off edges of the feathers which roughen the surface of the pot. When the pot cools again, water is put inside and the pot is placed beside the fire. To the water some backbones of fish are added and cooked all day long. This is done in order to give the pot a permanent fishy taste which is very much desired. (p. 147)

It must be kept in mind that these accounts are all from the Yukon–Kuskokwim River area, and further north. Firing techniques in the forested areas on Kodiak Island and the upper Alaska Peninsula were probably different from those on the Bering Sea coast further to the north, where the climate was harsher. Here a general lack of trees made (drift)wood a valuable commodity. Alternative fuels such as dung and bone may have been used instead, especially in the treeless north. Additionally, fuel could have been soaked in oil to assist the firing process further (Harry and Frink 2009; Anderson 2019) For example, ethnographic sources inform on the use of wood soaked in seal oil for the firing of pottery on the north slope (Spencer 1959, 472) and on St Lawrence Island (Geist and Rainey 1936, 129). Certainly, the addition of oil would have increased firing temperatures; the extent of this increase is, however, unclear. The appreciation that reaching high firing temperatures was more complicated in the northern treeless areas of Alaska also aids in an understanding of the replacement of Norton pottery by Thule pottery in Southwest Alaska. Dumond (2011) argues that it is very probable that the more brittle, low-fired Thule pottery of the Alaska Peninsula actually originated in the Yukon–Kuskokwim area. This could explain why Thule pottery was so different from Norton pottery because it was developed in an area with limited woody fuels. This also illustrates the fact that Norton pottery cannot simply be compared with ethnographic accounts that refer to the later Thule period, and it must be considered as a separate pottery type.

Firing temperatures of archaeological pottery from Alaska are largely unknown. However, Duelks (2015) investigated Thule firing temperatures using an experimental method based on re-firing the archaeological pottery, and the subsequent observation of differences in colorations of the ceramic. Duelks (2015, 39) concluded that all tested Thule pottery was fired at a minimum of 500°C and a maximum of 800°C. This suggests that Thule firing temperatures may not always have been as low as suggested in ethnographic reports. One of only a few statements made on the firing temperature of Alaskan archaeological pottery is by de Laguna (1939, 334), who describes Kodiak pottery as 'well-fired', but provides no further information. One may argue that very low-fired pottery would not have survived the wet burial environment (Rye 1981, 111), and as a result the sherds that did preserve may reflect a selection of the better fired pottery of a wider initial assemblage.

Little is also known about firing techniques in prehistoric Alaska. At Cape Espenberg, a shallow dish-like feature from late pre-contact times may have been used for the firing of pottery, as evidenced by the presence of numerous sherds and charcoal, burned bone and oxidized sand (Anderson 2019). However, in general, archaeological excavations have rarely yielded evidence associated with the firing of pottery in Alaska. This limited information, combined with ethnographic information, suggests the firing of pottery took place in open fires. It is also possible that

pottery was fired in cooking hearths to save fuel. In general, open fires do not reach temperatures > 1000°C (Rye 1981).

<div align="center">MATERIALS AND METHODS</div>

Firing temperature experiment

For the firing experiment, a total of 15 clay tiles ($12 \times 6 \times 1$ cm) were made (three sets of five). The clay (Sibelco EU K127) for each tile was mixed with a set amount of salmon oil (West Coast Select Wild Salmon Oil—NPN 8005088). The contribution of salmon oil to each set of tiles was 0.5% and 1.0%, respectively. The surface of the third set was coated with a single layer of salmon oil, and no oil was mixed into the clay of this set. The tiles were dried for 10 days at room temperature (about 20°C). Subsequently they were fired at different temperatures in an oxidizing environment using a Naber N100H 380V oven. One tile of each set was fired, wrapped in a single layer of aluminium foil at a maximum of either 200, 400, 600 or 800°C. The temperature, starting at room temperature was raised by $100°C\,h^{-1}$ until the maximum firing temperature was reached. It was held there for 15 min, after which the temperature was lowered again at the same rate. The total firing duration for tiles fired at 200°C was 4.25 h, at 400°C was 8.25 h, etc. (additional supporting information Table S1). One tile of each set was left unfired as a reference for the original lipid concentrations.

Lipid residue analysis

Samples were obtained by drilling about 5 mm into the experimental ceramic tiles and collecting approximately 1 g of ceramic powder. The surface layer (1 mm) of the ceramic was first removed in order to avoid any contamination. Subsequently lipid residue analysis was performed using an acidified methanol extraction following established protocols (Craig *et al*. 2013; Papakosta *et al*. 2015). Two internal standards (10 µL of C_{34} *n*-alkane before and 10 µL C_{36} *n*-alkane after extraction) were added to all samples before further analysis by gas chromatography-mass spectrometry (GC-MS).

The equipment used for GC-MS analysis was an Agilent 7890A series chromatograph attached to an Agilent 5975C Inert XL mass-selective detector with a quadrupole mass analyser (Agilent Technologies, Cheadle, UK). A splitless injector was kept at 300°C. The GC column was inserted into the ion source of the MS directly. Helium was used as a carrier gas with a constant flow rate of $3\,mL\,min^{-1}$. The ionization energy of the MS was 70eV and spectra were obtained by scanning between *m/z* 50 and 800. A DB-5 ms (5%-phenyl)-methylpolysiloxane column ($30\,m \times 0.250\,mm \times 0.25\,mm$; J&W Scientific, Folsom, CA, USA) was used for scanning. The temperature was set at 50°C for 2 min, then raised by $10°C\,min^{-1}$ until it reached 325°C, where it was held for 15 min. MSD ChemStation software (Agilent Technologies) was used to calculate lipid concentrations per sample, based on the known amount of internal standard, as well as for the identification of compounds in the GC-MS chromatograms.

Petrographic analysis of archaeological sherds to establish a firing temperature

Seven ceramic samples from different archaeological sites in Alaska (one Thule, four Norton and two Koniag sherds) were analysed by petrographic observation (additional supporting information Table S2). For the petrographic analysis, we used a polarizing microscope, which employs

transmitted plane-polarized light (PPL) or cross-polarized light (XP) to observe the mineralogical composition in order to reconstruct the technological steps carried out to process the clay (Reedy 1994; Quinn 2013). Such observations permit the characterization of the clay matrix, temper materials added to the clay (e.g., plastic and non-plastic inclusions), surface treatments and firing temperature. When observed under an optical microscope, the clay matrix may exhibit evidence to distinguish firing technologies and temperatures reached during the firing process (Quinn 2013). At < 800°C, the clay matrix tends to retain optical activity, while at higher temperatures the crystals lose their structures, turning into an amorphous glassy and isotropic matrix with new mineralogical phases (sintering stage). Thus, samples with optically active paste can be considered as being fired at < 800°C. Additionally some minerals transform colour at specific temperatures, which may be used as a marker for firing temperatures as well. For instance, at > 750°C muscovite changes from a colorful shade to a pale brown, while hornblende shifts from green to brown (Quinn 2013).

Water testing

In order to investigate whether the archaeological pottery was fired at high enough temperatures to reach a sintering stage, we tested each available sherd (13 Norton, four Thule and 20 Koniag; additional supporting information Table S3) by placing a small section of it in water. We then observed whether the ceramic started to disintegrate after being submerged for 1, 3, 6 and 24 h.
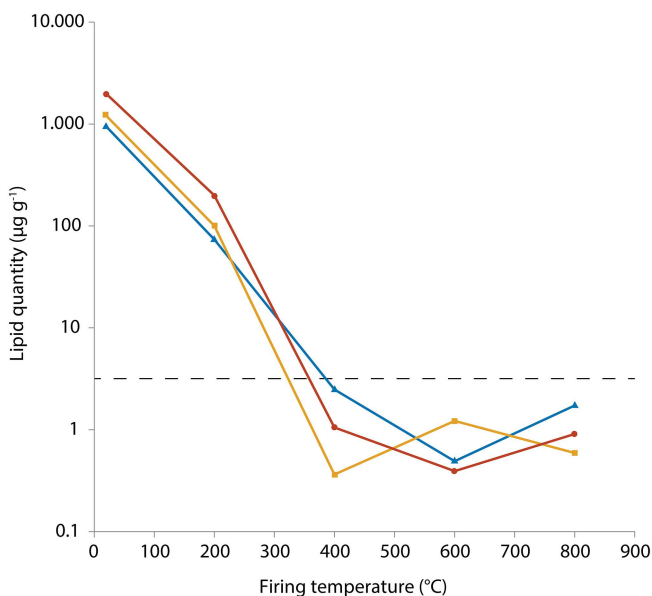

Figure 3 *Results of the firing experiment. The three coloured data lines refer to the different sets of tiles: blue triangles = 0.5% oil content; yellow squares = 1% oil content; and red circles = surface coating with oil. The dashed line indicates the limit of interpretable lipid concentrations (5 μg g⁻¹); data points below this line are viewed as negligible in archaeological samples [Colour figure can be viewed at wileyonlinelibrary.com]*

Table 1 *Presence of compounds in chromatograms at different temperatures in set 2; other sets yielded comparable results*

Firing temperature (°C)	Fatty acids	Unsaturated fatty acids	Diacids	ω-(o-Alkylphenyl) alkanoic acids (APAAs)	Isoprenoid acids	Branched	Other compounds
Unfired	C14–26	C16:1, C18:1, C20:5, C20:1, C22:6, C22:1, C24:1, C26:1	C8–17	–	Present	Ca15:0, Ca17:0, Ca18:0	Alcohol, *n*-alkanes, phenol
200	C14–24	C18:1, C20:1, C22:1, C24:1	C7–17	C16–22	Present	Ca17:0, Ca18:0	Alcohols, *n*-alkanes, phenol, B3CA
400	C16–18	C18:1-tr	–	–	–	–	Phenol, methylenebis, benzenamine, B3CA(2), B4CA-tr
600	C16–18	C18:1-tr	–	–	–	–	Phenol, methylenebis, benzenamine, B4CA-tr
800	C16–18	–	–	–	–	–	Phenol, methylenebis, benzenamine, B4CA-tr

B3/4CA, benzene tri/tetra-carboxylic acids; 'a' under Branched refers to anteiso; -tr, trace amounts.

RESULTS

Lipid concentrations

The results of the lipid residue analysis show a clear loss of lipids with increasing firing temperatures. The three samples that were dried at room temperature without firing showed very high lipid concentrations ranging from 1 to 2 mg g^{-1} (Fig. 3). The lipid concentrations dropped significantly after firing the ceramic tiles for 4 h at a maximum of 200°C, to between 70 and 200 μg g^{-1}. Around 90% of the lipid content was lost at this stage. After 8 h in the oven with maximum temperatures reaching 400°C, only small quantities (< 1.4 μg g^{-1}) of fatty acids C_{16}, C_{18} and $C_{18:1}$ remained (Table 1 and Fig. 4). These quantities are below the interpretable limit of 5 μg g^{-1} (Fig. 3) and may, therefore, be viewed as negligible, especially when compared with lipid concentrations found in Alaskan pottery that range from 12 to 3500 μg g^{-1} (Farrell *et al.* 2014).

Lipid profiles

The unfired clay tiles all show typical aquatic lipid distributions (Fig. 4, a) with fatty acids ranging from C_{14} to C_{26} and abundant unsaturated fatty acids including $C_{20:5}$ and $C_{22:6}$, branched
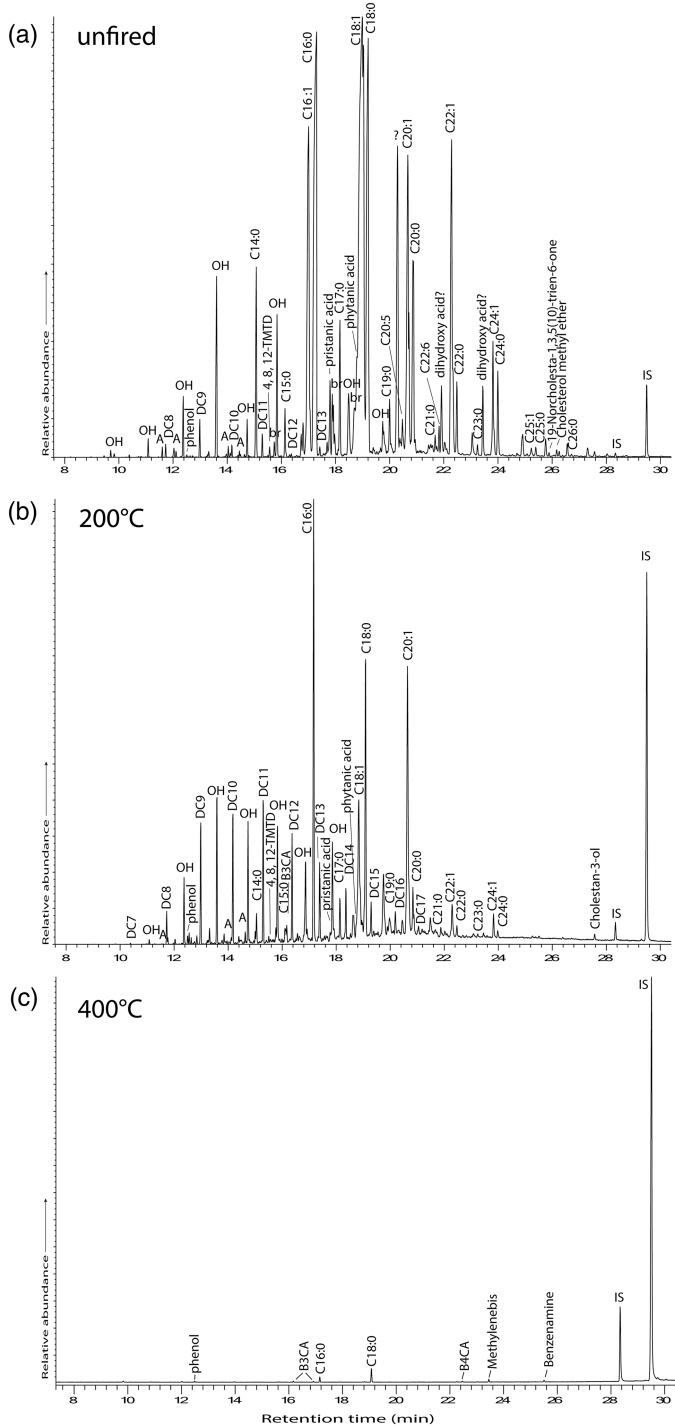
Figure 4 *Chromatograms of total lipid extracts of samples 2.1–2.3 showing the lipid profiles in (a) unfired clay and after firing at (b) 200°C and (c) 400°C. DC, dicarboxylic acid; OH, alkanol; IS, Internal standard n-alkanes C_{34} and C_{36}*

fatty acids and dicarboxylic acids. All isoprenoid acids—TMTD (4,8,12-trimethyltridecanoic acid); pristanic acid (2,6,10,14-tetramethylpentadecanoic acid); and phytanic acid (3,7,11,15-tetramethylhexadecanoic acid)—are present in these samples in high concentrations. Isoprenoid acids are an established biomarker for the presence of aquatic resources (Evershed *et al*. 2008; Cramp and Evershed 2014; Lucquin *et al*. 2016a). Mid-chain alcohols and *n*-alkanes are also present in the unfired samples.

The chromatogram changes after the clay tiles are fired at 200°C for 4 h (Fig. 4, b). Some (mainly long-chain) compounds are lost. While amounts of dicarboxylic acid increase, alcohols are reduced in concentration. ω-(*o*-Alkylphenyl) alkanoic acids (APAAs) of carbon length 16–22 are now detectable in the sample, though weakly. These compounds form during the prolonged heating of mono- and polyunsaturated fatty acids at ≥ 270°C, and the presence of C_{18}–C_{22} APAAs is considered to be a biomarker for aquatic resources. The weak appearance of APAAs in the sample may be explained by the firing temperature not reaching 270°C, which has been described as a precondition for APAAs to form (Cramp and Evershed 2014). At 400°C (8 h) hardly any lipids are detectable. Only fatty acids of carbon length 16 and 18 are still observed. Trace amounts of $C_{18:1}$ as well as a few other compounds are also present (Table 1). The chromatograms of samples fired at 600 and 800°C are nearly identical to samples fired at 400°C (Fig. 4, c).

Firing temperatures of Alaskan archaeological pottery

In general, the tested Alaskan ceramics (additional supporting information Table S2) show different mineralogical matrixes and manufacturing techniques. Interestingly, the samples show different firing technologies ranging from oxidizing (UGA1-1008b, UGA1-1009b, KAR1-88, KK1-19b and UGA2-21b) to reducing atmospheres (KAR31-74b and NAK8-12b). While the sample was too small to make any significant interpretation on cultural preferences for firing techniques, it is clear that all Norton pottery ($n = 4$) was fired under oxidizing circumstances, while the one Thule sherd was fired in a reducing environment. The two Koniag sherds showed variable firing technologies (additional supporting information Table S2). The clay used for vessel manufacture went through a sintering process, meaning that firing temperatures reached were at least 550–600°C for all samples (Rice 1987; Quinn 2013). Earthenware that does not reach this temperature range will eventually break down when soaked in water (Rice 1987,
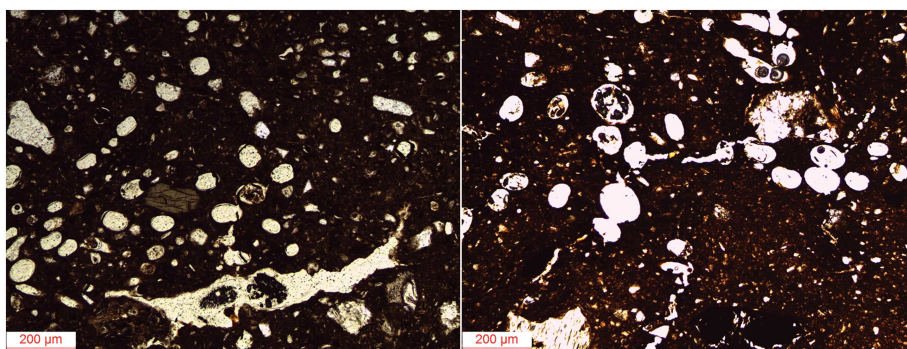

Figure 5   *Empty voids as observed in the general matrix XP of Norton samples UGA1-1009b (left) and KK1-19b (right), possibly the result of the evaporation of lipids in clay paste during the firing process. [Colour figure can be viewed at wileyonlinelibrary.com]*

90–93; Orton and Hughes 2013, 134–135). None of the tested Alaskan archaeological sherds showed any sign of disintegration after being submerged in water for 1, 3, 6 or 24 h. However, the ceramic paste of the seven samples tested by petrography yielded a high optical activity, suggesting the maximum firing temperature was $< 800°C$. Therefore, results indicate that all sherds analysed by petrography ($n = 7$) were fired at 550–800°C. All other sherds tested here ($n = 37$) were fired at temperatures of at least 550°C.

Samples NAK8-12b (Thule) and KAR31-74b (Koniag) yield a very coarse matrix structure in contrast with the other samples, the dark colour of the matrix may be the result of reducing firing conditions combined with the presence of organic matter. Norton samples UGA1-1009b and KK1-19b show a high number of round-shaped voids that may be connected to the addition of hydrophobic substances (e.g., animal fats and oils) to the clay mass during the manufacturing process, or the evaporation of gases during the firing process (Fig. 5). Gases can form as a consequence of the presence of organic materials (both solids and liquids) within the clay matrix. While there is some evidence of solid organic temper in sample UGA1-1009b, many of the voids in these samples do not show any evidence of carbonaceous plant remains, making it less likely that the presence of these voids is a consequence of solid organic materials (e.g., grasses, twigs) burning out. It is more likely that these voids were formed during the evaporation of liquids, such as oils or fats, during firing. This is, however, a novel idea that needs further experimental testing.

<div align="center">DISCUSSION</div>

Previous studies have investigated the degradation of lipids and carbon, which are naturally occurring in clay, during the firing process. While carbon will remain present in the ceramic up to very high temperatures (800–1000°C) (Johnson *et al.* 1988), Reber *et al.* (2018) showed that the majority of naturally occurring lipids in clay are thermally degraded to the point that they are no longer detectable by GC at 400°C. They concluded that pottery fired at $> 400°C$ may be considered a 'blank state', and lipid residue results from such pottery may be interpreted as resulting from the usage of the ceramic vessel. Our experiment confirms this; however, we stress that post-firing maintenance activities such as surface treatments may still contribute considerably to lipid residue results.

The added aquatic lipid concentration in the unfired pottery in our experiment was very high (1973 µg g^{-1} in unfired sample 3.1) when compared with naturally occurring lipids in clay, as reported by Reber *et al.* (2018) (maximum of 193 µg g^{-1}). Nevertheless, our experiment showed that even substantial amounts of aquatic lipids mixed into the clay, or applied as a surface coating, will be lost during the firing process at $\geq 400°C$. This is a significant finding, not only for Alaskan pottery but also in a global hunter–gatherer pottery context as the addition of organic materials to the clay paste of pottery is a well-known phenomenon among prehistoric cultures around the world. The results show that even substantial amounts of lipids are removed during firing at relatively low temperatures ($> 400°C$). Therefore, while the ethnographic descriptions of the addition of aquatic products during pottery manufacture are directly related to early historic Thule pottery, the conclusion that such practices would have little effect on lipid concentrations in pottery fired at $> 400°C$ is likely also applicable to Norton, Koniag and even other archaeological pottery worldwide, depending on the nature of the added organic material.

An important variable that remains to be investigated further is the role of firing duration on lipid degradation. In our experiment, the firing duration increased significantly with the increase in temperature. This possibly enhanced the degradation of lipids per firing temperature stage and may not be reflective of prehistoric Alaskan firing practices, as wasting fuel on lengthy firing

episodes would have been undesirable, especially in areas where wood is scarce. On the other hand, short firings (20–30 min) with high heating rates (a maximum temperature in 20 min), such as described by Gosselain (1992), also seem improbable considering the Alaskan climate often does not allow pottery to dry sufficiently before firing. Too high heating rates would significantly increase the risk of vessel breakage because of thermal stress due to steam build-up in the vessel walls. This problem may explain the porous nature of Thule pottery, as the porosity allows for the firing of not sufficiently dried clay pots (Gibson and Woods 1997; Harry *et al.* 2009b).

While very little is known about firing technologies of Alaskan pottery, it is assumed that firing generally occurred in an open fire. Open firings display great variety in firing temperatures, up to 300°C locally. Firing temperatures therefore may vary greatly between vessels and even within vessels themselves (Gosselain 1992). Petrographic results indicate variability in Alaskan firing environments, with some reducing and some oxidizing circumstances. Interestingly, all tested Norton pottery ($n = 4$) showed oxidizing firing circumstances. There were no differences in firing temperature detected between the three types of pottery.

The discerning ethnographic descriptions of the practice of repeated greasing of pots with oil and blood after firing remain a valid concern for lipid residue results on pottery from Alaska and possibly elsewhere in the world, especially when those results indicate a predominant presence of aquatic lipids (Farrell *et al.* 2014; Anderson *et al.* 2017). However, if we assume that the post-firing surface treatment of pottery with oil and blood was solely for the purpose of waterproofing the pottery, as described by Harry *et al.* (2009b), we may investigate whether such treatment was necessary in the first place. A simple water test showed that all 37 tested ceramic sherds were fired at temperatures high enough to reach a sintering stage ($< 550°C$). We argue that the extensive post-firing treatment using aquatic products for the waterproofing of the pottery may have been unnecessary. Possibly, such practices did not occur for this reason on well-fired pottery. Osgood (1940, 147) stated that a permanent fishy taste of the pottery was desirable and that it was for this reason that fish products were extensively boiled in newly made pottery. This suggests the possibility that the coating or greasing of pottery with fish or marine mammal oils and/or blood was a culinary practice, and might therefore be considered 'use' instead of 'manufacture'. We suggest here that it is likely that aquatic lipids on Alaskan pottery sherds originate from the use of the pottery as a cooking or storage vessel, rather than from the manufacture and/or maintenance of the pot itself, provided the pottery was fired at temperatures of at least 400°C. However, we acknowledge that the necessity to waterproof pottery not only is based on firing temperature but also is dependent on the porosity and subsequent permeability of the ceramic vessel (Rice, 1987). While Alaskan pottery was generally very porous (especially Thule pottery), the consequences of its permeability remain largely unknown. This needs further investigation in order to determine the necessity for surface treatments to make the pottery waterproof.

CONCLUSIONS

In this paper we tested whether abundant aquatic lipids added during ceramic manufacturing can survive the firing process. We found that high concentrations of added aquatic lipids to clay are removed during firing at 400°C or higher, for 8 h and over. Through petrographic analysis we showed that all the archaeological pottery from Southwest Alaska tested here, including Norton, Thule and Koniag pottery, achieved this firing temperature. Therefore, we conclude that the attribution of manufacture-derived lipids to these pottery samples is negligible. While ethnographic information indicates that surface treatments of pottery with aquatic oils and/or blood was a common practice in Alaskan early historic ceramic traditions, it must be emphasized that these

accounts often regard very low-fired, or even unfired, pottery vessels from historic times. Such vessels probably did not preserve in the archaeological record. All the tested pottery samples in this study were found to have been fired sufficiently to reach a sintering stage ($>550°$C). Possibly this makes post-firing treatments to waterproof the pottery redundant, and the reasons for these treatments were culinary, rather than practical. However, other factors could influence permeability (i.e. porosity) as well, and it should be stated that post-firing treatments are in fact a complex cultural practice, that may have differed from one vessel to the next. This needs further experimental work, testing the performance of cooking vessels with and without post-firing treatments, and under various firing circumstances. Nonetheless, we tentatively conclude that lipid residue results of well-fired Alaskan pottery, may be cautiously interpreted as resulting from vessel use, instead of manufacture. The contribution of aquatic lipids from manufacture or maintenance of the pottery cannot be excluded, but we consider their contribution for purely practical reasons unlikely for vessels that were fired at temperatures exceeding $550°$C.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

Table S1. Results of the firing experiment.

Table S2. Results of the petrographic analysis.

Table S3. Pottery samples for the water test sintering stage.