Maize consumption in pre-Hispanic south-central Andes: chemical and microscopic evidence from organic residues in archaeological pottery from western Tinogasta (Catamarca, Argentina)

I. Lantos a, J.E. Spangenberg b,**, M.A. Giovannetti c, N. Ratto a, M.S. Maier d,*

a Museo Etnográfico J. B. Ambrosetti, Universidad de Buenos Aires, Moreno 350, C1091AH Buenos Aires, Argentina
b Institute of Earth Surface Dynamics, University of Lausanne, CH-1015 Lausanne, Switzerland
c División Arqueología, Facultad de Ciencias Naturales y Museo, Universidad Nacional de La Plata, Paseo del Bosque s/n, B1900FWA La Plata, Argentina
d Unidad de Microanálisis y Métodos Físicos Aplicados a la Química Orgánica, Departamento de Química Orgánica, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Intendente Giraudo 2160, C1428ECG Buenos Aires, Argentina

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Abstract

Pre-Hispanic Andean societies depended economically on the cultivation of maize (Zea mays), the main staple food crop in the region after its introduction from highland Mexico. Here we report new data from residue analysis of potsherds recovered in archaeological sites in western Tinogasta, Catamarca province, Argentina, ca. 3rd to 16th centuries AD. Molecular and isotopic ($\delta^{13}$C values) compositions of fatty acids and microscopically identified maize starch granules from organic residues absorbed in archaeological potsherds were compared with Andean ingredients and food residues obtained from experimental replica pots, where traditional recipes were cooked. Complex mixtures of lipids and starch remains observed in archaeological cooking pots indicated combinations of Andean ingredients such as llama, beans, algarroba, and maize, and suggest continuity in the domestic foodways through time. The distribution and $\delta^{13}$C values of lipids preserved in vessels used for alcoholic beverage preparation, storage and transport in Inka sites suggested the possible consumption of two drinks with distinct patterns: traditional Andean maize beer (chicha) and a local fermented drink made from algarroba flour (aloja). This is potential evidence for consumption practices in festive contexts sponsored by the Inka state.

1. Introduction

1.1. Maize consumption in the Andes

Maize (Zea mays) has been a staple food for American societies since pre-Hispanic times (Johannessen and Hastorf, 1994; Staller et al., 2006); its domestication originated in highland Mexico ca. 8700 cal. BP and later spread to North and South America (Piperno et al., 2009). The earliest evidences of maize cultivation and consumption in South America are from the Pacific coastal regions of Peru and Ecuador ca. 3000 BC (Haas et al., 2013; Zarrillo et al., 2008). The expansion towards the south-central Andes occurred later (ca. 2000 BC), and new maize landraces characteristic to each region appeared (Oliszewski and Olivera, 2009). Archaeological evidences of maize based on microscopic remains of starch granules and phytoliths of Z. mays in the Southern Argentinean Puna (Catamarca province) date from ca. 2000 BC (Rodríguez and Aschero, 2007). Maize cobs and kernels found in several sites from 500 BC and 1st century AD in NW Argentina record the transition of hunter-gatherers to horticulture (Babot, 2005). Later periods showed an increasing dependence on maize as a staple food, as the population developed into complex organizations...
between the 1st and 14th centuries AD (Hastorf, 1990). During the Inka expansion between the 14th and 16th centuries AD the south-central Andes became the key region for state administered production and consumption of maize. Maize was consumed both in domestic contexts where food was shared by family members and was the setting for most of the basic socialization (Appadurai, 1981; Gumerman, 1997), and in centrally organized contexts where staple food was monopolized by the Inka administration. Consumption in the form of chicha beer was central for the symbolic domination of local societies (Logan et al., 2012), and has been associated to Inka festivities and rituals where the exhibition of maize and maize-based products was essential to the maintaining of power (Dietler, 2006; Goldstein, 2003; Hastorf and Johannessen, 1993; Moore, 1989).

In western Tinogasta (Catamarca province, Argentina) the earliest direct evidences of maize are archaeobotanic remains of cobs and kernels from Palo Blanco NH1 (AD 208–529) and Punta Colorada (AD 661–1020) (Fig. 1, sites 5 and 8). Later evidence comes from Batungasta (AD 1445–1558) and Lorohuasi (ca. AD 1550) (Fig. 1, sites 2 and 11). Three groups of local maize varieties were identified by morphological markers and ancient DNA: Andean complex, South American popcorns, and new races derived from varieties introduced from other regions after the Spanish conquest (Lia et al., 2007). Also, remains of Z. mays were found in funerary contexts at Las Champas (ca. AD 1400) and Bebé de la Troya (ca. AD 1330–1428) (Ratto et al., 2014). The importance of local cultivation was inferred from the agricultural installations at different altitude levels in the Fiambalá valley, such as those found for example at El Puesto 1 (Figs. 1 and 2E) (Orgaz and Ratto, 2013). These agricultural installations were used for food production by the agro-pastoralist societies during the first millennium AD, the Inka period ca. 14th to 16th centuries AD, and some are still in use today (Fig. 2F). During the 14th to 16th centuries AD, agricultural installations were reused and in some cases expanded in a context of interaction between local sociopolitical entities and foreign populations that were moved and established in the area by the Inka state (Orgaz and Ratto, 2013; Ratto and Boxaidos, 2012). Preliminary isotopic studies on bone collagen of bioarchaeological remains of individuals from the Fiambalá valley suggest differences in diet through time (Aranda et al., 2011). One case of a lactating individual from the first millennium AD indicated that the mother’s diet was based on C₄ plants, most probably maize. On the other hand, the samples from the Inka period had a wide range of values, but the general tendency suggested that during Inka state presence in the region (14th to 16th century AD), there was a mixed diet with an important C₄ component, a minor contribution of C₃ plants and limited access to animal protein. These results are preliminary, as more studies on the bone mineral fraction are currently in process. In summary, most of the archaeological evidence indicates an important reliance on maize in the Tinogastan diet, but the way in which this staple food was prepared and consumed in the study area is still largely unknown.

1.2. Detecting maize in food organic residues in archaeological ceramics

Organic residues are absorbed in ceramic vessel matrixes during food preparation or storage, thus allowing an exceptional preservation of organic compounds such as lipids and starch (Copley et al., 2005; Eerkens, 2005). Maize and maize-based food residues can be
detected in archaeological ceramics by a combination of microscopic analysis of preserved starch granules, and molecular and stable carbon isotope analysis of preserved lipids. Starch grains can be recovered from the inner walls of cooking potsherds (Crowther, 2005; Saul et al., 2012). Maize starch remains have been microscopically identified under reflected normal and polarized light in different archaeological samples, including stone artifacts, sediments, and coprolites from cultural layers in Central and South America (Babot and Apella, 2003; Pearsall et al., 2004; Perry, 2004). Maize starch grains have also been recovered from cooking residues adhered to potsherds from North and South American archaeological sites (Boyd et al., 2008; Zarrillo et al., 2008).

Chemical characterization of lipids can be achieved by gas chromatography coupled to mass-spectrometry (Malainey et al., 1999; Reber and Evershed, 2004a). The fatty acids (FAs) profile and the relatively high stable carbon isotope ratio ($\delta^{13}C$) expressed in $\delta^{13}C$ as % vs. Vienna Pee Dee Belemnite limestone standard (VPDB) characteristic of C4 plants can provide supporting evidence for the presence of residual maize oil in archaeological artifacts (Reber and Evershed, 2004b; Reber et al., 2004; Seinfeld et al., 2009). C3 and C4 plants have different photosynthetic pathways leading to distinct carbon isotope fractionations (Deines, 1980; O’Leary, 1993). C3 plants use the Calvin–Benson cycle for CO2 fixation and include most South American fruits, vegetables and cool season grasses, with $\delta^{13}C$ values clustering around −27‰ (Marshall et al., 2007). C4 plants use the Hatch–Slack cycle and are adapted to hot and arid environments. They include maize, sugar cane and warm season grasses, and their $\delta^{13}C$ values cluster around −14‰ (Marshall et al., 2007). Although C4 plants in NW Argentina also include pastures such as Muhlenbergia fastigiata, M. atacamensis, Sporobolus rigens, Pennisetum chilense, and Eragrostis nigricans which may have been used for herding, Z. mays was the main staple food consumed by humans derived from a C4 plant that can be distinguished from other foodstuffs by its $\delta^{13}C/\delta^{12}C$ ratio (Reber and Evershed, 2004b; Tykot et al., 2009).

2. The western Tinogasta study area

Western Tinogasta is part of the south-central Andes located in the southwestern tip of Catamarca province in NW Argentina (Fig. 1). It is comprised by the Fiambalá region and the Chaschuil region, separated by Las Planchadas and Narváez ranges, and has diverse and contrasting eco-zones, including the mesothermal valley (1400–2400 m above sea level — masl), the piedmont (2400–3500 masl), the transitional puna (3500–4000 masl), and the Andes range (4000–6700 masl). Western Tinogasta is limited by the southern puna highlands in the north, the Abaucán river in the south, the Fiambalá mountain ranges in the east, Chile’s III
Region in the northwest, and La Rioja province, Argentina, in the southwest.

The cultural landscape of pre-Hispanic western Tinogasta was characterized by discontinuous settlements of human populations due to environmental processes that made the area uninhabitable during certain periods (Ratto et al., 2013). Throughout the first millennium AD, western Tinogasta was populated by societies that developed herding and agricultural economies, while still maintaining hunting and gathering practices. Sparserly distributed villages were built with mud tapia (Fig. 2B) or stone pirca (Bonomo et al., 2010; Ratto et al., 2012). They were located both in the Fiambalá and Chaschuil regions, in different altitudinal levels and eco-zones, taking advantage of different local resources (Ratto et al., 2013).

Recent research shows that between the 10th and 13th centuries AD a synergy of environmental processes made lower eco-zones uninhabitable and triggered population movements and site abandonments in search of eco-refuges in higher valleys, where they continued to carry out their traditional ways of life (Ratto et al., 2013). The valley bottoms of the Fiambalá region were probably repopulated during the first centuries of second millennium AD when conditions slowly improved around the 13th century AD (Ratto, 2013). Then, when environmental conditions were optimal, the Inka expanded into the Fiambalá and Chaschuil regions from the 14th to 16th centuries AD. The Inka domination process promoted the mobilization of people from other areas with new cultural characteristics as part of the territorial domination strategy (Ratto and Boxaidós, 2012). Towards the 17th century AD, the Spanish colonial installation created new politically unstable conditions and caused community relocations as the area underwent a new depopulation process (Ratto and Boxaidós, 2012).

In this study we selected samples from archaeological sites settled during the first or the second millennia AD, distributed along the Fiambalá and Chaschuil regions (Table 1; Fig. 2). In the following paragraphs we briefly introduce the sites from which samples were selected.

The sites dating to the first millennium AD (Table 1) include: (i) La Troya LT-V50 situated at 1380 masl and dated in AD 641–784; (ii) Palo Blanco archaeological village (Fig. 2B–C) composed of various habitation units located at 1900 masl, dated in AD 208–529 (Palo Blanco NH1), AD 427–599 (Palo Blanco NH4), AD 458–639 (Palo Blanco NH3), and AD 693–985 (Palo Blanco NH6); (iii) Punta Colorada placed at 2290 masl and settled during AD 661–1020; (iv) Cardoso set at 1970 masl and with architectural pattern and ceramic technology indicating it was settled between the last centuries of the first millennium AD and the first centuries of the second millennium AD (radiocarbon dates in process); (v) Ojo del Agua situated at 2400 masl and dated in AD 994–1047; and (vi) El Zorro located at 4050 masl and settled from AD 322–1019. All dates are calibrated from radiocarbon dates with 1 sigma standard deviation, and were taken from Ratto (2013).

The sites from the second millennium AD (Table 1) include: (i) Quintar-1 (1750 masl) dated in AD 1123–1273, a period of environmental instability when most of the other sites in the mesothermal valley were abandoned; (ii) Mishma 7 (1760 masl) dated in AD 1405–1573 with local and Inka components; (iii) Batungasta (1480 masl) dated in AD 1445–1600, the central Inka administrative site of the region; and (iv) San Francisco (4000 masl) dated in AD 1400–1500 AD (Fig. 2A), a peregrination place used for feasting and religious activities previous to the ascension to Incahuasi Mt., where an Inka sacrificial site was found (Orgaz et al., 2007; Ratto et al., 2012).

In this paper we aimed to explore the potential changes and continuities in the maize preparation and consumption practices before and after the Inka state installation in order to provide insight into the foodways in western Tinogasta. We believe that domestic preparation of maize may have been part of the closely-knit social fabric of the agro-pastoral societies of the first millennium AD, and therefore domestic practices may have not changed substantially after the Inka occupation of the area during the second millennium. On the other hand, state-sponsored public rituals and festivities may have suffered changes by power disputes when the Inka administration took over the area during the fourth and fifth centuries of the second millennium. These issues inspired us to carry out an exploratory study aimed to assess the potential occurrence of maize and maize-based food remains within organic residues preserved in the ceramic matrices of archaeological pottery from western Tinogasta by molecular, carbon isotope and microscopic studies.

### 3. Materials and methods

#### 3.1. Samples

Organic residues were obtained from twenty-two potsherd samples (n = 22) (Table 1). Samples were taken from lip, neck, body...
or base sections of the vessel silhouette according to availability for sampling and presence of macroscopic signs of absorbed residues, such as stains or oiliness. Previously, we tested lip, body and base sections of our three replica pots (R-11, R-12, R-13, Table 2) and confirmed that although lipid concentration varied, FAs profiles were identical in all vessel sections. Therefore, we could safely compare archaeological absorbed residues from different vessel sections. In the field, potsherds were recovered using dustless gloves and immediately stored in aluminum foil paper to avoid contamination. In the lab, potsherds were carefully handled with dustless gloves and clean instruments. Potsherds had very little or no sediments attached to them given the extreme dryness of the sediment matrices in the field. When present, it was carefully removed with clean brushes. All potsherds remained unwashed. Organic residues were absorbed into the matrices of all samples, and no adhered crusts were visible. Samples of ca. 4 x 4 cm² were separated for residue analysis. Subsequent treatment is described in Section 3.2.

The potsherd samples were selected as representative of the vessel morphologies characteristic for specific functions. Following Skibo (1992) the vessel function was defined by technological and morphological characteristics, while vessel use by alteration evidences and presence of organic residues. The first functional category was “cooking pots” (Fig. 3, A-05, A-07 and A-11), characterized by a typical morphology showing a flat or round base, globular wide body, and slightly more restricted neck (Feely, 2013; Orgaz et al., 2007). The inner surfaces were untreated before firing, some were regular and smooth while others were irregular (Feely, 2010). The texture of the ceramic matrices, in terms of particle size and porosity, ranged from medium to coarse (Feely, 2010). In addition, use-alteration macroscopic features indicating their use as cooking pots were visible, such as soot in the outer surfaces, and/or dark and oily stains in the inner surfaces. The second functional category was “beverage-holding vessels”, including morphologies of aribalos, aribaloids and Belén vessels. Aribalos and aribaloids (Fig. 3, A-21) were characterized by their conic or semi-conic bases and constricted bottle-like necks (Orgaz et al., 2007) which indicate their function as liquid carriers. The inner surfaces were regular and smooth and the outer surfaces were treated with slip, polished and painted (Feely, 2010). The porosity of the ceramic matrices in aribalos and aribaloids was medium to fine. Various authors have stated that aribalos and aribaloids were designed to store, transport and pour alcoholic beverages for Inka ritual festivities (Bray, 2004, 2003; Giovannetti et al., 2013; Jennings and Bowser, 2009; Moore, 2013). In western Tinogasta, aribalos had classic Inka shapes with provincial decorative style, while aribaloids had a slightly modified shape and a provincial Inka decorative style (Calderari and Williams, 1991). Belén vessels are characterized by typical morphologies with conic bases, ovoid bodies, and wide necks, as well as distinctive Belén style decoration (Orgaz et al., 2007). The only studied Belén vessel sample (Fig. 3, A-08) represents a local style coexisting during the Inka occupation (Calderari and Williams, 1991). The inner surface was irregularly smoothed while the outer surface was also smoothed, bathed in slip and painted, and the porosity of the ceramic matrix was medium. An ongoing debate exists on Belén vessel function, as it has been associated with beverage production, funerary purposes, grain storage, and cooking (Amuedo, 2012; Marchegiani et al., 2009). Therefore, the Belén vessel sample studied in this paper was cautiously and temporarily assigned to the “beverage-holding” category as we believe in this case residue analysis could provide some information on its possible use as a beverage production vessel.

Lipid concentrations (µg/g) were tested against vessel antiquity, function, vessel section, ceramic matrix texture and surface treatment. Non-parametric Mann Whitney and Kruskal–Wallis tests showed that age, function, vessel section, matrix texture, and surface treatment had no statistically significant (P < 0.05) effect on the concentration of absorbed and preserved lipids (see Appendix A, Supplementary data).

Reference samples including eleven ingredients from traditional Andean cookery (n = 11) and potsherds from three replica cooking pots (n = 3) were also studied (Table 2). Four maize landraces native from NW Argentina were chosen as C4 plant references (pisingallo, chullpi, dentado blanco, and capia) and their starch granules were used as references for microscopic analysis. Algarroba pods and alubia beans from Catamarca province. NW Argentina, were selected as C3 plant references and their starch granules were used as references for microscopic analysis. Bovine fat from the central Pampas and NW Argentina were selected as references for animals fed on a diet composed of C4 pastures and some maize supplement. Samples of fat and jerky from llamas fed exclusively on C4 pastures were obtained from the puna area of Jujuy province, NW Argentina. Three replica ceramic pots were used for cooking experiments conducted with traditional corn-based Andean recipes (Table 3, Fig. 2 D, Fig. 3 R-13, R-12). Replica pots were crafted by an artisan ceramist using traditional firing techniques. Shape and volumetric characteristics of the pots, proportions of raw materials, porosity of the matrix and inner surfaces were reproduced from archaeological cooking pottery recovered at the study area (Feely, 2013). In replica pot A mazamorra (a sweet porridge generally consumed for breakfast) was made with dry kernels of sweet maize (Chullpi corn) boiled in water. In replica Pot B locro (a thick stew consumed for lunch) was made with dry kernels of starchy maize (Dentado Blanco corn), dry beans, and fresh

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**Table 2**

Reference samples selected for lipid analysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Material</th>
<th>Description</th>
<th>Locality</th>
<th>Altitude (masl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-01</td>
<td>Kernels</td>
<td>Pisingallo (Zea mays L., ARZM09963)</td>
<td>Tilcara, Jujuy</td>
<td>2460</td>
</tr>
<tr>
<td>R-02</td>
<td>Kernels</td>
<td>Chullpi (Zea mays L., ARZM09421)</td>
<td>Humahuaca, Jujuy</td>
<td>2500</td>
</tr>
<tr>
<td>R-03</td>
<td>Kernels</td>
<td>Dentado blanco (Zea mays L., ARZM12001)</td>
<td>Tiraí, Jujuy</td>
<td>1750</td>
</tr>
<tr>
<td>R-04</td>
<td>Kernels</td>
<td>Capia blanco (Zea mays L., ARZM09370)</td>
<td>Maimará, Jujuy</td>
<td>2400</td>
</tr>
<tr>
<td>R-05</td>
<td>Pods</td>
<td>Algarrobo (Prosopis alba Giserb.)</td>
<td>El Alto, Catamarca</td>
<td>940</td>
</tr>
<tr>
<td>R-06</td>
<td>Seeds</td>
<td>Alubia bean (Phaseolus vulgaris L.)</td>
<td>Fimialba Catamarca</td>
<td>1500</td>
</tr>
<tr>
<td>R-07</td>
<td>Fresh fat</td>
<td>Bovine fat I ( Bos taurus L.)</td>
<td>Cruz Alta, Tucumán</td>
<td>1300</td>
</tr>
<tr>
<td>R-08</td>
<td>Fresh fat</td>
<td>Bovine fat II ( Bos taurus L.)</td>
<td>San Antonio de Areqo, Buenos Aires</td>
<td>100</td>
</tr>
<tr>
<td>R-09</td>
<td>Fresh fat</td>
<td>Llama fat ( Lama glama L.)</td>
<td>La Candelaria, Jujuy</td>
<td>3950</td>
</tr>
<tr>
<td>R-10</td>
<td>Fresh fat</td>
<td>Llama fat ( Lama glama L.)</td>
<td>La Candelaria, Jujuy</td>
<td>3950</td>
</tr>
<tr>
<td>R-11</td>
<td>Potsherd</td>
<td>Replica pot A (Mazamorra)</td>
<td>Experimental site, Catamarca</td>
<td>1350</td>
</tr>
<tr>
<td>R-12</td>
<td>Potsherd</td>
<td>Replica pot B (Locro)</td>
<td>Experimental site, Catamarca</td>
<td>1350</td>
</tr>
<tr>
<td>R-13</td>
<td>Potsherd</td>
<td>Replica pot C (Pochocho)</td>
<td>Experimental site, Catamarca</td>
<td>1350</td>
</tr>
<tr>
<td>R-14</td>
<td>Kernels</td>
<td>Pisingallo from Punta Colorada (Zea mays L.)</td>
<td>Punta Colorada site, Catamarca</td>
<td>2290</td>
</tr>
</tbody>
</table>
beef fat. In replica Pot C pochoclo (popcorn) was made with kernels of another native race of maize (Pisingallo) from NW Argentina and a little fresh beef fat. The Maize Germplasm Bank of the Argentine National Institute for Agronomical Technology (INTA-Pergamino) provided the native landraces used in the recipes. Dry beans and beef fat were obtained from local farmers in the market of the modern town of Fiambalá, Catamarca, NW Argentina. In pre-Hispanic times, fat from llama, guanaco or vicuña would have probably been used but these products were not available at the time of the experimental cooking. The replica pots were broken and sherds were selected for microscopic starch analysis to obtain references of cooking alterations in starch granules (Crowther, 2012; Haslam, 2004; Raviele, 2011). Lipid analysis of the replica pot-sherds was performed to obtain references for the absorbed residues from cooked traditional Andean foods.

### 3.2. Lipid extraction

Lipid extraction was carried out on all archaeological and reference samples (Tables 1 and 2). Powder of the dry samples (kernels, beans, pods) was obtained by grinding with a coffee mill.
The fresh animal fats were frozen and ground using a porcelain mortar and pestle. Replica potsherds and archaeological potsherds were first rinsed on both surfaces with dichloromethane. They were then broken into small fragments with a hammer and then ground in a porcelain mortar and pestle. Lipids were extracted with dichloromethane:methanol (1:1, vol/vol). All solvents were of chromatographic quality (Merck, Buenos Aires, Argentina and Merck Darmstadt, Germany) and pre-distilled before use. Each sample was placed in an ultrasonic bath for 15 min and filtered; a few drops of distilled water were added, the organic phase was separated after centrifugation for 3 min (twice), evaporated at room temperature in the dark, weighed and then transferred with n-hexane to a 2 ml glass vial and stored at −20 °C. An aliquot of the extract was saponified with 1 ml of 1N potassium hydroxide in an ethanolic aqueous solution (9:1, vol/vol), at 60 °C for 2 h. After cooling at room temperature, the neutral fraction was extracted with 1.5 ml n-hexane and the aqueous fraction acidified with 1N HCl solution and extracted with 1.5 ml n-hexane. The organic phase was evaporated at room temperature in the dark and 0.5 ml of 1M HCl solution and extracted with 1.5 ml n-hexane and the neutral fraction was prepared by addition of 20 μl of N,O-bis (trimethylsilyl) trifluoroacetamide (BTSFA) with 1% trimethylchlorosilane (TMCS) (Supelco) and heating at 60 °C for 20 min. After cooling, the TMS derivatives were dried under a soft stream of nitrogen, n-hexane was added and the solution stored at 4 °C. Samples were analyzed within 24 h of derivatization. Procedure blanks for lipid extraction, saponification, methylation, and TMS derivatization were prepared and analyzed as the archaeological samples.

3.3. Chemical characterization of acid and neutral lipids

Chemical characterization of FAMEs was performed with an Agilent (Palo Alto, USA) gas chromatograph 6890 coupled to an Agilent 5973 quadrupole mass selective detector (GC–MS). The system was equipped with an Agilent free FAs phase (HP-FFAP) fused silica capillary column (150 m length, 0.20 mm i.d.) coated with nitroterephthalic acid modified polyethylene glycol stationary phase (film thickness 0.33 mm). He was used as carrier gas (1 ml/min flow rate) and manual injection was splitless at a temperature of 200 °C. After an initial period of 2 min at 100 °C, the column was heated to 240 °C at 5 °C/min followed by an isothermal period of 30 min. The MS was operated in the electron impact mode at 70 eV, source temperature of 250 °C, emission current of 1 mA and multiple-ion detection with a mass range from 50 to 600 amu. Compound identifications were carried out by comparing GC retention times of FAME standards (C14:0, C15:0, C16:0, C17:0, C18:0, C18:1, C18:2, Sigma, St. Louis, MO, USA) and mass spectrometric fragmentation patterns. The abundances of FAME in the organic residues relative to total FAME were calculated from total ion chromatogram peak areas.

Chemical characterization of the TMS derivatives of the neutral lipids was performed by gas chromatography–mass spectrometry on a Shimadzu GCMS-QP5050A (Shimadzu Corporation, Kyoto, Japan). The system was equipped with an Agilent Ultra 2 capillary column (50 m length, 0.20 mm i.d.) coated with (5% phenyl)-methylpolysiloxane (film thickness 0.11 mm). He was used as carrier gas (0.9 ml/min flow rate) and manual injection was splitless at a temperature of 250 °C. After an initial temperature of 100 °C, the column was heated to 240 °C at 10 °C/min followed by an isothermal period of 25 min, and then heated to 280 °C at 4 °C/min followed by and isothermal period of 30 min. The MS was operated in the electron impact mode at 70 eV with a source temperature of 290 °C.

3.4. Compound specific C isotope analysis of fatty acids (CISA)

Compound specific stable carbon isotope analyses (δ13C values) of the fatty acids (FAs) were performed on an Agilent 6890 GC coupled to a Thermo Fischer Delta V isotope mass spectrometer by a combustion (C) interface III (GC–C-IRMS) under a constant He flow of 1.2 ml/min. The gas chromatograph was operated with an HP-FFAP column and same temperature program as used for GC–MS analyses. The combustion interface consisted of two ceramic furnaces, an oxidation reactor with CuO/NiO/Pt wires at 940 °C and a reduction reactor with Cu wires at 600 °C. Water was removed from the effluent gas by passing a NaF tube (Perma Pure, Toms River, NJ, USA) with an annular back-flow of Helium. The background subtraction and calculations of δ13C values were performed using ISO-DAT 2.5 software (Thermo Fischer Scientific, Bremen, Germany). The repeatability and intermediate precision of the GC–C-IRMS procedure, and the performance of the GC and combustion interface were evaluated every five analyses by co-injection of isotope standards (eicosanoic acid methyl ester, δ13C20:0 = −24.3 ± 0.2% and naphthalene δ13C20:0 = −26.1 ± 0.3%) (Spanenberg et al., 2006). At least three replicate analyses of the reference and archaeological samples were carried out so averages and standard deviations could be calculated for each result. The accuracy of the GC–C-IRMS analyses was checked every ten analyses. The mean overall analytical error for the main FAMES was 0.8% and ranged between 0.1 and 2.7%. The stable carbon isotopic data are expressed in delta (δ) notation as the per mil (‰) deviations of the isotope ratio of the sample relative to that of a standard (δ13C = [(Rsample − Rstandard)/Rstandard] × 1000), where R = 13C/12C. The stable isotope composition of carbon (δ13C values) is reported relative to the Vienna Pee Dee Belemnite limestone (VPDB) standard. The isotopic shift due to the carbon introduced by methylation was corrected using a mass balance equation (Spanenberg et al., 1998). Post-industrial reference samples were corrected for anthropogenic CO2 emissions by adding +1.6% to the isotopic values obtained in the GC–C-IRMS analysis (Spanenberg et al., 2006).

3.5. Statistical analyses

Principal component analysis (PCA), Hierarchical cluster analysis (HCA), and Discriminant analysis (DA) were performed by statistical analysis software SPSS 18.0 (IBM) and PAST (Hammer et al., 2001) to gain insight into the nature of the multivariate dataset obtained from lipid analyses of the archaeological samples.

3.6. Starch separation and microscopic analysis

Starch granules were extracted in a controlled clean hermetic environment to avoid contamination. Dustless gloves and sterile materials were used for each sample and the workspace was cleaned carefully between each sample extraction. An area of 4 × 4 cm of the inner surface of each archaeological sample was gently scraped with a scalpel, and the detached residue was sieved with an N°35 US mesh (0.5 mm opening) and the finer fraction was recovered. The same procedure was used for the replica potsherd samples on a different day and after the archaeological samples preparation to avoid cross-contamination. A tip of each sample was mounted on a glass slide with a solution of distilled water and glycerol (50%). Microscopic study of starch grains was carried out on a Lancet XSZ-148 microscope at 40× alternating normal and polarized light. The light intensity was fixed at seven and the diaphragm opening was set at five. Samples were analyzed by sweeping through the complete slide. Micrographic images were obtained with a Samsung HZ10W camera with 10.2 megapixel resolution, which was equipped with an adaptor to the eyepiece.
4. Results

4.1. Fatty acid and neutral lipids composition

Relatively high amounts of lipids were recovered from the replica cooking potsherds (4200 μg/g mean value) and substantially less in the archaeological Tinogasta potsherds, with a mean value of 200 μg/g for all vessel categories.

The FAs relative abundances, palmitic to stearic acid ratios (P/S), and lipid concentrations of the reference and archaeological samples are detailed in Table 4. The gas chromatograms showed a series of methyl esters of carboxylic acids in the C_{12}–C_{18} range (Figs. 4–5). The main saturated fatty acids were myristic (C_{14:0}), pentadecanoic (C_{15:0}), palmitic (C_{16:0}), margaric (C_{17:0}), and stearic (C_{18:0}) acids, maximizing at C_{16} and C_{18}. Small to trace amounts of lauric (C_{12:0}) acid occurred in most of the archaeological samples. The most abundant unsaturated fatty acids were palmitoleic (C_{16:1}), oleic (C_{18:1}), linoleic (C_{18:2}), and linolenic (C_{18:3}) acids. The FAs distributions of the lipids extracted from modern maize landraces (R-01, R-02, R-03, and R-04) were similar to previously published data (Spangenberg and Ogrinc, 2001; Woodbury et al., 1995). The P/S ratios for modern maize samples ranged from 6.9 to 12.4. The FAs profile for archaeological pisingallo maize (R-14) was typical for degraded vegetable oil, with a loss of unsaturated fatty acids and relative increase of palmitic and stearic acid abundances, which is reflected in a P/S ratio of 5.1. The

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Archaeological samples

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<th>18:3</th>
<th>Other</th>
<th>P/S ratio</th>
<th>Lipid conc. (μg/g)</th>
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<td>5.6</td>
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Summary

- Fatty acid and neutral lipids composition
- Sample Description
- 12:0
- 14:0
- 15:0
- 16:0
- 16:1
- 17:0
- 18:0
- 18:1
- 18:2
- 18:3
- Other
- P/S ratio
- Lipid conc. (μg/g)
- Reference samples
- A-01 La Troya LV50; cooking pot
- A-02 La Troya LV50; cooking pot
- A-03 La Troya LV50; cooking pot
- A-04 Batungasta; cooking pot
- A-05 Batungasta; cooking pot
- A-06 Batungasta; cooking pot
- A-07 Mishma 7; cooking pot
- A-08 Mishma 7; beverage-holding vessel
- A-09 Quintar 1; cooking pot
- A-10 Palo Blanco NH1; cooking pot
- A-11 Palo Blanco NH3; cooking pot
- A-12 Palo Blanco NH6; cooking pot
- A-13 Palo Blanco NH4; cooking pot
- A-14 Ojo del Agua; cooking pot
- A-15 Cardoso; cooking pot
- A-16 Punta Colorada; cooking pot
- A-17 San Francisco; beverage-holding vessel
- A-18 San Francisco; beverage-holding vessel
- A-19 El Zorro; cooking pot
- A-20 Batungasta; cooking pot
- A-21 San Francisco; beverage-holding vessel
- A-22 San Francisco; beverage-holding vessel

In the archaeological Tinogasta potsherds, with a mean value of 200 μg/g for all vessel categories. The FAs relative abundances, palmitic to stearic acid ratios (P/S), and lipid concentrations of the reference and archaeological samples are detailed in Table 4. The gas chromatograms showed a series of methyl esters of carboxylic acids in the C_{12}–C_{18} range (Figs. 4–5). The main saturated fatty acids were myristic (C_{14:0}), pentadecanoic (C_{15:0}), palmitic (C_{16:0}), margaric (C_{17:0}), and stearic (C_{18:0}) acids, maximizing at C_{16} and C_{18}. Small to trace amounts of lauric (C_{12:0}) acid occurred in most of the archaeological samples. The most abundant unsaturated fatty acids were palmitoleic (C_{16:1}), oleic (C_{18:1}), linoleic (C_{18:2}), and linolenic (C_{18:3}) acids. The FAs distributions of the lipids extracted from modern maize landraces (R-01, R-02, R-03, and R-04) were similar to previously published data (Spangenberg and Ogrinc, 2001; Woodbury et al., 1995). The P/S ratios for modern maize samples ranged from 6.9 to 12.4. The FAs profile for archaeological pisingallo maize (R-14) was typical for degraded vegetable oil, with a loss of unsaturated fatty acids and relative increase of palmitic and stearic acid abundances, which is reflected in a P/S ratio of 5.1. The...
algarroba (R-05) contained C\textsubscript{16:0}, C\textsubscript{18:0}, and C\textsubscript{18:1}, followed by smaller amounts of C\textsubscript{18:2} (P/S ratio of 1.9), this FAs profile was similar to published data (Lamarque et al., 1994; Mazzuca and Balzaretti, 2003). The sample of native bean (R-06) showed abundant polyunsaturated fatty acids, especially C\textsubscript{18:2} and C\textsubscript{18:3}, followed by C\textsubscript{16:0}, C\textsubscript{16:1}, and C\textsubscript{18:0} in lower abundance, and P/S = 6.7, also similar to published FAs profiles (Grela and Günter, 1995). Cow fat samples (R-07, R-08) showed high abundance of C\textsubscript{16:0} and C\textsubscript{18:1}, presence of

![Figure 4](image_url)

**Fig. 4.** Total ion chromatograms of fatty acid methyl esters extracted from reference samples: A, R-02 chullpi maize; B, R-06 alubia beans; C, R-09 llama fat; D, R-12 test pot B. The fatty acids are myristic (14:0), pentadecanoic (15:0), palmitic (16:0), palmitoleic (16:1), margaric (17:0), stearic (18:0), oleic (18:1), and linoleic (18:2) acids.

![Figure 5](image_url)

**Fig. 5.** Total ion chromatograms of fatty acid methyl esters extracted from archaeological samples: A and B, A-05 and A-06 cooking pots from Batungasta; C, A-10 cooking pot from Palo Blanco NH1; D, A-14 cooking pot from Ojo del Agua. The fatty acids are lauric (12:0), tridecanoic (13:0), myristic (14:0), pentadecanoic (15:0), palmitic (16:0), palmitoleic (16:1), margaric (17:0), stearic (18:0), oleic (18:1), and linoleic (18:2) acids.
odd-numbered FAs and a low P/S ratio ranging from 2.6 to 4.0, typical of animal fats (Evershed et al., 2002). Llama fat samples (R-09, R-10) had typical animal fat profiles with high C_{16:0} and C_{18:1} acids abundance and a low P/S ratio ranging from 2.0 to 2.2, and FAs typical of ruminant and pseudo-ruminant animals (e.g., American camelids) (Coates and Ayerza, 2004; Maier et al., 2007; Vázquez et al., 2008) such as lauric (C_{12:0}), pentadecanoic and margaric acids, and trace amounts of ramified anteiso methyl-tetradecanoic and methyl-hexadecanoic acids. Myristic and palmitoleic acids were present in all animal fats—both cow and llama—while absent in all vegetable oil samples. The FA distribution for replica pot A (R-11) showed a vegetable oil profile with little signs of degradation and a P/S ratio of 5.6 (Fig. 6, Table 4). Replica pots B (R-12) and C (R-13) showed FAs profiles of mixtures of vegetable and animal ingredients and few signs of degradation, with P/S ratios of 2.4 to 1.8, respectively. In these last two cases, the mixtures were dominated by the animal fat component with respect to the vegetable oil component. This indicated that lipid concentrations (µg lipid extracted in 1 g of whole raw ingredient) in the vegetable ingredients used in both recipes were much lower (15,700 µg/g to 54,700 µg/g) than those in the animal fat ingredient (793,000 µg/g to 986,000 µg/g), and explains why the P/S ratio in pots B and C is similar to cow fat rather than to maize or beans. This supports previous findings by Reber et al. (2004), known as “masking effect”, where vegetable ingredients can be underestimated due to their lower lipid concentrations and higher abundance in more readily degradable unsaturated FAs. This is important for the interpretation of FAs profiles in archaeological samples.

The fatty acid distributions for the archaeological samples were typical of degraded fats and oils, and had a mean P/S ratio of 2.5 ± 1.3 (Fig. 7, Table 4). C_{16:1} and C_{18:1} acids were also found in most of the archaeological samples (A-01 to A-22). Small amounts of C_{18:2} were only detectable in a few samples. This is to be expected since the polyunsaturated FAs would have decomposed under the oxidative conditions during vessel use and subsequent burial at the archaeological sites. Some archaeological samples had trace amounts of ramified methyl-tetradecanoic and methyl-hexadecanoic acids equivalent to those found in the llama reference samples (R-09 and R-10). The FAs profiles of archaeological samples from sites dated to the first and second millennia AD were mostly dominated by an animal fat signature comparable to the llama reference samples (R-09 and R-10).


![Image](image_url)
triacanool (30-OH) (A-04, A-06, A-14). These long-chain alcohols are characteristic of plant waxes (Kolattukudy, 1970). Neither the archaeological samples nor the maize reference sample (R-03, dentado blanco maize) contained n-dotriaconol (32-OH), a long-chain alcohol that was proposed as a biomarker of North American maize (Reber and Evershed, 2004b; Reber et al., 2004). Samples A-01 and A-03 showed the presence of cholesterol, a lipid biomarker for meat, together with minor cholesterol degradation products. Sitosterol, a lipid biomarker for plants, was identified in sample A-11 as well as in maize and bean reference samples, which also contained campesterol and stigmasterol. The identification of cholesterol together with long-chain alcohols 24-OH, 25-OH, 26-OH, and 28-OH in archaeological samples A-01 and A-03 points to a mixture of vegetable and animal ingredients in these cooking pots.

4.2. Stable carbon isotope composition of individual fatty acids

Results of CSIA of the main FAs from lipid extracts of reference and archaeological samples are presented in Table 5. The δ¹³C values of the main FAs for maize (R-01, R-02, R-03, R-04, and R-14) were within the published range (Spangenberg and Ogrinc, 2001; Woodbury et al., 1995). Mean values for C₁₆:₀, C₁₈:₀, C₁₈:₁, and C₁₈:₂ were −16.9 ± 1.0‰, −19.2 ± 1.0‰, −15.5 ± 1.3‰ and −16.5 ± 1.2‰, respectively. The C₄ leguminous plant samples (bean R-05 and algarroba R-06) had mean δ¹³C values for C₁₆:₀, C₁₈:₀, C₁₈:₁, and C₁₈:₂ between −33.4 and −31.6‰. Bovine fat samples (R-07 and R-08) had values between −22.4 and −20.4‰ for C₁₆:₀, C₁₈:₀, C₁₈:₁, and −29.1‰ for C₁₈:₂. The fat samples of llamas (R-09 and R-10) fed exclusively on C₃ grasses had mean δ¹³C values between −27.5 and −24.5‰ for C₁₆:₀, C₁₈:₀, C₁₈:₁, and similarly to bovine fat had ¹³C-depleted C₁₈:₂ acids (−29.9‰). The lower mean values for C₁₈:₂ compared to the other main adipose FAs may be explained by a contribution of endogenous synthesized ¹³C-depleted cis-9,trans-11C₁₈:₂ acid (Richter et al., 2012a, 2012b). Replica pot A (R-11) had δ¹³C values ranging from −19.0‰ to −17.4‰. In replica pots B and C (R-12, R-13), the δ¹³C value of the FAs represented mixtures of animal and vegetable fats. They had similar δ¹³C values for C₁₆:₀, C₁₈:₀, C₁₈:₁, varying between −21.0‰ and −19.1‰. In replica pot B, the relatively lower δ¹³C value (−24.6 ± 1.7) is explained by the mixture of the recipe components: maize (−16.5 ± 1.2‰), bean (−34.8 ± 0.6‰) and bovine fat (−29.1 ± 4.5‰). In replica pot C, the δ¹³C value (−17.7 ± 0.4‰) is dominated by maize.

The δ¹³C values of the main FAs of the lipids extracted from the archaeological samples (A-01 to A-22) were −25.6 ± 1.6‰ (C₁₄:₀), −25.1 ± 1.7‰ (C₁₅:₀), −25.0 ± 1.7‰ (C₁₆:₀), −25.3 ± 1.9‰ (C₁₆:₁), −26.3 ± 1.9‰ (C₁₇:₀), −26.1 ± 1.7‰ (C₁₈:₀), −25.5 ± 2.7‰ (C₁₈:₁), and −31.7 ± 6.3‰ (C₁₈:₂). The mean δ¹³C values of each sample ranged from −28.8 to −21.5‰, indicating different biological sources of the organic residues.

The isotopic compositions of the main FAs in archaeological samples were compared with those from reference samples (Evershed, 2008; Spangenberg et al., 2006). We observed complex mixtures of different biological origins in the western Tinogasta archaeological samples. Biplots of the reference samples δ¹³C₁₆:₀ values against δ¹³C₁₈:₀ and δ¹³C₁₈:₂ (Fig. 6 A and B) showed a clear separation between vegetable oils from C₃ and C₄ plants. Animal fats were positioned in between C₃ and C₄ plants. Replica pot A was positioned in both biplots near maize reference samples. Replica pots B and C were positioned close to maize reference samples in biplot A, and in an intermediate position between maize and cow fat in biplot B. Biplots C and D of archaeological samples (Fig. 6C and D) showed that most isotopic values fell within the range of pre-industrial llama fat reference values. Only a few samples with higher values were positioned closer to the pre-industrial values for cow fat (A-09, A-14, A-18 and A-19). These higher values could indicate mixtures with a greater proportion of C₄ plant oils and a lower proportion of C₃ plant oils and animal fats.

4.3. Statistical analyses

Principal component analysis (PCA) was carried out on 33 samples (14 reference samples corrected to preindustrial values and 19 archaeological samples). We selected four variables for multivariate analysis: the main fatty acid δ¹³C values (δ¹³C₁₆:₀, δ¹³C₁₈:₀, and δ¹³C₁₈:₁) and palmitic to stearic acid (P/S) ratios. The first two principal components (PC) explain 97.5% of the total variance; PC1 explains 86.7% and PC2 10.8%. For PC1, the greatest loading was observed for δ¹³C₁₆:₀ (0.63), followed by δ¹³C₁₈:₀ (0.55), δ¹³C₁₈:₁ (0.49), and P/S ratio (0.25). For PC2, the greatest loading was observed for P/S ratio (0.96), followed by δ¹³C₁₆:₀ (−0.22),
Table 5

Δ13C values (% vs. VPDB) of the main fatty acids in lipids from reference samples and archaeological potsherds recovered at West Tintagoga.

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<td>R-01</td>
<td>Pisingallo</td>
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<td>–25.3 ± 0.3</td>
<td>–23.3 ± 0.4</td>
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<td>–25.7 ± 0.2</td>
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<td>D. Blanco</td>
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<td>–27.4 ± 0.9</td>
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<td>–26.1 ± 0.3</td>
<td>–25.4 ± 0.1</td>
<td>–25.1 ± 0.1</td>
<td>–27.0 ± 0.1</td>
<td>–36.5 ± 2.6</td>
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<td></td>
<td>R-12</td>
<td>Palo Blanco NH2</td>
<td>–25.4 ± 1.1</td>
<td>–26.9 ± 0.9</td>
<td>–27.4 ± 0.9</td>
<td>–29.4 ± 1.0</td>
<td></td>
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<tr>
<td></td>
<td>R-13</td>
<td>Palo Blanco NH4</td>
<td>–26.3 ± 0.3</td>
<td>–25.6 ± 0.2</td>
<td>–25.5 ± 0.1</td>
<td>–24.8 ± 0.2</td>
<td>–31.9 ± 2.9</td>
</tr>
<tr>
<td></td>
<td>R-14</td>
<td>Quintar 1; cooking pot</td>
<td>–24.0 ± 1.0</td>
<td>–24.8 ± 0.9</td>
<td>–25.0 ± 0.8</td>
<td>–25.1 ± 0.4</td>
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<td></td>
<td>R-15</td>
<td>Cardosco; cooking pot</td>
<td>–26.7 ± 0.6</td>
<td>–24.5 ± 0.2</td>
<td>–25.3 ± 0.1</td>
<td>–24.5 ± 0.7</td>
<td>–24.5 ± 0.1</td>
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<td></td>
<td>R-16</td>
<td>Pinta Colorada; cooking pot</td>
<td>–27.7 ± 0.1</td>
<td>–25.5 ± 0.3</td>
<td>–27.4 ± 0.2</td>
<td>–25.2 ± 0.3</td>
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<td></td>
<td>R-17</td>
<td>San Francisco; beverage-holding vessel (aribaloid)</td>
<td>–25.5 ± 1.5</td>
<td>–24.3 ± 1.3</td>
<td>–25.7 ± 1.5</td>
<td>–22.8 ± 1.6</td>
<td></td>
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<tr>
<td></td>
<td>R-18</td>
<td>San Francisco; beverage-holding vessel (aribaloid)</td>
<td>–21.7 ± 1.2</td>
<td>–20.2 ± 0.4</td>
<td>–23.4 ± 2.0</td>
<td>–21.8 ± 3.5</td>
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<td></td>
<td>R-19</td>
<td>El Zorro; cooking pot</td>
<td>–23.5 ± 0.5</td>
<td>–21.9 ± 0.4</td>
<td>–23.8 ± 0.4</td>
<td>–21.3 ± 0.1</td>
<td>–23.6 ± 0.8</td>
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<td></td>
<td>R-20</td>
<td>Batunrgasta; cooking pot</td>
<td>–28.8 ± 0.4</td>
<td>–28.3 ± 0.1</td>
<td>–28.9 ± 0.3</td>
<td>–30.8 ± 0.1</td>
<td>–31.1 ± 1.6</td>
</tr>
<tr>
<td></td>
<td>R-21</td>
<td>San Francisco; beverage-holding vessel (aribaloid)</td>
<td>–25.5 ± 0.6</td>
<td>–27.1 ± 0.8</td>
<td>–29.0 ± 0.5</td>
<td>–30.2 ± 0.3</td>
<td></td>
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<tr>
<td></td>
<td>R-22</td>
<td>San Francisco; beverage-holding vessel (aribaloid)</td>
<td>–25.0 ± 1.3</td>
<td>–25.8 ± 1.5</td>
<td>–26.8 ± 1.7</td>
<td>–28.7 ± 1.7</td>
<td>–28.3 ± 2.9</td>
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δ13C18:0 (−0.17), and δ13C18:1 (−0.05). PC1 represents mainly the FAs δ13C values, while for PC2 the P/S ratio was the most significant. We observed superposition of most archaeological samples with pre-industrial reference values for llama and cow fats (Fig. 8).


In order to test if the grouping of samples achieved by PCA and HCA was significant, we carried out a discriminant analysis (DA). The first three components resulting from PCA were used for such purpose. The samples were hypothetically assigned to the four groups that resulted from HCA. Three discriminant functions and four predictive groups were generated. The first two functions are plotted in Fig. 9. Overall, 97% of the original groups were correctly classified. Predictive groups 1, 2 and 4 had 100% correct classification, so their membership was identical to that in clusters 1, 2 and 4, respectively. Predictive group 3 had 92.9% correct classification, while 71% of the cases were classified into predictive group 4. Canonic correlations and Wilk’s Lambda values were satisfactory (value in caption of Fig. 9), indicating that the predictive model created by DA is reliable. The result of this analysis proves that the four HCA groups are significant and relevant for this study.

4.4. Microscopic identification and characterization of starch grains

Starch grains were recovered in five of the 22 archaeological potsherds and three replica potsherds. Maize starch grains were found in three replica potsherd samples R-11, R-12 and R-13 (Fig. 10 A, B, E, F), and additionally bean starch grains were found in R-12 (Fig. 10 M, N). Some starch grains in R-13 showed signs of heat alteration due to the gelatinization of the amylese and amylopectin layers, and could be observed microscopically by the loss of the extinction cross under polarized light (Fig. 10) (Raviele, 2011). Maize starch grains were also found in samples A-05, A-06, A-13, and A-14 (Fig. 10C, D, G, H, I, J, K, L). They were identified by the polyhedral or semi-polyhedral morphologies, maximum diameters ranging from 10 to 20 µm, pointed hilum in a central position, central fissures, straight angled polarized cross, and polarized light intensity of 4–6 in the 1–10 scale (Piperno and Holst, 1998). Sample A-06 contained a bell-shaped grain typical of maize (Fig. 10K, L) (Holst et al., 2007). Sample A-06 also contained one starch grain of Phaseolus vulgaris L. (bean) which was identified by its kidney-shaped morphology, a 33 µm maximum diameter, a polarized light intensity of 8, an eccentric pointed hilum, and the straight
angled polarized cross (Fig. 10 O, P) (Rabot et al., 2007; Piperno and Holst, 1998). A granule of Prosopis L. genera (algarroba) was also observed in sample A-06, which was identified by its irregular faceted morphology, a maximum diameter of 31 \( \mu \text{m} \), an eccentric hilum, a polarized light intensity of 4, and the thin broken arms of the polarization cross which thickened towards the ending (Fig. 10S, T) (Acosta et al., 2013; Giovannetti et al., 2008; Lema et al., 2012). The occurrence of starch granules from maize, bean, and algarroba in sample A-06 provided evidence for a mixture of vegetable ingredients. This could result from food recipes including the three ingredients, or from multiple uses of the vessel. The starch granules recovered in sample A-11 could not be identified at a species or genera level because they did not present any characteristic features and showed signs of degradation such as a partial loss of the extinction cross under polarized light.

5. Discussion

Starch and lipid organic residues from archaeological potsherd samples dating from the first millennium AD (A-01, A-02, A-03, A-10, A-11, A-12, A-13, A-14, A-15, A-16, A-19) indicated that the most common cooking practice was stewing a mixture of ingredients in the same pot. These mixtures could possibly be the result of a combination of ingredients being stewed together, or of multiple uses of the vessels for cooking separately each of the different ingredients. The organic mixtures included different proportions of South American camelid fat (such as llama, guanaco or vicuña), C3 plants such as bean or algarroba and C4 plants such as maize. The latter ingredient was detected by the presence of maize starch granules rather than by distinct FAs profiles and \( \Delta^{13} \text{C} \) values. This suggests that (i) the relative proportions of maize in the stews were not dominant, or (ii) that the contribution of maize lipids was masked by other ingredients, such as animal fat. Similar patterns were observed in two of our experimental replica pots (B and C), where the characteristic signature of maize in complex mixtures was observed mostly by relative high abundance of C18:2 with high \( \Delta^{13} \text{C} \) values, which can be rarely found in archaeological samples due to early diagenetic degradation. It is worth to point out that C18:2 was found in small amounts in 8 of the 22 samples (A-10, A-11, A-12, A-15, A-16, A-19, A-20; A-21), indicating that they were exceptionally well preserved. In these cases, only A-15 and A-19 had less negative \( \Delta^{13} \text{C} \) values that could indicate maize oil origin. The other samples had \( \Delta^{13} \text{C} \) typical for C3 plants. Maize starch granules were found in samples A-13 from Palo Blanco N4 (AD 427–599) and A-14 from Ojo del Agua (AD 994–1047) located at
1900 masl and 2400 masl, respectively. One cooking pot (A-19) from El Zorro (AD 322–1019) located at 4050 masl showed higher δ¹³C values (−23.3 ± 1.4‰), suggesting a contribution of maize residues. Given that maize cannot be grown for food purposes at such altitude, it might have been transported by herders from the lower Fiambá region for sustenance during flock tending in the San Francisco vega (or highland bog). Also in sample A-19, the δ¹³C₁₄:₀ value (−23.5 ± 0.5‰) falls within the ranges of modern samples of cows raised on C₃ pastures and fattened on maize before slaughter. The high isotopic value for this fatty acid of animal origin can be explained by the ancient herding practice of feeding llama herds with maize stubble during certain annual fallow periods (Dantas et al., 2014) or the use of other C₄ pastures to feed the animals.

In samples from the second millennium AD we observed continuity in the domestic cooking practices from the previous period. Cooking pots from Mishma 7 and Batungasta showed mixtures of llama, C₃ plants such as bean or *algarroba*, and C₄ plants such as maize, cooked either simultaneously or sequentially. On the other hand, samples from San Francisco and Mishma 7 that were associated with Inka rituals and festivities showed some changes in the way maize was prepared and consumed. Beverage-holding vessels used to store, transport and serve alcoholic beverages in Inka rituals had different chemical and isotopic profiles. While A-18 had δ¹³C value comparable to C₄ plants, A-21 and A-22 had δ¹³C values comparable with C₃ plants, and A-08 and A-17 had intermediate isotopic composition, suggesting a mixture of C₃ and C₄ plants (Table 5). The relatively higher δ¹³C values in sample A-18 could indicate preparation of maize beer *chicha*, while the relatively low δ¹³C values in samples A-21 and A-22 could indicate the preparation of another typical local fermented drink called *aloja* produced from the flour of *algarroba* pods. The mixed isotopic values in A-17 could indicate possible alternation between *chicha* and *aloja* storage and/or transport. The presence of some FAs of animal origin (myristic acid and ramified fatty acids) in samples A, 17, A-18, A-21 and A-22 could indicate the use of South American camelid fat to

Fig. 10. Starch grains from archaeological and replica pots: A and B, modern maize starch granule aggregates from R-11 under normal and polarized light; C and D, archaeological maize starch granule aggregates from A-06 under normal and polarized light; E and F, modern maize polyhedral starch granule from R-11 under normal and polarized light; G and H, archaeological maize polyhedral starch granule from A-06 under normal and polarized light; I and J, archaeological maize bell-shaped granule from A-06 under normal and polarized light; K and L, archaeological maize starch granule from A-14 under normal and polarized light; M and N, modern bean starch from R-11 under normal and polarized light; O and P, archaeological bean starch granule from A-06 under normal and polarized light; Q and R, modern algarroba starch granule under normal and polarized light; S and T, archaeological algarroba starch granule from A-06 under normal and polarized light. Bars represent 10 μm.
make the inner walls of the containers impermeable and avoid cooking stews.

The variations in the types of alcoholic beverages produced are potential evidence of the survival of certain local practices as a resistance to those imposed by the Inka administration. The production and consumption of traditional Andean chicha beer and local Catamarca alcohol drink in the same ritual scenarios are indication of some permeation of the Inka practices by local cultural traditions (Orgaz, 2012). This is supported by the ethno-historical accounts of consumption of alcohol during the early colonial period as part of local rituals carried out in defiance of the Spanish rule, which considered these practices as witchcraft and persecuted them (Arana, 1999; Cerrizo, 1942; Faberman, 2005; Quiroga et al., 1999).

Moreover, mixtures of imperial chicha and local alcohol were identified in Belén vessels and arbaloides, which are both beverage-holding vessels that mix local and Inka design and technological elements.

6. Conclusion

The three archaeometric techniques (FAs distributions, compound specific C isotope analysis, and microscopy of starch grains) used to study the organic residues preserved in ceramic potsherds from western Tinogasta, Catamarca, Argentina, allowed us to identify lipid and starch granule origins. Domestic foodways throughout the 3rd to 16th centuries AD were based on mixing a variety of ingredients into the stew pots, and cooking practices changed little through time. On the other hand, ritual feasting practices were part of the public life and therefore more subjected to the political transformations during the Inka domination period and later Hispanic conquest. Nevertheless, our results suggest that the survival of local traditional beverage production and consumption practices may have been a form of resistance to the Inka administration. In sum, residue analysis opened a window into the strong sociological and political significance of domestic and public foodways of pre-Hispanic agro-pastoral societies in the south-central Andes.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jas.2014.12.022.

References


Eerkens, J.W., 2005. GC-

14CAMS analysis and fatty acid ratios of archaeological po-


