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# Detailed fatty acids analysis on lithic tools, Cerro El Sombrero Cima, Argentina

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ABSTRACT

This paper describes results obtained through fatty acids analysis on a sample of lithic artifacts. Analyzed tools come mainly from the excavated assemblage of Cerro El Sombrero Cima (Tandilia, Argentina), where the occupation has been assigned to the Pleistocene/Holocene transition. They include fishtail projectile points (FTPP), retouched tools, and ground tools. A variety of resources have been identified which indicate the great diversity of organic materials used and highlights the importance of plants in past daily life. Also, through this method marine resources have been identified, giving support to the proposition that different environments, including the sea coast, were familiar to early hunter-gatherers in the region. In addition, results are relevant to the discussion of the hafting and recycling of FTPP and the generalized use of other tool types.

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## 1. Introduction

Many early archaeological sites in the Argentine Pampas have poor preservation conditions for organic material. Such is the case of Cerro El Sombrero Cima (CoSC). This site, with the largest early lithic assemblage identified, has both poor stratigraphy and low organic preservation. This situation has promoted the exploration of an analytical methodology that provides information about the organic resources on which lithic artifacts were used. Fatty acids analysis by gas chromatography has proved successful in recovering valuable information in the absence of macroscopic evidence. It thus constitutes a useful approach to understanding the resources used by people in the past and the way in which tools were employed.

This paper describes the results obtained on a sample of artifacts, mainly from the excavated assemblage of CoSC. It includes fishtail projectile points (FTPP), retouched tools, and ground tools. A variety of resources have been identified which are relevant to discuss the movements of early people and the environments they visited, as well as the resources which were part of their daily lives.

## 2. Regional environment

The case study is located in a hilly area in the center east of Buenos Aires province, currently approximately 80 km from the Atlantic coast (Fig. 1). These hills belong to the Tandilia ranges, one of the two mountain systems that interrupt the extensive Pampean plains. Tandilia consists of low hills crossing the plains over 350 km with a northwest-southeast orientation, which form groups disconnected by fluvial erosion (Zárate and Rabassa, 2005). In the section under study, the igneous and metamorphic Precambriam bedrock is overlain by late Precambrian sedimentary rocks and Palaeozoic quartzites (Zárate et al., 1993) forming typical buttes and mesas with flat summits. Water can be found mainly in springs and small streams which flow from the hills to the ocean. One major river, the Quequén Grande, collects water from Tandilia, traverses the southern plains and flows into the ocean. Water is also available in seasonal lagoons in the plains and in some coastal lagoons. The plain ends in a wide chain of sand dunes surrounding the seashore or in coastal cliffs up to 30 m high where the Tandilia ranges meet the Atlantic coast.

The Pampean landscape is covered by a loess mantle, nowadays rich agricultural land. The latest cycle of eolian sedimentation began during the last glaciation. Eolian deposition decreased dramatically in the area during the early Holocene when more stable conditions favored soil development. Loess deposits have been intensely affected by pedogenesis and biological activity, as well as by aqueous transport (Flegenheimer and Zárate, 1993; Zárate et al., 1993). The Tandilia ranges exhibit a great diversity of

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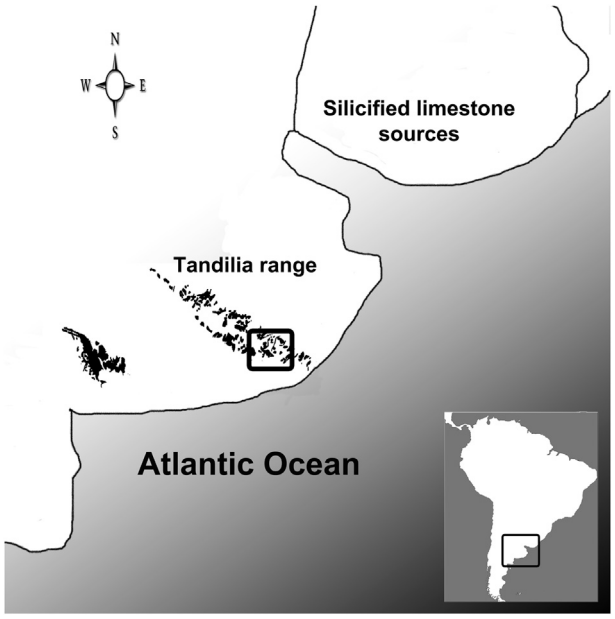


**Fig. 1.** Map of the study area.

microenvironments, and early archaeological occupations have been registered in many of them. Sites at higher elevations are set in environments with low eolian sedimentation rates, which may have been stabilized prior to human occupation. Early occupations located on the hill slope and in more protected rockshelters probably took place during the end of the depositional event and before the early Holocene interval of soil development. This stable interval was interrupted by the arid mid Holocene episode (Zárate and Flegenheimer, 1991; Zárate et al., 2000).

A grass steppe environment has been proposed for the time of early human occupation in the region (Paez et al., 2003). Recently, some indicators of the presence of shrub or arboreal components have been recorded at archaeological sites. The presence of charcoal indicates woody plants, and isolated micro particles related to Tala trees (*Celtis tala*) have been found in the hills and the Quequén Grande valley (Mazzanti, 2003; Martínez and Gutiérrez, 2011; Flegenheimer et al., 2013a).

The stratigraphic resolution in the valleys is greater than in the interfluves, with thick Holocene sequences in the floodplains of major rivers where alluvial sedimentation rates were higher (Zárate et al., 2000). Paleoclimatic conditions have been intensely studied in these sequences. In the Quequén Grande, several climatic pulses have been recorded and fluctuating climatic conditions inferred. A stable interval, following early human occupations, led to the development of the regional paleosol Puesto Callejón Viejo (Zárate et al., 2000; Gutiérrez et al., 2011; Martínez et al., 2013) which has been recently dated at Paso Otero archaeological locality giving ages of 10,000–9400 BP (Johnson et al., 2012).

Paleontological evidence suggests that since the Middle Pleistocene and through part of the Holocene, cold and arid climatic conditions prevailed in the region, alternating with more humid periods (Tonni et al., 1985). By the time of human occupation addressed in this paper a great variety of extant and extinct species were included in the assemblages with bone preservation, with some such as *Equus* (*Amerhippus*) *neogaeus* indicating arid conditions (Mazzanti, 2003; Martínez et al., 2013). The decrease of megamammals in the following millennia has promoted discussion about the nature of human intervention in their extinction in the region, in view of the absence of evidence indicating mass killings (Martínez et al., 2013).

Other environmental issues relevant to this paper are the location of the marine coast and the geomorphology of the Rio de la Plata during the time of human occupation. At this time, the sea level would have been lower than today, some 60 m below its current position (Guilderson et al., 2000; Parker et al., 2008; Ponce et al., 2011). This modified the coastline extending the plains mainly in the north and the south of the province of Buenos Aires, especially at the latitude of the Río de la Plata. Modifications were less dramatic in the central portion, where our study area is situated, which was then ~120 km inland. According to recent studies (Ponce et al., 2011), the occupation took place between two moments of inferred stabilization (between buried marine Terrace I and II). For that time, the rate of recession of the coastline has been estimated at an average of 27 m per year: therefore, changes in the sea coast must have been visible within a human lifetime. The different coastline affected the river distribution and drainage network. In this scenario, the Río de la Plata discharged eastwards from its present position, was narrower than today (Cavallotto et al., 2002), and its current course was mostly a coastal plain. There were no major geographical barriers between the plains in Uruguay and Buenos Aires province (Fig. 1).

## 3. Archaeology, case study

Hunter-gatherer groups inhabited the Pampean Region since the Late Pleistocene. Based on faunal remains, a generalized economy has been inferred for these early societies. Both extinct and extant species show signs of having been consumed and used (Mazzanti, 2003; Martínez and Gutiérrez, 2004; Martínez et al., 2013). Among them, some such as *Lama guanicoe*, *Ozotoceros bezoarticus*, *Hemiauchenia* sp., *Hippidion* sp. and *Equus* sp. that show anthropic intervention can reasonably be assumed to have been hunted with FTPP, although hunting sites with clear associations are elusive in the region. Information about the use of vegetal resources is scarcer, and except for the presence of charcoal, it is mainly indirect and comes from use wear studies.

Currently, twenty six archaeological sites assigned to the Late Pleistocene and Early Holocene bear witness of these early occupations: Cerro La China 1, 2 and 3, Cerro El Sombrero Cima and Abrigo 1, Los Helechos, Cueva Zoro, El Ajarafe, El Mirador, Abrigo La Grieta, Arroyo Seco 2, Paso Otero 5, Campo Laborde, La Moderna, Cueva Tixi, Abrigo Los Pinos, Cueva La Brava, Cueva El Abra, Cueva Burucuyá, Amalia 2, Loberia 1, El Guanaco 1 and 2, Arroyo de Frías, Laguna El Doce, and Pehuen Co paleoichnological site (Flegenheimer, 2003; Mazzanti, 2003; Bayón et al., 2004; Politis, 2008; Messineo and Politis, 2009; Mazzanti et al., 2010; Bayón et al., 2011; Martínez and Gutiérrez, 2011; Mazzia, 2011, 2013; Politis et al., 2011; Ávila, 2011; Mazzanti et al., 2012; Mazzia and Flegenheimer, 2012). Dates from these sites range between ca. 12,000 and 9000 $^{14}$C BP; in the microregion under study, sites firmly correlated to this case study range between 10,000 and 11,000 $^{14}$C BP (Mazzia and Flegenheimer, 2012).

Cerro El Sombrero Cima (CoSC) is an open air site located on the summit of El Sombrero hill, a butte where an early assemblage has been collected both from the surface and in stratigraphy (Flegenheimer, 2003; Flegenheimer et al., 2013b). These last remains are included in an A soil horizon which overlies either a B paleosol horizon or the quartzitic bedrock. No organic remains have been recovered at the site, as the sedimentary layer has been subject to active pedological activity and preservation is very poor. No radiocarbon dates associated to the occupation are available, which has been assigned to the Pleistocene–Holocene transition by comparison with nearby dated sites (Zárate et al., 2000/2002).

The assemblage under study includes 1501 flaked tools, of which 90 are fishtail projectile points (FTPP) in different moments

of their use life, and 11 tools manufactured by pecking, and grinding, one of them decorated by engraving. Toolstone has been highly selected, the most frequently chosen raw material being colored orthoquartzite of the Sierras Bayas Group (SBGO) found in quarries 40–60 km distant (Bayón et al., 1999; Colombo and Flegenheimer, 2013). Also, quartz, chert, silicified limestone, locally available orthoquartzites, dacite, silicified dolomite, and other rocks have been found in small proportions. Most of these rocks are exposed in the Tandilia ranges. Quarries for chert and silicified dolomite have been studied (Flegenheimer, 1991; Barros and Messineo, 2004, 2006) and potential sources for quartz and local orthoquartzites are known (Colombo, 2013). The only long distance transport identified involves silicified limestone, which probably traveled within social interaction networks. Its sources have been located 400–500 km to the northeast, crossing the Río de la Plata (Flegenheimer et al., 2003).

CoSC exhibits several characteristics which make it an exceptional site. The view from the hilltop is panoramic and reaches 40 km in most directions. It is denser and larger than most other early sites. The tool assemblage includes infrequently found tool types, the breakage ratio is very high (90%), fractures affect FTPP as well as other artifact types, bifacial tools are more frequent than in other regional early sites (42%), and debitage is restricted to the last moments of tool manufacture, resulting mainly from bifacial flaking with soft hammer percussion (Weitzel, 2012; Flegenheimer et al., 2013b). Microscopic use wear analysis on a small sample of tools from the site was useful to identify the importance of wood used by early peoples in an environment where this resource must have been scarce (Leipus, 2010).

The site is interpreted as a lookout and a place chosen for refurbishing weapons and discarding tools broken elsewhere. It has been recently proposed that this place was meaningful for early settlers and relevant in non-verbal communication. This proposal has been further sustained by comparison with another distant site, Cerro Amigo Oeste, which reveals a similar choice in social landscape (Flegenheimer et al., 2013b).

## 4. Gas chromatography analysis of lithic artifacts

### 4.1. Lipids and gas chromatography analysis

Organic residue analysis makes use of analytical organic chemical techniques to identify the presence and the origins of organic remains that cannot be described using traditional methods of archaeological investigation (Evershed, 2008). In this case study, this kind of analysis allows us to recover valuable information about organic resources which have not left macroscopic evidence. The study of the absorbed substances may provide information about dietary aspects or use of artifacts in the past (Evershead et al., 1992; Evershed, 2008). They reveal different kind of organic resources utilized and, when possible, their provenance.

When processing the archaeological objects, a small sample of fat and/or oil is obtained, that was trapped in the pores and fine cracks of the rocks while the objects were being used. Lipids, such as fats and oils, are organic molecules present in plant and animal tissues, composed of carbon, hydrogen, and oxygen atoms. These molecules are hydrophobic. They exhibit stability under high temperatures and a minimum breakdown over time in constant environmental conditions (Feiser and Feiser, 1960; Evershed, 1993; Gunstone et al., 2007). Thus, lipids can survive absorbed in the matrix of stone artifacts. In addition, due to their hydrophobic property, there is a minimum loss of substances when objects are washed with water in the absence of soap or detergents (Evershed, 1993; Babot, 2004).

Fatty acids are one of the natural compounds of lipids, with a linear chain and an even number of carbon atoms. They are classified according to chain length and the presence/absence of carbon double bonds. They are often divided into saturated and unsaturated forms: the carbon chains in saturated fatty acids are fully substituted with hydrogen, while unsaturated fatty acids have one or more double bonds between carbon atoms (Feiser and Feiser, 1960; Fankhauser, 1994; IUPAC, 1997; Bondia Pons, 2007; Gunstone et al., 2007).

The deterioration of polyunsaturated and very long chain fatty acids is more pronounced, but saturated fatty acids are less affected by decomposition. In archaeological samples, the presence of the first ones is important, as they indicate some stability of the substances over time (Malainey et al., 1999).

Gas chromatography is a widely used technique for the separation, identification, and quantification of lipids. It consists in the separation of mixtures of volatile or semi-volatile organic compounds through the use of protocols and specific equipment.

### 4.2. Methodological precautions

For this study, several methodological precautions were taken in order to ensure a more accurate interpretation of the results. First, as skin lipids may possibly be transferred to the artifacts, affecting the results of the chromatographic analysis (Evershead et al., 1992), a control sample was included. The aim was to consider whether a flake without use exhibited fatty acids due to its exposure to environmental conditions and our manipulation. According to the results, the archaeological samples under study are not polluted by manipulation during excavation or laboratory tasks (Mazzia, 2010–2011).

Second, since lipids are constituent parts of the environment, it is possible to mistakenly interpret lipids absorbed from the burial environment as evidence of past resources processed with archaeological artifacts (Evershed, 1993; Buonasera, 2007). Bearing in mind this possible contamination source, we also analyzed sediments of the A soil horizon where the assemblage was recovered. Based on the differences in the lipid record exhibited by the artifact and sediment samples, we consider that there is minimal post-burial absorption of substances. This can be explained in terms of the hydrophobic nature of the lipids that limits their migration by dissolution or dissemination. Fatty acids from the soil may be absorbed in the porosities of rocks, but this process is so slow that they are affected by degradation prior to accumulating in appreciable amounts (Charters et al., 1993; Evershed, 1993; Buonasera, 2007). These two methodological precautions provide greater certainty to the assessment of past organic substances in the archaeological samples.

Finally, a small experimental lithic collection was prepared in order to analyze absorbed substances from different origins. Experimental SBGO flakes were used with meat (*Bos taurus*), plants (including a mix of edible grass leaves, bulbs, roots, and fruits), wood (*Salix* sp.), vegetal mastic (made with heated *Pinus* sp. resin and ashes), and a mixture of meat and plants (Mazzia, 2010–2011).

### 4.3. Materials and method

The samples were processed at the Chemical Analysis Lab of Materia Hnos. Oleochemichals (Mar del Plata, Argentina). Artifacts with sizes between 2 and 10 cm were totally immersed in chloroform in a covered beaker for 24 h with an intermittent shakeup. As extraction involved the complete artifact, the fatty substances obtained come from the whole stone tool, not only from the edges. As a consequence, results may include a mix of substances coming from different edges and surfaces. Larger objects were treated

differently, as only selected parts were in contact with the solvent. After this first step, every extract was filtered and dried and treated under nitrogen. In all cases, the extraction process took place at a constant room temperature with nitrogen supply in order to prevent possible deterioration of lipids.

After the extraction of samples, a protocol of methylation was followed. Methylation involves the preparation of methyl esters derived from the samples of lipids. The protocol (EC 2-66 preparation of methyl esters) is based on the official methods of the American Oil Chemists adapted by the Materia Hnos. Lab. It included the following steps:

- the extract was diluted in 12.5 ml of a methyl solution of potassium hydroxide in a 150 ml ground-necked round-bottom flask,
- the round-bottom flask was connected to a refrigerant while boiling for 12 min,
- 25 ml of a 5% solution of sulphuric acid in methanol were added,
- the round-bottom flask was connected to a refrigerant while boiling for 12 min,
- it was cooled,
- for the phase separation, a 500 ml separatory funnel was used with 100 ml of distilled water and 50 ml of petroleum ether; the upper phase containing the methyl esters was kept,
- this extract was collected in a 100 ml beaker,
- the solvent was boiled off using a double boiler and completely dried in a 90 °C oven,
- it was diluted with petroleum ether and transferred into a vial,
- 2 μl of the sample were injected into the gas chromatograph.

When it is possible, the use of gas chromatography–mass spectrometry equipment is preferable to gas chromatographs because it is a more accurate technology for the identification of pure substances (Ábalos et al., 2003). However, gas chromatographs are widely available and also offer a reliable and effective method for identification and quantification of fatty acids feasible for correlation with natural resources (Malainey et al., 1999; Malainey, 2007; Costa Angrizani and Constenla, 2010). Although on this occasion the samples were processed with gas chromatographs, previously we had used gas chromatography–mass spectrometry equipment for other samples (Babot et al., 2007; Mazzia, 2010–2011). According to our experience with both types of equipment, the results have not shown significant differences.

In this case, a HP 6890N gas chromatograph with flame ionization detector (FID) and a back automatic injector were used for the analysis, along with a Supelcowax 10 capillary column. The column temperature was 200 °C, the injector temperature was 250 °C, and the detector temperature was 280 °C.

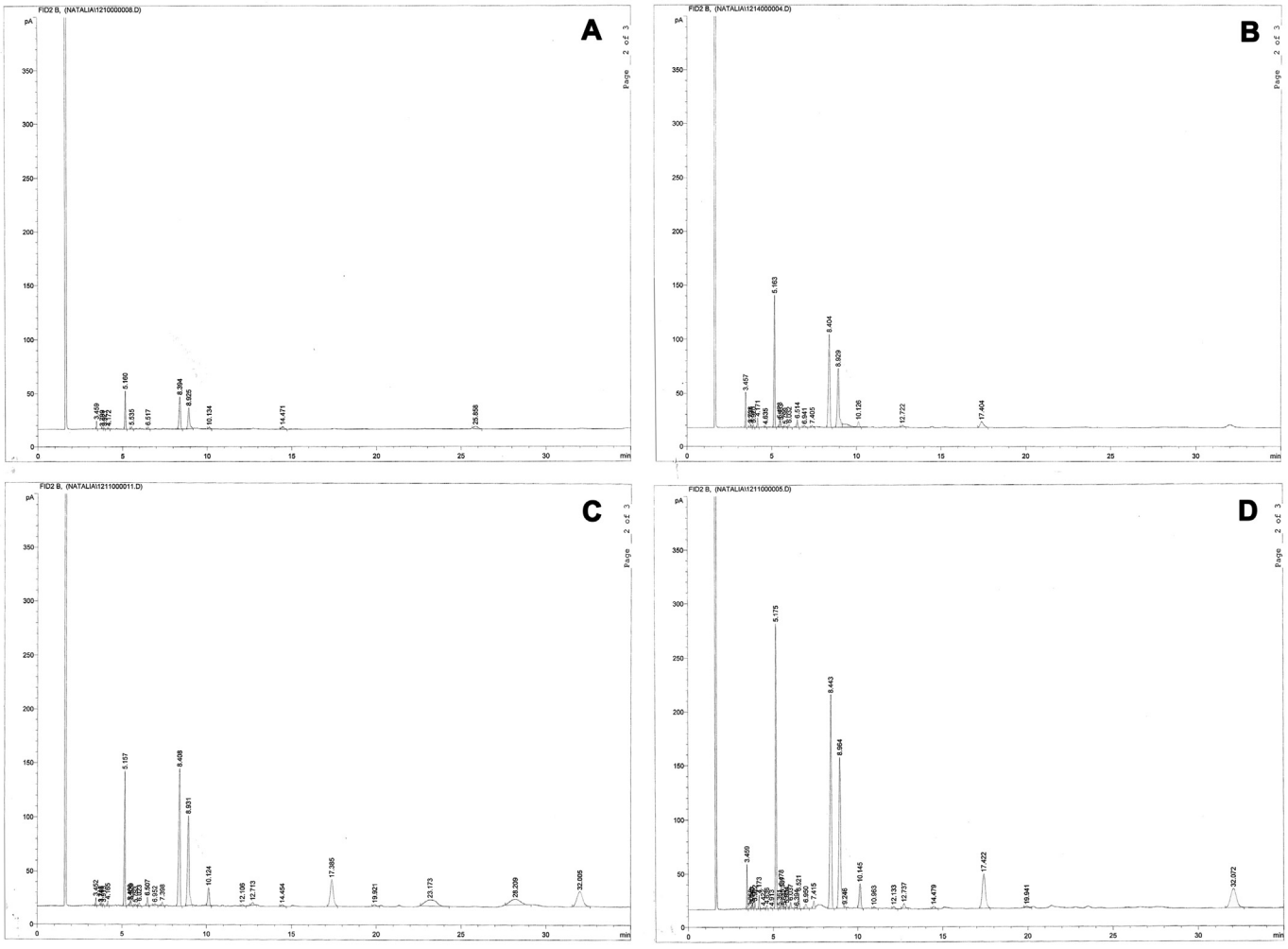


**Fig. 2.** Four chromatograms presented as examples: A. sample of sediments; B. S12 304 39 (fragment of an unidentified polished artifact); C. S13 905 3 (FTPP recycled as a drill); D. S7 102 1 (fragmented side scraper).

The next step consisted in determining the percentage of all the fatty acids in the chromatograms resulting from the injections (Fig. 2). These percentages and the relations between them were used for interpreting the results. The presence of some fatty acids, mainly saturated and short-chain ones, may be due to the action of degradation processes that have led to the disappearance of most volatile fatty acids (Malainey et al., 1999). These fatty acids are expected to be abundant in degraded samples.

The identification of substances is based on chemist-taxonomic principles. This implies relating a chemical property in the sample, such as the presence or absence of a typical compound or mixture of compounds, with that same property of contemporary plant and animal products taken as reference (Evershead et al., 1992). Thus, when interpreting each sample, the relative percentages of fatty acids were compared with the composition of animal fats and vegetable oils that are described in current databases, experimental information or archaeological papers (for example: U.S. Testing Company, N/D; Patrick et al., 1985; Rottländer, 1990; Robinson et al., 1991; A&G Técnica, 1993; Fankhauser, 1994; Cañabate Guerrero and Sánchez Vizcaíno, 1995; Fezler, 1995; Brenner and Bernasconi, 1997; Pond et al., 1997; Malainey et al., 1999; Sengör et al., 2003; Abd El-Baky et al., 2004; Babot et al., 2007; Buonasera, 2007; Frére et al., 2010; Mazzia, 2010–2011; Muhamad and Mohamad, 2012).

Among the materials recovered at Cerro El Sombrero Cima, different types of stone tools were selected for the analysis of the substances that could have adhered to their surfaces. The analyzed assemblage includes 29 lithic objects: five pecked and ground stone tools, nine fragmented FTPP, and 16 flaked artifacts such as scrapers and bifaces (Figs. 3–5). This selection includes a variety of artifacts favoring pecked and ground stone tools which were expected to preserve fatty acids according to previous work on this and other assemblages (Babot, 2004; Babot et al., 2007; Flegenheimer et al., 2013a). Also, several FTPP were analyzed, as these are the most conspicuous artifacts in the assemblage. In this group, points which were recycled into other tools were favored as they were expected to yield more information about a variety of resources used. Finally, in the third group, tools were chosen to represent the morphological variety exhibited at the hilltop. Most tools were recovered from within the A soil horizon at the site except for a small fragmented sphere (206) which is the only surface remain, and was included to test possible fatty acid preservation under unfavorable conditions. Most of the tools come from the centre of the hilltop in the main excavation area (S12 and S13), although examples from test pits in other areas of the hilltop were included (W130 and S7).

## 5. Results

The results are organized into three groups according to the characteristics of the analyzed objects (Tables 1–3). Each of the tables includes a first column containing the results of the gas chromatographic analysis of sediments: even though this column appears in the three tables, it describes the same sample. The lipid record in the sediment sample consists of seven fatty acids and 6.6% undetermined compounds. In the chromatogram (Fig. 2A), the peaks that represent these fatty acids have small areas. However, as mentioned in the following descriptions, they were taken into account when making inferences about stone tool samples.

**Table 1**
Results of chromatography analysis of sediment and pecked, ground and polished artifacts from CoSC. Fatty acids values are presented as percentages.

| Fatty acid | Sample | | | | | |
|---|---|---|---|---|---|---|
| | CoS Sed. | S12 105 2 | 206 | S12 204 1 | S12 304 23 | S12 304 39 |
| C11:0 – Undecanoic acid | – | – | – | – | 0.219 | – |
| C12:0 – Lauric acid | – | – | – | 0.089 | 0.571 | – |
| C13:0 – Tridecanoic acid | – | – | 0.186 | – | – | – |
| C14:0 – Myristic acid | 3.036 | 0.05 | 8.544 | 2.156 | 7.383 | 4.521 |
| C14:1 – Myristoleic acid | – | – | 0.432 | 0.329 | 0.372 | 0.5 |
| C15:0 – Pentadecanoic acid | 1.612 | – | 5.147 | 1.58 | 3.273 | 2.031 |
| C16:0 – Palmitic acid | 22.194 | 51.30 | 24.056 | 29.489 | 29.818 | 23.981 |
| C16:1 – Palmitoleic acid | 1.618 | – | 12.959 | 3.761 | 3.89 | 2.378 |
| C16:4 –Hexadecatetraenoic acid | – | – | – | – | 2.004 | – |
| C17:0 – Heptadecanoic acid | 1.608 | – | 2.321 | 2.834 | 2.507 | 2.68 |
| C17:1 – Heptadecenoic acid | – | – | – | 0.927 | – | 0.616 |
| C18:0 – Stearic acid | 32.447 | 14.1 | 22.507 | 18.41 | 22.316 | 28.194 |
| C18:1 – Oleic acid | 24.569 | – | 16.804 | 32.317 | 22.12 | 22.54 |
| C18:2 – Linoleic acid | – | – | 0.957 | 2.011 | 1.276 | 6.848 |
| C18:3n3 – ά-Linolenic acid | 1.976 | – | – | 0.592 | – | – |
| C18:4 – Stearidonic acid | – | – | 2.246 | 0.186 | – | 0.788 |
| C19:0 – Nonadecanoic acid | – | – | – | 0.111 | – | – |
| C20:0 – Eicosanoic acid | – | – | 0.646 | 0.142 | – | – |
| C20:2 – Eicosadienoic acid | – | – | – | 1.92 | – | 4.447 |
| Undeterminated fatty acids | 6.613 | – | 3.197 | 3.145 | 4.249 | 0.477 |

**Table 2**
Results of chromatography analysis of sediment and fishtail projectile points from CoSC. Fatty acids values are presented as percentages.

| Fatty acid | Sample | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | CoS Sed. | S13 905 3 | S11 W130 4 | S12 404 2 | S12 403 2 | S12 404 3 | S12 404 1 | S12 304 1 | S12 402 1 | S12 406 14 |
| C10:0 – Capric acid | – | – | – | 0.015 | 0.709 | 0.619 | – | – | – | 0.033 |
| C11:0 – Undecanoic acid | – | – | – | – | – | 0.954 | – | – | – | – |
| C12:0 – Lauric acid | – | – | – | 0.297 | 0.618 | 0.446 | – | – | – | – |
| C13:0 – Tridecanoic acid | – | – | – | 0.147 | 0.976 | 0.595 | – | – | – | 0.034 |
| C14:0 – Myristic acid | 3.036 | 0.511 | 2.607 | 2 | 3.546 | 1.571 | 29.412 | 0.188 | 4.281 | 5.327 |
| C14:1 – Myristoleic acid | – | – | 0.195 | 0.217 | 0.483 | 0.15 | – | – | 0.532 | 0.710 |

**Table 2** (*continued*)

| Fatty acid | Sample | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | CoS Sed. | S13 905 3 | S11 W130 4 | S12 404 2 | S12 403 2 | S12 404 3 | S12 404 1 | S12 304 1 | S12 402 1 | S12 406 14 |
| C15:0 – Pentadecanoic acid | 1.612 | 0.762 | 1.205 | 1.423 | 1.278 | 1.074 | 7.143 | – | 1.472 | 1.425 |
| C16:0 – Palmitic acid | 22.194 | 13.039 | 19.318 | 22.486 | 22.168 | 17.034 | 32.773 | 14.54 | 23.192 | 24.059 |
| C16:1 – Palmitoleic acid | 1.618 | 0.883 | 3.274 | 1.847 | 2.106 | 1.477 | 9.034 | 0.782 | 2.004 | 2.181 |
| C17:0 – Heptadecanoic acid | 1.608 | 1.703 | 6.368 | 2.34 | 2.781 | 2.604 | – | 2.503 | 2.596 | 2.647 |
| C17:1 – Heptadecenoic acid | – | 0.403 | 0.6 | 0.561 | 0.654 | 0.672 | – | – | 0.515 | 0.547 |
| C18:0 – Stearic acid | 32.447 | 23.655 | 29.709 | – | 32.641 | 28.994 | 14.076 | 43.53 | – | 27.08 |
| C18:1 – Oleic acid | 24.569 | 17.314 | 22.333 | 22.422 | 24.896 | 18.992 | 7.563 | 29.84 | 25.46 | 27.249 |
| C18:2 – Linoleic acid | – | 3.609 | 3.378 | 3.446 | 2.427 | 3.148 | – | 3.6 | 3.512 | 1.875 |
| C18:3n3 – ά-Linolenic acid | 1.976 | 0.302 | – | 0.371 | 0.648 | 0.685 | – | – | 0.492 | 0.462 |
| C18:4 – Stearidonic acid | – | 0.731 | – | 0.912 | 0.388 | 0.653 | – | – | 1.327 | 0.662 |
| C19:0 – Nonadecanoic acid | – | – | – | 0.192 | 0.306 | 0.335 | – | – | 0.195 | 0.188 |
| C20:0 – Eicosanoic acid | – | 0.445 | – | 0.396 | 0.309 | – | – | 0.735 | 0.428 | 0.29 |
| C20:2 – Eicosadienoic acid | – | 9.804 | 4.767 | 3.391 | – | 8.29 | – | 4.281 | 2.47 | 1.009 |
| C21:1 – Heneicosenoic acid | – | 0.364 | – | 0.134 | – | 0.453 | – | – | – | – |
| C21:2 – Heneicosadienoic acid | – | 8.586 | – | – | – | – | – | – | – | – |
| C22:2 – Docosadienoic acid | – | 10.217 | 5.993 | 5.118 | – | 7.287 | – | – | 2.547 | 0.786 |
| Undeterminated fatty acids | 6.613 | 7.669 | 0.251 | 32.293 | 3.066 | 3.966 | – | – | 28.976 | 3.298 |

### 5.1. Pecked and ground lithic artifacts

Table 1 lists the results obtained from the analysis of pecked and ground lithic artifacts. It does not include the decorated discoidal stone (Fig. 3A) as it has already been described in another paper (Flegenheimer et al., 2013a). The extract obtained from the decorated surface was too small, and it only consists of three fatty acids: myristic, palmitic and stearic. The ubiquity of these compounds in nature makes it impossible to infer any use for the discoidal stone.

The other four pecked and ground artifacts provided more abundant and heterogeneous lipid compositions than the discoidal stone, although one comes from the surface collection. It is artifact CoSC 206, a fragmented small stone sphere (Fig. 3B) manufactured on a yellow non-identified quartzitic rock. As this object was more exposed to oxidation processes than artifacts recovered during excavation, we expected to obtain a sample containing only saturated fatty acids, mainly of short and medium chains. However, we found polyunsaturated fatty acids, such as stearidonic acid. The high proportion of palmitoleic acid and the relative percentages of stearidonic, myristic, palmitic, oleic and linoleic acids are comparable to compositions that characterize various seed oils (U.S. Testing Company, N/D; Robinson et al., 1991). It is difficult at the moment to assess the implications of this result.

The extract S12 204 1 comes from another fragmented small stone sphere (Fig. 3C) that was made of the Balcarce Formation orthoquartzite. The relationship among the proportions of palmitic, palmitoleic, oleic, linoleic, stearidonic and eicosanoic acids is comparable with the composition of terrestrial animal fat (U.S. Testing Company, N/D; Robinson et al., 1991). This result would be consistent either with a leather wrap or thong used to tie the sphere or its use as a weapon: however, this last seems improbable due to its small size when compared to later regional bola stones known to have been used for hunting (Vecchi, 2010). Small spheres are found in other early assemblages in the Southern Cone both as manuports and as culturally modified objects of varied raw materials (Dillehay, 1997; Miotti et al., 2010; Flegenheimer et al., 2013a). Although small spheres were part of early assemblages, their function or significance is not yet clear.

A possible fragment of discoidal stone (S12 304 23, Fig. 3D), manufactured on Balcarce Formation orthoquartzite, had a significant lipid record. The presence of hexadecatetraenoic acid, a polyunsaturated fatty acid was identified: it has been found in the databases of the compositions of fish and marine mammal lipids, and is also present in some algae (Patrick et al., 1985; Brenner and Bernasconi, 1997; Pond et al., 1997; Sengör et al., 2003; Abd El-Baky et al., 2004; Muhamad and Mohamad, 2012). Therefore, this object is linked to the use of aquatic animal resources. As the function of discoidal stones is unknown so far (Flegenheimer et al., 2013a), this information is relevant if the fragment corresponds to this type of artifact.

Finally, a fragment of an unidentified polished artifact made of quartz (S12 304 39, Fig. 3E) was analyzed. It does not correspond to a small sphere, so, it either is part of a discoidal stone or of a third unknown type of ground tool. The amount of fat extracted from this fragment is remarkable, as its largest side is only 2 cm. In this sample there are relative values of linoleic, stearidonic, and eicosadienoic acids which can be related to the compositions of vegetable oils (U.S. Testing Company, N/D; Robinson et al., 1991; Mazzia, 2010–2011).

### 5.2. FTPP

The results of the chromatographic analysis of nine fragmented FTPP are presented in Table 2. From a typological analysis, some of these specimens were interpreted as recycled or reused artifacts with a function different from hunting (Flegenheimer et al., 2013b), and results were expected to reveal a variety of resources. The recycled points comprise two points that have been retouched, possibly after breakage, and currently exhibit bifacial scraping edges, one of them with a graver at the end. Another point has been reworked into a drill, and a fourth specimen has been used in strong abrasive work.

All the samples obtained were sufficiently abundant for the gas chromatograph injection. However, this does not mean that the past use of the projectile points could be identified in all the artifacts: such is the case of sample S12 404 1 (Fig. 4A). It was obtained from a fragmented and recycled FTPP that preserves the stem and part of the blade. It was manufactured on a brownish orthoquartzite (SBGO). The extract obtained was small with few fatty acids that are not diagnostic and that were also detected in the sedimentary matrix. Thus, it is not possible to infer the use of this object in the past.

The fragmented FTPP S12 404 2 (Fig. 4B) was manufactured on pinkish SBGO, and it also still has the stem and part of the blade. The lipid sample has a composition with a diversity of fatty acids. There was no record of stearic acid, which is widespread in nature. Eicosadieonoic, heneicosenoic, and docosadienoic acids point to a

**Table 3**
Results of chromatography analysis of sediment and retouched artifacts from CoSC. Fatty acids values are presented as percentages.

| Fatty acid | Sample | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | CoS Sed. | S12 106 6 | S12 203 38 | S12 404 8 | S12 405 11 | S7 102 1 | S12 205 bis5 | S13 27 12 | S12 203 7 | S12 401 10 | S12 4 2 | S13 904 14 | S12 4 12 | S12 305 2 | S12 4 11 | S12 303 3 |
| C9:0 – Nonanoic acid | – | – | – | – | – | – | – | 0.689 | – | – | – | – | – | – | – | – |
| C10:0 – Capric acid | – | – | 0.268 | – | 0.16 | – | – | 0.611 | – | – | – | – | – | – | – | – |
| C11:0 – Undecanoic acid | – | – | – | – | – | – | – | 1.416 | – | – | – | – | – | – | – | – |
| C12:0 – Lauric acid | – | – | 0.399 | – | 0.345 | – | 0.204 | 0.895 | – | – | – | – | – | – | 0.039 | 0.142 |
| C13:0 – Tridecanoic acid | – | – | – | – | 0.163 | – | – | 0.794 | – | – | – | – | – | – | 0.027 | 0.125 |
| C14:0 – Myristic acid | 3.036 | 5.947 | 6.649 | 1.598 | 1.983 | 2.026 | 4.183 | 8.338 | 2.669 | 0.235 | 2.875 | 2.361 | 0.541 | 1.065 | 4.537 | 7.998 |
| C14:1 – Myristoleic acid | – | 0.811 | 0.664 | 0.18 | 0.222 | 0.201 | 0.292 | 1.087 | 0.226 | – | 0.279 | – | – | 0.174 | 0.608 | 0.632 |
| C15:0 – Pentadecanoic acid | 1.612 | 1.684 | 2.44 | 0.842 | 1.544 | 1.281 | 2.075 | 2.061 | 1.705 | 0.207 | 1.117 | 1.139 | 0.451 | 0.746 | 1.428 | 2.629 |
| C16:0 – Palmitic acid | 22.194 | 23.5 | 32.565 | 17.336 | 22.33 | 19.459 | 26.363 | 23.773 | 21.825 | 15.203 | 21.915 | 20.532 | 18.13 | 14.239 | 23.285 | 23.043 |
| C16:1 – Palmitoleic acid | 1.618 | 1.966 | 2.547 | 1.854 | 3.212 | 2.735 | 2.798 | 2.569 | 3.459 | 1.235 | 1.878 | 2.912 | 1.59 | 1.015 | 2.348 | 6.153 |
| C16:4 – Hexadecatetraenoic acid | – | – | 1.468 | – | – | – | 1.612 | – | – | – | – | – | – | – | – | – |
| C17:0 – Heptadecanoic acid | 1.608 | 2.811 | 2.619 | 2.462 | 2.683 | 2.408 | 2.483 | 2.209 | 2.658 | 2.582 | 2.566 | 2.818 | 2.264 | 1.786 | 2.485 | 2.689 |
| C17:1 – Heptadecenoic acid | – | 0.409 | 0.442 | 0.467 | 0.643 | 0.638 | 0.734 | 0.609 | 0.618 | 0.523 | 0.554 | 0.821 | – | 0.394 | 0.549 | – |
| C18:0 – Stearic acid | 32.447 | 28.108 | 24.149 | 28.945 | 24.705 | 26.048 | 27.876 | 25.263 | 31.746 | 42.45 | 35.646 | 34.955 | 39.098 | 26.497 | 26.538 | 25.051 |
| C18:1 – Oleic acid | 24.569 | 21.411 | 20.709 | 23.6 | 25.376 | 21.226 | 25.026 | 23.387 | 21.893 | 31.485 | 25.18 | 30.55 | 26.136 | 17.455 | 28.715 | 21.897 |
| C18:2 – Linoleic acid | – | 2.153 | 3.549 | 3.561 | 3.565 | 3.312 | 5.048 | 3.311 | 2.603 | 3.117 | 3.888 | 3.276 | 4.436 | 2.611 | – | 1.506 |
| C18:3n3 – ά-Linolenic acid | 1.976 | 0.351 | – | 0.364 | 0.328 | 0.357 | – | – | 0.254 | – | – | – | – | – | 0.502 | 0.189 |
| C18:4 – Stearidonic acid | – | 0.199 | 0.931 | 0.568 | 1.122 | 0.779 | – | – | 0.079 | – | – | – | 1.017 | 0.614 | 0.59 | 1 |
| C19:0 – Nonadecanoic acid | – | 0.191 | – | – | – | 0.246 | – | – | – | – | – | – | – | – | 0.188 | 0.228 |
| C20:0 – Eicosanoic acid | – | 0.322 | – | 0.453 | 0.383 | 0.466 | – | – | 0.683 | – | – | – | – | – | 0.3 | 0.39 |
| C20:1 – Eicosenoic acid | – | – | – | – | – | – | – | – | – | – | – | – | – | – | 0.08 | – |
| C20:2 – Eicosadienoic acid | – | 3.842 | – | 9.131 | 3.806 | 8.468 | – | – | 3.963 | – | 3.611 | – | 5.612 | 7.22 | 1.569 | 1.194 |
| C21:1 – Heneicosenoic acid | – | 0.262 | – | – | – | 0.22 | – | – | – | – | – | – | – | – | – | – |
| C22:2 – Docosadienoic acid | – | 3.779 | – | 8.05 | 5.275 | 8.08 | – | – | – | – | – | – | – | – | – | – |
| Undeterminated fatty acids | 6.613 | 2.256 | 1.232 | 0.59 | 2.153 | 1.322 | 1.304 | 2.986 | 2.982 | – | – | – | – | 7.374 | – | 1.617 |

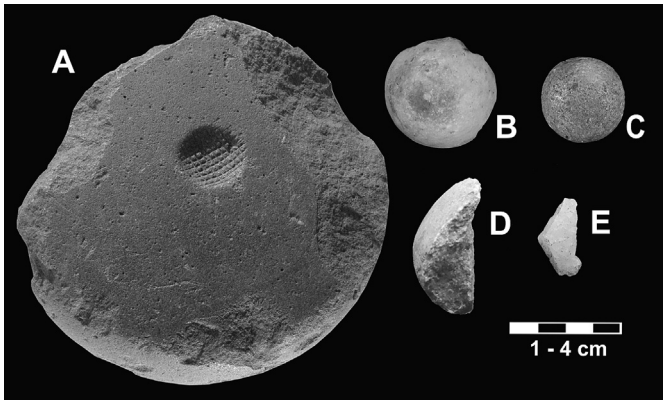


**Fig. 3.** Pecked, ground and polished artifacts from CoSC. A. S12 105 2; B. 206; C. S12 204 1; D. S12 304 23; E. S12 304 39.

plant contribution to the substances. However, the sample exhibits more than 32% undetermined compounds, making it impossible to infer the origin of the organic resources that have remained on it, as this situation masks the relationship among fatty acids.

Similarly, sample S12 402 1 (Fig. 4C) has almost 29% of undetermined fatty acids and no record of stearic acid. It is a recycled artifact, possibly originally a projectile point on red and white SBGO. The edges of this tool exhibit strong abrasion, most probably due to use. However, according to the results, its use in processing particular organic resources cannot be inferred from this analysis.

The lipid sample taken from specimen S13 905 3 (Fig. 4D) contains interesting information. It is a FTPP which has been recycled as a drill, manufactured on yellowish SBGO, and still has

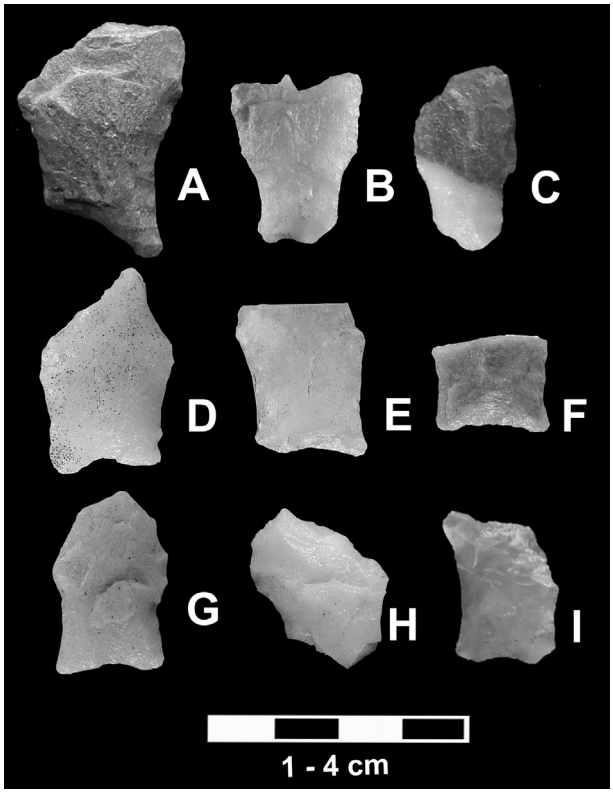


**Fig. 4.** Fishtail projectile points (FTPP) from CoSC. A. S12 404 1; B. S12 404 2; C. S12 402 1; D. S13 905 3; E. S11 130 4; F. S12 404 3; G. S12 406 14; H. S12 403 2; I. S13 27 12; J. S12 303 3.

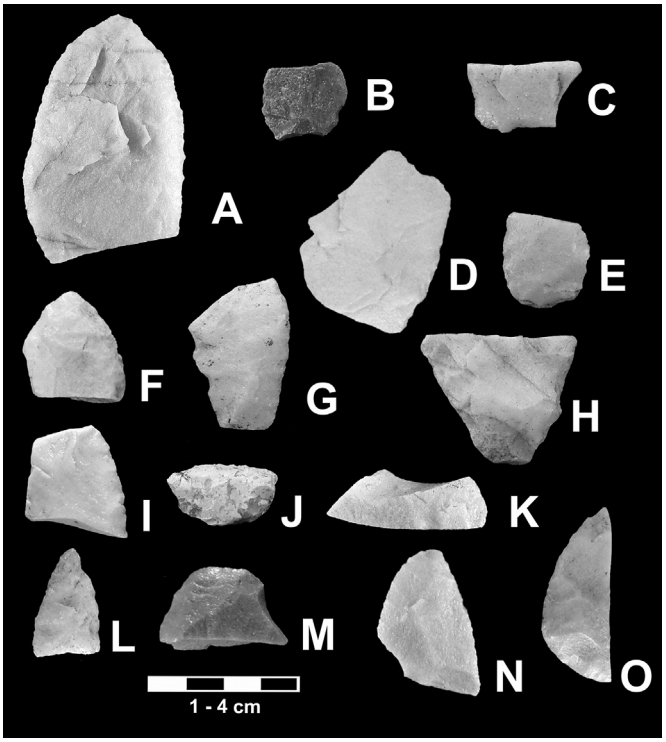


**Fig. 5.** Retouched artifacts from CoSC. A. S13 904 14; B. S12 4 2; C. S12 401 10; D. S7 102 1; E. S12 404 8; F. S12 405 11; G. S12 106 6; H. S12 203 7; I. S13 27 12; J. S12 303 3; K. S12 4 11; L. S12 305 2; M. S12 4 12; N. S12 205bis 5; O. S12 203 38.

the stem and part of the original blade. It exhibits a significant proportion of long/very long chain fatty acids, both saturated and unsaturated. Among them, eicosadienoic, docosadienoic, heneicosenoic, and heneicosadienoic are noteworthy. Eicosadienoic acid was identified in the experimental samples of wood, mastic, and plants. Docosadienoic acid was recognized in experimental samples of wood and plants, and the heneicosenoic and heneicosadienoic acids were detected only in plant samples (Mazzia, 2010–2011). In sum, it is probable that the analyzed substances are the result of the projectile point haft. However, the presence of fatty acids identified in vegetable oils, but not in wood or mastic, suggests the contribution of other substances once the point was fragmented and reutilized after recycling.

Sample S11 130 4 (Fig. 4E) comes from a fragmented FTPP made of quartz, and only the stem has remained. It presents a relatively high percentage of heptadecenoic acid. This is interpreted as the result of bacterial action on substances (Robinson et al., 1991; Buonasera, 2007). The presence of eicosadienoic and docosadienoic acids refers to the projectile's haft and/or the possible re-use of its edges on vegetal resources. This FTPP does not present macroscopic evidence of recycling.

Two other samples indicate that the projectile points were probably hafted. Extract S12 404 3 (Fig. 4F) comes from a pinkish SBGO stem. As discussed previously, relative proportions of eicosadienoic and docosadienoic acids are interpreted as evidence of hafting, as they were isolated in experimental samples of wood, mastic, and plants (eicosadienoic), and in experimental samples of wood and plants (docosadienoic). It is not possible to define other resources from the remaining compounds. The same two fatty acids were detected in sample S12 406 14 (Fig. 4G), although in different proportions. This sample corresponds to a complete and maintained FTPP worked on yellow SBGO. It is the only complete analyzed specimen which has not been recycled. It exhibits

evidence of a possible vegetal haft, and the relationship among the proportions of palmitic, palmitoleic, oleic, linoleic, stearidonic and eicosanoic acids is comparable with the composition of terrestrial animal fat (U.S. Testing Company, N/D; Robinson et al., 1991). This result is highly consistent with the expectations for a weapon and implies that this point was probably used after maintenance.

S12 403 2 (Fig. 4H) is a fragmented and recycled FTPP on whitish SBGO that preserves part of the blade and only a very small section of the stem. The point has been reworked into a composite tool with a small graver on the distal edge. No fatty acids related to hafting were identified, probably due to the small size of the remaining stem. The relative percentages of fatty acids in this lipid composition indicate that this specimen was used, but do not allow an unambiguous inference about the origin of the resources. Similarly, sample S12 304 1 (Fig. 4I) shows a general undetermined composition. However, this composition includes a significant proportion of eicosadienoic acid, possibly related to a vegetal haft. This is consistent with the object, which is a stem of a fragmented FTPP of chert.

### 5.3. Other flaked tools

The last group of results comes from 15 flaked artifacts that include different morphologies (Table 3): 14 are made of SBGO and only one is manufactured on silicified limestone. This group includes different manufacturing sequences. Five artifacts only have unifacial retouch, two have bifacial retouch and eight exhibit bifacial thinning.

Sample S13 904 14 (Fig. 5A) was extracted from a fragmented large double convergent side scraper. It has relative proportions of myristic, palmitic, stearic, oleic and linoleic acids comparable to terrestrial animal fats (U.S. Testing Company, N/D; Robinson et al., 1991; Mazzia, 2010–2011). Similarly, the extract taken from a fragmented small irregular biface (S12 4 2, Fig. 5B) exhibits the same fatty acids in a proportion indicating an animal origin. However, this biface also presents a relative percentage of eicosadienoic acid that indicates a plant contribution to the sample, possibly due to a vegetal haft, although no macroscopic indication of hafting is evident.

In a fragment of an unidentified composite tool (S12 401 10, Fig. 5C), a fatty acid profile similar to those described for terrestrial animal fats was registered. However, the proportion of the stearic acid appears augmented, probably due to the degradation of more unstable, long chain and unsaturated fatty acids. In consequence, it is not possible to infer an unequivocal origin of the organic resources.

Sample S7 102 1 (Fig. 5D) comes from a fragmented side scraper on a flat flake, possibly a bifacial thinning flake. Although the lipid record shows a variety of fatty acids, only a few can be differentiated from those detected in the sediments. Among them, linoleic, eicosadienoic, heneicosenoic and docosadienoic acids indicate a vegetable origin of the substances. The last three fatty acids were registered in the experimental samples of vegetables (C20:2 in wood, mastic and vegetables; C21:1 in vegetables and C22:2 in wood and vegetable samples: Mazzia, 2010–2011). Based on these evidences, the use of this tool on wood or/and on different vegetable tissues can be inferred: due to its morphology it is unlikely, though not impossible, that this object was hafted. Likewise, extract S12 404 8 (Fig. 5E) also has fatty acids that were identified in the sediments, as well as linoleic, eicosadienoic, and docosadienoic acids. According to the experimental references, these fatty acids can be related to wood, mastic or fruits and leaves of different plants. This fragment corresponds to a small bifacial tool with one regular edge and another sinuous edge. Acids possibly include substances from a vegetable haft or/and vegetable oils, as residues of plant processing.

Sample S12 405 11 (Fig. 5F) comes from a bifacial fragment, possibly a double convergent side scraper or an asymmetrical point tip. In this sample, capric and eicosanoic acids were registered at less than 1%. These fatty acids have a restricted distribution in nature, but they can be found in these proportions both in animal fats and vegetable oils (Babot et al., 2007; Buonasera, 2007). The presence of linoleic, eicosadienoic and docosadienoic acids is interpreted as indicative of vegetable substances (Mazzia, 2010–2011).

A composite tool, with notches on one edge and a side scraper on the opposite, manufactured on a white bifacial thinning flake (S12 106 6, Fig. 5G) presents ambiguous results. Compared with the sediment sample, this extract exhibits few diagnostic compounds. The presence of linoleic, eicosadienoic, heneicosenoic, and docosadienoic acids can be considered indicators of a plant origin, but their relative percentages are small. Therefore, it is difficult to make accurate inferences about the origin of the substances recovered. Similarly, sample S12 203 7, coming from a fragmented bifacial blank (Fig. 5H), presents low relative proportions of linoleic and eicosadienoic acids but no other clear indicators. Hence, these two specimens may have been used in the past on indeterminate organic resources that could include plants.

The sample obtained from a bifacial edge, possibly a side scraper (S13 27 12, Fig. 5I) shows a heterogeneous fatty acids profile but with non-diagnostic compounds. However, some peculiarities can be mentioned. Nonanoic acid is not found in nature, although it results from the oxidation of other fatty acids such as oleic, linoleic, and linolenic. It is often described for rancid vegetable oils or substances that suffered breakdown after discard of the artifact (Babot et al., 2007; Buonasera, 2007). The undecanoic, tridecanoic, pentadecanoic and heptadecanoic acids identified result from bacterial action on substances (Robinson et al., 1991; Buonasera, 2007). Among them, undecanoic and tridecanoic acids are less frequent in the reference databases, and they were detected only in the experimental sample that mixed meat and vegetables (Mazzia, 2010–2011).

A composite bifacial tool made of silicified limestone (S12 303 3 Fig. 5J) presents a fatty acids profile interpreted as a mixture of substances of different origins. This tool is expected to have a long life history as it was probably manufactured some 400–500 km from CoSC (Flegenheimer et al., 2003). It possibly is a recycled bifacial artifact and its morphology allows different functions (scraper, graver and abrupt edge). The relationship among the percentages of myristic, palmitic, stearic, oleic, linoleic, linolenic and stearidonic acids is comparable to the compositions of terrestrial animal fat (Robinson et al. 1991; U.S. Testing Company, Inc.). However, the presence of eicosadienoic acid was also identified at less than 2%, and indicates a minor contribution of vegetable oils. The extract S12 4 11 (Fig. 5K) exhibits similar results including a small proportion of eicosenoic acid. This extract comes from an unclassified fragment of artifact manufactured by bifacial thinning.

Another two samples present an important but not diagnostic lipid record that can be compared to the experimental sample corresponding to mixed meat and vegetables (Mazzia, 2010–2011). One of these samples comes from a fragment of a composite tool which ends in a drill (S12 305 2 Fig. 5L) and the other from a fragment of a scraper (S12 4 12 Fig. 5M).

Samples S12 205bis 5 (Fig. 5N) and S12 203 38 (Fig. 5O) exhibit very similar fatty acids profiles. The first one corresponds to a fragment of a unifacial double convergent side scraper, and the other comes from a fragment of a biface. Both have hexadecatetraenoic acid, a polyunsaturated fatty acid with a very restricted distribution in nature. This acid was also detected in a fragment of a possible discoidal stone. The only references found for this fatty acid are in compositions of fish and marine mammal lipids, and it is also present in some algae (Patrick et al., 1985; Brenner and

Bernasconi, 1997; Pond et al., 1997; Sengör et al., 2003; Abd El-Baky et al., 2004; Muhamad and Mohamad, 2012). The relative proportions of the other fatty acids identified in these archaeological samples are consistent with the interpretation assigning a marine origin to the sample.

In summary, twenty-nine lithic objects with different sizes and morphologies were analyzed by gas chromatography. Twenty-seven have lipid samples with heterogeneous fatty acids compositions that allow us to propose their use in the past for processing organic resources. Only two, a recycled point (S12 404 1) and a discoidal stone (S12 105 2), gave samples which do not provide information about their past use.

## 6. Discussion

As a first comment, we want to highlight the important preservation of lipid molecules absorbed in lithic artifacts used more than 10,000 years ago. This preservation occurred in an environment where no other organic remains survived and in stone tools that were water washed and then stored for more than twenty years in the lab. This application of a method usually used on other materials, such as pottery and grinding tools, is therefore very promising and will be further explored in order to obtain more accurate interpretations. Although most of the analyzed artifacts come from stratigraphy, one of the fragmented spheres (206) was recovered during surface collection. This sample shows good preservation. The size of the tools has to be emphasized, as they are smaller than those commonly analyzed: the sampled stone tools include a fragment measuring only 2 cm (S12 304 39, Fig. 2E). The sizes of the objects are not proportional to the amount of fatty acids they retain. For example, an extract from this small fragment has an abundant and heterogeneous fatty acids profile.

Regarding the absence of results in some cases, it is highly improbable that the recycled FTPP (S12 404 1, Fig. 3A) was not used: on the contrary, hafting and other fatty acids would be expected. However, it did not yield positive results. Therefore, the absence of results cannot be taken as indicating that the object was not used on organic remains. This is directly relevant to the interpretation of the discoidal stone, making it incorrect to assume that it was not used on organic resources.

Results obtained through this methodology do not necessarily reflect the last activities carried out. Rather, they yield a profile of the artifact's life history, a significant difference with results obtained through use wear studies. However, both methodologies have been used in the region to call the attention to the variety of resources used. Mainly, they have been relevant to enhance the importance of the vegetable world, specifically of wood, in the daily life of early hunter-gatherers (Leipus, 2004). As faunal remains are more frequently recovered, research about the peopling process has until recently over-emphasized the importance of hunting. The role of plants in the early Pampean hunter gatherers diet is understudied because of its scarce or null representation in the archaeological record. Despite of the lack of direct evidences, gas chromatography studies, use wear analysis and stable isotopes on human remains are introducing significant data. The study of plant resources utilization in past subsistence strategies involves more than their use as food. Some other related issues are the specific technologies used for their exploitation, the knowledge of the environment, and social meanings linked to their use.

According to current interpretations, most of the tools discarded at CoSC were previously used and broken in other places (Weitzel, 2010). As this method reflects tool history, the assemblage at the hilltop most probably represents a wider range of resources than those used specifically at this place. It might even constitute a large sample of the organic materials in use by these early Pampean societies. However, obtaining a truly representative sample requires including tools from several sites, as a high intersite variability has been registered in the microregion (Mazzia and Flegenheimer, 2012). This sample includes an important amount of vegetable resources, among which seeds and vegetable hafts (wood and mastic) can be distinguished, along with a smaller proportion of terrestrial animals and a few marine resources.

The FTPP are the group of artifacts where expectations are easier to discuss. This group has yielded very consistent results. Of the nine samples analyzed, five have evidence of hafting (S13 905 3; S12 130 4; S12 404 3; S12 304 1; S12 406 14); a sixth sample that comes from a recycled blade (S12 403 2), as expected, does not show evidence of hafting; and the other three specimens have unidentifiable results. The only complete point (S12 406 14) shows evidence of terrestrial animal fat, relating it to its use in hunting. Four recycled FTPP were analyzed: of these, results from one (S12 905 3) refer to its use on vegetable resources, and the others did not give identifiable results.

The group of pecked, ground, and polished stone tools has not yielded an identifiable pattern in the results. However, it is interesting that these artifacts, whose function is still unknown (Jackson and Méndez, 2007; Hermo et al., 2013, Flegenheimer et al., 2013a; Nami, 2013), gave identifiable results. These are very varied even within the same typological group: for example, small spheres have shown seed oil (206) and terrestrial animal fat (S12 204 1) and fragments have yielded samples assigned to vegetable resources (S12 304 39) and marine fatty acids (S12 304 23). Interpretations regarding these artifacts are still highly speculative, as many questions about their function remain.

The third group includes a greater number of objects: only one is complete and probably corresponds to a recycled tool on a long distance rock, the others are fragmented, and some cannot be classified due to breakage. This third group has produced a variety of results. Three objects register terrestrial animal fat (S13 904 14, S12 4 12, S12 401 10), one with a vegetable contribution and another with some uncertainty. Three other artifacts exhibit vegetable resources (S7 102 1, S12 404 8, S12 405 11), one of which might also be related to hafting and another might include other unidentified resources. The next two objects described (S12 106 6, S12 203 7) revealed use on indeterminate resources, possibly including plants. One artifact (S13 27 12) is also indeterminate, but some fatty acids refer to rancid substances and bacterial action. Four objects (S12 303 3, S12 4 11, S12 305 2; S12 4 12) have been used both on animal and plant resources and have mixed fatty acids. The last two objects (S12 203 38, S12 205bis 5) register use on marine resources. Analysis shows that all of these artifacts have been used in the past, but no relation has been identified between tool morphology and the kind of resource. This lack of standardization of form-function for several tool types has also been observed on other early assemblages through functional studies based on microscopic analysis (Leipus, 2004). Also, many artifacts exhibit traces of more than one resource, as many tools in the assemblage have been multifunctional.

The identification of marine resources in three different artifacts merits comment. As mentioned, the Atlantic coast must have been ~120 km from CoSC at the moment of occupation. This distance probably falls within the range covered by early people in a yearly round or even during logistical journeys (Kelly, 1995). Furthermore, as people occupying CoSC participated in interaction networks over 400–500 km towards the northeast (Flegenheimer et al., 2003), they were bound to know the Atlantic coast. At other early sites, Paso Otero 5 and Cueva Tixi, lithic coastal raw materials have been identified (Valverde, 2002; Martínez and Gutiérrez, 2011), and FTPP have been found along the present coast (Flegenheimer and Bayón, 1996; Bonomo, 2005). Information obtained through fatty acids

analysis is interesting because it gives support to the idea that early settlers in the Pampean region made use of marine resources and were familiar with this particular environment.

## 7. Conclusion

The good preservation of the analyzed substances through time is remarkable, and they do not show significant effects of degradation processes. This good preservation is indicated by the great proportion of samples with polyunsaturated and very long chain fatty acids. Good preservation of fatty acids was also found in other four early lithic assemblages in the micro-region (Mazzia, 2010–2011, 2011, 2013), but we cannot establish the taphonomic conditions that made it possible. However, in all of these cases, micro cracks produced by flaking and natural porosities of the rocks must have played a key role in protecting lipids from degradation. This matter should be addressed during future analysis.

The fatty acids profiles indicate that early Pampean people used their lithic tools on a diversity of organic resources including seeds, plants, terrestrial animals and marine resources. The results also indicate the existence of vegetable hafts and vegetable mastic used to hold some artifacts. Furthermore, chromatographic analysis provides evidence of different environments visited by early groups, and is useful to think about the distances travelled by these people.

Although gas chromatography analysis already has a long history in archaeological studies, mainly on pottery and grinding stone tools, (for example, Patrick et al. 1985; Rottländer, 1990; Cañabate Guerrero and Sánchez Vizcaíno, 1995; Malainey et al. 1999; Buonasera, 2007; Evershed, 2008; Costa Angrizani and Constenla, 2010; in Argentina: González de Bonaveri and Frère, 2002, 2004; Babot, 2004; Babot et al., 2007; Babot and Hocsman, 2008; Babot et al., 2008; Frére et al., 2010; Mazzia, 2011, 2012; Bonomo et al., in press) the results are still generalized and imprecise. It is not possible yet to define the kind of vegetable or animal identified. More accurate distinctions require precise regional databases where native plants and animals are characterized. These are now being produced and will permit more detail in future interpretations in order to obtain more reliable identifications of resources, tasks, and movements of early people.

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