Multi-analytical study of ceramic pigments application in the study of Iron Age decorated pottery from SW Iberia

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ABSTRACT

A non-invasive multi-analytical approach combining optical microscopy (OM), micro-X-ray diffraction (μXRD), in-situ X-ray fluorescence spectroscopy (XRF), variable pressure scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (VP-SEM-EDS) and Raman micro-spectroscopy has been employed for the first time to investigate the chemical composition of ceramic pigments in Iberian Iron Age ceramics. The methodology was applied in the study of red, black and white pigments on Iron Age decorated pottery from the archaeological site of Garvão (SW Portugal). The complementary methodology adopted in this study minimized the damage to the ancient artefacts and turned out to be essential in achieving a complete chemical and mineralogical characterization of pigment composition.

Results suggest that haematite (Fe_2O_3) and pyrolusite (MnO_2) are the main mineral carriers of the Fe and Mn chromophore ions, responsible respectively for the red and black colour. While illite ($K(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_2$), a common clay mineral, is giving the white colour. It is the first time that the use of illite as a pigment on decorations of ancient pottery has been reported in western societies.

The potters used local raw materials, compatible with the regional geological context and the archaeometric study seems to demonstrate that the society that produced the painted ceramics had limited access to long commercial routes.

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1. Introduction

Since ancient times, potters from early civilizations have been making extensive use of natural pigments for colouring ceramic artefacts. The chemical and mineralogical characterization of painted ceramic objects recovered from archaeological excavations is an essential instrument to: (a) identify the pigments used in the painted ceramic workshops, (b) provide evidence on the availability and sources of natural pigment, (c) contribute to understand the ancient pottery production techniques mainly on the application of pigments [1,2]. Naturally occurring compounds such as iron oxides and oxyhydroxides were extensively used as pigments by ancient civilizations. They can be used to produce bright colours with different shades, ranging from light yellow to black, including

deep red, brown and violet [3–5]. Their widespread use results from their availability and physical stability after application [3,4].

The studied specimens are recovered Iron Age artefacts from the Garvão votive deposit site (Fig. 1) and they have been interpreted as representing votive offerings left in the sanctuary and afterwards, carefully placed in a secondary deposit to liberate space in the sanctuary. From a typological perspective, the existence of local pottery production workshops cannot be ruled out. Nevertheless, Garvão ceramics can be understood as representing Iberian societies characterized by a merge of strong Mediterranean cultural inspirations with cultures from the central regions of the Peninsula under the influence of Celtic traditions [6,7], between the 3th and 1st centuries BC. The closeness with an important mining area of the Iberian Pyrite Belt must also be considered.

The Iberian Pyrite Belt (IPB) is part of South-Portuguese Zone (SPZ), the southernmost segment of the Variscan Iberian Massif. The presence of Cu-Pb-Zn-(Au, Ag) and Mn-(Fe) ore deposits are the main distinguish features of IPB and attracted the attention
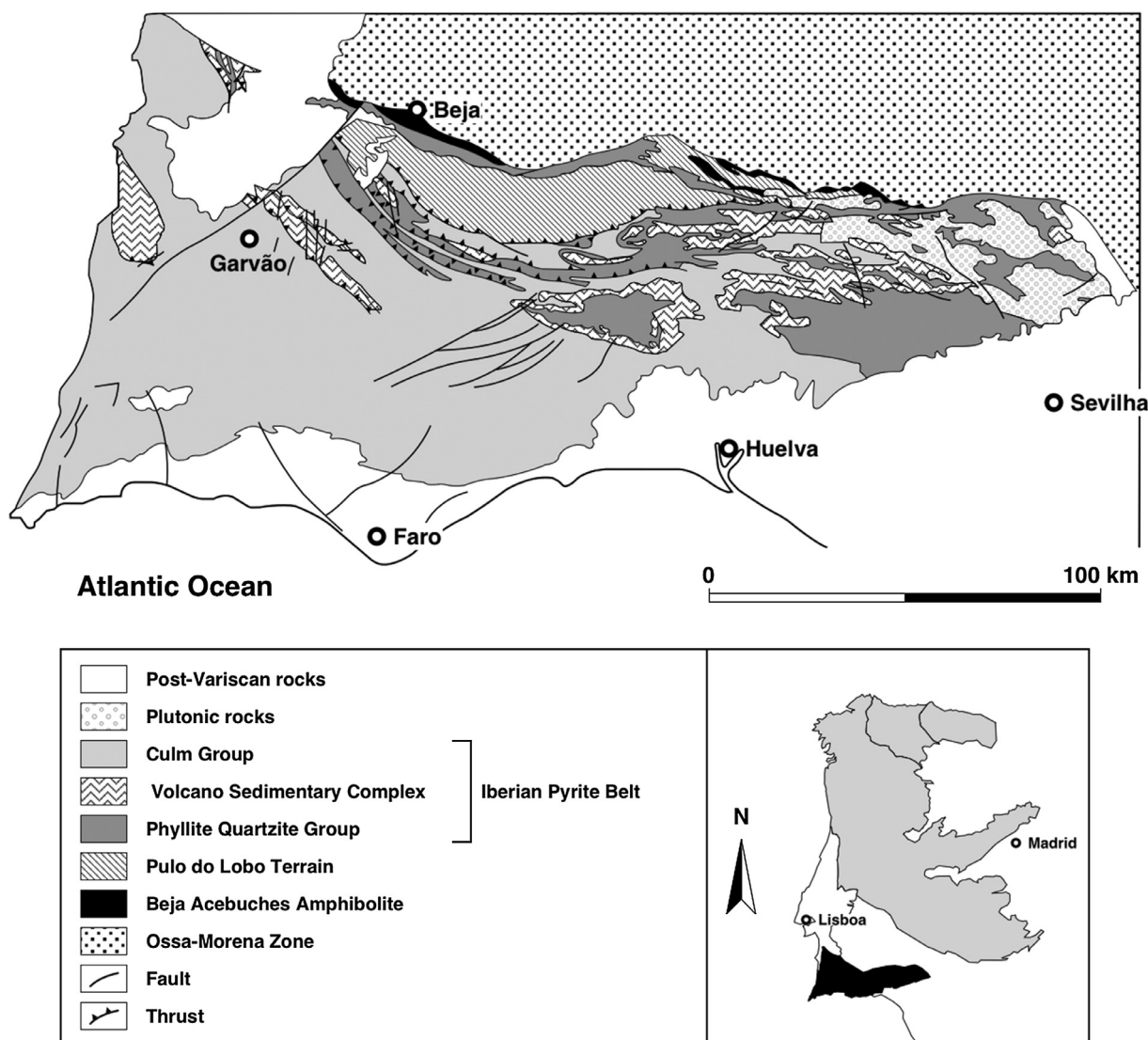

Fig. 1. Geological map of SW Iberia with the position of Garvão archaeological site (adapted from [8]). The sulphide ore deposits and the Mn-(Fe) oxide mineralizations are widespread to Volcano-Sedimentary complex.

of several societies since the chalcolithic period. The Garvão votive deposit lays on the rocks of the Baixo Alentejo Flysh group (Fig. 1). This geologic unit is the uppermost unit in Iberian Pyrite Belt and South-Portuguese Zone and consists of alternating layers of shale and greywacke. From the economic point of view, the rocks of the Volcano-Sedimentary complex are the most important because they host some important massive sulphide ore deposits and innumerable Mn-(Fe) oxide mineralizations. The Phyllite-Quartzite group is the oldest geological formation in the IPB and consist of a repetitive succession of shale and sandstone. The boundary between the low grade metamorphic SPZ rocks with the plutonic rocks and higher grade metamorphic rocks outcrops of Ossa-Morena Zone underlines the main tectonic suture in the region. The post-Palaeozoic rocks in SW Iberia are mainly sandstones North of Garvão and limestones or clastic rocks South of Garvão [8].

The aesthetic style, the manufacturing procedure and the materials employed are the main parameters in the classification of these ceramics attributed to Iron Age historical period. The decorated ceramics and the material study of pigments may therefore contribute to the knowledge of the evolution of Iberian ceramic technology during the Iron Age. Moreover, the determination of the pigments chemical and mineralogical composition can contribute to evaluate the most probable sources of raw materials used for pottery manufacturing.

When investigating material culture, it is often necessary to use more than one technique in order to achieve unambiguous results [9,10]. Therefore, chemical, mineralogical and microstructural characterisation of the pigments was performed combining different complementary techniques: optical microscopy (OM), micro X-ray diffraction (µXRD), in-situ X-ray fluorescence (XRF), variable pressure scanning electron microscope (VP-SEM-EDS) and micro-Raman spectroscopy (µRaman). As it is the case with any archaeological and/or Cultural Heritage objects, the main priority of the scientist is the safeguard of the artefact under investigation. Therefore, the authors envisaged an analytical methodology based on non-invasive techniques hence avoiding sampling.

Previous research on Iberian pottery has been focusing primarily on typological and aesthetical characterization, whereas available studies on the pigments used for their decoration using spectroscopic techniques are rare [11–13]. Pérez and Esteve-Tébar (2004) investigated the chemical nature of red, white and black pigments of Greek pottery from the end of the 5th century and the first half of the 4th century BCE in the Iberian burial site

of Cabezo Lucero (Guardamar del Segura, Spain) using Raman micro-spectroscopy. This study showed magnetite and haematite as the main mineralogical constituents respectively of the black and red pigments with the white pigment composed by alumina obtained through thermal decomposition of aluminium hydroxides. Further, local productions of Iberian pottery were not considered [11].

Parras et al. (2009) investigated pigments found on decorated antique Iberian pottery from Puente Tablas (Jaén, Spain) also by Raman spectroscopy. Different types of iron oxide pigments (haematite and goethite) were identified, along with amorphous carbon. In some samples, the presence of chalk or gypsum could be verified [12].

Ayora-Cañada et al. (2011) employed Raman spectroscopy for the chemical characterization of the ceramic body and brownish-red pigments found in ancient Iberian pottery from the archaeological site of *La Vispesa* (Huesca, Spain). Calcite, quartz and haematite were found to be the main mineralogical constituents with anatase as a minor component. Haematite was identified in both the ceramic body and the decorative elements [13].

When compared with others previous studies, the present work intends to demonstrate that a multi-analytic approach is essential to completely characterize these cultural materials. This is also the first attempt to understand the use of pigments in the Iron Age ceramics from south-western Iberia, not so close of Mediterranean cultures colonies of southern and southeastern Iberia.

2. Experimental set-up

2.1. Specimens/samples

Pottery fragments belonging to ovoid vases and plates and whole pieces dating from the Second Iron Age were collected from archaeological excavations in Garvão (Portugal). All specimens are hand-painted with black, white, red and dark red pigments generally after the slip application and before the firing. The decoration with the red pigment is the most common. Parallel and horizontal bands and lines are the main motives but the presence of geometric drawings was also registered. In the plates, the decorative elements occur as concentric circles in various shades of red.

The analytical work was conducted in unbroken ceramics and in fragments of decorated pottery (Fig. 2). The sampling was minimized and restricted to the observation and micro-analyse of some pigments in thin-section or cross-section.

2.2. Experimental methods

2.2.1. Optical microscopy

All samples were observed by optical microscopy through a stereo-zoom microscope (Leica M205C, with a Leica DFC290HD camera for image acquisition). The surface of the pigments was examined and their texture and pigment particle distribution was evaluated. Some micro-samples from ceramic fragments were
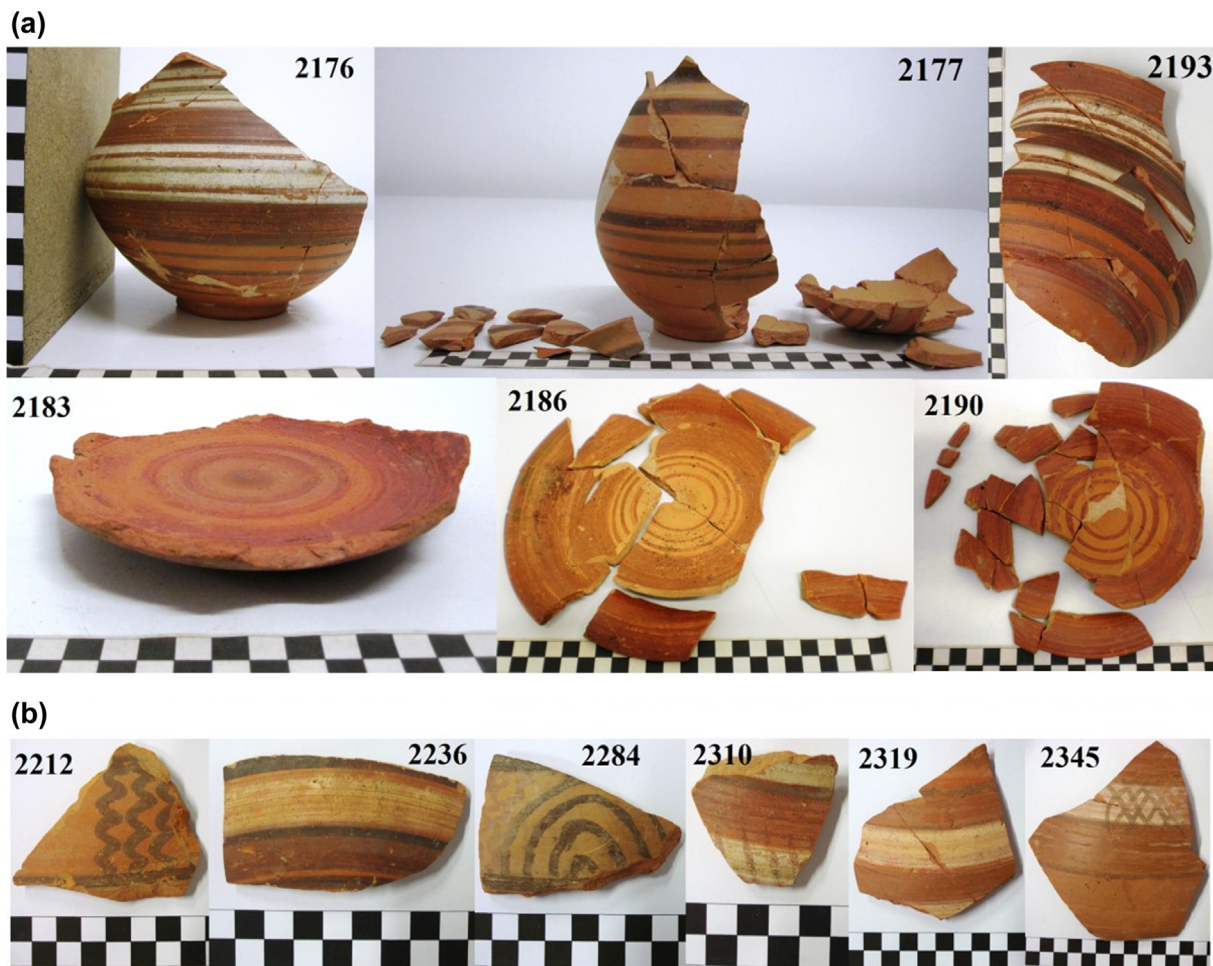

Fig. 2. Type of analysed samples (a) almost complete ovoid vases and plates and (b) fragments of decorated pottery, ■ 1 cm.

mounted in epoxy resin. Polished cross sections and thin sections of these samples were examined using a microscope (Leica DM2700 M) in reflected darkfield and transmitted brightfield modes, respectively.

2.2.2. Micro-X-ray diffraction (µXRD)

µXRD experiments were carried out directly on the objects using a commercial Bruker D8 Discover diffractometer (daVinci design) with a Cu Kα radiation source, a 1 mm collimator and a Lynxeye 1-D detector. The diffractograms was collected from 3 to 75° 2θ with a step of 0.05° and 2sec by step.

This technique enables identification of crystalline compounds directly in painting sections of different artefacts without any additional damage. However, it is not useful when the pigments are composed of amorphous material and for a complete characterization, it is also required the chemical elemental composition recognition.

2.2.3. Portable X-ray fluorescence (pXRF)

The use of in-situ pXRF allows non-invasive and multi-elemental chemical analysis. The X-ray fluorescence experiments were performed in air with an Ag anode X-ray generator (Amptek Mini-X) and an SDD detector (Amptek SDD X-123). Data was collected over a live time of 300 s for each analysis. An accelerating voltage of 30 kV and an electron beam current of 15 µA was used. The X-ray spot in the sample have a diameter of 5 mm.

The analysed volume in each pigment thin layer is bound to include some of the underlying ceramic body. Therefore, to understand which elements were characteristics of the pigment, the area of the ceramic paste immediately adjacent to the painted layer was also analysed.

2.2.4. Variable Pressure Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (VP-SEM-EDS)

Characterization of the chemical microstructure is one of the most important applications of the conventional Scanning Electron Microscope (SEM) equipped with an Energy Dispersive X-ray Spectrometer (EDS). This technique can provide textural information, point analysis and elemental mapping showing the spatial distribution of the chemical elements within the analysed area.

The specimens were investigated using a Variable Pressure Scanning Electron Microscope HITACHI S3700N interfaced with an Energy Dispersive X-ray Bruker Xflash 5010 SDD spectrometer utilizing the Esprit1.9 software. By SEM-EDS three types of samples were analysed: (a) original ceramic shards without any treatment, (b) polished surfaces and (c) thin sections of selected microsamples. The last two types were carbon coated before examination and analysed under high vacuum. The original shards were left uncoated to preserve them in their original state and analysed in variable pressure mode (VP-SEM-EDS).

2.2.5. Raman spectroscopy

Raman microscopy is becoming increasingly popular in heritage studies and archaeometric research because it has proven itself as a very reliable, sensitive, specific, non-destructive technique that can be applied in situ and therefore avoiding any sampling and consequently any damage to the object under examination [10,11,13–15]. Raman spectroscopy is particularly useful when used in conjunction with XRD in the identification of non-crystalline compounds. Raman microscopy is also a suitable technique for the identification of individual microscopic particles of pigment.

Furthermore, specially controlled atmosphere or sample-coating are not required in Raman spectroscopy [11]. Its high spatial and spectral resolution [12,16] allows the analysis of very thin ceramic coatings without any interference from the substrate [11].

Selected specimens were analysed using a dispersive confocal micro-Raman microscope (Horiba Xplora) equipped with an Olympus BX41 microscope and a motorized XYZ stage. The wavenumber stability and the accuracy were checked by recording the Raman spectra of a silicon standard (520.7 cm^{-1}). A colour video camera attached to the microscope allowed the visual inspection of the specimens and the selection of the areas from which the Raman spectra are collected. Measurements were carried out on the decoration and a range of spectra were obtained from different spots on each sample. The samples were analysed without any preliminary preparation and all spectra were collected through a 100× objective with a laser spot size of <4 µm. A 638 nm laser line with maximum power of 10 mW was used as the excitation source. The laser power at the sample was always kept as low as possible and usually ranged between 0.1 and 1 mW in order to avoid thermal degradation of sensitive Fe and Mn materials, especially oxides and hydroxides. A 600 lines/mm grating was used and accumulation times per spectrum were set between 10 and 300 s.

3. Results and discussion

3.1. Red pigment

The red pigment investigated under the stereomicroscope provides information about the texture and homogeneity of the pigment layer. The pigment thickness appears to differ from one sample to another, although the coverage of the ceramic surface remains fairly good.

The µXRD results revealed the presence of haematite, quartz and illite (Fig. 3a). These phases are also present in the ceramic body but the first is more abundant in the painted sections. pXRF elemental analysis showed that Fe is a major component both in the red decoration and in the ceramic paste (Fig. 3b and c). Nevertheless, pXRF in most of the samples reveal enrichment in Fe and also Mn in the area of the red pigment and higher content in Mn in the dark red areas, the data are not conclusive. The presence of Si, K, Ti and Al observed indicates that the iron containing compound was applied using an ochre raw material since these elements are related to the earth nature of these pigments.

The VP-SEM-EDS experiments allow to distinguish between the painted and unpainted surface area of the original shards archaeological ceramics. The painted area is enriched in Fe if compared with the ceramic paste (Fig. 4a) validating the preliminary XRF results. The pigment is heterogeneous. The Fe-rich grains coexist with several Mn-rich ones (Fig. 4b). Elements like K, Al and Si are present suggesting the application of a clayish iron earth pigment (i.e. an ochre). The SEM-EDS results, obtained on the thin sections, show a superposition of a Fe-rich layer over the ceramic body. The thickness of the pigmented layer is about 5–6 µm (Fig. 4c).

Raman spectra of the red pigment revealed the presence of haematite and quartz. Besides some differences in band positions and relative intensities, the presence of haematite is evidenced by the presence of the bands at 220, 285, 400, 601, 655 and 1312 cm^{-1} (Fig. 5) [2,15,17–20]. The α–quartz bands at 460, 199 and 120 cm^{-1} [17] are frequently present (Fig. 5). In some spectra a band at 660 cm^{-1} was observed, which could be assigned to residual magnetite (Fe_3O_4) [20–24].

Iron oxides are affected by the firing conditions. In fact, the different colours were obtained through the use of different firing conditions. For example, under oxidizing conditions, the oxidized forms like haematite are dominant whereas under reducing conditions haematite is converted to magnetite between 650 °C and 900 °C [21,24].

The abundance of haematite therefore must be connected with the prevalence of oxidizing conditions during firing. The magnetite
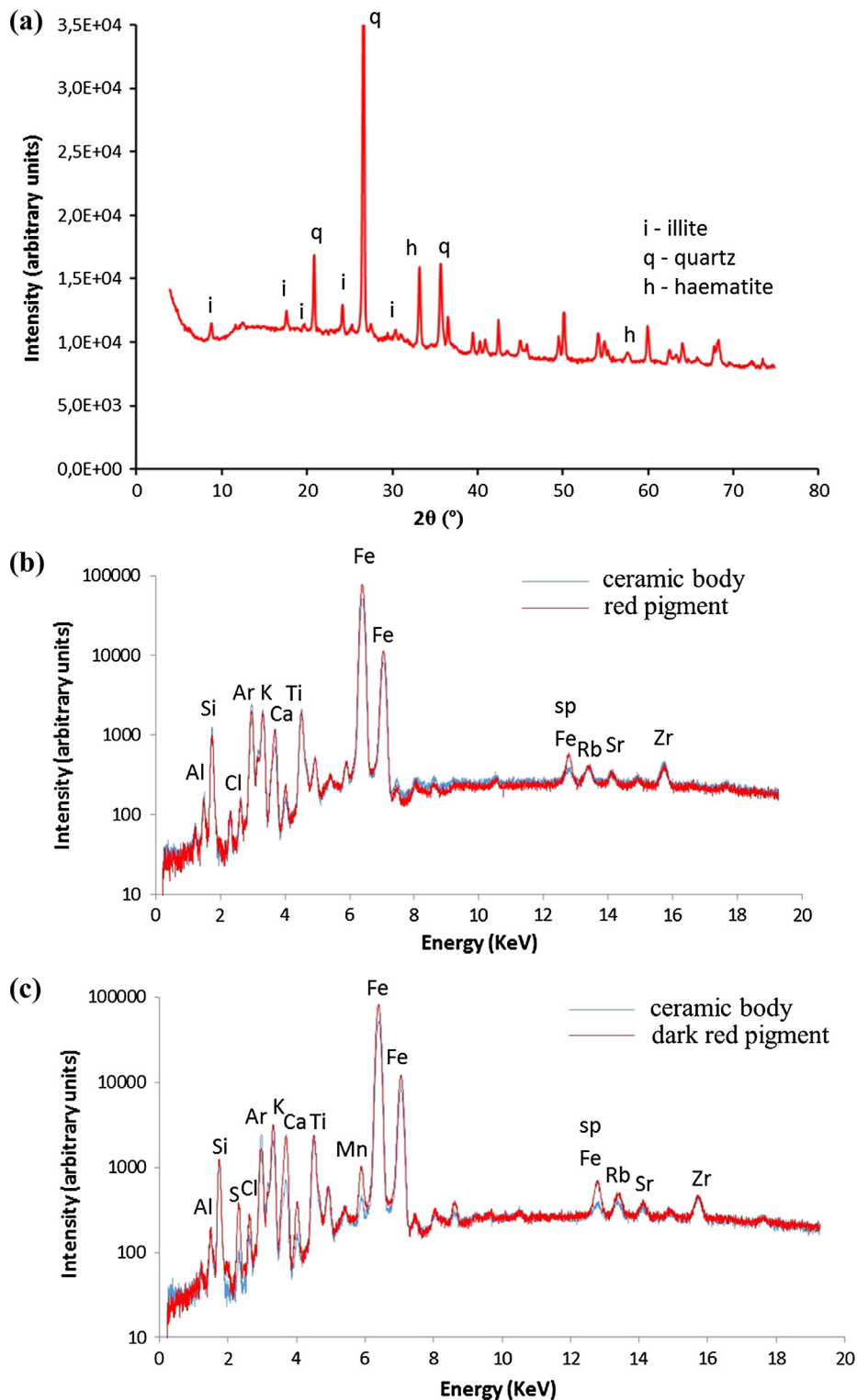
Fig. 3. (a) micro-diffractogram of the red pigment (sample 2291) (b) XRF spectrum of the red pigment and (c) XRF spectrum of the dark red pigment. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

inclusions should be inherited from the natural raw material source, where magnetite frequently coexists with haematite. The absence of goethite (and of its typical yellow colour) must be attributed to its thermal instability above 200 °C [25].

The presence of iron, as detected by in situ XRF and the phases identified (i.e. illite, quartz and haematite) by μXRD provides

evidence that ochre were used as red pigment. Although μXRD and XRF provided useful information about the pigments only by using high spatial resolution techniques, micro-Raman spectroscopy and VP-SEM-EDS, it was possible to unequivocally associate iron and haematite to the red decoration thin layer. A darker red hue corresponds to the presence of Mn.
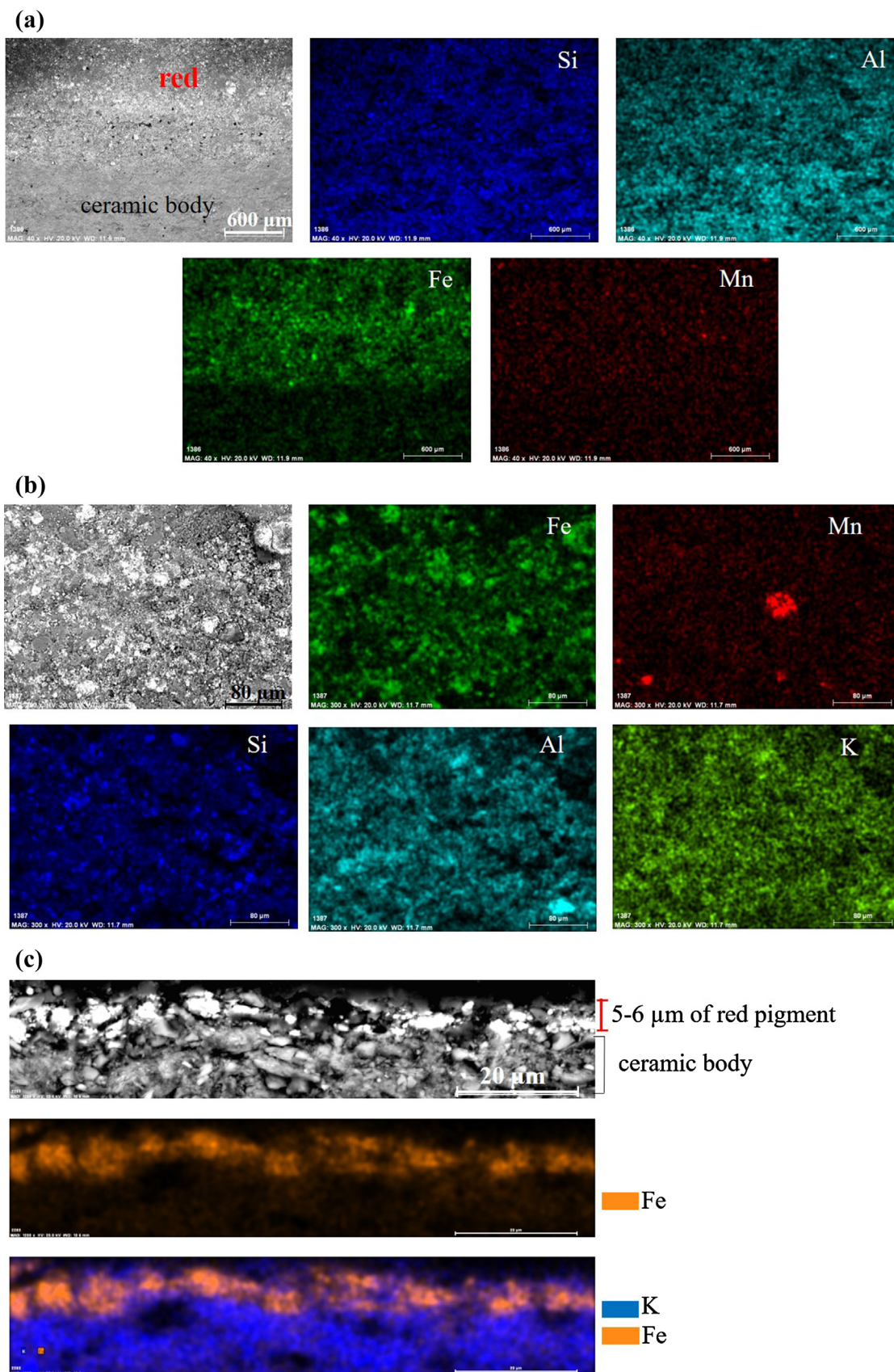
Fig. 4. (a) VP-SEM Back-Scattered Electron photomicrograph and VP-SEM-EDS elemental map of the red pigment and paste surface (sample 2236); (b) a detail of the red pigment in the same sample and (c) SEM-EDS elemental map on thin section (sample 2291).
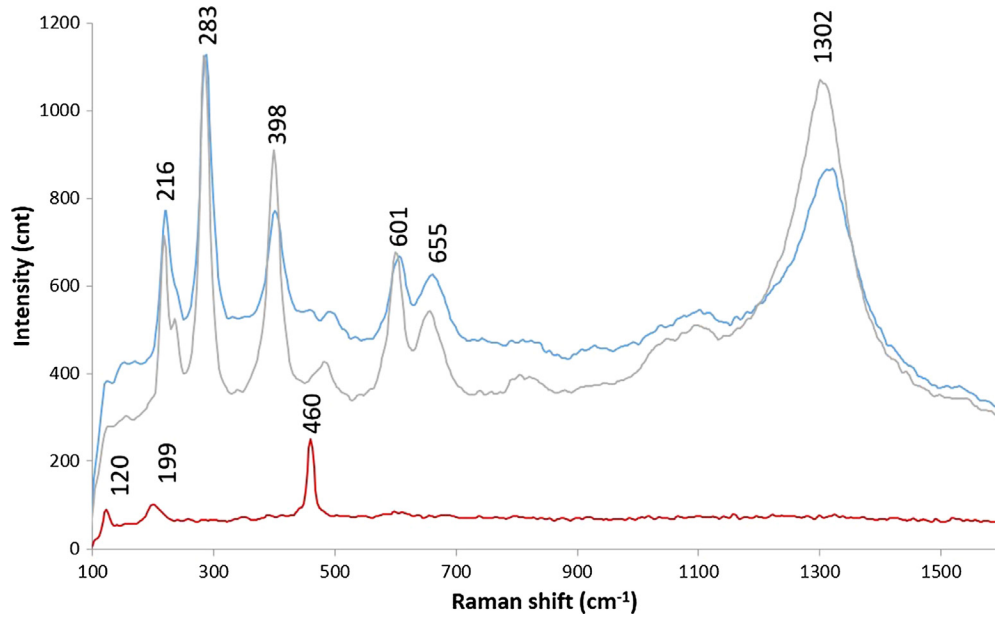
Fig. 5. Raman spectrum of red pigment attributed to haematite and magnetite (■ sample 2252, ■ sample 2193) and quartz (■ sample 2193). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
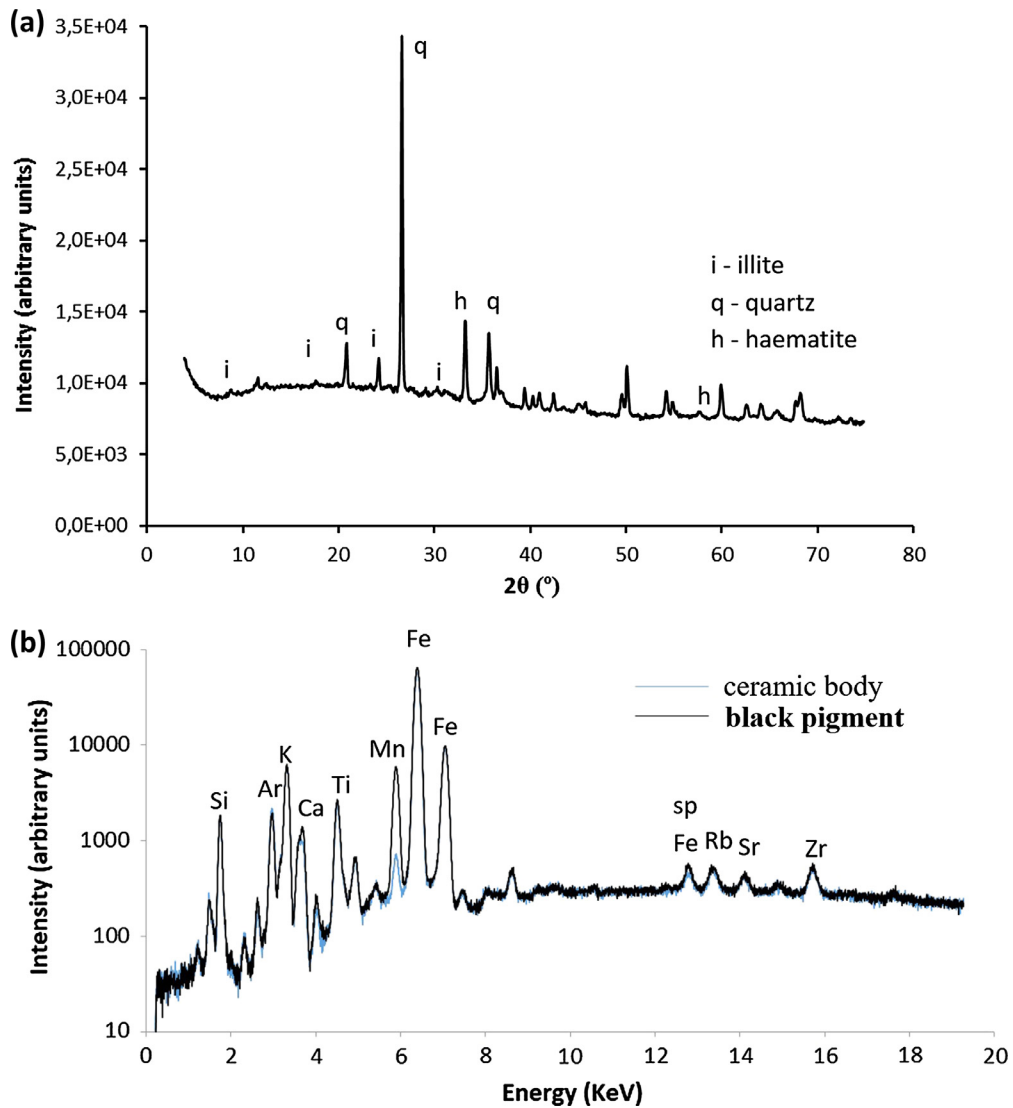

Fig. 6. (a) Micro-diffractogram of the black pigment (sample 2176) and (b) XRF spectrum of the black pigment (sample 2212).

3.2. Black pigment

Despite some local conservation problems, under stereomicroscopic observation the black pigment shows a homogeneous texture suggesting that the pigment application technique adopted was quite efficient and allowed a uniform coating of the ceramic surface. The μXRD analysis, performed on microscopic samples detached from the black decoration and in shards, revealed the presence of quartz as a major phase, with haematite and illite as minor components (Fig. 6a). Therefore, none black pigment was identified by μXRD.

XRF spectra of the black painted surfaces revealed Fe and Mn as abundant elements with higher concentrations of Mn in comparison with the ceramic clay body (Fig. 6b). The high Mn concentrations suggest that the black pigment in decorated Garvão ceramics was obtained using Mn oxides. All the other elements have similar concentrations as the ceramic body and must be attributed to the ceramic natural clay raw material.

VP-SEM-EDS compositional maps from the ceramic paste and the areas painted with black pigment (Fig. 7a) show clearly that Mn is associated with the black colour. At higher magnifications the painted area appears heterogeneous and made up by a mixture
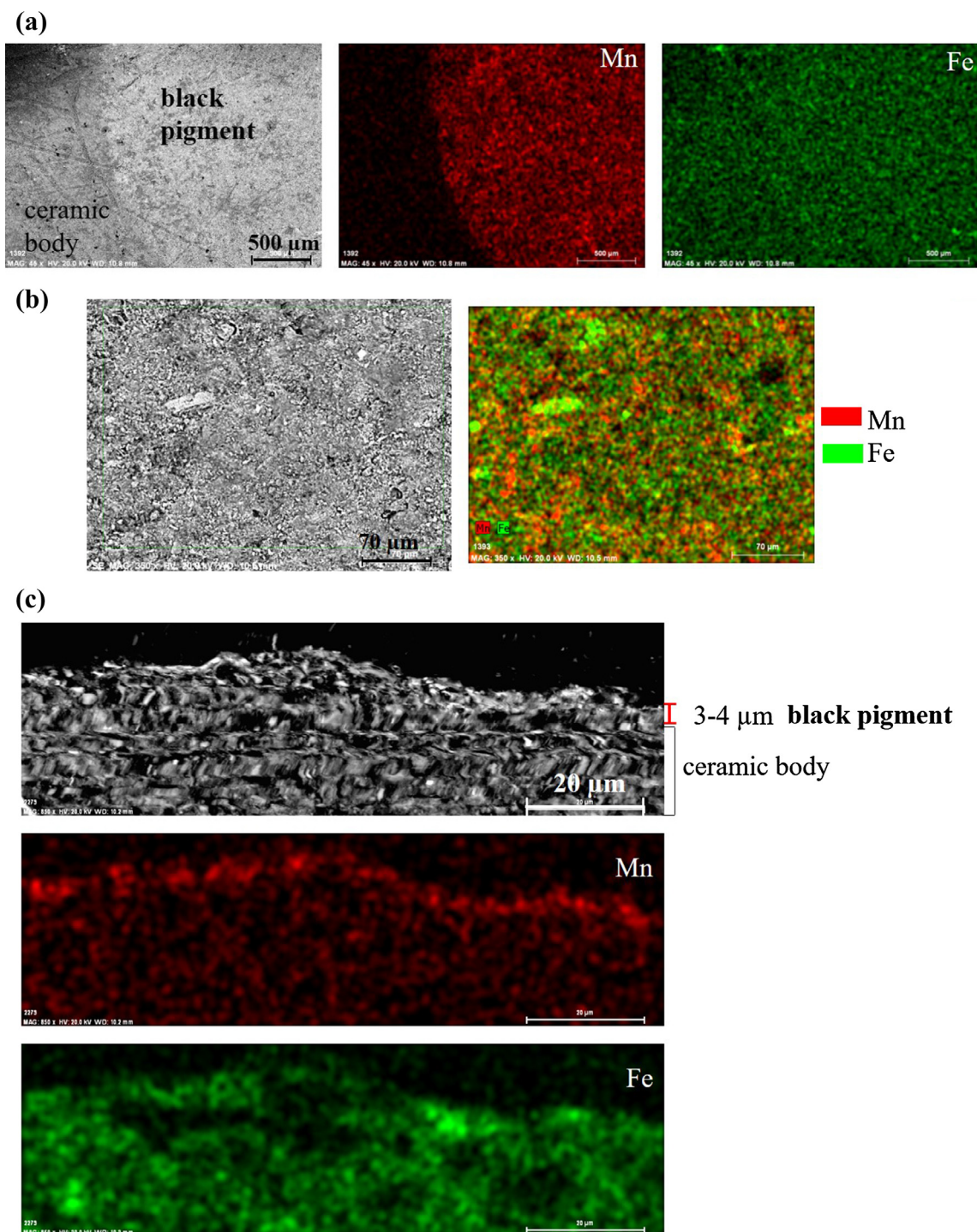

Fig. 7. (a) VP-SEM-EDS elemental map of the black pigment and paste surface of the sample 2212; (b) a detail of the black pigment in the same sample and (c) SEM-EDS elemental map on thin section (sample 2212).

of Fe and of micrometric tiny Mn particles (Fig. 7b). In thin section (Fig. 7c), it is possible to see that the layer of the black pigment is very thin (3–4 μm) when compared with the red pigment. Therefore, the elemental analyses by SEM-EDS confirm the results obtained by XRF and it is possible to sustain that in the black decorations a Mn black pigment was used. Nevertheless, the μXRD does not show the presence of any manganese crystalline phase.

The broad bands at 217, 283, 398, 603, 660 and 1308 cm^{-1} in the micro-Raman spectrum of the red coloured particle in black surface (Fig. 8) indicate the presence of haematite [17–19]. The presence of a broader band at around 660 cm^{-1} can also be assigned to residual magnetite [21–24]. But more important, the Raman spectra of the black particles (Fig. 8) show a broad band at 634 cm^{-1} that can be attributed to pyrolusite [26].

The assignments attributed for the Mn-O stretching vibrations are controversial. The ranges expected are between 600 and 750 cm^{-1} and the position of the characteristic band of bixbyte is reported at 592 cm^{-1} [27]. However, this band has also been reported at 680 cm^{-1} with three major features for pyrolusite at 500–510, 575–580 and 630–640 cm^{-1} [26]. The identification of Mn-containing compounds by Raman spectroscopy is indeed difficult because these compounds are known to be sensitive to laser-induced thermal decomposition [18,28]. Actually, some difficulties in the identification of the iron and manganese oxides must be associated with the structural complexity of these compounds, sometimes involving solid solutions, or their frequent intermixing with similar iron and chromium compounds [18].

Therefore, the association of Mn with the black colour was demonstrated by XRF and SEM-EDS. The impossibility to detect any Mn phase by XRD means that these compounds are not crystalline or its concentration is below the detection limit of this technique. Since the vibrational spectrum depends mainly on short-range order, micro-Raman spectroscopy allows us to identify a compound with similar molecular structure of pyrolusite, often associated with haematite, quartz and residual magnetite.

To reach a black colour, carbon- and iron-based black pigments require firing in a reducing atmosphere, while the colour of manganese pigments is independent of the firing atmosphere [28]. Pyrolusite (MnO_2), bixbyte (Mn_2O_3), and hausmannite (Mn_3O_4) mineral phases were described as stoichiometric manganese oxides. Pyrolusite transforms into bixbyte at 500 °C and the latter is stable until approximately 800 °C. At higher temperatures (900–1000 °C) bixbyte reacts with haematite to form jacobsite [$MnFe_2O_4$] [27]. However, it is impossible to estimate the firing temperature, since information about the composition of the original Mn-containing ores would be needed.

The proximity of the Iberian Pyrite Belt, well known for its manganese ore deposits [29] is consentaneous with a regional source of this Mn-rich black pigment. In this important mining region, pyrolusite is major component in the mineralogy of Mn deposits [30].

3.3. White pigment

The observation of the white pigment under stereomicroscope shows that it is constituted by small white crystals. The painting layer is quite fragile and sometimes the surface layer of the ceramics is not uniform (Fig. 9a).

Several crystalline phases have been indicated as main mineral components of white pigments found in ancient ceramics: kaolinite [15,31], aluminium oxide [11], carbonates [1,32], hydroxyapatite [33], Ca and Ca-Mg rich clays [34,35]. The use of a mixture of illite and silicon oxide was reported as a white pigment on painted ceramics excavated from the Yangqiaopan Tombs of the late Western Han Dynasty, China [36].

In Garvao, the mineralogical composition of the white pigment as obtained by μXRD shows, the predominance of quartz and the presence of illite (Fig. 9a). In this case, XRF proved to be inefficient in providing a chemical signature of the white pigment and to distinguish it from the bulk ceramic. The XRF spectra in the white pigment contains relatively higher amounts of K and some Al, Cl and Ca compared to the ceramic substrate. Fe, Si, Al, Ti, Mn, Rb, Sr and Zr were found to be present both in the ceramic and in the pigment (Fig. 9b). The presence of Cl and Ca can be attributed to the burial environment. In fact, in some samples white salt deposits are visible on the surface of the fragments and SEM-EDS analyses identified particles of halite and gypsum, consistent with the presence of Ca, S and Cl observed by XRF.

The VP-SEM-EDS elemental maps obtained in the white decorated areas, allows us to check the distribution of the chemical elements. The pigment seems to be depleted in Fe and enriched in K, Al and Si (Fig. 10a) supporting the weak XRF data. In thin section, the chemical distribution of the elements shows that the white
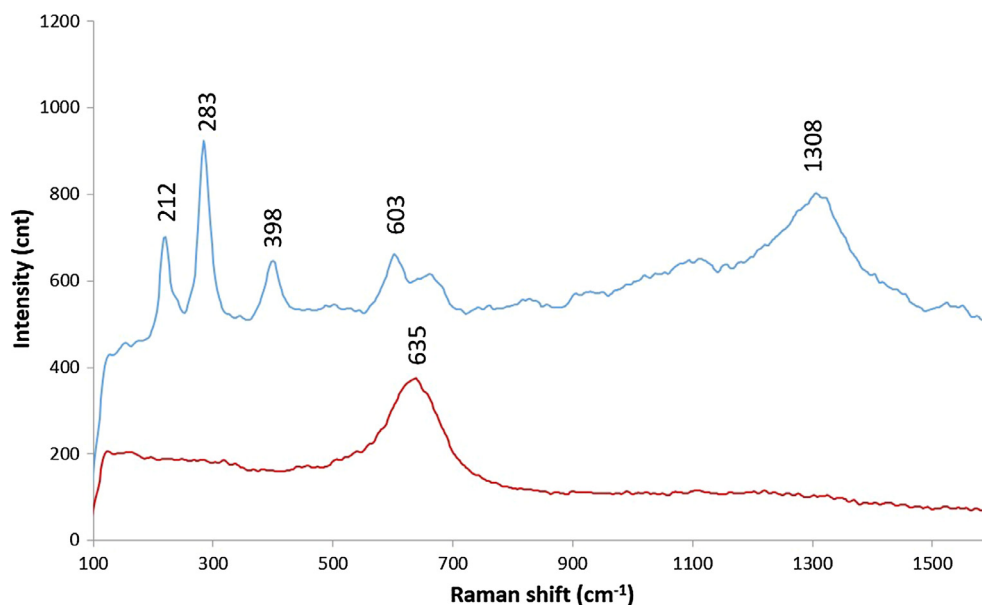

Fig. 8. Raman spectrum of black pigment (■ sample 2212) attributed to haematite with residual magnetite and to ■ pyrolusite.
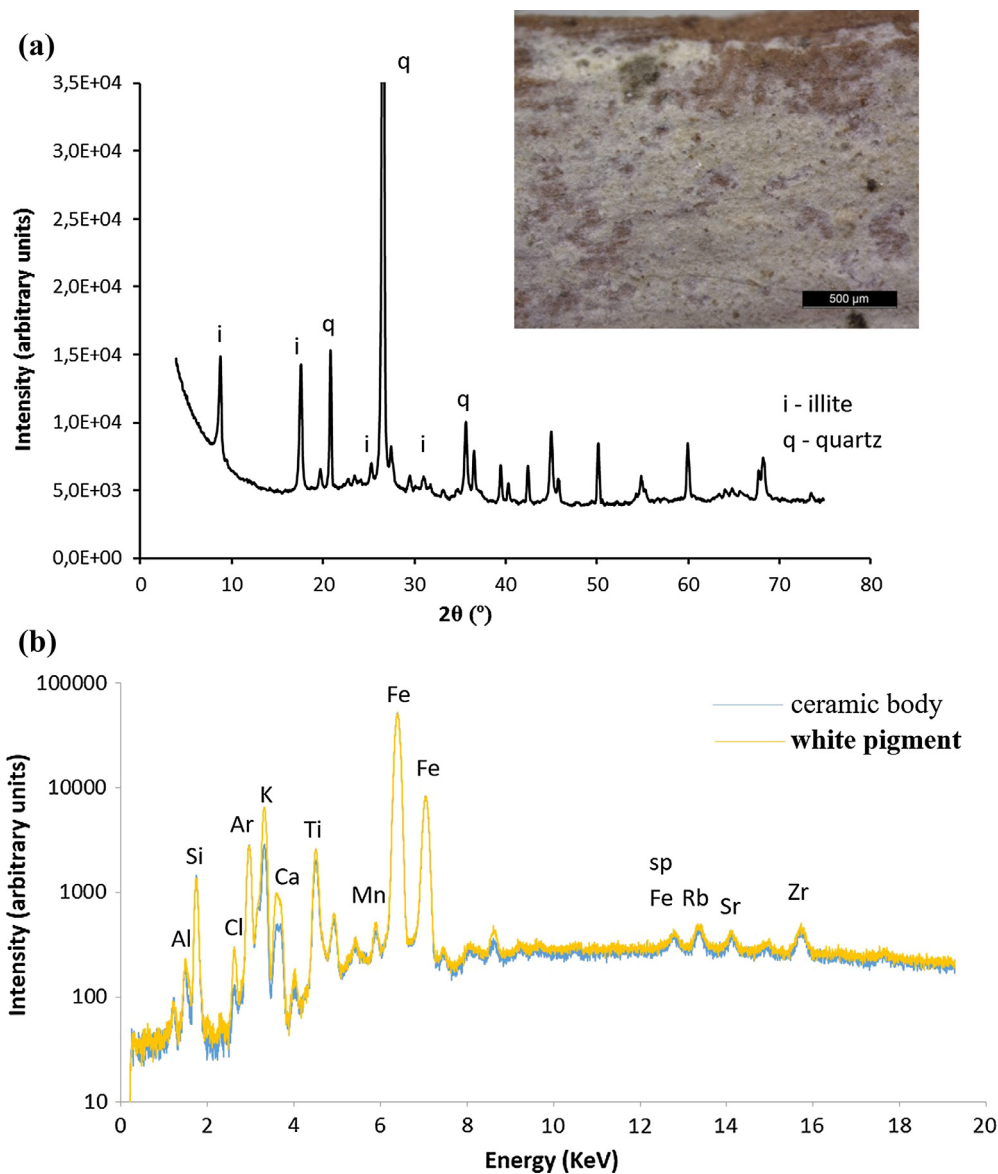
Fig. 9. (a) White pigment under stereomicroscope and micro-diffractogram of the white pigment (sample 2291) and (b) XRF spectrum of the white pigment (sample 2193).

pigment layer is thicker when compared with red and black pigments (Fig. 10b). The superficial enrichment in K is evident.

Raman spectra of the white pigment reveal the presence of quartz, anatase and rutile (Fig. 11). The very intense Raman band around 142 cm^{-1} together with others (194 cm^{-1}, 391 cm^{-1}, 511 cm^{-1} and 634 cm^{-1}) can be attributed to the vibrational modes of the anatase structure [15,28,31,37]. There is also rutile in the white pigment, as evidenced by the presence of characteristic Raman bands of this TiO$_2$ polymorph at 442 and 605 cm^{-1} [9,15,31,37]. As only small amounts of anatase and rutile was detected and there are not enrichment in Ti detected by XRF or SEM-EDS, they are a part of the clay raw material composition and are not responsible by the white colour.

Therefore, on Garvão Iron Age votive deposit, illite was the white pigment used. This statement is based on the μXRD data and in the pigment enrichment in K detected by XRF and SEM-EDS. Illite is a very weak Raman scatterer, so the technique lacks sensitivity to this material. The associated minerals anatase and rutile, on the other hand, are very good Raman scatterers and tend to overwhelm the spectrum of illite by several orders of magni-

tude. They are the most common crystalline forms of TiO$_2$ and occur in nature as minerals [9] and may remain as residual phases in clays [28,31]. It was reported that the presence of anatase can mask the Raman bands of clay minerals due the intense Raman bands given by the strongly covalent Ti—O bonds [28].

Some authors investigated the composition of white pigments used in decorated ancient pottery and concluded that the pigments used for white coating was only anatase and they propose the possibility of the application of the coating after firing because anatase would change into rutile at higher temperatures [i.e. 38]. Otherwise, the analyses of the white pigments in pre-Columbian estucado ceramics shows that the anatase has not been used by itself as a pigment but it is instead present as an impurity in the white clay used as pigment [15]. In the case of the pigment from Garvão's archaeological site, the presence of natural anatase and rutile in the white pigment was detected via Raman analysis but the content of Ti obtained by XRF and SEM-EDS is low and therefore, insufficient to justify the white colour. The presence of rutile and anatase must be attributed to a mineralogical impurity in the white pigment.
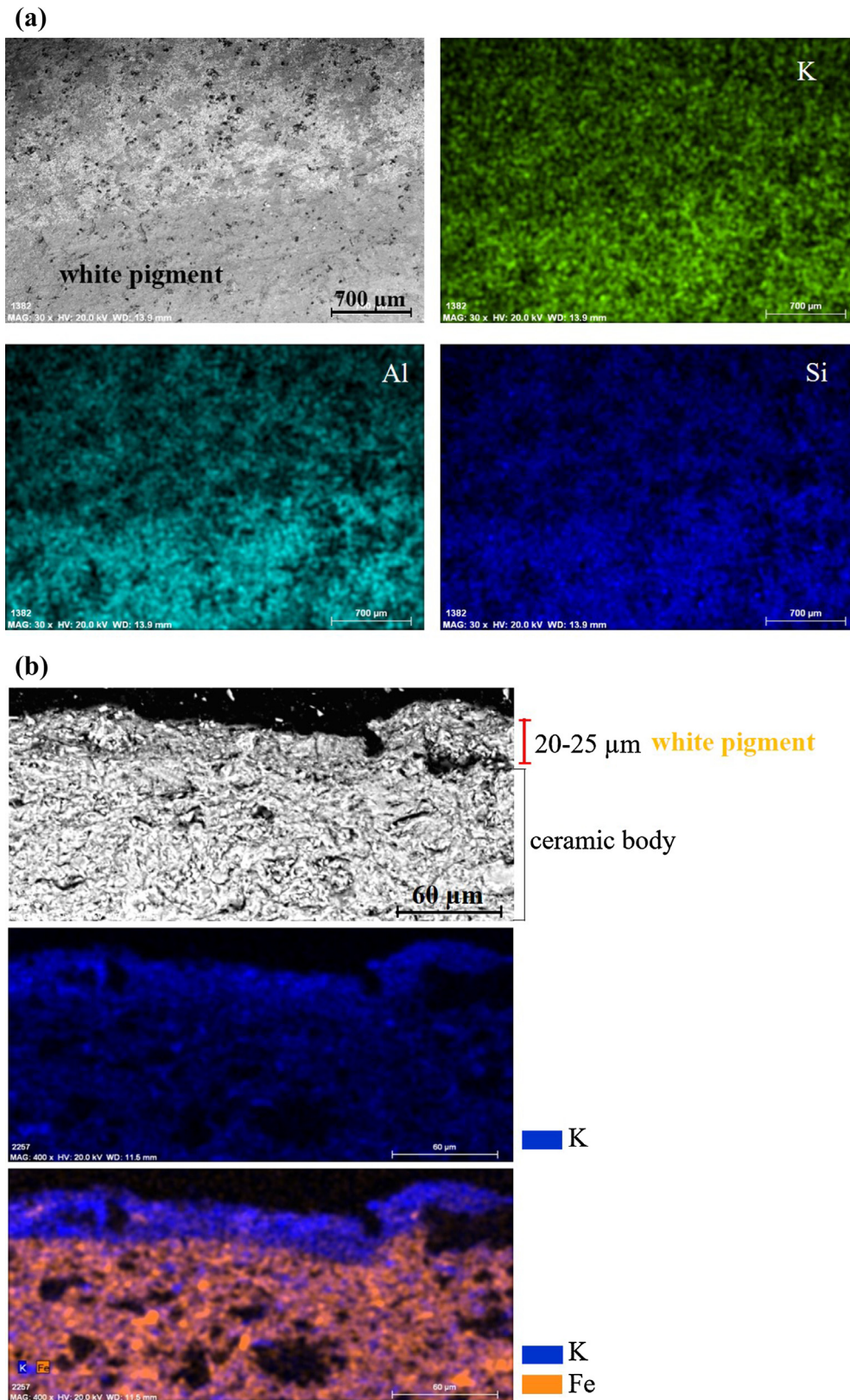
(a)

(b)

Fig. 10. (a) SEM-EDS elemental map of surface of small shards. The area comprises white pigment and bulk ceramic (sample 2236) and (b) SEM-EDS elemental map on thin section (sample 2291).

This quite unique pigment can be found in low grade metamorphic rocks that are common in southern Portugal geology. This seems to indicate a quite isolated society with no access to more efficient raw materials to be used as white pigments. It must be underlined that sources of carbonates can be found at less than 100 km and that kaolinite is a common mineral in the north of Por-
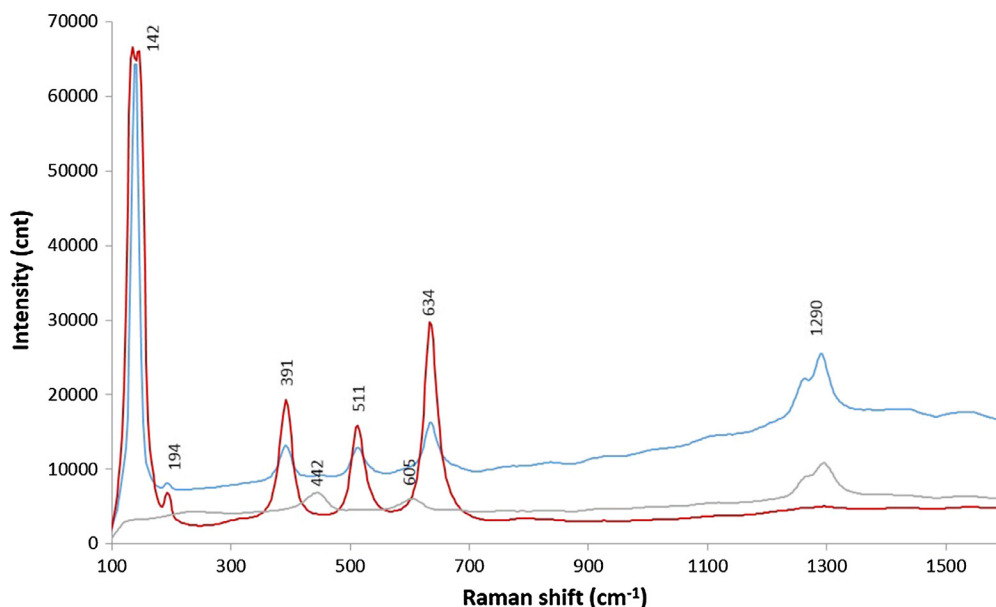
Fig. 11. Raman spectrum of white pigment (sample 2193) atributed to ■■ anatase and to ■ rutile.

tugal, associated to the weathering of granites or to small sedimentary deposits.

4. Conclusion

The combination of several complementary analytical techniques has proved essential to investigate the mineralogical and chemical composition of the pigments used to decorate the pottery artefacts from the Garvão site. μXRD and Raman spectroscopy together with VP-SEM-EDS and XRF show great potential for the study of pigments, for their identification and therefore to understand the technology used in ancient historical contexts, as is the case of Garvão during the Iberian Iron Age.

The presence of haematite, clay and quartz identified by μXRD and Raman spectroscopy, and the abundance of iron detected mainly by SEM-EDS but also by in-situ XRF, are strong evidence that the red colour was obtained using ochre pigments. The presence of haematite suggests oxidizing conditions during firing. The darkening of the red was obtained adding accidentally or intentionally Mn compounds and it was not an effect of a reducing kiln atmosphere.

The identification of Mn-containing compounds by X-ray diffraction is sometimes problematic because of their amorphous nature. Therefore, XRD experiments performed in the black decoration did not reveal the presence of manganese compounds. On the other hand, the combination of XRF and SEM-EDS with Raman spectroscopy allowed us to identify the presence of pyrolusite-like (MnO_2) compounds as amorphous phase in the black decorations. The combination of these techniques is therefore important to overcome the difficulties which are normally encountered in the analysis of black and brown manganese-containing compounds. The combination of all techniques showed also the presence of aluminosilicates, quartz, albite and iron oxides (haematite and magnetite) as contaminants in the black pigment.

XRF is unable to provide a chemical signature of the white pigments and to distinguish it from the paste, and μRaman did not identify any chromophore phase. On the other hand, SEM-EDS analysis showed that this colour is attained by a white clay material. The abundance of potassium, aluminium and silicon make

illite a very probable choice. This hypothesis was confirmed by μXRD. The use of a single technique, such as Raman spectroscopy, can erroneously identify the white pigment as anatase or rutile.

The technology involved in the application of pigments in archaeological pottery is one of the most interesting aspects of ancient ceramic processing. In this case study, the application of paintings on the surface of the vessels was carried out at the end of the drying phase, before firing as shown in the cross-section microscopy data. The results obtained revealed that these ceramics achieved firing maximum temperatures lower than about 950 °C under oxidizing conditions. The very residual presence of magnetite (Fe_3O_4) in the red hematite (Fe_2O_3) pigment indicate oxidizing firing conditions and that firing temperature would not be high enough to convert hematite into magnetite, that should happen at 950–1250 °C [38]. The main contribution of pyrolusite (MnO_2) to the black pigment validates also the oxidizing firing conditions. The presence of illite clay mineral as white pigment and the absence of cristobalite and mullite indicate a firing temperature under 1000 °C. Actually, at this temperature it is expected that all phyllosilicates including muscovite are lost and spinel are formed, followed by mullite and cristobalite [39].

The raw material for the red paint derives probably from iron oxides from local ochre associated to weathering of sulphides ores or iron-rich clay deposits. For the black paint the raw materials used contain iron and manganese oxides. This kind of materials is commonly associated with the nearby exhalative deposits associated with submarine volcanic rocks in the Iberian Pyrite belt [29]. In the case of the white paint the raw material source is probably an illite-rich clay metamorphic rock as slates. Therefore, all the pigments can be found near the Garvão religious centre and this tends to suggest a regional production of the decorated offerings that were examined in this study.

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