



## Chemical analyses of the earliest pigment residues from the uttermost part of the planet (Beagle Channel region, Tierra del Fuego, Southern South America)

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### ABSTRACT

This paper presents the results of chemical analyses of the organic and inorganic fractions of pigment residues found in three archaeological sites located in the Beagle Channel region, Tierra del Fuego, Southern South America. Twenty-one archaeological samples have been analysed through XRD, SEM–EDX, FT-IR and GC–MS in order to characterise their inorganic colouring components and to search for the presence of organic substances used as binders. Lipids found in some samples are considered as potential binders. These organic components are compared to those found in archaeological sediment samples from the same layers where the pigments have been found, in order to search for potential taphonomic contaminations of the latter by the former. Results show that such contaminations are unlikely, hence the lipid contents are deemed of anthropic origin. The pigment sample results are also compared to data from analyses of natural sediment samples collected in several localities of the Beagle Channel in order to search for potential natural pigment sources. Results show that organic and inorganic components of these sediments are not the same than those present in the archaeological pigment samples, hence the pigment raw material sources have not been yet located. All these data provide for the first time evidence of the existence of ancient activities of pigment sourcing and paint preparation with organic binders which range from 6000 BP to 1900 BP in the southernmost region of the planet.

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### 1. Introduction

The Beagle Channel is located at the southern portion of the Fuegian Archipelago: it runs approximately West–East and it is bordered by the islands of Tierra del Fuego (in the North) and Hoste and Navarino (in the South; Fig. 1). The Northern shore of the Beagle Channel region has been subject of systematic and continuous archaeological surveys and excavations from 1975 onwards (Orquera and Piana, 1999). The excavations have led to the definition of a long archaeological sequence which starts at 6900 BP (uncalibrated radiocarbon dates) and ends in the 19th century (Orquera and Piana, 1999). From 6200 BP onwards, the sequence was characterized by a specialization in the exploitation of littoral resources, which focused on the consumption of pinnipeds (especially fur seals, *Arctocephalus australis*) through the development of a highly efficient bone tool technology (Orquera, 2005, p. 107). Fish,

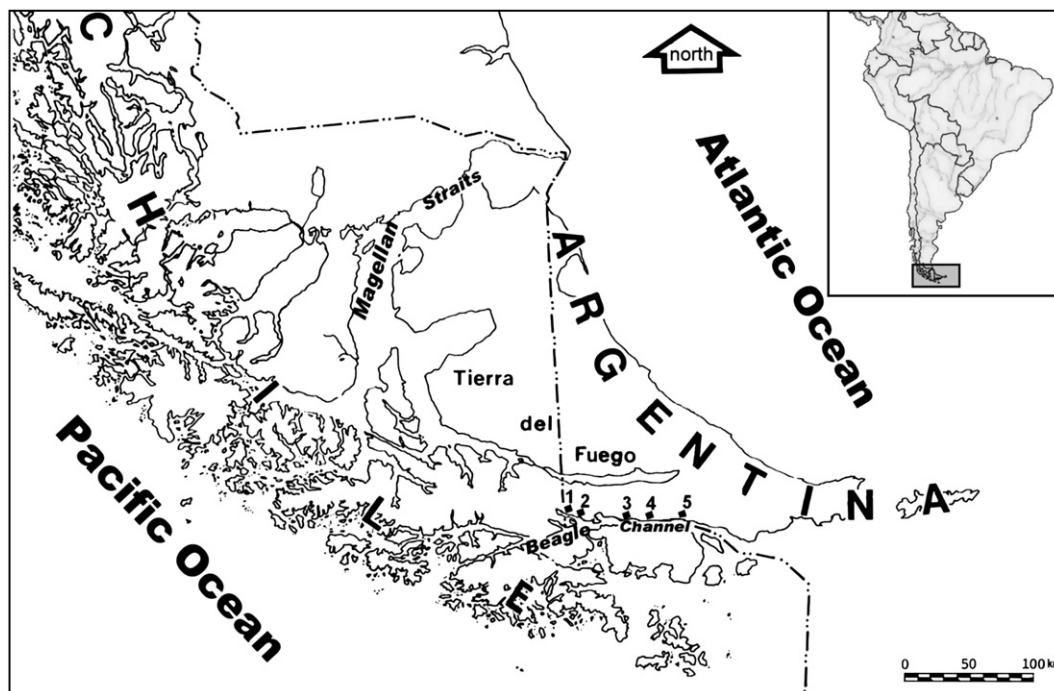
shellfish, guanacos and birds were also frequently consumed (Orquera and Piana, 1999; Zangrando, 2003).

These hunter–gatherer–fisher groups also developed a number of other activities, some of which have a considerably low archaeological visibility. Among these is the use of pigments, which usually appear in the archaeological record as small lumps of coloured substances, and less frequently as small powder stains in archaeological layers. Prior to this paper, these materials had not been subjected to any systematic studies. Therefore, the aims of this paper are as follows.

- (a) To present the results of pigment residues' analyses of three archaeological sites of the Beagle Channel region, which include the identification of the components of their organic and inorganic fractions in order to discuss whether pigments were used directly in their natural state or whether they were mixed with organic binders in order to produce paint.
- (b) To discuss the data about the samples' organic components in comparison to parameters obtained from analyses of archaeological sediment samples, in order to analyse potential taphonomic contamination problems.

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**Fig. 1.** Map of the Beagle Channel region, Tierra del Fuego (Southern South America). Key: 1 – Lapataia Bay; 2 – Ensenada Bay; 3 – Túnel I site; 4 – Shamakush I site; 5 – Imiwaia I site.

(c) To discuss the data about the samples' inorganic and organic components in comparison to information obtained from analyses of natural sediment samples, in order to search for potential natural pigment sources.

The integration of these three lines of evidence can shed new light on the development of technologies of paint production – which were previously unknown for the Beagle Channel region – including off-site activities of pigment procurement and on-site activities of paint preparation. In addition, the fact that we are analysing samples from three archaeological sites situated in three different locations and covering a wide chronological range, allows us to search for possible spatial and/or temporal similarities and differences in these activities. Moreover, these analyses can also contribute to a methodological discussion about the taphonomy of the pigment residues once they were incorporated to the archaeological record.

## 2. Materials and methods

### 2.1. Archaeological pigment samples

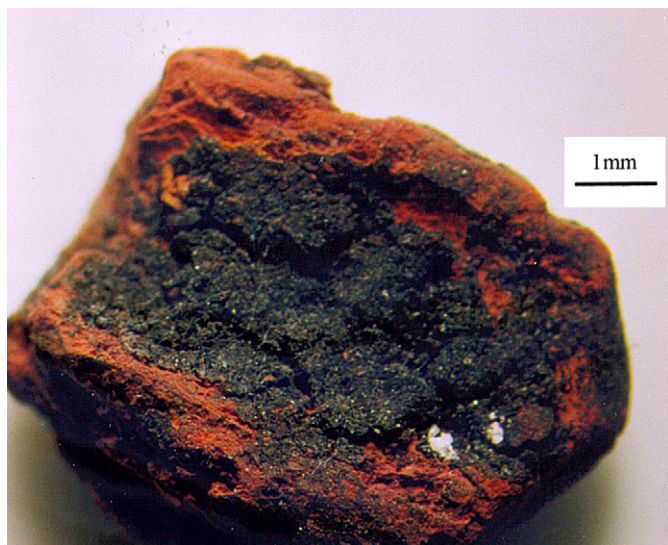
Fourteen sites have been excavated in the Beagle Channel region; pigment residues have been found in three of these sites: Túnel I, Shamakush I and Imiwaia I (Fig. 1). Túnel I is situated in the homonymous locality (54°15'S Lat., 68°09'W Long.), over a slope at 15 m above current sea level. A total of 150 m<sup>2</sup> have been excavated in this site, and 63 m<sup>3</sup> of sediments have been removed; the findings have allowed the identification of an archaeological sequence that ranges from 6900 ± 70 BP (Beta 6780) to 450 ± 60 BP (Beta 4388) (Orquera and Piana, 1999). This sequence is discontinuous and includes some chronological gaps, which, nevertheless, are mostly covered by findings in other archaeological sites (Orquera and Piana, 1999).

Shamakush is situated at Remolino locality (54°51'S Lat., 67°51'W Long), 19.2 km East of Túnel. It is characterized by its horizontal coasts and by a plain area of land which is approximately 2.5 km long and 600 m wide. A total of 64 m<sup>2</sup> have been excavated in site Shamakush I, and 20.20 m<sup>3</sup> have been removed, defining a sequence which ranges from 1927 ± 120 BP (AC1291) to 940 ± 110 BP (AC 1047) (Orquera and Piana, 1999, p. 39).

Site Imiwaia I is located within the lands of Estancia Harberton (54°52.38'S Lat., 67°17.75'W Long.), 53.6 km East from Túnel I. It is situated in Cambaceres Interior bay, in a flat landscape. A total of 56 m<sup>2</sup> have been excavated in this site, while 34.47 m<sup>3</sup> have been removed. Its radiocarbon dates range from 5872 ± 147 BP (AC 1397) to 150 ± 70 BP (AC 1579) (Orquera and Piana, 2001).

These sites are shell-middens and contain abundant archaeological evidence, including stone tools, bone tools, bone and shell ornaments, faunal remains and pigment residues. Given their particular formation process, the shell-middens have been excavated using a specific technique, which allows the separation of layers of inter-locked shells and the recording of archaeological remains within them, with a more accurate relative chronology (Orquera and Piana, 1992). Shell-midden excavations exposed artefacts, ecofacts and, occasionally, pigment residues. These residues were identified due to their colour (mostly reddish) and texture (lumps of powder), which clearly differ from that of the archaeological matrix (Figs. 2 and 3). Moreover, archaeological analyses and actualistic studies of shell-midden formation processes in the Beagle Channel indicate that burial happens fast (Orquera and Piana, 1992), which reduces the possibility of contamination. These data provided a first indication of the transportation of pigments to the sites by human agents.

The samples were collected with conventional trowels and placed in plastic containers. Care was taken in order to minimise touching the samples with bare hands to reduce potential contamination processes. Sample labels were placed in separate plastic bags so that the label material (paper) was not in direct contact



**Fig. 2.** Pigment sample TI 7, site Túnel I, layer E. Magnified 10 $\times$ . Note the intense red colour, compact powder lump texture and distinctive black sedimentary remains from the archaeological layer where it was found. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

with the sample. The samples were stored away from light, in dry conditions and at room temperature.

A total of 69 pigment samples were recovered during the excavations: 35 in Túnel I, three in Shamakush I and 31 in Imiwaia I (Fiore et al., 2007). Of these, 21 are analysed in this paper: 10 from Túnel I, two from Shamakush I, and nine from Imiwaia I (see Table 1). These were selected following these aims and criteria:

- at an inter-site level, samples from different archaeological localities and different sites were selected, in order to establish comparisons between different micro-regions within the Beagle Channel region;
- at an intra-site level, a representative sample of the number of pigment residues found in each site was selected, i.e. a proportional number of samples according to the total number of samples recorded in each site;



**Fig. 3.** Pigment sample TI 19, site Túnel I, layer D. Magnified 10 $\times$ . Note the red colour and compact powder lump texture. Small black stains correspond to sedimentary remains and white spots are shell remains from the archaeological layer. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Table 1**  
Beagle Channel sites, layers, pigment samples and radiocarbon dates

Site	Component and layer	Number of pigment samples	Radiocarbon dates
Túnel I	IV $\alpha$	1	2660 $\pm$ 100 BP (AC 1030)
	II D	5	4590 $\pm$ 130 BP (AC 833) to 6150 $\pm$ 220 BP (AC 883)
	II E	4	6200 $\pm$ 100 BP (Beta 3270)
Shamakush I	D	2	940 $\pm$ 100 BP (AC 1047)
Imiwaia I	B	1	154 $\pm$ 70 BP (AC 1579)
	C	1	–
	K	2	–
	L	1	4900 $\pm$ 120 BP (AC 1730)
	M	3	5000 $\pm$ 140 BP (AC 1731)
	N	1	5750 $\pm$ 170 BP (AC 1582) 5872 $\pm$ 147 BP (AC 1397)

- at an intra-site level, when pigment residues were found in more than one layer, samples were selected in order to represent the different layers and thus the chronological range found in the site.

The pigments were found as small lumps of coloured sediment, usually resting directly in the archaeological layers. Only one potential “crayon” (sample TI 8) was found: its consistency is much harder than the rest of the samples and it bears some macroscopic and several microscopic striations (observed with a stereomicroscope at magnifications ranging from 10 $\times$  to 63 $\times$ ); these striations may have resulted from rubbing this “crayon” on a relatively harder surface (Couraud and Laming-Empeaire, 1979). The potential function of this sample as a “crayon” needs to be confirmed experimentally, and will not be discussed further in this paper. Most of the samples are red, although two of them are yellowish (see Table 2).

## 2.2. Archaeological sediment samples

The study of the organic fraction of the pigment samples was complemented with the analysis of the organic fraction of archaeological sediment samples. These were studied with the aim of

**Table 2**  
Archaeological pigment samples from Beagle Channel sites

Sample number	Component, layer and quadrant	Sample colour
<i>Site Túnel I</i>		
T1 32	IV $\alpha$ XIII	Red
T1 24	II D38 XV	Red
T1 25	II D38 XV	Red
T1 15	II 22 D-sub4 XIII	Red
T1 27	II D20 XIII	Yellow-greyish
T1 20	II 5D XI	Yellow
T1 8	II E3 XII	Red
T1 3	II E10 XVI	Red
T1 5	II E10 XVI	Red
T1 35	II E inf XVIII	Red
<i>Site Shamakush I</i>		
SHI 1	D 184 sector 2	Red
SHI 2	D 180 sector 6	Red
<i>Site Imiwaia I</i>		
Imi 11	B IV	Red
Imi 10	C IV	Red
Imi 27	K235 III	Red
Imi 28	K290 III	Red
Imi 20	L5 IV	Red
Imi 1	M180V	Red
Imi 3	M180V	Red
Imi 5	M180V	Red
Imi 24	N25 I	Red



determining which kind of organic compounds were present in the sediment matrix of each archaeological site. The results obtained were used as parameters to evaluate the potential taphonomic contamination of the pigment samples: a similarity between the organic fractions of pigment residues and archaeological sediment samples would suggest a potential contamination of the former by the latter; a difference between these components would suggest that the organic fraction of the pigment samples was not of taphonomic origin and possibly responded to the inclusion of these substances as a result of human activities, namely, the mixing of pigments with organic binders during the preparation of paint.

The archaeological sediment samples were collected as a routine process during the excavation of each site. When the sites were excavated, the excavation protocol did not include taking a sediment sample from each particular spot where pigments were found; nevertheless, sediment samples were routinely collected from each archaeological layer. Therefore, we analysed the available relevant samples of archaeological sediments from layers that contained pigment residues, which include two samples from Túnel I, two from Imiwaia I and one from Shamakush I (see Table 3).

### 2.3. Natural sediment samples

The study of the inorganic components of the pigment residues was complemented with the analysis of natural sediment samples which macroscopically looked similar in colour and texture to the archaeological pigment samples. The aim of such analyses was to search for potential pigment sources that might have been used by ancient populations to collect these colouring substances along the Beagle Channel region.

The natural sediment samples were collected in five localities along the Beagle Channel: Lapataia Bay, Ensenada Bay, Túnel, Shamakush–Remolino, and Imiwaia–Harberton (see Table 4 and Fig. 1). Lapataia and Ensenada are located in the West portion of the Beagle Channel region, and not where the archaeological sites and samples under study were found; yet they have been included in our pigment survey since pigment quarries could have been situated in these localities and could have been exploited as sources of raw material by the ancient populations of the region.

Given that red is the most commonly found colour among the archaeological pigment samples, this was the criterion followed to collect the samples. Yellow samples were also searched for, but not found during this fieldwork. Each sample was taken at spots where reddish sediments appear in the landscape, mostly near water sources (which act as oxidation factors) or in sedimentary layers exposed in natural profiles. A total of nine samples were analysed.

### 2.4. Sample preparation and analysis

The inorganic fraction of the archaeological pigments and the natural sediment samples was studied using XRD, FT-IR and SEM-EDX. XRD analyses were carried out on a Philips diffractometer PW

1050, using copper radiation and nickel anticathode. SEM-EDX analyses were performed on a Philips XL 30 ESEM scanning electron microscope. FT-IR spectra were collected using a Nicolet Magna 550 spectrometer. The samples were dispersed in KBr disks. Spectra of 4 cm<sup>-1</sup> resolution were acquired by coaddition of 32 scans from 4000 to 400 cm<sup>-1</sup>.

The organic fraction of the archaeological pigments, the archaeological sediments, and the natural sediment samples was analysed through FT-IR, GC and GC-MS. All the solvents were of a quality suitable for chromatography (Merck, Darmstadt). Samples were crushed to a powder and extracted three times using chloroform:methanol (2:1 (v/v), 15 min sonication) at room temperature. The total lipid extracts were then centrifuged (15 min, 3200 rpm), decanted and filtered through celite under vacuum. The filtrates were then dried under a stream of nitrogen and analysed by FT-IR prior to derivatization. Fatty acid methyl esters (FAME) were prepared by treating the extracts with 2% HCl in methanol (0.5 ml) at 60 °C for 2 h. After cooling, water (0.5 ml) was added. The mixture was extracted with chloroform (3 × 0.5 ml) and the solvent evaporated under nitrogen. The FAME were stored at -25 °C until gas chromatographic analysis. GC was performed on a Hewlett-Packard 5890A chromatograph equipped with a flame ionization detector and an ULTRA 2 column (30 m × 0.25 mm i.d.). Temperature program: 1 min of isothermal at 100 °C and then 100–290 °C at 10 °C min<sup>-1</sup>, followed by a 10 min hold at 290 °C. Gas chromatography-mass spectrometry (GC-MS) was performed on a TRIO-2 VG mass spectrometer coupled to a Hewlett-Packard 5890 chromatograph.

## 3. Results

### 3.1. Analysis of archaeological pigment samples: inorganic fraction

The study of the inorganic fraction of archaeological pigment samples from Túnel I site by XRD indicates the presence of hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) in six out of 10 samples (TI 3, TI 5, TI 8, TI 24, TI 25, TI 35; see Table 5) together with accessory minerals often associated with earth pigments, such as quartz, clays and carbonates. The four remaining samples that did not show presence of hematite by XRD were studied by SEM-EDX; this analysis revealed that these four samples (TI 15, TI 20, TI 27 and TI 32) include Fe in different amounts, which presumably had not been detected by XRD due to its amorphous structure or low concentration (see Table 5). FT-IR data recorded directly from the samples showed characteristic hematite bands at 550–560 and 480–485 cm<sup>-1</sup> (Ruan et al., 2001) and strong peaks at 1100–1000 cm<sup>-1</sup> due to Si–O–Si stretchings (Barone et al., 2003) for samples TI 5, TI 8, TI 24, TI 25 and TI 35, confirming the results previously obtained by XRD. While red earth pigments are generally coloured by hematite, most of the yellow or yellow-brown earths are coloured primarily by the iron oxide hydroxide ( $\alpha$ -FeOOH) goethite, as might be the case of the yellowish coloured samples TI 20 and TI 27, containing 13% and 8% Fe, respectively, as determined by SEM-EDX. The presence of quartz and

**Table 3**  
Archaeological sediment samples from Beagle Channel sites

Sample	Site	Layer and quadrant	Relations to pigment samples number	FT-IR extract (cm <sup>-1</sup> )	GC-MS
Sedarq 1	Túnel I	D38 IV/XV	TI 24 and TI 25 (and indirectly to TI 27, TI 20, TI 15)	3428 (s), 2926 (s), 2856 (m), 1743 (sh), 1645 (sh), 1565 (s), 1414 (s)	Fatty acids: C <sub>16:0</sub> ; Minor components: C <sub>14:0</sub> , C <sub>15:0</sub> , C <sub>18:0</sub>
Sedarq 2	Túnel I	$\alpha$ XIII/XIV	TI 32	3420 (m), 2927 (s), 2861 (s), 1736 (w), 1650 (sh), 1571 (s), 1459 (m), 1419 (w)	Fatty acids: C <sub>16:0</sub> , C <sub>18:0</sub> ; minor components: C <sub>14:0</sub> , C <sub>15:0</sub> , C <sub>17:0</sub> , C <sub>18:1</sub> , C <sub>20:0</sub> , C <sub>22:0</sub>
Sedarq 3	Shamakush I	D 184 I	SHI 1 (and indirectly to SHI 2)	3434 (s), 2934 (s), 2861 (s), 1652 (sh), 1743 (w), 1565 (s), 1420 (m)	Fatty acids: C <sub>16:0</sub> , C <sub>18:0</sub> , C <sub>18:1</sub>
Sedarq 4	Imiwaia I	K 235 III	Imi 27	3421 (w), 2927 (s), 2855 (m), 1742 (w), 1650 (w), 1571 (w), 1460 (w)	Fatty acids: C <sub>14:0</sub> , C <sub>16:0</sub> , C <sub>18:0</sub> , C <sub>18:1</sub>
Sedarq 5	Imiwaia I	K 290 III	Imi 28	2927 (m), 2861 (m), 1729 (w), 1460 (w), 1374 (w)	Fatty acids: C <sub>16:0</sub> , C <sub>18:0</sub> ; minor components: C <sub>14:0</sub> , C <sub>15:0</sub> , C <sub>17:0</sub> , C <sub>18:1</sub> , C <sub>20:0</sub> , C <sub>22:0</sub> , C <sub>24:0</sub>

**Table 4**

Natural sediment samples from Beagle Channel localities

Sample	Layer and quadrant	Location	XRD	SEM–EDX	FT-IR extract (cm <sup>-1</sup> )	GC–MS
Pignat 1	Lapataia	54°51'16.1"S, 68°34'32.1"W	Quartz, plagioclase, clorite, moscovita, potassium, feldspar*	Na (6%), Mg (2%), Al (14%), Si (51%), S (1%), Cl (<1%), K (2%), Ca (2%), Ti (<1%), Mn (1%), Fe (20%)	3421 (s), 2934 (m), 2855 (w), 1736 (sh), 1656 (sh), 1572 (s), 1413 (s)	Fatty acid: C <sub>16:0</sub>
Pignat 2	Lapataia	54°51'19.3"S, 68°43'25.1"W	Quartz, plagioclase, clays	Na (4%), Mg (2%), Al (12%), Si (19%), S (2%), Cl (1%), K (1%), Ca (1%), Ti (<1%), Fe (57%)	3414 (w), 2927 (s), 2855 (m), 1723 (m), 1460 (w), 1387 (w), 1292 (w), 1160 (w), 1052 (w)	Fatty acids: C <sub>16:0</sub> , C <sub>18:0</sub> , C <sub>18:1</sub> , Minor components: hydrocarbons
Pignat 3	Ensenada	54°50'49.9"S, 68°29'40.7"W	Quartz, plagioclase, clorite, moscovite*, clays	Na (6%), Mg (2%), Al (18%), Si (61%), Cl (<1%), K (5%), Ca (<1%), Ti (1%), Fe (6%)	3414 (m), 2934 (m), 2855 (w), 1729 (sh), 1637 (m), 1413 (w)	Fatty acids: C <sub>16:0</sub> , C <sub>18:0</sub> , C <sub>20:0</sub> , C <sub>22:0</sub> + hydrocarbons
Pignat 4	Ensenada	54°50'49.9"S, 68°29'40.7"W	Quartz, plagioclase, clorite, moscovite*, clays*, calcite*	Na (4%), Mg (2%), Al (18%), Si (58%), K (3%), Ca (1%), Ti (1%), Fe (13%)	3447 (s), 2925 (sh), 2855 (sh), 1644 (m), 1558 (w), 1420 (w)	Fatty acids: C <sub>16:0</sub> , C <sub>18:0</sub> , C <sub>18:1</sub> , C <sub>20:0</sub> , C <sub>22:0</sub> , C <sub>23:0</sub> , C <sub>24:0</sub>
Pignat 5	Ensenada	54°51'25.9"S, 68°30'38.0"W	Quartz, plagioclase, clorite, moscovite, potassium feldspar*, hematite*	Na (2%), Mg (2%), Al (17%), Si (60%), K (4%), Ca (1%), Ti (1%), Fe (13%)	3434 (s), 2933 (sh), 2854 (sh), 1650 (sh), 1578 (m), 1420 (m)	–
Pignat 6	Túnel	54°49'11.02"S, 68°08'59"W	Plagioclase, moscovita, clorite*, quartz*, potassium feldspar*, hematite*	Na (13%), Mg (1%), Al (19%), Si (47%), K (2%), Ca (2%), Mn (1%), Fe (15%)	3447 (s), 2931 (sh), 2855 (sh), 1651 (m), 1565 (m), 1414 (m)	–
Pignat 7	Imiwaia	54°49'54.8"S, 67°29'57.3"W	Quartz, plagioclase, clorite, moscovite, dolomite*, anfibol*, clays*	Na (3%), Mg (4%), Al (10%), Si (58%), Cl (<1%), K (1%), Ca (1%), Mn (<1%), Fe (22%)	3414 (s), 2940 (sh), 2854 (sh), 1637 (m), 1407 (w)	C <sub>16:0</sub> , C <sub>18:0</sub>
Pignat 8	Remolino	54°51'33.9"S, 67°49'33.6"W	Quartz, plagioclase, clays	Na (8%), Mg (1%), Al (14%), Si (63%), K (2%), Ca (<1%), Ti (<1%), Fe (11%)	3441 (s), 2927 (s), 2855 (s), 1736 (m), 1650 (sh), 1572 (s), 1414 (s)	Fatty acids: C <sub>16:0</sub> , C <sub>18:0</sub> , C <sub>18:1</sub> , C <sub>20:0</sub> , C <sub>22:0</sub> , C <sub>23:0</sub> , C <sub>24:0</sub> , C <sub>25:0</sub> , C <sub>26:0</sub> , C <sub>28:0</sub> + hydrocarbons
Pignat 9	Imiwaia	54°51'57"S, 67°16'40.6"W	Quartz, plagioclase, clays, clorite, moscovite*, anfibol*	Na (5%), Mg (3%), Al (14%), Si (52%), K (2%), Ca (1%), Ti (<1%), Fe (22%)	3408 (m), 2934 (s), 2855 (s), 1743 (m), 1466 (m), 1383 (m), 1292 (w), 1170 (m), 1066 (w)	Fatty acids: C <sub>16:0</sub> , C <sub>18:0</sub> , C <sub>18:1</sub> , C <sub>20:0</sub> , C <sub>22:0</sub> , C <sub>24:0</sub>

\*Minor component.

clays as accessory minerals in these samples masks the characteristic goethite bands at 892 and 795 cm<sup>-1</sup> (Helwig, 2007) and makes a precise identification by FT-IR difficult. The FT-IR spectra of both samples also show characteristic hematite bands at 545–482 and 580–490 cm<sup>-1</sup>, respectively. This is probably due to the fact that hematite is frequently found in mixtures with goethite, since the latter rarely occurs in nature in pure form (Hradil et al., 2003). On the other hand, the FT-IR spectra of the red archaeological samples TI 15 and TI 32 were dominated by the bands of their main components: quartz (1100–1000 cm<sup>-1</sup>) and calcite (1490–1380 and 889 cm<sup>-1</sup>), respectively, and no hematite bands were observed. This may presumably be due to a low crystalline structure of the iron oxides which give colour to both samples.

Regarding the two pigment samples from Shamakush I site, XRD of one of the samples (SHI 2) shows that it contains hematite as the only crystalline component; this is particularly interesting since this sample shows the most pure composition of the whole 21 samples analysed in this paper. Such composition suggests that the pigment source for this sample must have been a different one than the source exploited from Túnel I. The other sample from this site (SHI 1) was analysed by Raman spectroscopy, which also showed the presence of hematite (Maier et al., 2006).

The nine samples of site Imiwaia I were also studied by XRD: four of them (Imi 3, Imi 5, Imi 10 and Imi 24; see Table 5) contain hematite. The remaining five samples were studied by SEM–EDX. The results showed that all four of these samples (Imi 1, Imi 20, Imi 27 and Imi 28) contain Fe in different amounts, ranging from 7% (Imi 1) to 83% (Imi 28). Again, these Fe contents of these five samples had not been detected by XRD due to their amorphous structure or low concentrations (see Table 5). The Fe contents of sample Imi 11 could not be quantified due to its high contents of carbon and oxygen.

### 3.2. Analysis of archaeological pigment samples: organic fraction

Recent analytical investigations provide evidence for the survival and preservation of organic biomolecules in archaeological

environments (Regert et al., 2003; Copley et al., 2005). For example, preserved animal fats are by far the most commonly occurring organic residues absorbed in archaeological ceramics (Spangenberg et al., 2006). Lipids have also been used as binders in painting residues. Recently, we have identified the presence of an animal fat in two samples of ochre painting residues (crayons) from the archaeological site Loncomán Cave (Río Negro, Argentina) (Maier et al., 2007). Plant and animal lipids consist predominantly of triacylglycerols containing straight chain carboxylic acids (C<sub>x,y</sub>, where *x* is the number of carbons in the chain and *y* is the number of carbon double bonds (C=C) in the chain). The more important saturated fatty acids in oils and animal fats are the lauric (C<sub>12:0</sub>), myristic (C<sub>14:0</sub>), palmitic (C<sub>16:0</sub>), and stearic (C<sub>18:0</sub>) acids, together with the unsaturated palmitoleic (C<sub>16:1</sub>), oleic (C<sub>18:1</sub>), linoleic (C<sub>18:2</sub>) and linolenic (C<sub>18:3</sub>) acids. Lipids are sensitive to various alteration processes, both chemical and biological. Hydrolytic degradation releases fatty acids from triacylglycerols and β-oxidation and reduction processes lead to the loss of unsaturated acids. Given that short- and medium-chain fatty acids arising from oxidation processes are more soluble in percolating ground water than long-chain fatty acids; degraded lipids in archaeological samples are identified by high concentrations of palmitic (C<sub>16:0</sub>), and stearic (C<sub>18:0</sub>) acids.

Analyses by FT-IR of the pigment samples from Túnel I site showed no clear sign of organic compounds in the spectra, which were dominated by the inorganic components. Aiming at the detection of any residual organic compounds, the samples were extracted with a chloroform:methanol (2:1) mixture and the extracts were analysed by FT-IR: the results indicated the presence of organic components, most likely lipids. The most important features were the presence of a carbonyl absorption band at 1717–1741 cm<sup>-1</sup> and bands at 1558–1583 and 1400–1422 cm<sup>-1</sup> together with bands attributable to C–H stretchings of CH<sub>3</sub> and CH<sub>2</sub> groups at 2950–2845 cm<sup>-1</sup> (see Table 5). The carbonyl band at 1717–1741 cm<sup>-1</sup> could arise from fatty acids or from acylglycerol groups. FT-IR spectra of vegetable oils and animal fats contain a strong,

**Table 5**  
Archaeological pigment samples: results

Sample	Layer and quadrant	XRD	SEM-EDX	FT-IR sample (cm <sup>-1</sup> )	FT-IR extract (cm <sup>-1</sup> )	GC-MS
<i>Túnel I site</i>						
TI 3	E 10 XVI	Plagioclase, hematite, quartz*	–	Not performed due to low amount of sample	3431 (s), 2950 (m), 2933 (m), 2851 (m), 1718 (sh), 1662 (m), 1573 (s), 1422 (s)	–
TI 5	E 10 XVI	Hematite, quartz, moscovita, plagioclase	–	3700–3000 (s), 1618 (m), 1000 (s), 1033 (s), 560 (s), 482 (s)	3423 (s), 2924 (s), 2867 (m), 1733 (w), 1650 (sh), 1583 (s), 1419 (s)	–
TI 8	E 3 XII	Hematite, quartz, plagioclase, clays, tridimite*	–	3700–3000 (s), 1643 (m), 1085 (s), 1041 (s), 657 (s), 582 (s), 550 (s), 482 (s)	3438 (m), 2950 (s), 2934 (s), 2854 (s), 1736 (m), 1580 (m), 1473 (w), 1400 (w)	Fatty acids: C <sub>16:0</sub> and C <sub>18:0</sub> Minor component: C <sub>18:1</sub>
TI 15	22 D-sub4 XIII	Quartz, clorite	Fe (77%), Al (2%), Si (9%), Ca (6%), Mg (4%), P (3%)	3000–2500 (s), 1617 (m), 1458 (m), 1100–1000 (s), 656 (m), 472 (s)	3400 (w), 2931 (s), 2881 (s), 1733 (m), 1580 (w), 1455 (m), 1400 (w)	–
TI 20	5 D XI	Quartz, clorite, ilite, plagioclase	Fe (13%), Al (10%), Si (33%), Ca (44%)	3150–2800 (s), 1448 (m), 1350–900 (s), 792 (m), 545 (m), 482 (s)	3439 (s), 2950 (s), 2854 (m), 1739 (w), 1632 (sh), 1571 (s), 1400 (m), 1071–1000 (s), 546 (s), 480 (s)	–
TI 24	D 38 XV	Hematite, quartz, potassium, feldspar, moscovite, plagioclase*, clays*	–	1071–1000 (s), 546 (s), 480 (s)	3400 (w), 2934 (s), 2870 (m), 1741 (w), 1650 (sh), 1575 (w), 1400 (w)	Fatty acids: C <sub>16:0</sub> and C <sub>18:0</sub> Minor component: C <sub>18:1</sub>
TI 25	D 38 XV	Hematite, quartz, plagioclase, moscovita, clays*	–	3700–3100 (s), 1650 (w), 1100–950 (s), 552 (s), 485 (s)	3444 (w), 2925 (s), 2845 (m), 1717 (w), 1650 (sh), 1558 (s), 1458 (w), 1400 (w)	Fatty acids: C <sub>16:0</sub> and C <sub>18:0</sub> minor component: C <sub>18:1</sub>
TI 27	D 20 XIII	Quartz, clays	Fe (8%), Al (23%), Si (55%), K (10%), Ca (2%), Mg (1%), Ti (1%)	3639 (m), 3600–3000 (s), 1628 (m), 1200–900 (s), 580 (s), 490 (s)	3445 (s), 2834 (s), 2861 (s), 1734 (w), 1650 (sh), 1583 (s), 1444 (sh), 1408 (m)	Fatty acids: C <sub>16:0</sub> and C <sub>18:0</sub> minor component: C <sub>18:1</sub>
TI 32	α XIII	Calcite, magnetite*	Fe (44%) Al (1%), Si (3%), P (5%), Ca (42%), Mg (2%), Mn (2%)	3700–3100 (s), 1600 (s), 1490–1380 (s), 1065 (m), 889 (s), 800–550 (s)	3415 (m), 2934 (s), 2854 (m), 1717 (sh), 1647 (sh), 1571 (s), 1418 (s)	Fatty acid: C <sub>16:0</sub>
TI 35	E. inf.	Hematite, quartz, potassium, feldspar, ilite, moscovite	–	3170–295 (s), 1642 (s), 1280–900 (s), 560 (s), 472 (s)	2942 (s), 2854 (m), 1731 (m), 1458 (m)	–
Sample number	Layer and quadrant	XRD	FT-Raman sample	FT-IR sample	GC-MS	
<i>Shamakush I site</i>						
SHI 2	D 180	Hematite	–	3419 (m), 2931 (m), 2860 (m), 1744 (m), 1463 (m), 1250–900 (s), 543 (s), 470 (s)	Fatty acids: C <sub>15:0</sub> , C <sub>16:1</sub> , C <sub>16:0</sub> , iso-C <sub>17:0</sub> , C <sub>17:1</sub> , C <sub>18:0</sub> , C <sub>18:1</sub> Minor components: C <sub>14:0</sub> , iso-C <sub>16:0</sub> , C <sub>17:0</sub> + saturated hydrocarbons (23, 24, 25, 26, 27, 28 C)	
SHI 1	D 184	–	2746, 1603, 1291, 615, 469, 415, 298, 230, 148	–	Fatty acids: C <sub>14:0</sub> , iso-C <sub>16:0</sub> , C <sub>16:0</sub> , C <sub>18:0</sub> + saturated hydrocarbons (23, 24, 25, 26, 27, 28, 29 C), minor components: C <sub>15:0</sub> , C <sub>18:1</sub>	
Sample number	Layer and quadrant	XRD	SEM-EDX	FT-IR extract	GC-MS	
<i>Imiwaia I site</i>						
Imi 1	M180V	Quartz, plagioclase	Fe (7%), Na (7%), Mg (2%), Al (11%), Si (66%), K (2%), Ca (4%), Ti (<1%)	3440 (m), 2924 (m), 2862 (m), 1751 (w), 1650 (sh), 1573 (m), 1458 (w)	–	
Imi 3	M180V	Quartz, plagioclase, hematite, potassium, feldspar*	–	3449 (m), 2927 (m), 2854 (m), 1733 (w), 1587 (m)	–	
Imi 5	M180V	Quartz, feldspar, hematite	–	3421 (s), 2922 (w), 2856 (w), 1650 (sh), 1567 (m)	–	
Imi 10	C IV	Hematite	–	3431 (s), 2926 (m), 2870 (w), 1747 (w), 1650 (sh), 1578 (s), 1426 (m)	–	
Imi 11	B IV	Calcite, quartz, feldspar, hematite*	Fe (not quantified). High contents of C and O	3434 (s), 2933 (w), 2862 (w), 1570 (w)	–	
Imi 20	L5 IV	Quartz, calcite, goethite	Fe (45%), Al (5%), Si (15%), K (1%), Ca (31%), P (3%)	3421 (w), 2936 (w), 2857 (w), 1741 (sh), 1650 (sh), 1577 (w), 1425 (w)	Fatty acids: C <sub>16:0</sub> , C <sub>18:0</sub> + hydrocarbons	
Imi 24	N25 I	Quartz, calcite, feldspar, aragonite*, hematite	–	3468 (m), 2936 (m), 2870 (m), 1739 (w), 1650 (sh), 1570 (w), 1473 (w)	–	
Imi 27	K 235 III	Quartz, clorite, calcite, mica	Fe (49%), Al (2%), Si (35%), Ca (14%)	3455 (m), 2937 (s), 2855 (m), 1748 (w), 1650 (sh), 1575 (m), 1412 (m)	Fatty acids: C <sub>14:0</sub> , C <sub>16:0</sub> , C <sub>18:1</sub> , C <sub>18:0</sub> + hydrocarbons (23, 24, 25 C)	
Imi 28	K 290 III	Quartz*, calcite*, clorite*	Fe (83%), Si (12%), Ca (5%)	3459 (w), 2936 (s), 2851 (m), 1758 (s), 1464 (w), 1250 (w), 1169 (m), 1100 (w)	–	

\*Minor component.

sharp carbonyl band at 1750–1740  $\text{cm}^{-1}$  due to the ester group (Derrick et al., 1999) while fatty acids of these sources show the carbonyl band around 1715  $\text{cm}^{-1}$  (Maier et al., 2007).

Therefore, the carbonyl bands at 1717 and 1718  $\text{cm}^{-1}$  in the spectra of samples TI 3, TI 25 and TI 32 can be assigned to free fatty acids of vegetable and/or animal origin, while the bands at 1731–1741  $\text{cm}^{-1}$  in the rest of the archaeological samples of Túnel I site indicate the presence of acylglycerols of plant and/or animal provenance. Broadening of the latter band has been observed in most of the spectra of organic extracts of the archaeological pigment samples and this could be attributed to the formation of free fatty acids. On the other hand, the strong bands at 1558–1583 and 1400–1422  $\text{cm}^{-1}$  could be assigned to carboxylate asymmetric and symmetric stretchings on comparison with previous data (Maier et al., 2007). The position of these bands can vary for different metals (Robinet and Corbeil, 2003). Probably, hydrolysis of triacylglycerols to free fatty acids and further reaction of the latter with minerals in the samples have led to the formation of fatty acid salts.

Analyses by GC of the fatty acid methyl esters (FAME) prepared from the lipids extracted from the pigment samples of Túnel I site, indicated that the main fatty acids were the saturated palmitic ( $\text{C}_{16:0}$ ) and stearic ( $\text{C}_{18:0}$ ) acids, as established by comparison with retention times of authentic compounds. Four of the samples (TI 8, TI 24, TI 25, and TI 27) were selected in order to study them by GC–MS. The results showed that these samples have the same components: palmitic ( $\text{C}_{16:0}$ ) and stearic ( $\text{C}_{18:0}$ ) acids as the major components together with minor amounts of the unsaturated oleic ( $\text{C}_{18:1}$ ) acid. Representative total ion chromatograms of the lipids extracted from Túnel I samples are shown in Fig. 4. These fatty acid distributions, with a greater abundance of palmitic acid ( $\text{C}_{16:0}$ ) than stearic acid ( $\text{C}_{18:0}$ ), are typical of degraded animal fats (Spangenberg et al., 2006; Copley et al., 2005).

An interesting difference rises when comparing these results with those from samples from Shamakush I site. In this latter case, FT-IR analysis of sample SHI 2 without any prior preparation clearly showed signals of organic components, probably lipids, which suggested that their proportion was higher than that in Túnel I samples. The presence of a carbonyl band at 1744  $\text{cm}^{-1}$  was consistent with the presence of acylglycerols as the predominant lipids. GC–MS analysis of the fatty acid methyl esters (FAME) prepared

from the lipids extracted from the archaeological samples of Shamakush I site showed that the main organic constituents of both samples (SHI 1 and SHI 2) were myristic ( $\text{C}_{14:0}$ ), palmitic ( $\text{C}_{16:0}$ ), stearic ( $\text{C}_{18:0}$ ) and oleic ( $\text{C}_{18:1}$ ) acids, and a mixture of saturated hydrocarbons of 23, 24, 25, 26, 27, 28 and 29 carbons (Table 5). Sample SHI 2 also contains margaric acid ( $\text{C}_{17:0}$ ), the branched-chain *iso*-palmitic (*iso*-16:0) and *iso*-margaric (*iso*-17:0) acids and the monoene acids palmitoleic ( $\text{C}_{16:1}$ ) and heptadecenoic ( $\text{C}_{17:1}$ ) acids (Fig. 5).

Analysis by FT-IR of the chloroform–methanol extracts of the nine pigment samples from site Imiwaia I showed the presence of a mixture of acylglycerols (carbonyl band at 1733–1758  $\text{cm}^{-1}$ ) and fatty acid salts (1567–1587  $\text{cm}^{-1}$ ) in eight of the nine samples. The FT-IR of sample Imi 28 showed a sharp carbonyl band at 1758  $\text{cm}^{-1}$  and a clear triplet of peaks at 1250, 1169 and 1100  $\text{cm}^{-1}$  (C–O stretchings), characteristic of esters and indicative of the presence of triacylglycerols as the main lipidic components. The samples were analysed by GC but most of the extracts showed few peaks or poorly defined chromatograms. Two samples (those with most peaks) were selected to run GC–MS analyses: Imi 20 and Imi 27. Both samples contain palmitic ( $\text{C}_{16:0}$ ) and stearic ( $\text{C}_{18:0}$ ) acids and a mixture of saturated hydrocarbons as the main components. Imi 27 also showed the presence of oleic acid ( $\text{C}_{18:1}$ ).

In short, pigment samples from Túnel I differ from those in Shamakush I in that the organic components of the former contain palmitic ( $\text{C}_{16:0}$ ), stearic ( $\text{C}_{18:0}$ ) and oleic ( $\text{C}_{18:1}$ ) acids while the latter contain not only these acids but also a mixture of hydrocarbons. Both samples from Shamakush I site (SHI 1 and SHI 2) contain branched-chain fatty acid *iso*-palmitic (*iso*-16:0) and SHI 2 also contains *iso*-margaric (*iso*-17:0) acid and the monoene acids palmitoleic ( $\text{C}_{16:1}$ ) and heptadecenoic ( $\text{C}_{17:1}$ ) acids. Samples from both sites also differ from those from Imiwaia I because the latter contain, in general terms, very few organic components. No polyunsaturated fatty acids characteristic of plant oils were detected in the archaeological samples, since these fatty acids would have decomposed readily under burial at the archaeological site. This shows relative intra-site homogeneity and inter-site differences which might respond to technical factors (Clottes, 1993). Yet there is the possibility that these organic components are present in the pigment samples as a result of taphonomic contamination. The following section deals with this problem.

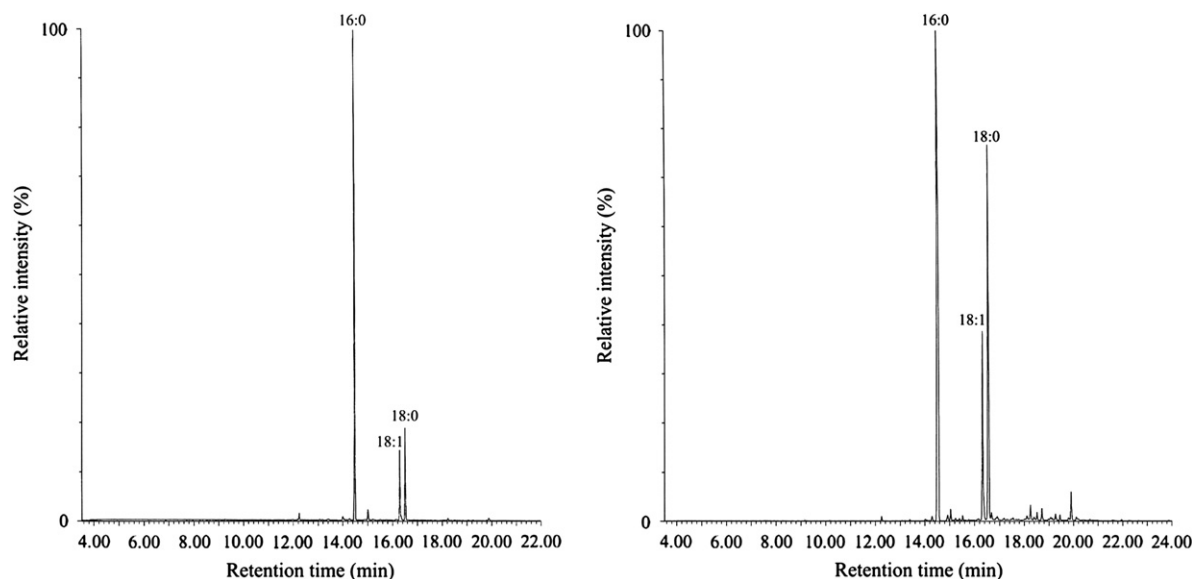


Fig. 4. GC–MS total ion chromatogram of the fatty acid methyl esters in lipids extracted from archaeological samples TI 27 and TI 24 from Túnel I site. The fatty acids are the palmitic (16:0), stearic (18:0) and oleic (18:1) acids.

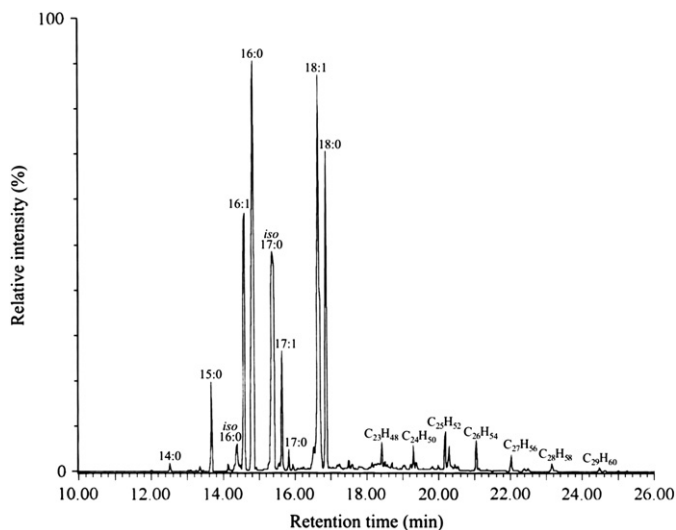


Fig. 5. GC–MS total ion chromatogram of the fatty acid methyl esters in lipids extracted from archaeological sample SHI 2 from Shamakush I site.

### 3.3. Analysis of archaeological sediment samples in search of potential taphonomic contamination of pigment samples

Five samples of archaeological sediments of sites Túnel I (sedarq 1 and sedarq 2), Shamakush I (sedarq 3) and Imiwaia I (sedarq 4 and sedarq 5) were extracted with a chloroform:methanol (2:1) mixture and the extracts containing organic compounds in concentrations of 101 mg/g (sedarq 1), 185 mg/g (sedarq 2), 128 mg/g (sedarq 3), 14 mg/g (sedarq 4) and 78 mg/g (sedarq 5) were analysed by FT-IR. The results summarized in Table 3 show the presence of lipids in the samples. The most important features in the spectra (carbonyl absorption bands at 1729–1743, 1565 and 1571  $\text{cm}^{-1}$ ) indicate that the lipids are present as a mixture of acylglycerols and fatty acid salts, with predominance of the latter in four of the five samples (sedarq 1–4). FT-IR data of sample sedarq 5 showed the presence of acylglycerols (carbonyl band at 1729  $\text{cm}^{-1}$ ) as the main components. The organic extracts of the archaeological sediment samples were analysed by GC–MS as their fatty acid methyl esters.

Sample sedarq 1 was taken from layer D38, quadrant IV/XV of site Túnel I, which is the same layer where pigment residues TI 24 and TI 25 were found. The GC–MS results indicate that the major fatty acid of this sample is palmitic acid ( $\text{C}_{16:0}$ ), together with myristic ( $\text{C}_{14:0}$ ) and stearic ( $\text{C}_{18:0}$ ) acids as minor components. This composition differs from that of the organic fraction of archaeological pigment samples TI 24 and TI 25, which contain palmitic and stearic acids as the main components together with the unsaturated oleic ( $\text{C}_{18:1}$ ) acid as the minor component.

Sample sedarq 2 was taken from layer  $\alpha$ , quadrant XIII/XIV of Túnel I site, which is the layer where pigment sample TI 32 was found. GC–MS results indicate that the major peaks of this sediment sample correspond to palmitic ( $\text{C}_{16:0}$ ) and stearic ( $\text{C}_{18:0}$ ) acids, while several minor peaks assigned to myristic ( $\text{C}_{14:0}$ ), pentadecanoic ( $\text{C}_{15:0}$ ), margaric ( $\text{C}_{17:0}$ ), oleic ( $\text{C}_{18:1}$ ), arachidic ( $\text{C}_{20:0}$ ) and behenic ( $\text{C}_{22:0}$ ) acids are also observed (see Table 3). Comparison with pigment sample TI 32 indicates that palmitic acid is present in both kinds of samples (sediment and pigment), while the other fatty acids are lacking from TI 32. These results suggest that the organic components in the Túnel I pigment samples are not present due to taphonomic contamination.

The same analyses were carried out on an archaeological sediment sample (sedarq 3) from site Shamakush I, taken from layer D184 quadrant I, where pigment sample SHI 1 was found. The GC–

MS results show that sedarq 3 includes major peaks corresponding to palmitic ( $\text{C}_{16:0}$ ), stearic ( $\text{C}_{18:0}$ ) and oleic ( $\text{C}_{18:1}$ ) acids. Comparison with sample SHI 1 indicates that its organic fraction contains myristic ( $\text{C}_{14:0}$ ), palmitic ( $\text{C}_{16:0}$ ), *iso*-palmitic (*iso*- $\text{C}_{16:0}$ ) and stearic ( $\text{C}_{18:0}$ ) acids and a mixture of hydrocarbons with 23, 24, 25, 26, 27, 28 and 29 carbons as the major components together with minor pentadecanoic ( $\text{C}_{15:0}$ ) and oleic ( $\text{C}_{18:1}$ ) acids, which are not present in the sediment sample sedarq3. This hints towards the possibility that the organic contents of the pigment samples are not a result of taphonomic contamination.

Finally, two sediment samples from layers from site Imiwaia I in which pigment residues were found were also studied by GC–MS. Sample sedarq 4 corresponds to layer K235, quadrant III, where pigment sample Imi 27 was found. Sample sedarq 5 was taken from layer K290, quadrant III, where pigment sample Imi 28 was found (unfortunately, comparisons with pigment sample Imi 28 are not possible since its organic contents are minimal and GC–MS does not reveal the contents of any acid.). Both samples contain myristic ( $\text{C}_{14:0}$ ), palmitic ( $\text{C}_{16:0}$ ), stearic ( $\text{C}_{18:0}$ ) and oleic ( $\text{C}_{18:1}$ ) acids; sample sedarq 5 also contains margaric ( $\text{C}_{17:0}$ ), arachidic ( $\text{C}_{20:0}$ ), behenic ( $\text{C}_{22:0}$ ) and lignoceric ( $\text{C}_{24:0}$ ) acids (see Table 3). Comparison with the organic fraction of pigment sample Imi 27 hints to the existence of some differences. Firstly as mentioned above, the organic contents in Imiwaia pigment samples are considerably low, which contrasts with those in the layers where these pigments were found. Secondly, the archaeological Imi 27 contains a mixture of hydrocarbons (23, 24 and 25 carbons) which are absent from the archaeological sediments.

To sum up, when comparing the GC–MS results of all archaeological pigment samples with those of archaeological sediments, it is noticeable that both kinds of samples contain palmitic ( $\text{C}_{16:0}$ ), stearic ( $\text{C}_{18:0}$ ) and oleic ( $\text{C}_{18:1}$ ) acids. The archaeological pigments lack arachidic ( $\text{C}_{20:0}$ ), behenic ( $\text{C}_{22:0}$ ) and lignoceric ( $\text{C}_{24:0}$ ) acids present in the archaeological sediments. On the other hand, the archaeological pigment samples contain hydrocarbons, absent in the archaeological sediments. This marks an interesting difference that suggests that the presence of the organic fraction in the pigment samples is not the result of taphonomic agents, but rather of intentional anthropic actions, such as their inclusion as binders during the process of paint preparation. Nevertheless, there are two alternative possibilities to consider that (a) these organic components came from rubbing pigments over an organic surface to be treated or painted with them (e.g. leather, skin, etc); and (b) these organic components were attached to the pigments if these were kept in bags made of organic material, such as animal entrails. In the first case the archaeological remains found in the sites would actually be residues of the painting process, in the second case they would be residues generated by the pigments' storage. However, we have not found any independent lines of evidence to support these two alternatives against the most likely possibility that these are binder remains in paint residues.

### 3.4. Analysis of natural sediment samples in search of potential pigment sources

As noted above, nine samples of natural sediments which might represent pigment sources were studied. The inorganic fraction of these samples was firstly analysed by XRD; the results showed that they contain quartz and plagioclase, plus other components such as clays, and that only in two cases did they contain a potential component of hematite (see Table 4). The nine samples were then studied by SEM–EDX, which indicated that they all contained Fe in different proportions, usually ranging from 6% to 22%, with only one exception of 57% (see Table 4). These results convey a difference between these natural sediment samples and the pigment samples



found in the three archaeological sites, in so far as the latter either contain hematite or higher proportions of Fe. This suggests that the natural sediment samples of the five Beagle Channel localities under study were not the potential sources from which pigments were obtained in the past, which hints towards a specific selection of the pigments' sources by the prehistoric inhabitants of the region. Yet it should be noted that it is also possible that the natural pigments found in these locations could have been decanted, sieved and heated in order to obtain a more pure form of hematite (Couraud, 1988; Lorblanchet et al., 1990): experiments will be conducted in the future to explore this possibility.

In spite of the fact that these natural sediments seem not to have been the sources of pigments found in the archaeological sites, their organic fraction was studied by FT-IR and GC-MS in order to assess whether they contained similar components to those found in the archaeological pigments. If the same components were found in both kinds of samples, then the hypothesis of the anthropic origin of the organic fraction of archaeological pigments would be weakened. The natural sediment samples (pignat 1–pignat 9) were extracted with a chloroform:methanol (2:1) mixture and the extracts containing organic compounds in concentrations of 280 mg/g (pignat 1), 1090 mg/g (pignat 2), 690 mg/g (pignat 3), 456 mg/g (pignat 4), 282 mg/g (pignat 5), 2582 mg/g (pignat 6), 102 mg/g (pignat 7), 559 mg/g (pignat 8), and 676 mg/g (pignat 9) were analysed by FT-IR (Table 4). Samples pignat 2 and pignat 9 show carbonyl bands at 1723 and 1743  $\text{cm}^{-1}$ , respectively, together with a triplet of peaks at 1292, 1160–1170 and 1052–1066  $\text{cm}^{-1}$ , characteristic of triacylglycerols. The FT-IR spectra of the rest of the samples showed the presence of fatty acid salts (carboxylate bands at 1558–1578 and 1407–1420  $\text{cm}^{-1}$ ) as the main lipidic components. Analysis by GC-MS of the FAME prepared from the organic extracts of the samples indicated that natural sediment samples contain palmitic ( $\text{C}_{16:0}$ ), stearic ( $\text{C}_{18:0}$ ), arachidic ( $\text{C}_{20:0}$ ), behenic ( $\text{C}_{22:0}$ ), tricosanoic ( $\text{C}_{23:0}$ ), lignoceric ( $\text{C}_{24:0}$ ), pentacosanoic ( $\text{C}_{25:0}$ ), cerotinic ( $\text{C}_{26:0}$ ) and montanic ( $\text{C}_{28:0}$ ) acids. These compositions show a difference between the natural sediment and the archaeological pigment samples, which lack the fatty acids of 20, 22, 23, 24, 25, 26 and 28 carbons. This reinforces the possibility that the organic fraction of archaeological pigments may not be a natural feature but a cultural product.

#### 4. Discussion and conclusions

The inorganic fraction of the archaeological pigment residues contains in all cases hematite or Fe (usually in medium to high proportions). This suggests that the pigments were intentionally selected in terms of their colour, which is attributed to their iron content. Inter-site differences do occur, and are particularly noticeable in Shamakush I samples, which are constituted by almost pure hematite. This indicates that pigment residues found in each site may come from different sources.

The potential sources of these pigments have not been identified yet, since the samples of natural sediments of similar colours to the archaeological pigments lack hematite and usually contain Fe in low proportions. This indicates that in spite of the fact that several spots with reddish sediments are visible in at least five Beagle Channel localities, the pigment sources were not ubiquitous, thus implying a special selection of pigments among all those available in the landscape. Furthermore, this suggests that the ancient populations who used pigments in the region had specific knowledge about where the adequate sources were located. Further sampling and analyses will be required to locate and identify these sources, including other less-accessible sources such as peat-bogs.

Analyses by FT-IR of the pigment residues of the three archaeological sites gave preliminary information on the presence of organic components in the samples. While the FT-IR spectra of

pigment residues from sites Túnel I and Imiwaia I were dominated by the inorganic components, one of the samples from site Shamakush I (SHI 2) showed the presence of lipids together with hematite as the inorganic component. This fact suggested a higher proportion of organic components in the Shamakush I sample than that in the samples from Túnel I and Imiwaia I. Further analysis by FT-IR of the chloroform–methanol extracts of the pigment samples of the latter sites also revealed the presence of lipids. The components of the residual organic phase in most of the archaeological pigment samples are mainly free fatty acids and their salts indicating that the triacylglycerols originally present underwent hydrolysis and reacted with the samples' mineral matrix. Analysis by GC-MS of the FAME of the organic components of the samples from the three sites (Túnel I, Shamakush I and Imiwaia I) showed clear inter-site differences: those from Túnel I and Imiwaia I contain fatty acid distributions typical of degraded fats, with a greater abundance of palmitic ( $\text{C}_{16:0}$ ) than stearic ( $\text{C}_{18:0}$ ) acid as the main components, together with minor oleic ( $\text{C}_{18:1}$ ) acid (Spangenberg et al., 2006; Evershed et al., 1997). On the other hand, the organic fractions of the archaeological pigment samples of Shamakush I contain a complex mixture of fatty acids with the presence of palmitic ( $\text{C}_{16:0}$ ), *iso*-margaric (*iso*- $\text{C}_{17:0}$ ) and stearic ( $\text{C}_{18:0}$ ) acids as the main saturated components and the unsaturated palmitoleic ( $\text{C}_{16:1}$ ), heptadecenoic ( $\text{C}_{17:1}$ ) and oleic ( $\text{C}_{18:1}$ ) acids. Both samples also showed the presence of saturated hydrocarbons of 23, 24, 25, 26, 27, 28 and 29 carbons. These *n*-alkanes have also been detected in sample Imi 20 and in three of the nine natural pigment samples but they were not found in the archaeological sediment samples. This fact could be attributed to a biogeological origin in the inorganic components of the pigment residues and it rules out the use of a bitumen as binder because no steroid hydrocarbons (steranes, sterenes) or terpanes were detected (Wendt and Lu, 2006).

Branched-chain fatty acids containing 15 and 17 carbon atoms are well known as bacterial markers (Dudd et al., 1998) but they also arise in the fats of ruminant animals, such as cattle and sheep. Also, heptadecenoic acid ( $\text{C}_{17:1}$ ) has been recognized as a minor constituent of ruminant fats of bovine, ovine and caprine origin produced by endogenous desaturation of heptadecanoic acid ( $\text{C}_{17:0}$ ) (Alves et al., 2006). Taking into account that guanacos are ruminants, another possibility is that the fatty acids present in the Shamakush samples are the result of the use of their fat as a paint binder. Recently, we have determined the fatty acid composition of the marrow lipid of a guanaco from Patagonia (*Lama guanicoe*) (Maier et al., 2007). Comparison of the fatty acid distribution of the organic fraction of sample SHI 2 pigment with that from the marrow of *L. guanicoe* (which inhabits Patagonia and Tierra del Fuego) suggests a similar composition for  $\text{C}_{16:0}$ ,  $\text{C}_{16:1}$ ,  $\text{C}_{18:0}$  and  $\text{C}_{18:1}$  fatty acids.

Another potential source of binders would be the fur seals (*A. australis* and, in a much lower proportion, the sea lions *Otaria flavescens*; Orquera and Piana, 1999; Schiavini, 1993), which have a much greater proportion of body fat than guanacos. In fact, after weaning, fur seals contain 9–11.4% of body fat – variations being related to sex, age and season (Orquera and Piana, 1999; Schiavini, 1999). Instead, guanacos contain approximately less than 1% of body fat (De Nigris and Mengoni Goñalons, 2004). As far as we know, there are no reports on the fatty acid composition of the fats of these fur seals and sea lions, and we have yet not obtained a sample to analyse it for the reasons stated above. Yet comparison with fatty acids of Californian sea lions, such as *Zalophus californianus*, indicate that they contain saturated pentadecanoic ( $\text{C}_{15:0}$ ) and heptadecanoic ( $\text{C}_{17:0}$ ) acids and the monounsaturated acids palmitoleic ( $\text{C}_{16:1}$ ) and heptadecenoic ( $\text{C}_{17:1}$ ) in their lipids (Castro-González et al., 2003). This is interesting in so far as pentadecanoic ( $\text{C}_{15:0}$ ), heptadecanoic ( $\text{C}_{17:0}$ ), palmitoleic ( $\text{C}_{16:1}$ ) and heptadecenoic ( $\text{C}_{17:1}$ ) acids are present in the archaeological

pigment samples of Shamakush I. Although these data do not come from the same sea lion species which inhabits the Beagle Channel region, these comparative parameters point to the possibility that sea lions may have been in some cases the source of ancient organic binders in Tierra del Fuego. The presence of *iso*-margaric acid in pigment sample SHI 2 does not rule out the contribution of microbial contamination in addition to the lipid substrates initially present.

Based on comparisons between GC–MS results of the pigment residues versus samples from the archaeological layers where these residues were found, these organic components seem not to be contaminations of taphonomic origin. Straight chain fatty acids such as pentadecanoic (C<sub>15:0</sub>) and heptadecanoic (C<sub>17:0</sub>) acids are present as minor components in the archaeological sediment samples from Túnel I and Imiwaia I sites, but not in the sediment sample from Shamakush I, the site where samples containing these fatty acids as well as their branch chain isomers were found. Archaeological sediment samples from Túnel I and Imiwaia I also contain minor even chain fatty acids (C<sub>20:0</sub>, C<sub>22:0</sub>, C<sub>24:0</sub>) not present in the pigment samples. On the other hand, four of the nine natural sediments of similar colours than the archaeological pigments also contain these compounds together with minor C<sub>26:0</sub> and C<sub>28:0</sub> fatty acids as components of their lipids. This suggests that the lumps of coloured substances found in these archaeological sites were not just pigment remains but residues of paint prepared with pigments plus lipids as organic binders.

These first results presented in this paper show that the inhabitants of the Beagle Channel region had developed a paint production technique which spanned from 6200 BP to at least 940 BP and involved the management of mineral pigments and organic binders. The use of these resources has been documented in three archaeological sites, while search for off-site activities, such as pigment sourcing, have been initiated but have not been fulfilled so far. Further studies may shed light on these still unknown aspects of the earliest paint remains from the uttermost part of the planet.

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