



Combined use of gas chromatography and HPLC-ESI-Q-TOF to assess the culinary uses of archaeological *Santa María* style ceramic vessels from El Colorado (Catamarca, Argentina)

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Received: 12 March 2020 / Accepted: 14 May 2020 / Published online: 1 June 2020
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Abstract

In this paper, an interdisciplinary investigation was carried out to study if *Santa María* tricolor style vessels were used as culinary equipment in a 14th century AD domestic cooking space in El Colorado (Yocavil valley, Catamarca, Northwest Argentina) and to question the long-established idea that *Santa María* vessels were exclusively funerary objects. The combined use of gas chromatography (GC-FID), gas chromatography–mass spectrometry (GC-MS), and high-performance liquid chromatography coupled to electrospray ionization and quadrupole time-of-flight mass spectrometry (HPLC-ESI-Q-TOF) to study residual lipids from *Santa María* style vessels provided valuable information on their ancient use. Also, an ordinary striated style ceramic pot with distinct visible soot marks, as well as sediments from the cooking area, was studied for comparative purposes. Fatty acid, sterol, and acylglyceride profiles were characterized, and markers of food sources were searched in the complex mixtures. We identified intact triacylglycerides (TAGs) in the archaeological samples, even unsaturated, indicating exceptional preservation of lipids in the ceramic matrixes. Cholesterol or cholesterol oxidation products were observed in all ceramic containers, as well as plant sterols (stigmasterol, sitosterol) in two containers. Markers for ruminant lipids, such as TAGs that contain odd-chain fatty acids, were found, supported by the identification of odd-chain and branched-chain fatty acids with GC-FID and GC-MS. This evidence contributes to the hypothesis that *Santa María* vessels were used for culinary purposes in this archaeological domestic cooking space.

Keywords Lipid residues · TAGs · gas chromatography · HPLC-ESI-Q-TOF · *Santa María* ceramics

Irene Lantos and Valeria P. Careaga contributed equally to this work.

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s12520-020-01085-3>) contains supplementary material, which is available to authorized users.

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Introduction

Food and drink preparation, storage, and service are commonly carried out in cooking areas within archaeological households. These culinary activities result in organic residues that are preserved in the porous matrixes of ceramic containers (Cramp 2018; Evershed and Roffet-Salque 2018; Degano et al. 2018), as well as in sedimentary deposits in hearths and kitchen floors due to the spillage of food substances in the process of their manipulation (Pecci et al. 2017). The complex mixtures of residual organic compounds found in ceramics often result from the intentional coating of the inner surfaces and from their multiple subsequent uses (Henrickson and McDonald 1983; Schiffer 1990; Skibo 1992; Roffet-Salque et al. 2016). The integration of data from the context of discovery and from techno-morphological, use-alteration, and organic residue analyses can contribute to the knowledge on specific ceramic type use.

Studies of archaeological lipids frequently comprise appropriate chemical treatment such as hydrolysis and derivatization for identification of fatty acids and sterols by gas chromatography–mass spectrometry (Vázquez et al. 2008; Lucquin et al. 2016; Bonaduce et al. 2017, among others). Recently, different high-resolution mass spectrometry techniques have been successfully applied to the characterization of underivatized residual acylglycerides in objects of cultural heritage (Mottram et al. 1997, 2001; Kimpe et al. 2001, 2004; Mirabaud et al. 2007; Romanus et al. 2007; Garnier et al. 2009; Saliu et al. 2011, 2014; La Nasa et al. 2015; Tirat et al. 2016; Degano et al. 2016; van Dam et al. 2017; Shevchenko et al. 2017; Tuñón-López et al. 2017; Oras et al. 2017; Blanco-Zubiaguirre et al. 2018; Lucejko et al. 2018; Hammann and Cramp 2018). Considering that lipids in food sources are mostly in the form of triacylglycerides (TAGs), the advantage of studying non-decomposed TAGs in ceramic residues is that they can be more specific to the original source than their decomposition products. The identification potential is further increased if TAG characterization is combined with the analysis of fatty acid and sterol profiles.

In this paper, an interdisciplinary investigation was carried out to study if *Santa María* style tricolor vessels were used as culinary equipment in a 14th century AD (Late Intermediate Period) domestic cooking space in El Colorado archaeological locality (26°54'33.12"S 66°8'13.91"W¹), in the Yocavil valley (Catamarca, Northwest Argentina) (Fig. 1). The *Santa María* style flourished and became dominant in the Calchaquí and Yocavil valleys during the Late Intermediate Period (11–15th centuries AD) (González 1950, 1977).

Particularly, *Santa María* tricolor vessels have smooth surfaces, a white or cream slip, and complex designs painted in black and red. *Santa María* ceramic assemblages can be categorized in two main morphologies: jars (*tinajas*) and bowls (*pucos*), although there are other minor morphologies (Palamarczuk 2014). Jars and bowls were usually associated with funerary practices (Nastri 2003; Marchegiani et al. 2009). This was established since the first expeditions in the late 19th and early 20th centuries, which targeted the excavation of cemeteries and the recovery of funerary material remains (Podgorny 2004; Ramundo 2007). In many cases, jars were used as urns to hold human remains—of young children—and bowls were used as lids, although both morphologies were also used as accompaniments in adult burials. However, several recent studies reported the recovery of this style in significant proportions within household floors and dump areas, even exceeding 50% of sherd sets depending on the quantification criteria, and with no link to funerary use (Roldán and Funes 1995; Piñeiro 1996; Nastri 1999; Rivolta and Salazar 2006; Orgaz et al. 2007; Palamarczuk 2008; Greco et al. 2012). Moreover, previous preliminary studies of some *Santa María* jar and bowl examples suggested they were possibly used to contain foods or beverages (Lantos et al. 2017, 2018). In order to obtain further compelling evidence of their culinary uses in a specific context, a detailed study of two *Santa María* jars and one *Santa María* bowl from El Colorado was carried out in this paper (Fig. 2). These containers had no indication of association with human burial remains. An ordinary striated style ceramic pot with visible soot marks and sediments from the cooking area were also studied for comparative purposes. Gas chromatography (GC-FID), gas chromatography–mass spectrometry (GC-MS), and high-performance liquid chromatography coupled to electrospray ionization and quadrupole time-of-flight mass spectrometry (HPLC-ESI-Q-TOF) were combined to study residual lipids, to search for markers of original food sources, and to assess if *Santa María* vessels were used as culinary equipment in this particular domestic cooking space.

An archaeological cooking context in El Colorado, Catamarca, Northwest Argentina

Archaeological households in the Late Intermediate Period were characterized by the coexistence of domestic activities and craft production (Quiroga 2007; Salazar 2007; Tarragó 2007; Váquer 2007). In these spaces, food was processed, prepared, cooked, stored, consumed, and sometimes discarded (Nash 2009). These activities are inferred from the occurrence of hearths, cooking implements, zooarchaeological and archaeobotanical remains, and organic residues in artifacts and in sediments in residential structures.

¹ The geographical coordinates 26°54'33.12"S 66°8'13.91"W correspond to Structure E3 of the El Colorado archaeological locality. The measurement error was 3 m. The datum is WGS84. The coordinates were collected by Dr. Palamarczuk with a GPS Garmin etrex 30. The points on the map in Fig. 1 represent exact geolocations.

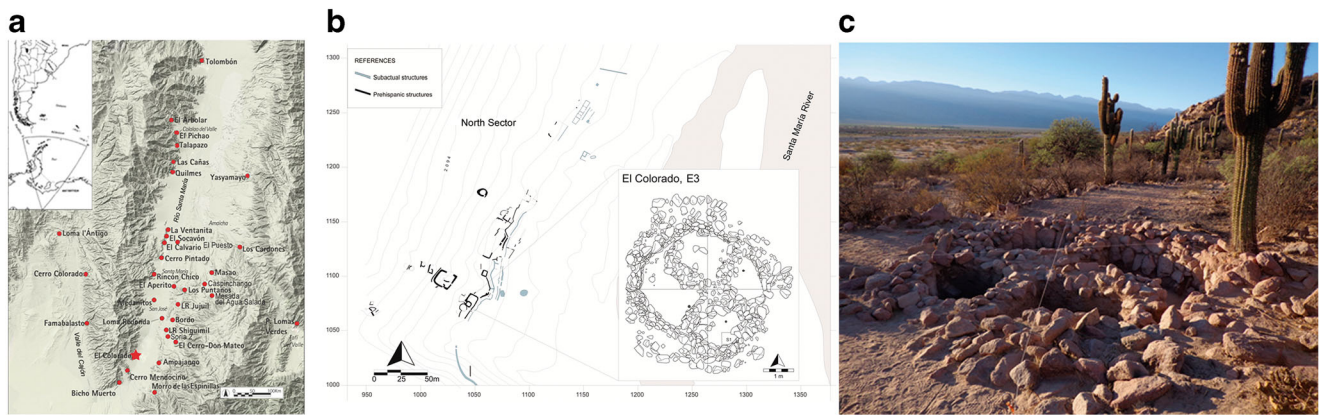


Fig. 1 El Colorado archaeological locality. **(a)** El Colorado and other archaeological sites in Yocavil Valley and surrounding areas. **(b)** Detail of E3 architecture. **(c)** View of E3 excavation from the North

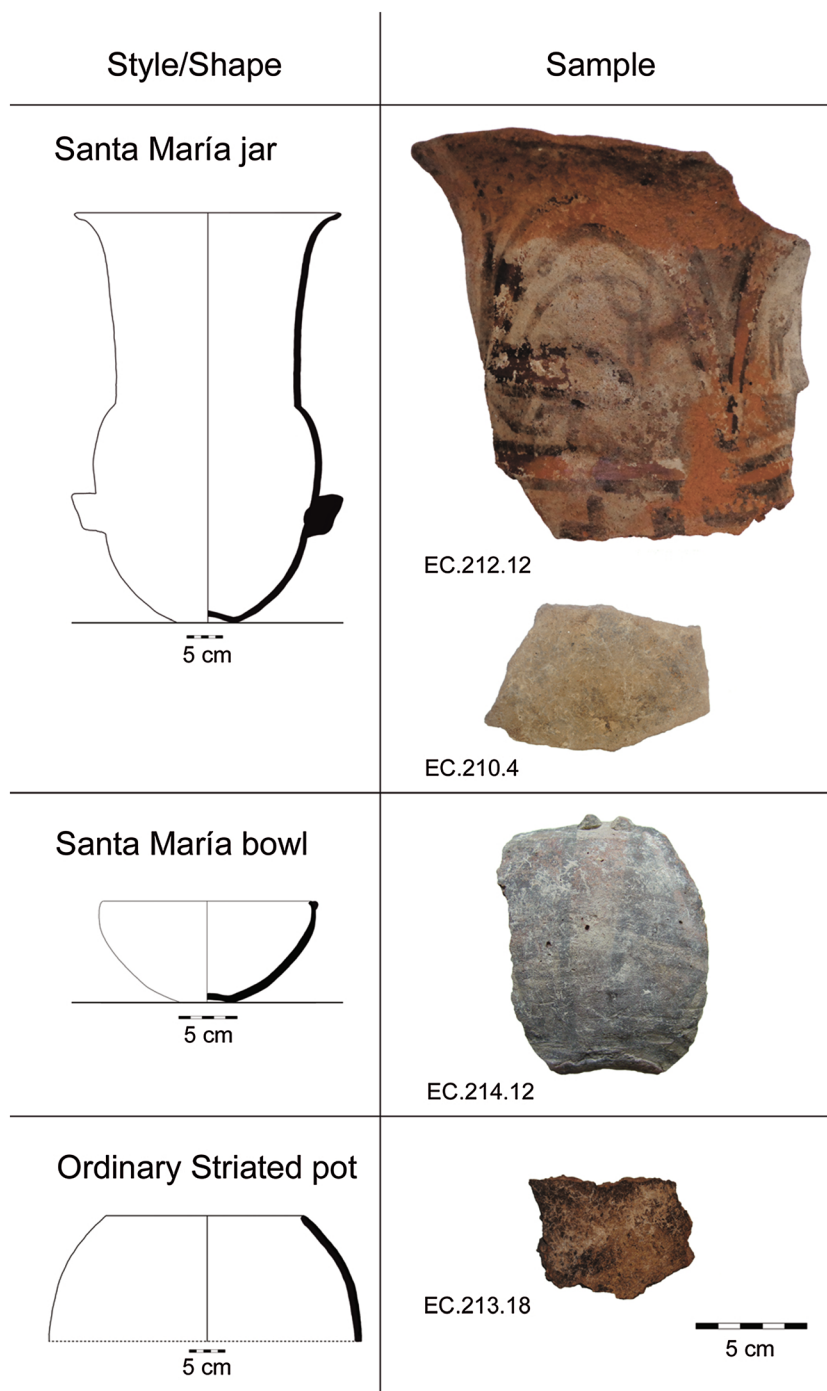
The archaeological cooking context in this study is situated in El Colorado archaeological locality (60 ha), which was inhabited by small agro-pastoralist communities from the Early Period, toward the beginning of the first millennium to recent times. A small cluster of buildings located in the North Sector was constructed during the Late Intermediate Period. Within this cluster is Detection 2, a residential complex with seven orthogonal structures built with stone walls (Palamarczuk 2016). One of the structures, named E3, was completely excavated in an open area (Barker 2003) during four field seasons (2012–2016) reaching sterile deposits.

Different surfaces of occupation were recognized and four radiocarbon dates were obtained (Palamarczuk et al. 2016). It was concluded that E3 was built in the early 14th century and remained occupied until the early Colonial Period during the 16th century. Specifically, our study focuses on the first occupation floor of structure E3, at an average depth of 70 cm from the current surface, represented by Stratigraphic Levels 8 and 9. Its features include a combustion area or hearth, thermo-altered sediments, carbonaceous spots, and horizontally arranged findings (ceramic fragments, scarce lithic artifacts, faunal bone remains, charred seeds, etc.). A sample of small charred branches from the hearth was dated in 624 ± 20 years BP (YU-4564). The initial examination of faunal remains identified Camelidae family. Camelidae are South American autochthonous pseudoruminant ungulates (Esteban and Thompson 1988). In the Late Intermediate occupations of Yocavil valley, they are the most frequent taxa, followed by Cervidae (also ruminant) (Belotti López de Medina 2015, 2017). The recovery of plant remains was achieved by employing a 2-mm sieve in 90% of the sediments, while the remainder was processed by a SMAP flotation device (Watson 1976). All recovered remains were analyzed by stereoscopic microscope, although only charred plant remains of edible species were separated for further analysis; the carbonization ensures the association to the hearth and to the archaeological occupation under study. The taxonomic identification was carried out by observation under stereoscopic and

photographic incident lighting microscopes, guided by diagnostic features described in the literature (Winton and Winton 1932, 1935), catalogues of regional flora (Cabrera 1976), and the scientific plant collection from the Ethnobotany and Applied Botany Lab (FCNyM, UNLP). Wild and domesticated species of nutritional importance were identified. A total of 84 remains were recovered with the sieve: *Zea mays* ($n = 31$), *Geoffroea decorticans* ($n = 3$), *Prosopis* sp. ($n = 34$), *Prosopis torquata* ($n = 15$), and *Phaseolus vulgaris* ($n = 1$). With the flotation device, an additional 78 specimens were recovered: *Chenopodium quinoa* ($n = 63$), *Ch. carnosulum* ($n = 9$), *Prosopis* sp. ($n = 1$), and *Z. mays* ($n = 5$) (Petrucci and Palamarczuk 2019).

The ceramic collection was analyzed considering stylistic and technological aspects, and its quantification was carried out according to the criteria of families of fragments (Orton et al. 1997). Fresh cross-sections of the matrixes were observed under a binocular microscope in order to group sherds into families. A total of 152 ceramic fragments were recovered and grouped into 86 families. Twelve of these families correspond to *Santa María* style vessels: four belong to jars, one belongs to a bowl, and the remaining are of undetermined morphology. For this study, we selected samples only from families with unambiguous morphology (Fig. 2). Two samples belonging to two *Santa María* jar families were included: vessel EC.210.4 (*Santa María*) and vessel EC.212.12 (*Santa María* tricolor). The jar shape is characterized by a large elongated body, a wide everted neck, and a narrow base. Due to size and proportions, jars are unstable and heavy. Vessels EC.210.4 and EC.212.12 do not have visible traces of use, such as abrasion, or of exposure to fire, such as darkening of paste, cracking, or soot, although a big fragment of the neck of EC.212.12 was found in the vicinity of the hearth. All this suggests that they were not used on fire, so other culinary uses, such as storage or service, had to be explored. The third sample is from a small *Santa*

Fig. 2 Ceramic samples analyzed in this study

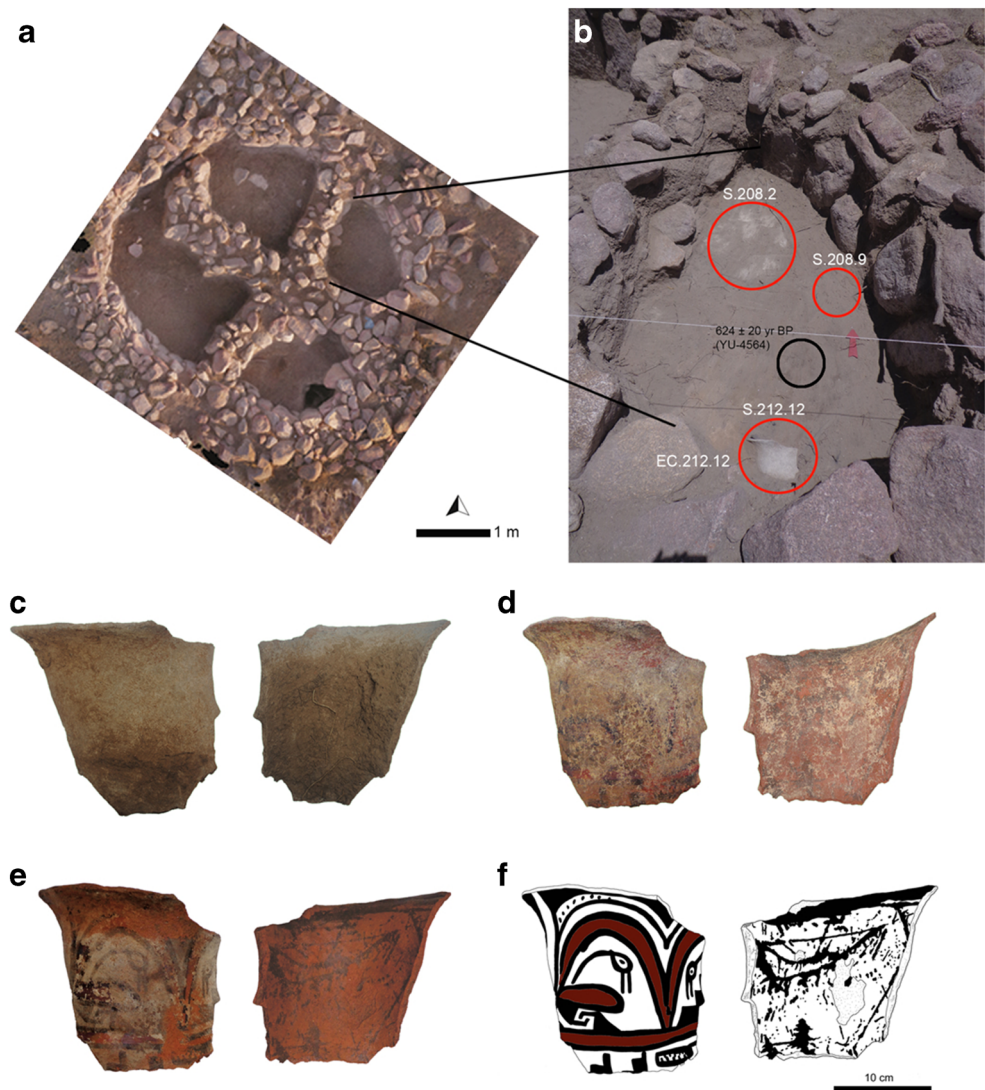


María tricolor bowl (Vessel EC.214.12), which has an open mouth and shallow body (Fig. 2). This vessel does not have macroscopic marks of use or wear so, as with jars, evidence of culinary use had to be searched. The fourth sample corresponds to the family of an ordinary striated pot (vessel EC.213.18) with a restricted mouth and globular body (Fig. 2). This sample was selected due to visible soot marks and cracking as a result of the exposure to fire, which strongly implies its use as a cooking pot. The study of this last specimen with clear

macroscopic evidence of use on fire, compatible with culinary use, is important in our case study because it was recovered in the same context as the *Santa María* style fragments under analysis. It is plausible to consider that it was subjected to similar post-depositional processes and provides a point of comparison with the decorated vessels whose functionality we intend to investigate.

Due to the maintenance and sweeping of the occupation floor, fragments have a low level of reassembly. However,

Fig. 3 (a) Orthomosaic of E3 (PhotoScan 1.2.5); (b) detail of combustion area in the northeast area of E3, Stratigraphic Level 8, the recovery place of vessel EC.212.12 and of the sediment samples analyzed is shown; (c) vessel EC.212.12 with adhered sediments; (d) after a sample was taken for organic residue analysis, the remaining fragment was then washed with distilled water; (e) minerals were removed with an acetic acid solution; (f) the painted designs in the internal and external surfaces were reconstructed



one of the *Santa María* jars (EC.212.12) is represented by a big neck, rim, and lip fragment and by a body fragment, and the *Santa María* bowl (EC.214.12) is composed by two large sherds from the base, body, rim, and lip sectors, which strongly suggest in situ deposition. Thus, in situ rupture and association to the activities carried out in the enclosure is supported.

A second set is made up of sediment samples collected in Stratigraphic Level 8: (1) sediment from the activity area floor which was adhered to the internal surface of the neck of vessel EC.212.12 (S.212.12), (2) ashen sediment of the whitest tone on the periphery of the hearth (S.208.2), and (3) sediment of the same stratigraphic level, outside the thermoaltered area (S.208.9) (see Fig. 3). Post-depositional processes may have affected the presence and/or degradation of lipid residues in ceramic matrixes; therefore, the analysis of sediment samples contributes to the evaluation of results.

Materials and methods

Recovery of the samples in the field

Recovery in the field was planned ahead by the interdisciplinary group, anticipating the unearthing of a food processing area. Precautions to avoid contamination were considered. Gardening cloth gloves were used throughout the excavation. Ceramic samples were not cleaned in the field, and were wrapped in aluminum foil immediately after recovery, labeled, and stored in plastic bags. Sediment samples were stored in labeled aluminum cups. The ceramics were then brushed in the laboratory, and the adhered sediment was stored and labeled. After this step, a sample of each sherd (10 g approximately) was broken off with pincers. These samples were used for organic residue analyses. The remainder was washed with distilled water, which revealed the deposition of minerals on the surfaces. In order to correctly

characterize the decorative style and morphology, minerals were removed with a solution of acetic acid (5%). This process allowed us to categorize samples EC.210.4, EC.212.12, and EC.214.12 as *Santa María* vessels (Fig. 3).

Chemicals and reagents

All the solvents used were HPLC grade or pesticide grade: chloroform (CHCl₃), methanol (CH₃OH), dichloromethane (CH₂Cl₂), *n*-hexane (C₆H₁₄), and diethyl ether ((C₂H₅)₂O) (Merck). As derivative reagents, 20% boron trifluoride (BF₃) in methanol and *N,O*-bis(trimethylsilyl) trifluoroacetamide (BTSFA) with 1% trimethylchlorosilane (TMCS) were obtained from Merck and Supelco.

HPLC-MS-grade solvents isopropanol (*i*-PrOH), ammonium acetate (C₂H₇NO₂), and methanol (CH₃OH) were obtained from Sigma-Aldrich and Merck.

Commercial standards

All commercial standards of cholesterol, stigmaterol, glyceryl tristearate, glyceryl tripalmitate, glyceryl trimyristate, glyceryl monostearate, dipalmitin, and distearoylglycerol mixed isomers were purchased from Sigma-Aldrich, and FAME C4-C24 Mix from Supelco.

Procedure

Lipid extraction was carried out on ceramic and sediment samples (7–10 g). Sherds were mechanically cleaned with a hand lathe tool (Dremel) in order to remove all external surfaces, and then ground to dust in a porcelain mortar and pestle. Sediments were also homogenized in a porcelain mortar and pestle. Lipids were extracted with chloroform/methanol (2:1; vol/vol) (Folch et al. 1957), 10 mL per gram of sample. Each sample was placed in an ultrasound bath for 15 min (twice) and filtered, drops of distilled water were added, the organic phase containing the total lipid extract (TLE) was separated after centrifugation for 3 min (twice), evaporated under nitrogen stream, weighed, and stored at – 18 °C. An aliquot of the TLE (5 mg) was saponified with 1 mL of 4% potassium hydroxide in an ethanolic aqueous solution (2:1, vol/vol), at 60 °C for 2 h. After cooling at room temperature, the neutral fraction was extracted with 1.5 mL *n*-hexane. This procedure, adapted from Colombini et al. (2003), allows the obtainment of an enriched neutral compound fraction. The aqueous fraction was acidified with 2 N HCl solution to pH 3 and extracted with 1.5 mL diethyl ether. The organic phase containing the free fatty acids was evaporated under N₂ stream and 0.5 mL of 20% boron trifluoride in methanol was added and heated in a boiling water bath for 3 min. After cooling, 1.5 mL of chloroform and a drop of water were added, and the organic phase

containing the fatty acid methyl esters (FAMES) was recovered and stored at – 18 °C. FAMES were redissolved in dichloromethane before injection. The stability of FAMES allowed for a first analysis with GC-FID and a second analysis with GC-MS. Trimethylsilyl derivatives (TMS) of the neutral compounds were prepared by addition of 20 µL of *N,O*-bis(trimethylsilyl) trifluoroacetamide (BTSFA) with 1% trimethylchlorosilane (TMCS) and heating at 60 °C for 20 min. After cooling, the TMS derivatives were dried under nitrogen stream and analyzed by GC-MS within 24 h. TMS derivatives were redissolved in chloroform before injection.

Analytical blanks to check for procedural contamination during lipid extraction, saponification, methylation, and TMS derivatization were prepared and analyzed.

GC-FID was carried out to identify FAMES by retention time comparison with standards. Relative abundances of individual FAMES were calculated from peak areas and expressed as percentages of total fatty acids. GC-MS was carried out to confirm the identity of FAMES previously identified by GC-FID by retention time comparison with standards, and by the interpretation of the fragmentation patterns of each compound, as well as by comparison with mass spectra libraries. GC-MS was also used to identify those compounds for which no standards were available, and other compounds present in trace amounts that remained undetected by GC-FID. GC-MS of TMS derivatives was used to identify neutral compounds by comparison with available standards, and/or by the interpretation of the fragmentation patterns. TMS derivatives were not analyzed or quantified by GC-FID, as their concentration in organic residues in archaeological ceramics was very scarce. TLE was filtered with PTFE syringe filters (0.22 µm pore size) and diluted with CH₂Cl₂/MeOH before injection in HPLC-ESI-Q-TOF. This technique was used because it is a high-resolution mass spectrometry technique that allowed the separation and detailed characterization of the residual underivatized acylglycerides in the ceramic samples.

Instrumental parameters

Gas chromatography (GC-FID) of FAMES was carried out on a Focus GC (Thermo Finnigan Corporation), equipped with an Innowax capillary column (Agilent, 100% polyethylene glycol, 30 m length, 0.25 mm i.d., 0.5 µm film thickness). Nitrogen was used as carrier gas (0.8 mL/min continuous flow rate). Manual injection was operated in splitless mode at 220 °C. Flame ion detector temperature was set at 275 °C. The temperature program was 100 °C (1 min), 15 °C/min to 200 °C (1 min), and 2 °C/min to 240 °C (17 min).

Gas chromatography–mass spectrometry (GC-MS) of FAMES was performed with a Shimadzu GCMS—QP5050A (Kyoto, Japan). The system was equipped with an Innowax capillary column (Agilent, 100% polyethylene glycol, 30 m length, 0.25 mm i.d., 0.25 µm film thickness).

Helium was used as carrier gas (1.1 mL/min continuous flow rate) and manual injection was in split mode at a temperature of 250 °C. The temperature program was 90 °C (2 min), 15 °C/min to 200 °C (1 min), and 2 °C/min to 240 °C (15 min). The GC-MS interface was maintained at a temperature of 280 °C. The mass spectrometer was operated in electron ionization mode at 70 eV, source temperature at 290 °C. The mass range was scanned from 41 to 450 m/z at 0.5 s/scan in full-scan mode. Analysis of fragmentation patterns and comparison with a reference library allowed compound identification.

Gas chromatography–mass spectrometry (GC-MS) of TMS derivatives was carried out on a Shimadzu GCMS—QP5050A (Kyoto, Japan) following the method described in Lantos et al. (2018).

High-performance liquid chromatography coupled to electrospray ionization and quadrupole time-of-flight mass spectrometry (HPLC-ESI-Q-TOF) analyses were carried out using a RRLC Agilent 1200 HPLC (Agilent Technologies, Wilmington, DE, USA) coupled to a Bruker micrOTOF-QII mass spectrometer (Bruker Daltonics, Billerica, MA, USA), equipped with an ESI source. The instrument was operated in the positive ion mode at a capillary and end plate offset voltages were set to 4.5 kV and –450 V, respectively. Nebulizer (nitrogen) flow was 6.0 L/min, nebulizer pressure 2.7 bar, and dry temperature 200 °C using N₂ as dry gas. Multi-point mass calibration was carried out using a sodium formate solution from m/z 50 to 1500 in positive ion mode. Bruker Compass Data Analysis (version 4.0) software was used for data acquisition and processing. TAGs were researched as $[M + NH_4]^+$ and $[M + Na]^+$ ions by the “SmartFormula” algorithm provided by the software. Formula matching was set at 10 ppm tolerance. Mass spectrum in the total ion current (TIC) mode was also acquired in the range of 50–1300 m/z .

Chromatographic separation was achieved with a Luna C18 column (2.0 mm × 100 mm, 3 μm; Phenomenex, Torrance, CA, USA) and the column temperature was set to 20 °C. The injection volume was 5 to 10 μL, depending on the extract’s concentration (400 μg/mL diluted in CH₂Cl₂/MeOH, 50:50).

Flow rate was set to 0.3 mL/min. Methanol with ammonium acetate (0.03 mM) and isopropanol were used respectively as mobile phase components A and B. The mobile phase was delivered at a flow rate of 0.3 mL/min in gradient mode: 0 min 100% A, 0–10 min linear gradient to 80% A, 10–12 min 80% A isocratic, 12–42 min 40% A linear gradient, 42–43 min 40% A isocratic, 43–50 min 100% A linear gradient, and 50–55 min 100% A isocratic.

Results and discussion

TLE concentrations (micrograms of lipids per gram of extracted matrix) were within an acceptable range for analysis

(Evershed 2008). The highest lipid yields were found in the ordinary striated pot EC.213.18 (740 μg/g) and in the bowl EC.214.12 (470 μg/g). *Santa Maria* jars EC.212.12 and EC.210.4 had lower lipid concentrations (240 μg/g and 99 μg/g, respectively). As expected, the highest lipid concentration was found in the pot EC.213.18, given its noticeable use on fire.

The chromatograms from GC-FID and GC-MS analyses of the archaeological vessels showed a series of methyl esters of carboxylic acids in the C8–C20 range (Table 1, Fig. 4). The most abundant saturated fatty acids (FAs) were C16:0 and C18:0, followed by C14:0 and C12:0. Unsaturated FAs were C16:1, C18:1, and C18:2. All ceramic samples showed some odd-chain FAs, such as C15:0 and C17:0. Also, branched-chain FAs of C13, C14, C15, and C16 were identified in all ceramic samples. The presence of branched-chain FAs in combination with the odd-chain FAs suggest the presence of ruminant animal fat (Evershed et al. 2002; Spangenberg et al. 2006; Vázquez et al. 2008; Salvá et al. 2009; Regert 2011; Lantos et al. 2015; Miyano et al. 2017). Small amounts of dicarboxylic acids, such as diC9 (azelaic acid), were detected in all samples, which are usually linked to plant degradation products (Dunne et al. 2016). The hydroxylated FA C18:1-OH was observed in three of the samples. Although this FA can derive from an original source, it can also be an oxidation product.

The C16:0/C18:0 ratio, although largely debated in the literature, is still used to propose the origin of fatty substances (Kimpe 2003; Romanus et al. 2007; Regert 2011). In our samples, EC.210.4 has a low P/S ratio (1.34) that could indicate ruminant animal fat due to the higher proportion of C18:0 in ruminant (Romanus et al. 2007) (Table 1). On the other hand, the other three vessels (EC.212.12, EC.213.18, and EC.214.12) have higher ratios (3.06, 3.28, and 2.75, respectively) that possibly suggest mixtures of plant oils with animal fats as original sources (Table 1). These values are in accordance with those reported for reference samples from plant and animal sources from Northwest Argentina (Lantos et al. 2015).

Sterol analysis showed the presence of cholesterol or cholesterol oxidation products in all vessels, as well as plant sterols (stigmasterol, sitosterol) in two containers (EC.212.12 and EC.213.18). Cholesterol is a marker of animal sources, while stigmasterol and sitosterol are the most common sterols in plants, including species such as *Z. mays* (Ryan et al. 2007; Harrabi et al. 2008), *Prosopis* (Lamarque et al. 1994), *Phaseolus vulgaris* (Ryan et al. 2007), and *Ch. quinoa* (Ryan et al. 2007; Fanali et al. 2015) that are present in the archaeological record of El Colorado (Petrucci and Palamarczuk 2019). Finally, ergosterol, a marker of microbial activity, was not found in any sample.

Sediment samples from the cooking area (S.212.12 and S.208.2) had significant TLE concentrations (320 μg/g and

Table 1 Fatty acid (FA) relative abundances (%) calculated from peak areas in GC-FID chromatograms (ratio between C16:0 and C18:0 is also shown)

Sample FA (%)	EC.210.4	EC.212.12	EC.214.12	EC.213.18	S.212.12	S.208.2	S.208.9
C8:0				1.61			
C9:0		0.86		2.99			
C10:0	0.33	0.77		4.18			
C11:0		0.28	0.03	2.17			
C12:0	1.25	1.85	0.81	3.85	5.09	10.28	
C12:0 11-Me		0.02	0.09				
C13:0	0.97	0.79	0.63	0.42			
C13:0 12-Me	0.76	0.18	0.18	1.74			
C14:0	2.27	12.06	11.78	8.94	66.95	13.60	
C14:1		0.94		0.64			
C14:0 13-Me	0.82	0.82	1.01	0.42			
C14:0 12-Me	0.48	0.44	0.69	0.78			
C15:0	2.61	2.96	3.43	2.18	6.13	8.88	
C15:0 14-Me	1.23	0.54	0.48	0.34			
C16:0	41.85	47.73	49.05	44.55	9.29	39.50	
C16:1	1.18	3.61	1.83	0.82			
C16:0 15-Me		0.61	0.58	1.07			
C16:0 14-Me	0.54	0.43	0.38	0.59			
C17:0	1.54	1.92	1.33	1.61	3.99		
C18:0	31.12	15.62	17.84	13.61	3.63	20.51	
C18:1	1.13	3.69	2.32	1.65			
C18:2		0.38		1.19			
C19:0		0.29	0.13				
C20:0	1.01	1.65	0.64	0.86			
C18:1-OH	9.26		6.62	2.08			
diC9	1.64	1.27	0.14	1.70	4.91	7.22	
diC11		0.29					
Other (trace amounts)	C16:0 br; C19:0	diC6; diC7; diC8; diC10	C12:0 br; diC11		C13:0; C22:0; C24:0; C26:0; diC8; diC10	C17:0; C20:0; C22:0; C24:0; diC8	C14:0; C16:0; C18:0
C16:0/C18:0	1.34	3.06	2.75	3.28	2.56	1.93	—

111 $\mu\text{g/g}$, respectively), although the contribution of FAMES was low (ESM 1). The sample taken outside of the cooking area (S.208.9) did not show a significant concentration (17 $\mu\text{g/g}$). The sediment samples showed poor FA profiles with low intensity peaks for the most common saturated FAs in the C12–C26 range. Profiles were not as diverse and did not match any of the profiles of the ceramic containers (Table 1).

The high concentrations and FA diversity in the ceramic vessel samples suggest that absorbed lipids are the result of culinary use, although migration of lipids cannot be ruled out.

Acylglyceride identification was carried out using HPLC-ESI-Q-TOF. Lipids were largely found as intact TAGs mainly in the range of m/z 700–1000, and the errors were all within 10 ppm (Table 2). Monoacylglycerides and diacylglycerides were found only as minor components (data not shown). The retention time of intact TAGs is ruled by the equivalent carbon

number (ECN) defined as $\text{ECN} = \text{CN} - 2\text{DB}$, where CN is the number of carbon atoms and DB is the number of double bonds (Plattner et al. 1977; Líska and Holčápek 2008).

As reported in the literature (Herrera et al. 2010; Degano et al. 2016), the *sn*-1 and *sn*-3 losses were favored compared to the loss from the *sn*-2 position—the latter is energetically disfavored—and thus the corresponding diacylglycerol ions were more abundant in the MS/MS spectrum. However, we were not able to assign the position of the acyl chains in all the identified TAGs given that, in some cases, the co-elution of positional isomers cannot be ruled out.

Under the employed conditions, the ESI ionization provided TAG ammonium and sodiate adducts $[\text{M} + \text{NH}_4]^+$ and $[\text{M} + \text{Na}]^+$ as the most common base peaks. The TAG species were identified by high-resolution mass spectrometry and by the interpretation of the characteristic MS/MS fragmentation

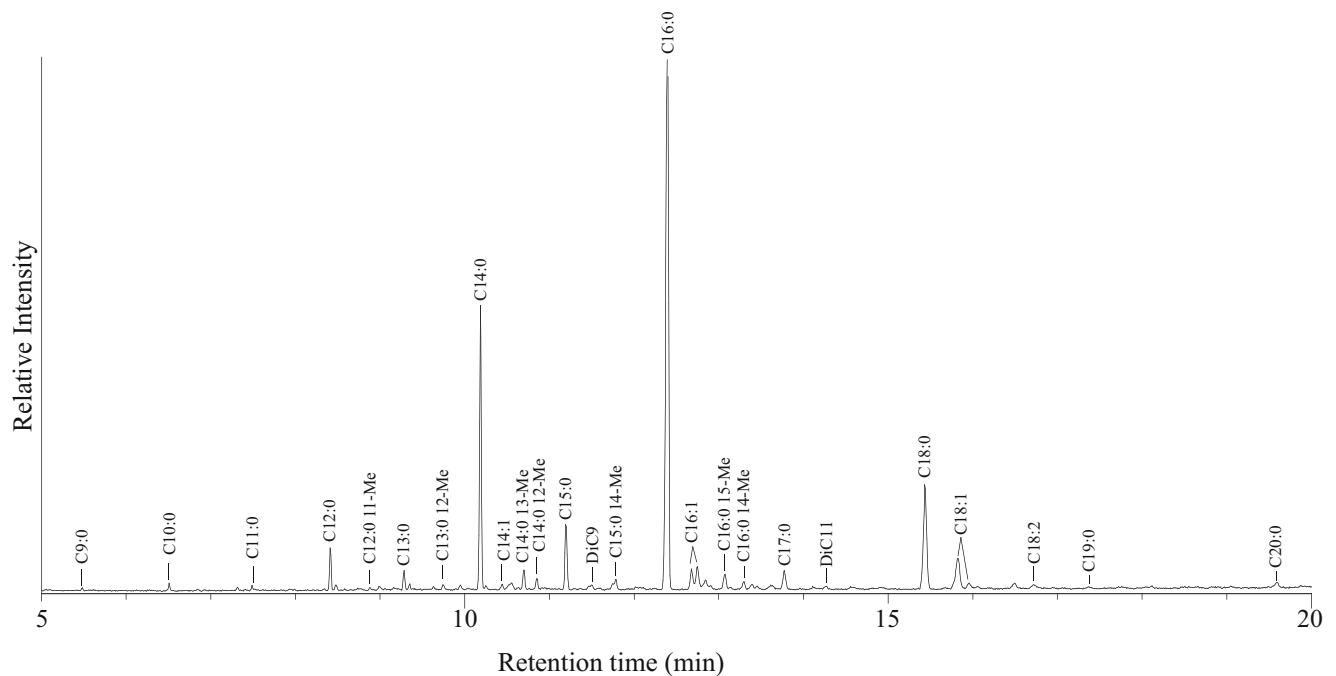


Fig. 4 Total ion chromatogram obtained by GC-MS of fatty acid methyl esters (FAMES) recovered in sample EC.212.12, a *Santa María* jar from El Colorado, Catamarca, Argentina

pattern of $[M + NH_4]^+$ adducts. For example, the fragmentation of $[M + NH_4]^+$ adduct ion at m/z 892.8325 results in three fragment ions at m/z 591.5, 605.6, and 593.6, which correspond to the loss of C18:0, C17:0, and C18:1 acids, respectively. They are assigned as $[C17:0C18:1]^+$, $[C18:0C18:1]^+$, and $[C18:0C17:0]^+$ (Fig. 5a). Additionally, the fragmentation of $[M + NH_4]^+$ adduct ion at m/z 904.8340 results in two fragment ions at m/z 605.6 and 603.5, which correspond to the loss of C18:1 and C18:0 acids, respectively. They are assigned as $[C18:0C18:1]^+$ and $[C18:1C18:1]^+$ (Fig. 5b).

Oxidized TAG products were detected in three vessel samples due to the presence of additional oxygen atoms. The assignment of these TAGs is based on $[M + Na]^+$ and $[M + NH_4]^+$ adduct ions, and in some of these cases we observed pseudomolecular $[M + H]^+$ that was not observed in the case of intact TAGs (Table 3).

The results obtained from the archaeological vessel samples EC.212.12, EC.213.18, and EC.214.12 showed TAGs in a range from ECN 40 to ECN 54, compatible with the presence of mixtures containing animal fat, the latter typically range from ECN 46 to ECN 54 (Garnier et al. 2009; Saliu et al. 2014). In the sample EC.214.12, it was possible to identify TAGs of up to ECN 58. Sample EC.210.4 presented only a few intact TAGs, and no TAGs with unsaturated FAs, suggesting a poor lipid profile. This is in accordance with the scarce lipid yield recovered from the matrix in this sample.

For all samples, it is interesting to highlight the presence of TAGs with odd-chain FAs in their structure. Although we acknowledge that the presence of odd-chain FA in residual lipids could have a microbial origin, it has been shown that

they only contribute to a minor extent to the overall lipid distribution of the absorbed lipids (Dudd et al. 1998). On the other hand, their recurrent presence in all ceramic samples, and their absence in the FA profile of sediment sample S.208.9 recovered outside the cooking space, suggest that TAGs with odd-chain FA could be original to the lipids in the food sources processed in the ceramic vessels. Among them were C16:0C14:0C17:0, C16:0C15C16:0, and C16:0C15:0C18:1. In the case of sample EC.214.12 and EC.212.12, it was also possible to assign TAGs carrying more than one odd-chain FA, including C13:0, C15:0, C17:0, and C19:0 (see Table 2). It was observed that some TAGs with the same ECN and MS/MS spectrum eluted at very close retention times, although the positions and number of branchings cannot be exactly determined by HPLC-MS (Lísa and Holčápek 2008). Considering that the information provided by GC-MS analyses indicates the presence of both linear and branched odd-chain FAs in the samples, it is possible that these closely eluting TAGs contain either a linear or a branched-chain FA. In absence of published TAG profiles of South American ruminants, we compared our results with available published TAG profiles of Old World ruminant species (Haasmann 1998; Mottram et al. 2001; Kimpe et al. 2002; Romanus et al. 2007; Regert 2011; Lísa et al. 2011; Saliu et al. 2014; Tuñón-López et al. 2017). In the literature, ruminant fats typically contain odd-chain FAs in their TAG structures, such as C16:0C17:0C18:0 and C17:0C18:0C18:0, as reported in lamb (Mottram et al. 2001). The first was found in samples EC.210.4, EC.212.12, and EC.214.12. The latter and/or its positional isomer were found in samples EC.210.4 and EC.214.12.

Table 2 Triacylglycerides (TAGs) of archaeological vessel samples with molecular formulae, CN:i, ECN, precursor and fragment ions, and relative error, in cases where the TAG is present in the sample

Molecular formula	CN:i	ECN	TAG	Theoretical m/z [M + NH ₄] ⁺	Error (ppm)		Measured m/z [M-R ₁ CH ₂ CO ₂ H] ⁺		Measured m/z [M-R ₂ CH ₂ CO ₂ H] ⁺		Measured m/z [M-R ₃ CH ₂ CO ₂ H] ⁺	
					EC:210.4	EC:212.12	EC:214.12	EC:213.18	EC:210.4	EC:212.12		EC:214.12
C ₄₃ H ₈₂ O ₆	C40:0	40	C12:0-C12:0-C16:0 ^b	712.6450			-8.3	-2.4	-9.7	495.4	495.4	439.4
			C16:0-C10:0-C14:0 ^b	712.6450			-8.3	-2.4	-9.7	439.4	439.4	467.4
			C14:0-C12:0-C14:0 ^b	712.6450			-8.3	-2.4	-9.7	467.4	467.4	467.4
C ₄₄ H ₈₄ O ₆	C41:0	41	C15:0-C12:0-C14:0 ^a	726.6606		2.8			467.4	467.4	481.4	
			C14:0-C12:0-C16:0 ^b	740.6763		0.1	-1.1	-9.7	495.4	495.4	467.4	
C ₄₅ H ₈₆ O ₆	C42:0	42	C15:0-C13:0-C14:0 ^b	740.6763		0.1			481.4	481.4	495.4	
			C16:0-C13:0-C13:0 ^b	740.6763		0.1	-1.1	-9.7	467.4	467.4	509.5	
C ₄₅ H ₈₄ O ₆	C42:1	40	C14:0-C10:0-C18:0 ^b	740.6763					439.4	439.4	495.4	
			C16:0-C8:0-C18:1 ^b	738.6606		4.6			495.4	495.4	439.4	
C ₄₅ H ₈₂ O ₆	C42:2	38	C12:0-C12:0-C18:1 ^b	738.6606		4.6			521.5	521.5	439.4	
			C16:1-C8:0-C18:1 ^a	736.6450		-2.1			495.4	495.4	437.4	
C ₄₆ H ₈₈ O ₆	C43:0	43	C14:0-C14:0-C15:0 ^b	754.6919		-6.6	-0.1		509.5	509.5	495.4	
			C15:0-C12:0-C15:0 ^b	754.6919		-6.6	-0.1		481.4	481.4	481.4	
C ₄₆ H ₈₆ O ₆	C43:1	41	C16:0-C13:0-C14:0 ^b	754.6919		-6.6	-0.1		481.4	481.4	509.5	
			C16:0-C12:0-C15:0 ^b	754.6919		-6.6	-0.1		481.4	481.4	495.4	
C ₄₇ H ₉₀ O ₆	C44:0	44	C16:1-C13:0-C14:0 ^b	752.6763		-4.3			481.4	481.4	507.4	
			C14:0-C14:0-C16:0 ^b	768.7076		-4.3			523.5	523.5	507.4	
C ₄₇ H ₈₈ O ₆	C44:1	42	C16:0-C10:0-C18:0 ^b	768.7076		5.4	9.9	3.0	495.4	495.4	495.4	
			C16:0-C12:0-C16:0 ^b	768.7076		5.4	9.9	3.0	495.4	495.4	495.4	
C ₄₈ H ₉₂ O ₆	C45:0	45	C18:1-C10:0-C16:0 ^a	766.6919		-7.1	-0.8	-7.8	467.4	467.4	493.4	
			C16:0-C14:0-C15:0 ^a	782.7232		-7.9			509.5	509.5	523.5	
C ₄₈ H ₈₈ O ₆	C45:2	41	C14:1-C15:0-C16:1 ^b	778.6919		-6.8			535.5	535.5	507.4	
			C16:1-C13:0-C16:1 ^b	778.6919		-6.8			507.4	507.4	507.4	
C ₄₉ H ₉₄ O ₆	C46:0	46	C14:1-C13:0-C18:1 ^b	778.6919		-6.8			535.5	535.5	479.4	
			C16:0-C14:0-C16:0 ^b	796.7389		0.6	1.5	-8.2	523.5	523.5	523.5	
C ₄₉ H ₉₂ O ₆	C46:1	44	C15:0-C15:0-C16:0 ^b	796.7389		0.6	1.5	-8.2	537.5	537.5	523.5	
			C14:0-C18:0-C14:0 ^b	796.7389		0.6	1.5	-8.2	551.5	495.4	551.5	
C ₄₉ H ₉₀ O ₆	C46:2	42	C16:0-C14:0-C16:1 ^b	794.7232		-8.2	-9.7	5.1	521.5	549.5	523.5	
			C15:0-C15:0-C16:1 ^b	794.7232		-8.2			535.5	535.5	523.5	
C ₄₉ H ₉₀ O ₆	C46:2	42	C14:0-C18:1-C14:0 ^b	794.7232		-8.2	-9.7	5.1	549.5	495.4	549.5	
			C16:1-C14:0-C16:1 ^b	792.7076		-9.6		-3.1	521.5	547.5	521.5	
C ₄₉ H ₉₀ O ₆	C46:2	42	C18:1-C14:1-C14:0 ^b	792.7076		-9.6		-3.1	493.4	549.5	547.5	
			C16:1-C16:0-C14:1 ^b	792.7076		-9.6			521.5	519.4	549.5	

Table 2 (continued)

Molecular formula	CN:i	ECN	TAG	Theoretical m/z [M + NH ₄] ⁺	Error (ppm)		Theoretical m/z [M-R ₁ CH ₂ CO ₂ H] ⁺	Measured m/z [M-R ₁ CH ₂ CO ₂ H] ⁺	Measured m/z [M-R ₂ CH ₂ CO ₂ H] ⁺	Measured m/z [M-R ₃ CH ₂ CO ₂ H] ⁺
					EC:210.4	EC:212.12				
C ₄₉ H ₈₈ O ₆	C46:3	40	C18:1-C14:1-C14:1 ^b	790.6919	-8.1		491.4	547.5	547.5	547.5
			C16:1-C14:1-C16:1 ^b	790.6919	-8.1		519.4	547.5	547.5	519.4
C ₅₀ H ₉₆ O ₆	C47:0	47	C16:0-C15:0-C16:0 ^b	810.7545	-3.6	-6.0	537.5	551.5	537.5	537.5
			C16:0-C14:0-C17:0 ^b	810.7545	-3.6	-6.0	537.5	565.5	537.5	523.5
			C15:0-C18:0-C14:0 ^b	810.7545	-3.6	-6.0	551.5	509.5	509.5	565.5
			C15:0-C17:0-C15:0 ^b	810.7545	-3.6	-6.0	551.5	523.5	523.5	551.5
C ₅₀ H ₉₄ O ₆	C47:1	45	C16:0-C15:0-C16:1 ^b	808.7389	0.9	3.3	535.5	549.5	549.5	537.5
			C14:0-C17:0-C16:1 ^b	808.7389	0.9	3.3	563.5	521.5	521.5	537.5
C ₅₀ H ₉₂ O ₆	C47:2	43	C16:1-C15:0-C16:1 ^b	806.7232	-5.2		535.5	547.5	547.5	535.5
			C18:1-C14:1-C15:0 ^b	806.7232	-5.2		507.4	563.5	563.5	547.5
C ₅₁ H ₉₈ O ₆	C48:0	48	C16:0-C16:0-C16:0 ^a	824.7702	6.8	-2.5	551.5	551.5	551.5	551.5
			C16:0-C14:0-C18:0 ^b	824.7702	6.8	-2.5	551.5	579.5	579.5	523.5
			C15:0-C18:0-C15:0 ^b	824.7702	6.8	-2.5	565.5	523.5	523.5	565.5
			C17:0-C14:0-C17:0 ^b	824.7702	6.8	-2.5	537.5	579.5	579.5	537.5
C ₅₁ H ₉₆ O ₆	C48:1	46	C16:0-C14:0-C18:1 ^a	822.7545	-4.1	-3.6	549.5	577.5	577.5	523.5
C ₅₁ H ₉₄ O ₆	C48:2	44	C18:1-C14:0-C16:1 ^b	820.7389	-8.5		521.5	575.5	575.5	549.5
			C16:1-C16:0-C16:1 ^b	820.7389	-8.5		549.5	547.5	547.5	549.5
C ₅₁ H ₉₂ O ₆	C48:3	42	C16:1-C16:1-C16:1 ^a	818.7232	-2.9		547.5	547.5	547.5	547.5
			C16:1-C18:1-C14:1 ^b	818.7232	-2.9		547.5	519.4	519.4	575.5
C ₅₂ H ₁₀₀ O ₆	C49:0	49	C16:0-C15:0-C18:0 ^b	838.7858	7.7	-0.3	565.5	579.5	579.5	537.5
			C16:0-C16:0-C17:0 ^b	838.7858	7.7	-0.3	565.5	565.5	565.5	551.5
			C18:0-C14:0-C17:0 ^b	838.7858	7.7		537.5	593.6	593.6	551.5
C ₅₂ H ₉₈ O ₆	C49:1	47	C16:0-C17:0-C16:1 ^b	836.7702	-9.2		563.5	549.5	549.5	565.5
			C16:0-C15:0-C18:1 ^b	836.7702	-9.2	5.2	563.5	577.5	577.5	537.5
			C16:0-C17:1-C16:0 ^b	836.7702	-9.2		563.5	563.5	563.5	563.5
C ₅₃ H ₁₀₂ O ₆	C50:0	50	C16:0-C18:0-C16:0 ^b	852.8015	-2.6	-2.5	579.5	551.5	551.5	579.5
			C17:0-C15:0-C18:0 ^b	852.8015	1.4	-2.5	565.5	593.6	593.6	551.5
C ₅₃ H ₁₀₀ O ₆	C50:1	48	C16:0-C16:0-C18:1 ^b	850.7858	1.4	-3.1	577.5	577.5	577.5	551.5
			C18:0-C14:0-C18:1 ^b	850.7858	1.4	-3.1	549.5	605.6	605.6	551.5
C ₅₃ H ₉₈ O ₆	C50:2	46	C16:1-C16:0-C18:1 ^b	848.7702	1.8	-3.1	577.5	575.5	575.5	549.5
			C18:1-C14:0-C18:1 ^b	848.7702	1.8	-3.1	549.5	603.5	603.5	549.5
C ₅₄ H ₁₀₄ O ₆	C51:0	51	C18:0-C17:0-C16:0 ^b	866.8171	-1.4	-3.4	565.5	579.5	579.5	593.6
			C18:0-C15:0-C18:0 ^b	866.8171	-1.4	-3.4	565.5	607.6	607.6	565.5
C ₅₄ H ₁₀₂ O ₆	C51:1	49	C18:0-C15:0-C18:1 ^b	864.8015	5.0	4.3	563.5	605.6	605.6	565.5

Table 2 (continued)

Molecular formula	CN:i	ECN	TAG	Theoretical <i>m/z</i> [M + NH ₄] ⁺	Error (ppm)			Measured <i>m/z</i> [M-R ₁ CH ₂ CO ₂ H] ⁺	Measured <i>m/z</i> [M-R ₂ CH ₂ CO ₂ H] ⁺	Measured <i>m/z</i> [M-R ₃ CH ₂ CO ₂ H] ⁺
					EC:210.4	EC:212.12	EC:214.12			
						EC:213.18				
C ₅₅ H ₁₀₆ O ₆	C52:0	52	C18:1-C17:0-C16:0 ^b	864.8015	5.0	4.3	565.5	577.5	591.5	
C ₅₅ H ₁₀₄ O ₆	C52:1	50	C18:0-C16:0-C18:0 ^a	880.8328	1.5	5.7	579.5	607.6	579.5	
C ₅₅ H ₁₀₂ O ₆	C52:2	48	C18:1-C16:0-C18:1 ^a	878.8171	-5.6	0.5	579.5	605.6	577.5	
C ₅₅ H ₁₀₀ O ₆	C52:3	46	C18:1-C16:1-C18:1 ^b	876.8015	-0.7	1.4	577.5	603.5	577.5	
			C18:2-C16:0-C18:1 ^b	874.7858	0.3	5.6	575.5	603.5	575.5	
			C18:2-C16:0-C18:2 ^a	874.7858	0.3		577.5	601.5	575.5	
C ₅₆ H ₁₀₈ O ₆	C53:0	53	C18:0-C17:0-C18:0 ^b	872.7702	-4.1	2.2	575.5	599.5	575.5	
			C18:0-C16:0-C19:0 ^b	894.8484	1.6	2.2	593.6	607.6	593.6	
			C18:0-C17:0-C18:1 ^a	892.8328	0.9	0.3	579.5	621.5	593.6	
C ₅₆ H ₁₀₄ O ₆	C53:2	49	C18:1-C17:0-C18:1 ^b	890.8171	-0.5	-2.2	591.5	605.6	593.6	
			C18:1-C16:0-C19:1 ^b	890.8171	-0.5		591.5	617.5	577.5	
			C18:1-C15:0-C20:1 ^b	890.8171	-0.5		591.5	631.6	563.5	
C ₅₇ H ₁₁₀ O ₆	C54:0	54	C18:0-C18:0-C18:0 ^a	908.8641	-1.8	5.6	607.6	607.6	607.6	
C ₅₇ H ₁₀₈ O ₆	C54:1	52	C18:0-C18:1-C18:0 ^a	906.8484	2.1	5.0	605.6	607.6	605.6	
C ₅₇ H ₁₀₆ O ₆	C54:2	50	C18:1-C18:0-C18:1 ^a	904.8328	-8.5	-1.3	605.6	603.5	605.6	
C ₅₇ H ₁₀₄ O ₆	C54:3	48	C18:1-C18:1-C18:1 ^a	902.8171	2.8	5.8	603.5	603.5	603.5	
C ₅₇ H ₁₀₂ O ₆	C54:4	46	C18:1-C18:2-C18:1 ^a	900.8015	-1.8	-8.9	601.5	603.5	601.5	
C ₅₇ H ₁₀₀ O ₆	C54:5	44	C18:2-C18:1-C18:2 ^a	898.7858	-2.9	-4.7	601.5	599.5	601.5	
C ₅₇ H ₉₈ O ₆	C54:6	42	C18:2-C18:2-C18:2 ^a	896.7702	4.0		599.5	599.5	599.5	
C ₅₈ H ₁₁₂ O ₆	C55:0	55	C18:0-C19:0-C18:0 ^b	922.8797		1.7	621.5	607.6	621.5	
			C18:0-C21:0-C16:0 ^b	922.8797		1.7	621.5	579.4	649.6	
			C18:1-C19:0-C18:0 ^b	920.8641		4.9	621.5	605.6	619.5	
			C18:1-C16:0-C21:0 ^b	920.8641		4.9	621.5	647.6	577.5	
			C18:1-C17:0-C20:0 ^b	920.8641		4.9	621.5	633.6	591.5	
C ₅₉ H ₁₁₄ O ₆	C56:0	56	C18:0-C20:0-C18:0 ^b	936.8954	-1.7		635.6	607.6	635.6	
			C20:0-C16:0-C20:0 ^b	936.8954	-1.7		607.6	663.6	607.6	
C ₅₉ H ₁₁₂ O ₆	C56:1	54	C18:0-C20:0-C18:1 ^b	934.8797	-7.9	0.5	633.6	605.6	635.6	
			C18:0-C20:1-C18:0 ^b	934.8797		0.5	633.6	607.6	633.6	
C ₅₉ H ₁₁₀ O ₆	C56:2	52	C18:1-C20:0-C18:1 ^a	932.8641	-2.3		633.6	603.5	633.6	
C ₆₁ H ₁₁₈ O ₆	C58:0	58	C20:0-C20:0-C18:0 ^b	964.9267		3.4	635.6	635.6	663.6	
			C22:0-C20:0-C16:0 ^b	964.9267		3.4	607.6	635.6	691.6	
C ₆₁ H ₁₁₄ O ₆	C58:2	54	C18:1-C22:0-C18:1 ^a	960.8954	2.2		661.6	603.5	661.6	

In TAGs labeled as (a), positional distribution of the fatty acids was determined. In TAGs labeled as (b), the positional distribution of the fatty acids was not determined; therefore, the listing of fatty acids is random

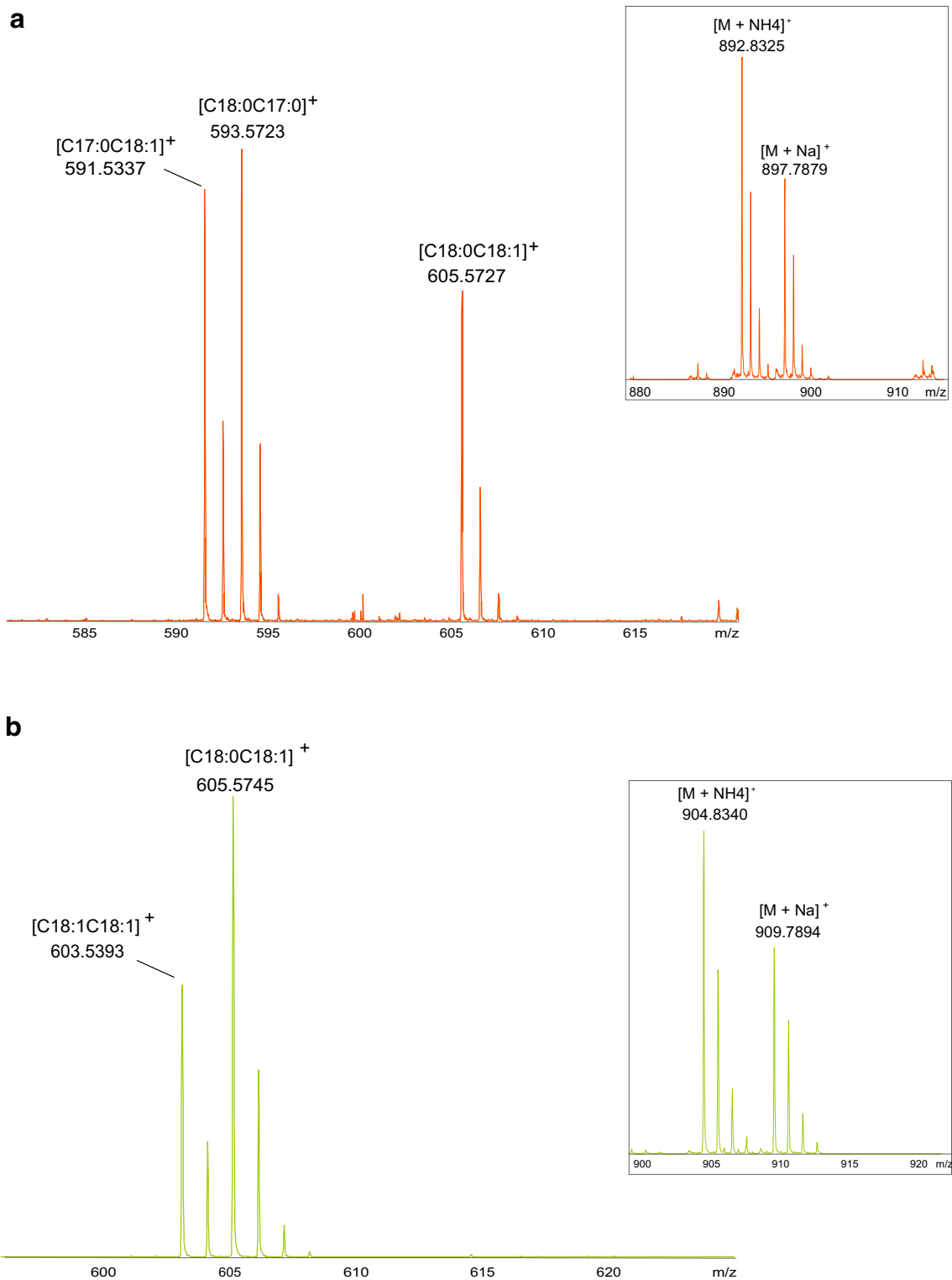


Fig. 5 MS/MS spectrum for the fragmentation of $[M + NH_4]^+$ adduct ions at (a) m/z 892.8325 and (b) 904.8340, showing their fragment ions, in sample EC.214.12

The TAG C18:0C18:0C18:0 was found in all of our archaeological samples. This TAG is usually present in ruminant fat and it is absent—or in low proportions—in non-ruminant animal fat (Mottram et al. 2001; Romanus et al. 2007).

The identification of TAGs with unsaturated FAs in their structures is evidence that lipid residues in archaeological vessels are well preserved. We compared lipid profiles with available reports of plant species that are present in the

Table 3 Oxidized triacylglycerides (TAGs) identified in samples EC.210.4, EC.214.12, and EC.213.18, (a) more than one molecular formula is possible in these cases

Molecular formula	Measured m/z [M + H] ⁺			Measured m/z [M + NH ₄] ⁺			Measured m/z [M + Na] ⁺		
	EC.210.4	EC.214.12	EC.213.18	EC.210.4	EC.214.12	EC.213.18	EC.210.4	EC.214.12	EC.213.18
C ₄₅ H ₈₄ O ₈				770.6517			775.6090		
C ₄₇ H ₈₈ O ₈				798.6870			803.6413		
C ₅₃ H ₁₀₂ O ₈		867.7786			884.7948			889.7531	
C ₅₄ H ₁₀₂ O ₈						896.7898			901.7413
C ₅₅ H ₁₀₄ O ₈ /C ₅₆ H ₁₀₈ O ₇ ^(a)		893.8096			910.8248			915.7754	
C ₅₅ H ₁₀₆ O ₈		895.8175			912.8268			917.7926	
C ₅₇ H ₁₀₆ O ₇				920.8204			925.7766		
C ₅₆ H ₁₀₆ O ₈ /C ₅₇ H ₁₁₀ O ₇ ^(a)					924.8433			929.7949	
C ₅₇ H ₁₀₈ O ₈ /C ₅₈ H ₁₁₂ O ₇ ^(a)		921.8296			938.8519			943.8028	
C ₅₇ H ₁₁₀ O ₈		923.8234			940.8526			945.8019	

archaeological botanical record of El Colorado (Petrucci and Palamarczuk 2019), such as *Ch. quinoa* (Fanali et al. 2015), *Z. mays* (Holcapek et al. 2003; Harrabi et al. 2010; Zeb and Murkovic 2010), *P. vulgaris* (Yoshida et al. 2005), and *Prosopis* spp. (Siano et al. 2018). Most of these studies used samples from European markets, with the exception of Siano et al. (2018) who collected Argentine samples. The survival of TAGs containing C18:2 in archaeological lipid residues suggests that the original source contained this compound in abundance, which is the case of plants (Zeb and Murkovic 2010; Kraujalis et al. 2013). Particularly, TAG C18:2C18:2C18:2 is present in both *Ch. quinoa* (Fanali et al. 2015) and *Z. mays* (Holcapek et al. 2003; Harrabi et al. 2010). In the case of *Ch. quinoa*, more than 60% of TAGs contained at least one C18:2 (Fanali et al. 2015). In samples EC.212.12 and EC.213.18, we found C18:2C18:1C18:2, and in sample EC.212.12 we found C18:2C18:2C18:2. These results, combined with the identification of plant sterols and higher C16:0/C18:0 ratios, suggest the presence of plant lipids in the residues in accordance to the previously mentioned modern samples.

Interdisciplinary interpretation

The interpretation of vessel use was an interdisciplinary activity that required the integration of the contextual archaeological information, the techno-morphological and use-alteration examination of the ceramic artifacts, and the results of residue analyses.

This archaeological cooking context has a combustion area, abundant charred macrobotanical remains, faunal remains and, in contemporaneous association to these features and ecofacts, a ceramic fragmentary assemblage—including samples EC.210.4, EC.212.12, EC.213.18, and EC.214.12—with stylistic characteristics that situate them chronologically in the

Late Intermediate Period, which is consistent with the radio-carbon date obtained (Palamarczuk et al. 2016).

The techno-morphological features of *Santa María* jar EC.212.12, large and unstable, combined with the absence of visible use-alteration traces, suggest its possible function for food or beverage service or storage. The open shape and smaller size of *Santa María* bowl EC.214.12 indicate its potential use as crockery for food or drink consumption. It is relevant to point out that the profusely painted *Santa María* jars and bowls were probably not everyday ware, but used in special occasions of commensality within the households. The lipid residues recovered in the ceramic matrix of these two samples indicate the presence of well-preserved mixtures of ruminant animal and plant lipids. Ruminant fat could have been used to seal inner surfaces for liquid storage (Cremonte et al. 2009; Miyano et al. 2017), or its presence could be the result of holding foods such as stews that combine animal and vegetable ingredients. The *Santa María* jar EC.210.4 has similar techno-morphological characteristics to EC.212.12 and absence of use-alteration features. However, scarce lipids were recovered and the profile indicates mainly the presence of ruminant fat. This could imply that it was sealed and hardly used, or rather it was used to contain water or liquids that leave no significant residue. Finally, in the case of EC.213.18 striated pot, the techno-morphological characteristics and the visible soot and cracks from exposure to fire suggest it was a cooking pot. The residues support this inferred use, given the abundant and well-preserved mixture of animal and plant lipids, which point toward the boiling of stews. The results obtained in this study are supported by previous preliminary findings from an Inca feasting context in the archaeological site of Fuerte Quemado-Intihuatana (15th–16th centuries AD) in the Yocavil valley (Catamarca, Argentina) (Lantos et al. 2017). Lipid residues recovered in one *Santa María* jar and two *Santa María* bowls indicated that this local ceramic

style—in association with other Inca style containers—were used for culinary purposes in a context of political commensality sponsored by the Empire. The absence of soot marks in these vessels suggested the use of jars for storage/service and bowls for service. In some of these examples, markers for ruminant lipids were also found, supporting our hypothesis that camelid lipids could have been used to seal the vessel walls. The comparison between results obtained from the Late Period *Santa María* jars from El Colorado and the Inca Period *Santa María* jars from Fuerte Quemado–Intihuatana raises the question of the possible continuity in the use of local styles for culinary practices in context of domestic and/or political commensality, even after the Inca conquest.

Conclusion

The characterization of FAME, sterol, and TAG profiles by combining analytical techniques (GC-FID, GC-MS, and HPLC-ESI-Q-TOF) resulted advantageous for the characterization and interpretation of lipid residues in archaeological samples. Although the FA profiles obtained with GC techniques in this study provided valuable information, they were insufficient to determine lipid origin on their own. The characterization of intact TAGs with HPLC-ESI-Q-TOF in archaeological samples allowed us to (1) consider the preservation of lipid residues in samples, and (2) provide a first approach to the identification of TAG markers of original food sources. Moreover, this is the first study to characterize intact TAGs recovered from South American archaeological ceramics with HPLC-ESI-Q-TOF, while previous similar studies analyze European examples (Mottram et al. 1997, 2001; Kimpe et al. 2001, 2004; Mirabaud et al. 2007; Romanus et al. 2007; Garnier et al. 2009; Saliu et al. 2011, 2014; La Nasa et al. 2015; Tirat et al. 2016; Degano et al. 2016; van Dam et al. 2017; Shevchenko et al. 2017; Tuñón-López et al. 2017; Oras et al. 2017; Blanco-Zubiaguirre et al. 2018; Lucejko et al. 2018; Hammann and Cramp 2018).

The results obtained in this study provide initial evidence to discuss the culinary use of *Santa María* vessels within the cooking space of a 14th century AD household in El Colorado (Catamarca, Argentina). These results and the preliminary data from an Inca context (Lantos et al. 2017) raise the question on the possible continuity in the use practices of the *Santa María* style over time. The evidence in this paper is a contribution to a larger debate in archaeology on the role of *Santa María* ceramics in daily life during the Late Intermediate Period in Northwest Argentina, challenging the traditional view that they were strictly funerary objects, for which further investigation on a wider chronological and spatial scale is warranted in the future.

Acknowledgments We thank Dr. Myriam Tarragó and Dr. Norma Ratto for their support and guidance. We thank all participants of the fieldworks in El Colorado (Yocavil Archaeological Project). Y.A. thanks the University of Buenos Aires for a Doctoral Fellowship. I.L., V.P.C., V.P., and M.S.M. are Research Members of CONICET. E.B. is Research Support Staff of CONICET. N.S.P. is a researcher at FCNYM–UNLP.

Funding information This work was supported by the University of Buenos Aires (UBACYT 20020170100340BA to M.S.M.; UBACYT-20020170100318BA to Dr. Myriam Tarragó), the National Agency for Promotion of Science and Technology (ANPCYT) (PICT-2016-0480 to I.L.; PICT-2015-2123 to V.P.C.), and the National Research Council of Argentina (CONICET) (PIP-11220130100288CO to M.S.M.; PIP-11220130100178CO to Dr. Myriam Tarragó).

Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

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