INTEGRATED ANALYTICAL TECHNIQUES FOR THE STUDY OF COLOURING MATERIALS FROM TWO MEGALITHIC BARROWS*

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We have determined the composition of rock art pigments from two megalithic barrows located in the north of Portugal. The use of XRD, SEM–EDS and FT–IR spectroscopy confirmed the presence of hematite and kaolinite in the red pigments from the Eireira barrow, and kaolinite in the white pigment from the Leira das Mamas barrow. The organic composition of the pig- ments was studied by GC–MS, suggesting that the red sinuous lines and dots from the Eireira barrow were prepared with cooked or heated algae and/or aquatic plants, with egg as binder, while the white pigment from the Leira das Mamas barrow revealed a mixture of vegetable oils for kaolinite moulding, which could be stabilized by temporary exposure to high temperatures. The multi-analytical approach used on this study of megalithic pigments allowed the recovery of important data about north-western prehistoric communities, namely the way in which they exploited existing resources and their ability to transform them.

***KEYWORDS**:* MEGALITHIC BARROWS, PIGMENTS, COLOURING MATERIALS, GAS CHROMATOGRAPHY – MASS SPECTROMETRY (GC–MS), CHEMICAL ANALYSIS

INTRODUCTION

Paintings in chambers and corridors of megalithic barrows are well known in Western Europe (Shee 1974; Bueno-Ramírez and de Balbín-Behrmann, 2002; Bueno-Ramirez *et al.* 2012). Despite their dissemination throughout Europe, they are mostly found in north-west Iberia, more specifically in the Galicia region (Spain), together with the north and centre-north of Portugal (Vasconcelos 1907; Correia 1924; Coelho 1931; Shee 1974, 1981; Jorge 1994, 1997; Carrera 1997, 2005, 2011; Silva 1997a,b; Cruz 1998, 2001).

This phenomenon has prompted many different studies related to the dating of art and mega- lithic phenomenon (Cruz 1995; Carrera 2002; Carrera and Valcarce 2006, 2008), the interrelationship between painted and carved motifs (Jorge 1997, 2003; Bradley and Valcarce 1999; Bueno-Ramírez and de Balbín-Behrmann, 2002; Carrera 2005; Valcarce and Vázquez 2006; Ramírez *et al.* 2008; Bueno-Ramírez *et al.* 2009), the organization and interpretation of the motifs in their micro-contexts (Sanches 2006a,b, 2008–9) and on painting conservation techniques and methodologies (Carrera 1999, 2003, 2011, 2014; Carrera and Valcarce 2003). However, a systematic research programme aiming to study the chemical composition of colourants and binders used to illustrate the symbolic world of the builders and users of dolmens from north-west Iberia is lacking. In fact, this kind of interdisciplinary study is crucial to determine how the prehistoric communities of north-west Iberia took advantage of the existing resources and to analyse their ability to transform them.

The study of cultural heritage material, which is often precious and fragile, calls for non- destructive micro-analytical methods. Some analytical techniques were used for the study of the composition (e.g., hematite, goethite or charcoal) of the pigments, and/or on the methodolo- gies used in their preparation, such as grinding, mixing or heating. Pigments may be mixed with extenders (clay, calcite, bone, talc, potassium feldspar, micas etc.) and with binders (water, vegetable oil or animal fat) (Chalmin *et al.* 2003). Additionally, extensive physicochemical analysis of ancient paintings can allow the identification of the elemental and structural compo- sition of pigments and, sometimes, their possible geographical origin (Chalmin *et al.* 2003).

In the context of the project ‘Funerary and Ceremonial Practices between the Neolithic to the Bronze Age Approached by Archaeometry’—the ARQUEOM Project, the present study has been focused on the characterization of painted art found on two megalithic monuments located in different areas of north-western Portugal: (i) the Eireira barrow, on the coast, and (ii) the Leira das Mamas or Lamas barrow, in the hinterland (Fig. 1). It is intended to identify the pigment composi- tion and the preparation method (extenders and/or binders). It is important to state that as pigment and extender sometimes come from the same natural mineral or compound, our use of the term 'pig- ment' includes both pigment and extender. Combinations of different techniques were used to iden- tify the crystalline phases of the pigments (XRD), carry out morphological observations (SEM) coupled with an assessment of the elemental composition (EDS), identify the mineralogical and or- ganic components (FT–IR) and identify the composition of the binders (GC–MS).

THE ARCHAEOLOGICAL CONTEXTS

The Eireira barrow

The Eireira barrow is a Neolithic monument located in Afife, Viana do Castelo, in the foothills of the north-western slope of Santa Luzia mount, 400 m from the coast and near the valley of the Cabanas River. The local geological substrate is composed of medium to fine-grained two-mica granite (Teixeira *et al.* 1972; Pereira 1992).

The site was excavated by Eduardo Jorge Lopes da Silva, between 1986 and 1989, but only a few papers with architectural features of the monument and some carving descriptions were pub- lished (Silva 1988, 1994, 1997a, 2003). Thus, there is a gap in the knowledge regarding funerary rites (in which we include the paintings) and the chronology within the fifth to fourth millennia or the third millennium BC, during which the barrow was erected and reused, respectively. Some lithic and ceramic artefacts from this monument, exhibited in the Casa dos Nichos Museum, in Viana do Castelo, support these chronologies.

The monument has an oval shape tumulus, about 24.50 m long from east to west and 19.9 m from north to south, and an undifferentiated chamber and corridor. The chamber was made with

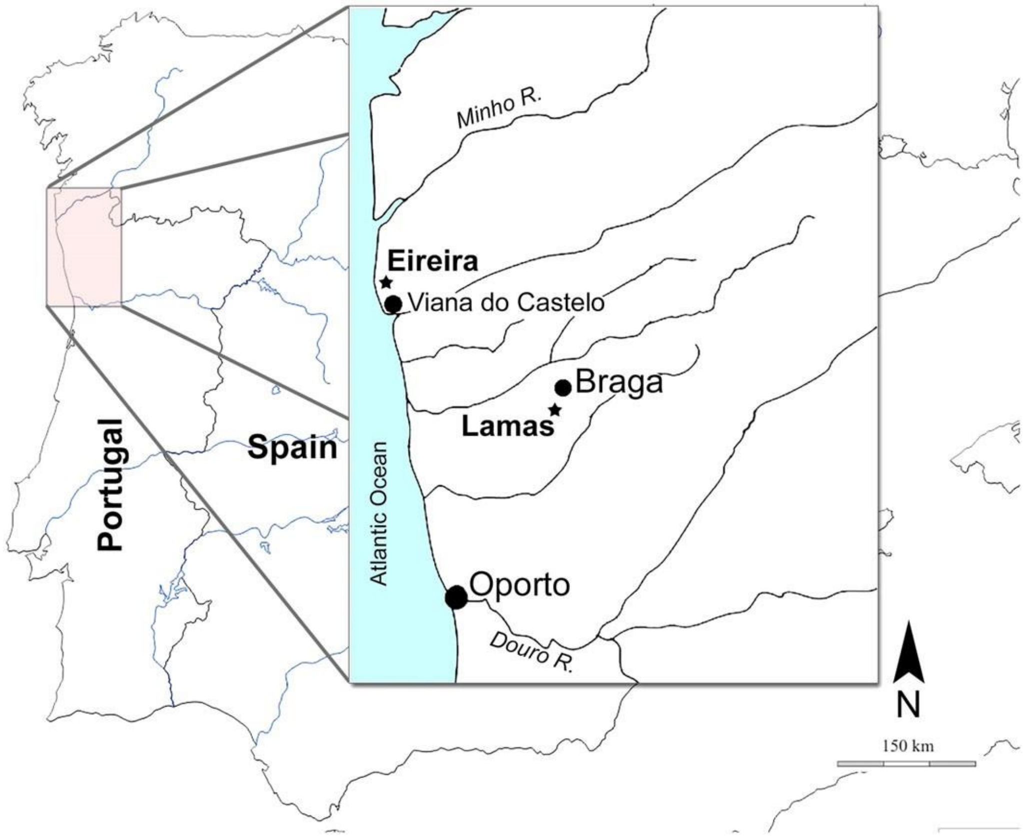

Figure 1 *The location of the two case studies in north-west Iberia*

local granitic orthostats, many of them polished, engraved and with some remains of paintings. However, after the archaeological excavations, the *in situ* orthostats remained exposed to the elements; consequently, the paintings are in a worrying state of degradation. Fortunately, a granitic orthostat in the form of a pillar had been previously removed to the Museum of Decorative Arts of Viana do Castelo, allowing these paintings to be preserved from the environmental degradation and vandalism.

This painted pillar was found in 1987 near the head orthostat, during the second archaeological intervention on the Eireira barrow (Silva 1988). It is about 1.53 m in height, 0.74 m wide and 0.24 m thick (Almeida 2008; Carrera 2005). The engraved surface was previously polished and shows four red-coloured wavy lines, mostly well preserved, arranged horizontally at the bottom of the pillar. Nineteen more traces of paint on the top of the pillar were also identified, generally little circles and dots, as well as two engraved cup marks. All the motifs were painted in red with the exception of the engraved cup marks, which are not painted (Fig. 2 (a)).

The Leira das mamas barrow

The barrow of Leira das Mamas is a Neolithic funerary monument located in Lamas, Braga, on a hill in the valley of the river Ledo or Veiga (Fig. 1). The local geological substrate is

Figure 2 *The painted orthostats from (a) Eireira and (b) Leira das Mamas.*

composed of medium to fine-grained biotitic granite (Teixeira *et al.* 1972; Ferreira *et al.* 2000). The site was accidentally discovered in February 1993, during the preparation of earthworks for a new housing development. Between 1993 and 1999, three archaeological excavations were carried out at this monument and, in 2000, its reconstruction was completed through the initiative of the Lamas village hall authorities together with the Museum of Archaeology D. Diogo de Sousa, in Braga, where the offerings deposited during the funerary practices are exhibited.

The archaeological works concluded that the Leira das Mamas barrow contained a chamber with a short open corridor facing south-east. The barrow is approximately 34 m in diameter and was constructed with compacted dark brown soil containing dispersed charcoal elements. The ceramic and lithic offerings (hemispherical containers; polished stone artefacts such as axes, adzes and one gauge; arrowheads; microliths; lamellas; flakes etc.) had no indication of use. The typology of the deposited objects suggests that the monument was constructed and used during the regional Middle to Late Neolithic, between the end of fifth and the end of fourth millennia BC. Indicators of its reuse during other moments in prehistory are disappointing and inconclusive (Bettencourt 2013).

Two orthostats from this monument present reticular motifs that Silva (2003) describes as being composed of white and red paint. However, the presence of these two colours was not confirmed, as we were able to detect only white pigment. Both orthostats, one 1.08 m in height,
1.10 m long and 0.11 m wide and the other 1.12 m in height, 0.76 m long and 0.125 m wide, present on their polished surface irregular reticulated figurines of a whitish colour (Fig. 2 (b)) (Bettencourt 2013). Fortunately for this study, these two orthostats were not used on the reconstruction of the monument but were deposited in Lamas village hall, which has allowed a better preservation of the painted motifs.

MATERIALS AND METHODS

All glassware was decontaminated by immersion for 24 h in a chromosulphuric bath and rinsed with deionized water. The pigments were scraped *in situ* with new sterile scalpels to gather small aliquots of about 0.5 g, and the samples were collected and wrapped in aluminium foil and stored in Eppendorf tubes until analysis. As the pigments were most certainly mixed with granite fragments from the orthostats, they were ‘cleaned’ in the laboratory by manual sorting under a binocular microscope, in order to remove as many silicates and other particles from the rock as possible. Besides the pigments, different aliquots of the pillar material were also collected and analysed, to study the possible contamination of the pigment samples with minerals from the stone.

Four different analytical techniques were selected to examine the collected materials: X-ray diffraction (XRD); scanning electron microscopy with energy-dispersive spectrometry (SEM– EDS); Fourier transform infrared spectroscopy (FT–IR) and gas chromatography – mass spectrometry (GC–MS). The first two techniques were used to characterize the micromorphology and mineral content of the samples, while the last two methodologies were focused on the study of the organic materials of the paint layer (Table 1).

The instrumental analyses were performed within the following experimental conditions.

FT–IR

Room-temperature Fourier transform infrared (FT–IR) spectra of solid samples in KBr pellets were measured using a Bomem MB104 spectrometer in the transmittance mode (range 4000–500 cm^{-1}) by averaging 32 scans at a maximum resolution of 4 cm^{-1}.

Before the analysis, all samples were dehydrated at 60°C under vacuum, to minimize the presence of bands from adsorbed water.

XRD

The identification of the crystalline phases was performed on samples that had been manually ground in an agate mortar, using a Philips PW 1710 diffractometer with a graphite monochroma- tor, Cu–Kα radiation and operating at 40 kV and 30 mA. The powder XRD patterns were examined in the region of 2° to 65° with a step size 0.02° for 2θ and scan speed of 2 s per step. The identification of the mineral phases was achieved by comparison with a database based on JCPDS–ICDD patterns.

Table 1 *The analysed samples*

Site	*Sample*	*FT–IR*	*XRD*	*SEM–EDS*	*GC–MS*
Eireira barrow	Paint layer from red sinuous lines	+	+	+	+
	Paint layer from red dots	–	–	–	+
	Rock support	+	+	+	+
Leira das Mamas barrow	White paint layer	+	+	+	+
	Rock support	+	+	+	+

+, Analysed; -, not analysed.

SEM–EDS

The SEM–EDS analyses were carried out using a scanning electron microscope from the Nova NanoSEM 200-FEI Company (USA), equipped with an EDAX-Pegasus X4M integrated system (EDS—energy-dispersive spectrometer/EBSD—electron backscatter diffraction) in low-vacuum mode, operated at an accelerated voltage of 30 kV.

GC–MS

The organic remains from each sample were extracted sequentially with dichloromethane and methanol (HPLC grade from Fisher Scientific) in a Soxhlet apparatus, filtered with 0.20 μm PTFE syringe filters and concentrated on a rotary evaporator to ~2 mL. The concentrated extracts were transferred to vials, dried with a gentle nitrogen flow, dissolved in pyridine and derivatized with N,O-bis(trimethylsilyl)trifluoroacetamide:trimethylchlorosilane (Sigma- Aldrich) in a 99:1 *v*/v ratio for the analysis of the most polar compounds. A GC–MS Varian 4000 Performance ion-trap device was operated with the following conditions: (a) 1 μL injection in SCAN mode, 250°C injector temperature, (b) column ZB-5MSi, 30 m × 0.25 mm × 0.25 μm;

(c) helium as carrier gas, at a constant flow of 1 mL min^{-1}; (d) a heating programme of 45 min in total: 60°C (1 min), 60–80°C (10°C min^{-1}), 80–290°C (7°C min^{-1}) and 290°C (12 min); (e)

acquisition mode, electronic impact at 70 eV; (f) interface and ion source at 290°C; and (g) scanned masses from 50 to 600 *m/z*. Compound identification was based on comparison of the resulting spectra with mass spectra libraries (Wiley 6 and Nist08), co-injection with authentic standards and analysis of fragmentation patterns.

RESULTS

Eireira barrow orthostat

FT–IR The data analysis can be easily achieved by focusing the discussion on two separate sec- tions of the FT–IR spectra. Therefore, we can consider both a fingerprint region due to the influence of the clay structure (from 500 to 1300 cm^{-1})

and, in the second part of the representation (from 1300 to 4000 cm^{-1}), the functional group region with information related to the pigment structure (Fig. 3 (a)) (Aroke *et al.* 2013).

The band at 3620 cm^{-1} is usually considered as being due to the presence of hydroxyl groups, and the peak at 1040 cm^{-1} as corresponding to the stretching vibration of Si–O and Si–O–Si groups. Additionally, the spectra of the pigment also present bands at 3690, 3612 and 1647 cm^{-1}. The presence of well-defined absorption bands at 3690 and 3612 cm^{-1} is typical for kaolinite (Gardolinski *et al.* 2000; Rong *et al.* 2008), suggesting either that the pigment consists of kaolinite clay and a red-coloured additive or that the kaolinite is from the stone material. The band at 1647 cm^{-1} is due to the presence of physisorbed water, namely (O–H) deformation. Hematite was not detected by FT–IR analysis of the Eireira pigment as it is transparent to FT–IR in the mid-infrared spectral region (Solla *et al.* 2015).

XRD The study by XRD provided diffractograms with information about the crystalline phases present in the pigment and rock samples (Fig. 3 (b)). It is necessary to emphasize that the crystalline phases can be identified by conventional XRD only if the amount in the sample is enough to give a good signal-to-noise ratio (Duran *et al.* 2010; Rogerio-Candelera *et al.* 2013). Consequently, minority compounds can be masked by the background noise. In spite of the low signal-to-noise ratio, it was possible to detect the presence of hematite (Fe_2O_3) as the main crystalline compound associated with the red colour of the pigment, and kaolinite ($Al_2Si_2O_5(OH)_4$). Also, different mineral phases related to the granite support pillar were identified: quartz (SiO_2), feldspars ($KAlSi_3O_8$–$NaAlSi_3O_8$–$CaAl_2Si_2O_8$) and micas (biotite $K(Mg,Fe)_3(AlSi_3O_{10})(F,OH)_2$ and muscovite $KAl_2(AlSi_3O_{10})(F,OH)_2$). The samples from undecorated areas provided diffractograms that confirm the composition of the substratum (quartz, feldspars and micas), the same crystalline phases as identified in the pigment samples, but with the absence of hematite.

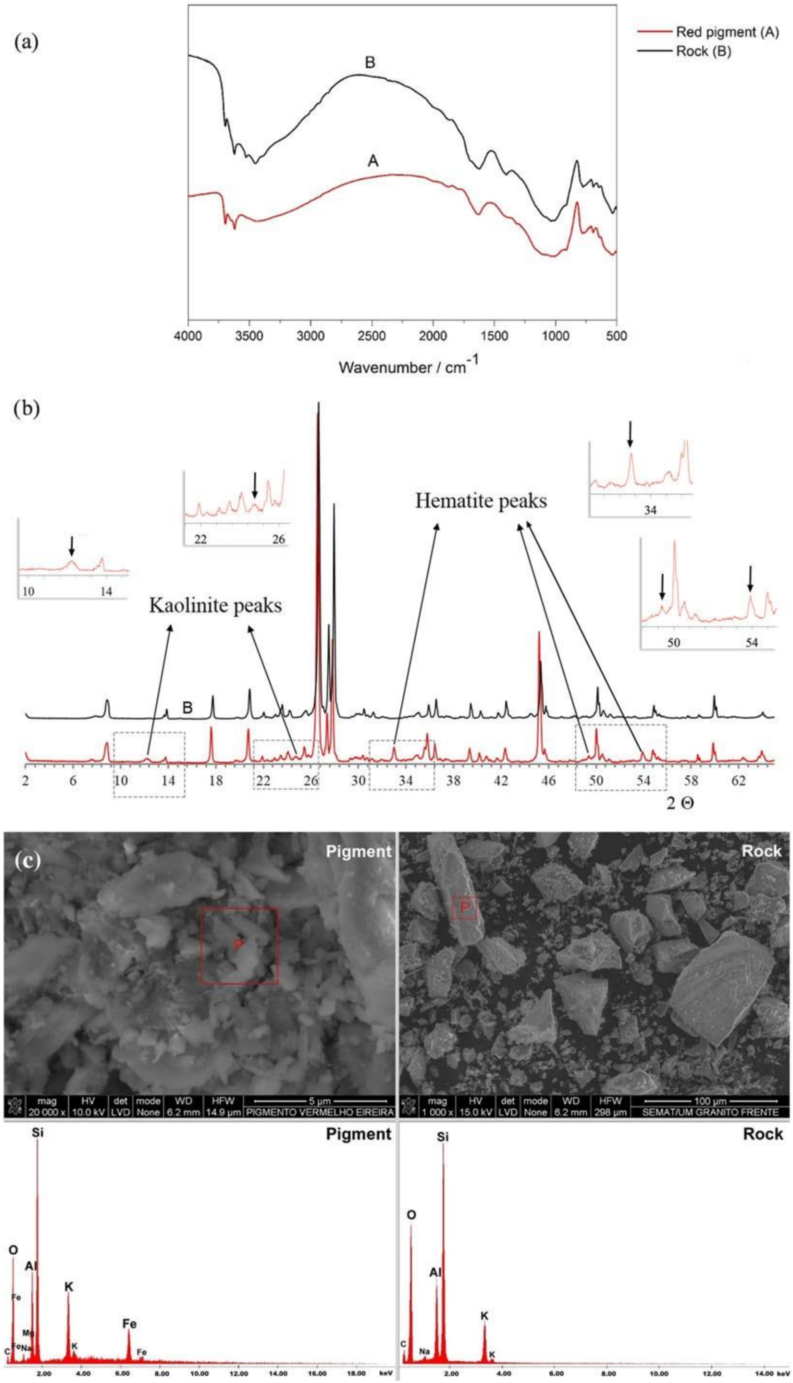

Figure 3 *An analysis of the Eireira orthostat red pigment: (a) FT–IR spectra of the red pigment (A) and rock from an undecorated area (B); (b) XRD diffractograms of the red pigment (A) and rock from an undecorated area (B); (c) SEM images from the red pigment (top left) and undecorated rock (top right), and EDS spectra from the red pigment (bottom left) and undecorated rock (bottom right)*

SEM–EDS The SEM–EDS analysis (Fig. 3 (c)) confirmed the presence of iron in the red pigment samples. Silicon, aluminium, potassium and sodium were also detected. These results are consistent with the presence of hematite in the pigment, also reflecting the orthostat granitic composition (quartz, micas and feldspars). The SEM observations strengthen these conclusions, showing iron oxide flakes (of less than 5 μm) and several crystalline grains with structural and textural characteristics from the minerals referred above. The analysis of samples from undecorated areas indicated a residual presence of iron, probably associated with the biotite mica. In this case, the SEM observations showed only the presence of the granite mineral phases. Small quantities of carbon were also detected, this element probably being associated with the organic material in the pigments and/or with biological or human contamination, or only being due to the SEM manipulation in a low vacuum. Hematite could be the source of the red colour of the pigment. Kaolinite could have been added to serve as an extender or, if hematite is from a sedimentary origin, it could have been present in the sediment/soil that was used. Thus, the presence of bands characteristic of kaolinite in the red pigment is justified here, especially when Fe_2O_3 was not detected in the measured FT–IR region.

GC–MS Figure 4 presents the chromatograms of the Eireira methanolic extracts of the red pigments, taken from the sinuous lines (Fig. 4 (a)) and small red dots (Fig. 4 (b)). Some of the detected compounds are characteristic of algae and/or aquatic plants, such as phytol, an alcoholic diterpene constituent of chlorophyll (Schwender *et al.* 1997), and linalool, which also belongs to the terpene group, and is usually present in flowers, plants and spices (McGovern *et al.* 2009). Oleanitrile and 9-octadecenamide could be due either to a reaction of oleic acid in a basic environment or to the presence of plant oils in the sample (Vaccaro *et al.* 2013). Quercetin is a plant pigment found in fruits, vegetables, leaves and grains (Ferreira and Quye 2002) and β-sitosterol is a vegetal sterol frequently found in vegetable oils (Baeten *et al.* 2013). Cholesterol is a sterol part of animal cell membranes; it is usually considered to be a tracer for animal-based products such as meat, animal oils or milk (Kimpe *et al.* 2001, 2002; Baeten *et al.* 2013). However, although not as abundant as in meat products, it can also be found in lipids from marine products (Solazzo and Erhardt 2007). Phytanic acid is also considered to be a tracer indicating fish deriv- atives (Hansel *et al.* 2004; Craig *et al.* 2007; Evershed *et al.* 2008; Baeten *et al.* 2013). The fatty acid amides 9-octadecenamide, 11-eicosenamide and 13-docosenamide are found in grasses and microalgae (Kawasaki *et al.* 1998; Dembitsky *et al.* 2000; Bertin *et al.* 2012). The combined results provide good evidence for processing of algae and/or aquatic plants. Tracers from vegetal biomass burning were also detected, comprising both levoglucosan and dehydroabietic acid. Levoglucosan, a pyrolysis product of cellulose, which is widely present in wood or vegetation from various species, is frequently used as a tracer for biomass burning because it is produced at relatively high levels and is very stable (Simoneit *et al.* 1999; Simoneit 2002; Zhang *et al.*

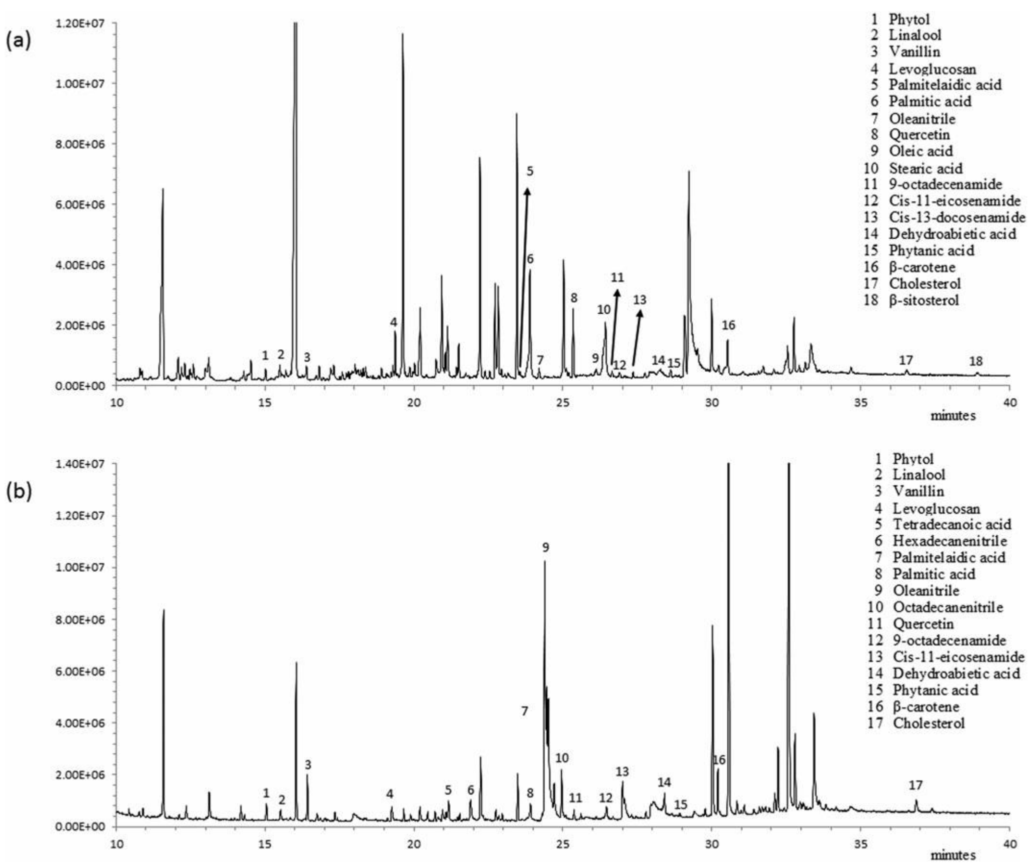

Figure 4 *GC–MS chromatograms of the Eireira orthostat red pigment from (a) the reticular motifs and (b) the small spots.*

2013). Dehydroabietic acid is a diterpenic compound, one of the main components in resins of Pinaceae origin, produced by the heat of abietic acid throughout a dehydrogenation process (Jerković *et al.* 2011). The presence of these two compounds in the samples suggests that the algae and/or aquatic plants detected were heated or cooked on a fire beforehand, and hence subjected to the influence of smoke.

The chromatogram of the pigment from the small dots (Fig. 4 (b)) also presents traces of cholesterol, hexadecanenitrile and octadecanenitrile. These compounds are markers related to the presence of egg proteins, evidencing the use of egg as a glue or binder for the pigments (Ospitali *et al.* 2007; Bonaduce and Andreotti 2009; Brecoulaki *et al.* 2012). The detection of amino acids (alanine and glycine) is also compatible with the presence of egg traces (Brecoulaki *et al.* 2012).

Small amounts of sugar compounds were detected in both the sinuous lines and small spots (compounds not pointed out in chromatograms). Their existence is most probably related to the degradation of vegetal cellular walls or simply due to the biological activity of micro- organisms deposited on the barrow over the years (Harding 2012).

GC–MS analysis of the rock surface close to the paintings was also conducted as a control, but no organic matter was found.

Leira das mamas barrow orthostats

FT–IR Figure 5 (a) shows the IR spectra of the ‘rock’ and ‘pigment’ samples. Both spectra show the intense bands at about 3620, 3450, 1630 and 1010 cm^{-1}, and some in the 1000– 500 cm^{-1} region suggesting that both materials are of an aluminosilicate type (Aroke *et al.* 2013). The bands at 3450 and 1630 cm^{-1} could be due to the presence of physisorbed water, namely the ν(O–H) stretching frequency at 3450 cm^{-1} and the δ(O–H) deformation band at 1630 cm^{-1}. The band at around 3620 cm^{-1} is usually assigned to surface hydroxyl groups (Kuzniarska-Biernacka *et al.* 2005). The band in the low-energy region, with a maximum peak at 1010 cm^{-1}, is usually assigned to Si–O and Si–O–Si stretching vibrations (Kuzniarska-Biernacka *et al.* 2005). In addition to the bands mentioned above, the ‘pigment’ spectrum shows bands at 3695, 1110, 915 and 755 cm^{-1}. The presence of strong, sharp absorption bands at 3695 and 3620 cm^{-1} is typical for kaolinite clays (Granizo *et al.* 2000) and the frequency at which these bands appear is determined by the distance of OH groups from the oxygen of neighbouring groups. The other low-energy bands are assigned to Si–O and Si–O–Si stretching vibrations and are due to O–H bending vibration from adsorbed water (Bourlinos *et al.* 2004). Combined with the XRD results, this supports the conclusion that the ‘pigment’ was based on kaolinite clay.

XRD The XRD diffractograms from the Leira das Mamas (Fig. 5 (b)) samples allowed the identification of kaolinite ($Al_2Si_2O_5(OH)_4$) as the white pigment. Quartz (SiO_2), feldspars ($KAlSi_3O_8$–$NaAlSi_3O_8$–$CaAl_2Si_2O_8$), micas (biotite $K(Mg,Fe)_3(AlSi_3O_{10})(F,OH)_2$ and musco- vite $KAl_2(AlSi_3O_{10})(F,OH)_2$) were also detected, reflecting the presence of these minerals in the composition of the granitic substratum. The analysis from undecorated areas of the granitic pillar revealed the same mineralogical content but without the presence of kaolinite.

SEM–EDS The SEM–EDS analysis from the white pigment (Fig. 5 (c)) shows a strong signal for aluminium. These results are consistent with the presence in the pigment of kaolinite (an aluminosilicate). The identification of small quantities of sodium, potassium, calcium, magne- sium and iron also reflects the granitic composition (quartz, micas and feldspars) from the orthostat. The SEM observations strengthen these conclusions, kaolinite flakes (of less than 10 μm) being visible, together with several crystalline grains that have structural and textural characteristics from the granite mineral phases. Samples from undecorated areas had a smaller quantity of aluminium, which is consistent with the absence of kaolinite (aluminosilicate). Small quantities of carbon were also detected, and this element is probably associated with organic residues in the pigment, biological or human contamination, or result from the use of SEM in low-vacuum mode.

GC–MS The results of the chromatographic analysis on the white pigment (Fig. 6) from Lamas point to the use of plant oils in the preparation of the pigment. In fact, the pigment exhibited the presence of oleanitrile, which is characteristic of vegetable oils (Vaccaro *et al.* 2013), and quer- cetin, a vegetal compound tracer also used as a dye on ancient textiles (Ferreira and Quye 2002). Other detected plant oil tracers were β-sitosterol, a vegetal sterol (Baeten *et al.* 2013), β-carotene and lycopene, both antioxidant pigments present in various plants, vegetables and fruits (Paiva and Russell 1999; Goñi *et al.* 2006). The detection of levoglucosan indicates the thermal degra- dation of cellulose (Simoneit *et al.* 1999; Simoneit 2002), while the presence of pimaric and dehydroabietic acids suggests the use of resins of Pinaceae origin that were exposed to a thermal dehydrogenation process (Jerković *et al.* 2011).

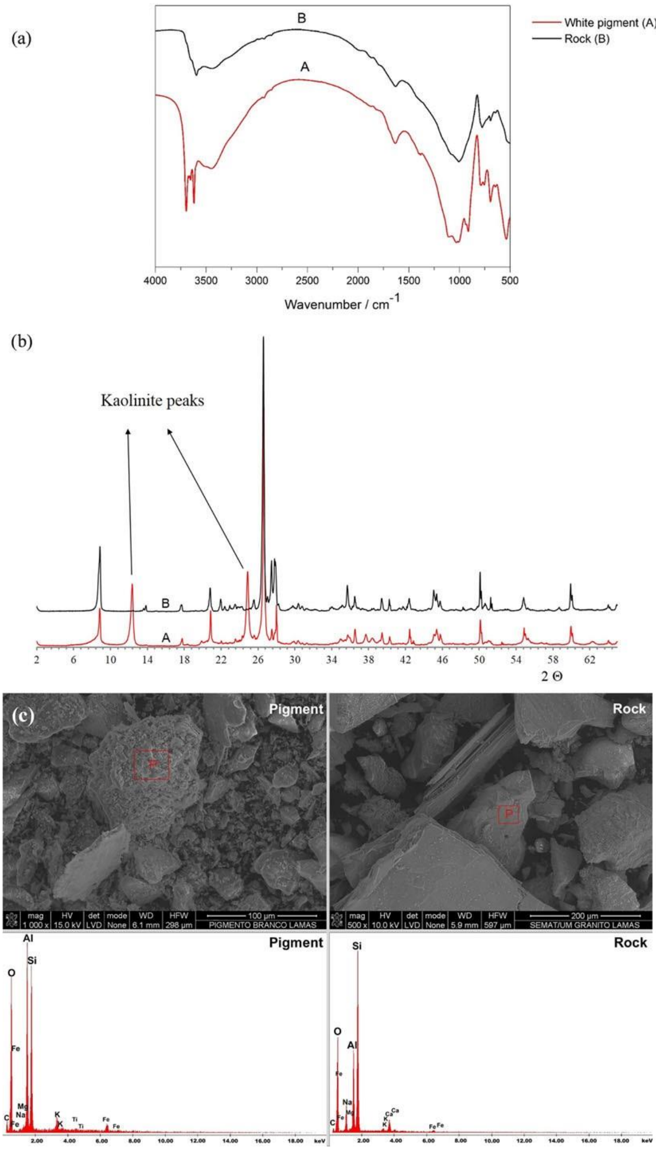

Figure 5 *An analysis of the Leira das Mamas orthostat white pigment: (a) FT–IR spectra of the white pigment (A) and rock from an undecorated area (B); (b) XRD diffractograms of the white pigment (A) and rock from an undecorated area (B); (c) SEM images from the white pigment (top left) and undecorated rock (top right), and EDS spectra from the white pigment (bottom left) and undecorated rock (bottom right).*

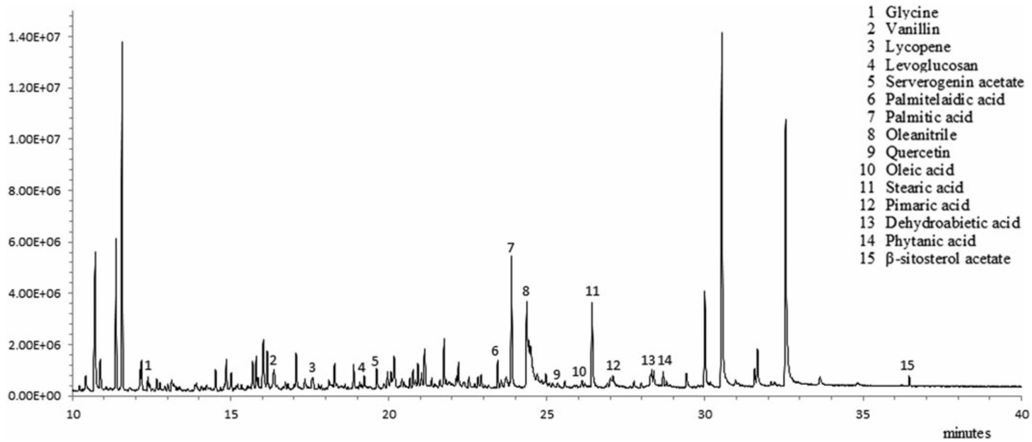

Figure 6 *The GC–MS chromatogram of the Leira das Mamas white pigment.*

These results, combined with the information that no organic matter has been detected (by GC–MS analysis) upon the rock surface, suggest that the pigment was prepared using vegetal oils as organic additives, in a mixture that was heated and stabilized using cellulosic material of Pinaceae origin.

DISCUSSION AND CONCLUSIONS

A range of techniques—XRD, SEM–EDS, FT–IR and chromatographic analysis—were applied on sample pigments collected on painted granitic orthostats from the Eireira and Leira das Mamas barrows.

Kaolinite was detected in the FT–IR analysis of the Eireira pigment.

The XRD and SEM–EDS analyses showed that the reddish colour of the pigment found in the Eireira barrow is due to the presence of iron oxide minerals, particularly hematite, while the white colour from the pigment found in Lamas comes from kaolinite. The detection of micas (biotite and muscovite) and potassium feldspars reflects the granitic nature of the orthostats, but it is also possible that these minerals could have been used as extenders in the paint composition.

The composition of the organic additives was studied using gas chromatography with mass detection. The red pigment of the Eireira barrow revealed both traces of algae and/or aquatic plants, and markers of vegetal biomass burning. The main conclusion of these analyses was that the red colourant contained algae and/or aquatic plants that were cooked or heated using wood or leaves. The white pigment of the Leira das Mamas barrow presented traces of vegetal oils, together with vegetal biomass burning tracers and resin acids of Pinaceae origin, suggesting the use of vegetal oils as organic additives, in a mixture that was prepared and stabilized by heating.

The most usual pigments found in the megalithic monuments of north-west Iberia are the red colourants and occasionally also black and white dyes (Carrera 2005, 2011; Rivas and Carrera 2010). Red pigment samples from megalithic monuments located in north-west Iberia have already been analysed, showing hematite as a common mineral (Rivas and Carrera 2010). This fact is in line with our results for the Eireira pigment, which show that the use of this mineral in funerary rituals during the Middle and Late Neolithic periods was widespread throughout north-west Iberia.

Hematite, as a pigment, was commonly used in the Iberian Peninsula during the Upper Palaeolithic (Arias *et al.* 2011), sometimes mixed with pyrite (Zilhão *et al.* 2010). It was also applied during the Early Neolithic together with goethite and/or cinnabar (Domingo *et al.* 2012), and in combination with goethite in schematic art paintings from the late prehistoric rock shelters of western Iberia (Gomes 2015). Hematite is also the main component of red pictographs from megalithic contexts of Western Europe and Brittany (France) (Hernanz *et al.* 2016). It was frequently used together with ligands or binders, as their adhesion characteristics do not allow effective bonding (Arias *et al.* 2011).

Another discussion that is common in some studies is the pigment provenance (Jezequel *et al.* 2011; Bonneau *et al.* 2012; Domingo *et al.* 2012; Rogerio-Candelera *et al.* 2013). As the colourant minerals identified for Eireira and Leira das Mamas are very common in the region (Teixeira *et al.* 1972; Pereira 1992), we can accept that these pigments were probably made using local materials.

The preparation of red pigments by heating seems to be a common technique in prehis- tory (Pomiès *et al.* 1999). Binders can present different compositions, depending on their purpose and the availability of materials. In fact, as an example we can present the formula used on the Dombate dolmen, at Corunha, Galicia, which seems distinct from the one used by the Eireira painters. In fact, Rivas and Carrera (2010) describe the use of animal fats as binders, with particular emphasis on cow fats (Rivas and Carrera 2010), in contrast to the Eireira pigment, which features a combination of aquatic plants and eggs (both easily collected in the surroundings) subjected to thermal treatment. Such regional variants in the composition of binders could be due to distinct cultural contexts or easy access to ingredients. The use of diverse analytical methodologies can also be responsible for some dissimilarities among results.

Studies on the composition of white pigments are still scarce; a few known examples deal with the use of kaolinite clay in the megalithic monuments of north-west Iberia (Rivas and Carrera 2010). The technique consisted of combining kaolinite with plant oils, the preparation mixture being heated by burning Pinaceae vegetal material. The use of the Pinaceae tree makes evident, once again, the intrinsic knowledge that those communities acquired from the environment, bearing in mind that these Pinaceae family trees are found in the vicinity of the monument. The composition of the pigment found in the Leira das Mamas paintings is consistent with the remaining monuments of Galicia, Spain in the same period (Steelman *et al.* 2005; Carrera 2011), showing that this formula was commonly used in funerary rites in the Middle to Late Neolithic.

Published studies of pigments from the megalithic monuments of the north-west Iberian Peninsula reveal the frequent use of animal fats as binders (Rivas and Carrera 2010). This is a significant area of research, as it allows us to evaluate the technical level of development of the Neolithic communities, to establish their interaction with the surrounding environment, and to propose new interpretations about the symbolism of death from the perspective of an animistic world in which the colourants were chosen for their physical, and simultaneously symbolic, properties. The interpretation of the meanings of colourants during the funerary rites is an interesting field of study, although difficult and based mainly on ethnographic data (Zagorska 2008); it is important to stress that they represent a transformation of the animistic world elements associated with the great transformation of the human being—death—probably as a phenomenon of mimicry.

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