Journal of
RAMAN
SPECTROSCOPY

Received: 14 April 2011 Revised: 10 June 2011 Accepted: 11 June 2011

(wileyonlinelibrary.com) DOI 10.1002/jrs.3030

Raman Microspectroscopic study of Iberian pottery from the *La Vispesa* archaeological site, Spain

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Raman microspectroscopy has been employed for the characterization of 16 samples of ancient Iberian pottery. These sherds of vessels were found in the archaeological site of *La Vispesa* in *Tamarite de Litera* (Huesca, Spain) and correspond to the Iberian time. The composition of certain mineral phases such as non-plastic inclusions has been particularly considered with a view to obtaining information on the source materials and their provenance, as well as the technological conditions of ceramic production. Typical minerals such as calcite and quartz were found in most of the samples. The presence of anatase in a group of the samples suggested the use of different clays in the production of the vessels. Furthermore, the absence of rutile in these samples, together with the identification of calcite, is indicative of a mild firing temperature. Hematite was identified in all samples, both in the ceramic body and in the decoration. Differences in the position of the bands and relative intensities characterized hematite in terms of crystallinity and origin. An attempt to assign the samples to different production centers was made according to their chemical composition and morphology. Copyright © 2011 John Wiley & Sons, Ltd.

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Keywords: Iberian pottery; Raman microscopy; archaeometry; firing conditions; hematite

Introduction

Pottery is one of the oldest human technologies and art forms, and its remains can reveal much about the culture and lifestyle of previous civilizations. For this reason, it constitutes an interesting area of investigation in archaeology.[1] In terms of features and function, most antique ceramics can be divided into three general categories: the transport *amphorae* and storage vessels, *doliae*; the cooking ware, pots, casseroles, lids, plates; and fine-ware, that is mostly employed as drinking vessels or for serving liquids and foods. The last were often treated with a fine slip and brush-decorated. Apart from the utilitarian functions, pottery can be used for sociopolitical and ritual purposes and as prestige objects to display success or power.[2]

Among the issues addressed by archeologists in the study of pottery are the provenance of raw materials for the ceramics and the fabrication processes. Answers to these items require first analyses of the materials that make up the pots, as well as the ability to relate such analyses to the raw materials that might have been used in the production.[3,4] Provenance studies of ceramic materials can be aided by determining the mineral phases presents in sherds excavated from an archaeological site; this allows discrimination of locally produced objects from imported wares and getting information on trade routes and relations concerning the excavation site.[5] Moreover, it is also important to recognize similarities and differences among pots that might have been fabricated from similar materials using similar techniques.

Furthermore, the knowledge of the fabrication conditions of ancient ceramics, such as firing temperature, is of interest because it provides information on the performance of the kilns used in their manufacture and on the technological capabilities of the potters. A good estimation of the firing temperature can be obtained from thermal expansion measurements of the ceramics.[6,7] The analysis of the mineralogical phases can also provide information about the transformations experienced by some minerals, which can be indicative of the conditions of the firing process, i.e. atmosphere and temperature.[8,9] In this way, both technological and provenance information can be obtained.[10]

When studying archaeological artifacts, it is mandatory to protect them from damage, and in this sense Raman spectroscopy is becoming increasingly important in heritage studies because the measurement can be performed without any contact with the studied object.[11,12] The coupling of the Raman spectrometer with an optical microscope allows the nondestructive examination of molecular species with a good spatial resolution.[13] Furthermore, a remarkable benefit of Raman microspectroscopy is the possibility to investigate objects without tedious sample preparations.[14] This technique has been demonstrated as a particularly useful tool for the characterization of ceramics even when the characterization of this kind of objects is complicated due to the heterogeneity of the samples.[15–19] Raman spectroscopy can provide useful information about the presence of different crystalline and amorphous phases, as well as distinguishing between the polymorphs.[20]

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The mineralogical changes induced by the firing during the production can be investigated using Raman spectroscopy too.[21] In fact, the results obtained by Raman spectroscopy are in agreement with those obtained from thermal expansion measurements on different types of ceramics. The conclusions proved that the Raman technique could be an alternative, fast, and easy way to estimate the composition and structure of such ceramics.[22–24] Furthermore, infrared spectroscopy can aid in the identification of clay and carbonate structures, helping in the assessment of firing conditions.[25]

This research is aimed at the study of the materials used for the wares' body and decoration of some Iberian pottery specimens recovered in the archaeological site of *La Vispesa* (Fig. S1, Supporting Information). The *oppidum* of *La Vispesa*, (*Tamarite de Litera*, Huesca, Spain)[26,27] has been recently declared as an Interesting Cultural Item (BIC).[28] *La Vispesa* is located on a small hill 320 m high, on the left side of the Ebro River in the oriental foothills of the junction of the Alcanadre and Segre rivers.

According to the stratigraphy and the archaeological materials found in the successive excavations between 1984 and 2002,[26,29,30] five occupations that overlapped on the site have been differentiated until 2nd century AD when it was definitely abandoned. Only three of these occupations conserve architectural remains, which were consolidated years ago.[26] The first Iberian settlement on the hill took place between the end of 4th and 3rd century BC,[30] overlapping with the earliest occupation in Iron Age Urnfield Period (4–5th century BC). Dating of this first Iberian settlement is based on the presence of Attic and Protocampanian pottery together with the discovery of two Carthaginian coins among a wide collection of regional and local pottery. The excavations in this *oppidum* have revealed Iberian quadrangular houses up to 30 m^2 with adobe walls and supported by foundation stones. No interior partition walls were found even when different uses were recognized by the remains, namely textile activities, food transformation, and storages. The access to the domestic areas was through a paved street with sandstone flagstones, well identified on the Northern side sector of the hill and which connected the housing. The communication between the different terraces was through stairs or ramps. In conclusion, it is a town planning marked by a road network following the direction and slope of the contour lines, making easier access to the household as well as the drainage of waste water.[31] The second Iberian period, which constitutes the maximum height of the village, matches with the Romanization process. This period can be identified by some objects dated between the last years of the 3rd century and the last quarter of 2nd century BC, mainly Hellenistic black varnish pottery, Greco-Italic and Dressel I *amphorae*.[32] This imported ceramic appeared together with local and regional productions, such as Ilergetian red varnish pottery and Iberian grey ceramic. However, the overwhelming majority of the vessels of this period are the Iberian coarse and fine decorated ware, such as the sherds investigated in this work.

Experimental

Materials

Sixteen different sherds of vessels retrieved in excavations from *La Vispesa* were analyzed. The selected sherds were found in houses excavated both in the Western sector of the hill (S2, S3, S4, S12, S13, S15, and S16) and in the Northern side sector (S1, S5, S6, S7, S8, S9, S10, S11, S14). Specimens were in the form of medium to small fragments (4–6 cm width). Figure 1 shows how the ceramic bodies varied in color from reddish to creamy. Generally, pastes are compact and refined, with small reddish-orange inclusions. Three of the samples show a sandwich-type cross section (S11, S12, and S15) with a grey central core. All samples were decorated with geometric forms such as bands, lines, concentric circles, and ribs of various shades in brownish-red colors.

Figure 1. Sherds of Iberian pottery from *La Vispesa* (*Tamarite de Litera*, Huesca, Spain).

Instrumentation and procedure

Raman spectra were obtained with a Renishaw (in Via Reflex) spectrometer equipped with a Peltier-cooled CCD detector coupled to a Leika confocal microscope. The 520.7 cm^{-1} peak of a silicon standard was employed for calibration. A 514-nm ion Ar laser with maximum power of 20 mW was used as the excitation source. A color television camera attached to the microscope allowed the visual inspection of the samples and the selection of the sample areas from which to collect the Raman spectra. The samples were analyzed without any preliminary preparation except for placing them under the microscope objective (×50). The laser power was always kept below 2 mW in order to avoid thermal degradation. Measurements were carried out on the decoration, the surface without the decoration, and the inner body. A range of spectra were collected from different spots on each sample.

Infrared spectra of the samples were recorded with a Bruker Tensor 27 Fourier transform infrared spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. A horizontal DuraSamplIR single-reflection diamond attenuated total reflection (ATR) accessory (SensIR Technologies) with a torque-limited pressure applicator was employed. All spectra were recorded at 4 cm^{-1} resolution (128 scans). A spectrum of the clean and dry ATR crystal against air was used as background.

Principal component analysis was performed directly on the Raman spectra only with baseline correction using a toolbox from Eigenvector for Matlab.

Results and Discussion

The 16 ceramic specimens studied in this work correspond to *kalathoi* vessels that were used in the past for different purposes. Some of them were employed to collect, store, and transport honey and also other export goods such as lard and cereal.[33] They were classified in terms of the texture, color, finish, and paint, among other characteristics. Visual inspection under the microscope revealed a strong heterogeneity on a microscopic scale; samples were composed of grains of different sizes, shapes, and colors. The predominant colors were orange, red, and brown scattered over a pale background in the ceramic body. The decoration showed more intense red and brown colors. The sandwich cross sections were found in samples S11, S12, and S15. This type of structure can be due to firing under reducing conditions with an oxidizing cooling stage, or to firing organic matter-rich clays under oxidizing conditions.[34,35] Tables S1 and S2 (Supporting Information) summarize the minerals identified in all samples, together with the diagnostic bands employed for each case.

Phyllosilicates in general and clay minerals in particular are very weak Raman scatterers. Thus, the Raman spectra of the sherd matrix material were extremely weak, and it was difficult to assign the bands to specific clay minerals. Furthermore, a significant luminescence background was observed in most samples. In most cases, broad bands were observed in the region 600–750 cm^{-1} but they were difficult to assign. They may be attributed to highly disordered phases originating during the firing process.[36]

When focusing on inclusions of non-plastic phases, high-quality Raman spectra (Fig. 2) were acquired.

These minerals can be either naturally present as impurities in the initial clay, or were added purposely by the potters in order to strengthen the clay when still wet to prevent the walls from collapsing in on themselves.[2] Among the main Raman bands that appear in many samples are the characteristic band of α-quartz at 462 cm^{-1} and a medium intense band at 511 cm^{-1} that can be assigned to albite (Na-feldspar).[37] Calcite was also found in all the samples, with a narrow band at 1085 cm^{-1}. Decomposition of calcite is often considered irreversible, and the calcite impurity in ancient ceramics is used as a marker for the reconstruction of the firing conditions.[38] Although calcite starts to decompose at 600–700 °C, only firing temperatures above 900 °C make this process irreversible because the quicklime (CaO) formed by decomposition of calcite reacts with the amorphous phases resulting from the dehydroxylation of clays and calcium silicates are formed.[9] Thus, the presence of calcite could suggest that this pottery was fired at relatively low temperatures, around 850 °C. Similar firing temperatures have been proposed for other Celtiberian pottery productions from the Central Iberian's Chain.[39] However, taking into account the fact that sherds of ancient ceramics are stored in the earth for thousands years under ambient conditions, calcite could also be a result of a post-burial recarbonation process. Calcium silicates and aluminosilicates on storage in contact with water and CO_2 decompose and produce again $CaCO_3$.[8] In order to gain more information about the origin of calcite in the samples and the presence of calcium silicates, we have registered ATR-FTIR spectra of the samples. Infrared spectroscopy has been reported as a useful technique for materials analysis in ancient pottery and for the determination of firing temperatures.[25,40]

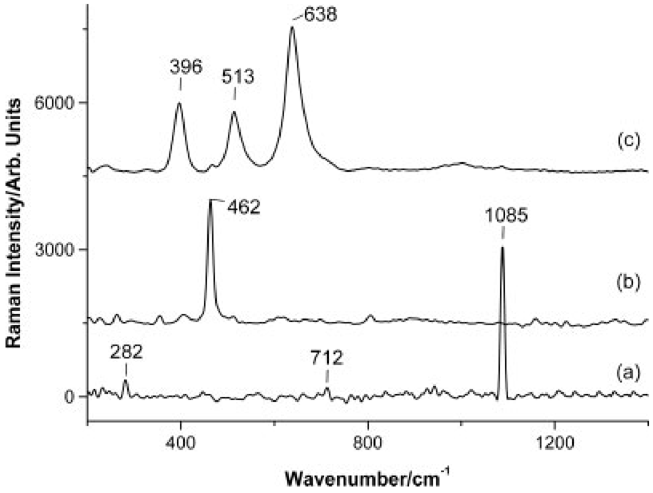

Figure 2. Typical Raman spectra of different mineral compounds found in the ceramic body of the samples: (a) sample S8, calcite; (b) sample S5, quartz; and (c) sample S10, anatase.

Figure 3 shows representative FTIR spectra of the samples in the range 1900–600 cm^{-1}. These spectra are characteristic of calcareous or slightly calcareous ceramics with strong Si–O vibrations in the region of 900–1100 cm^{-1} along with the typical bands of calcite, i.e. a sharp band at 875 cm^{-1} together vibrations in the region of 1420 cm^{-1}.[41] In the samples from *La Vispesa*, the region ~1420 cm^{-1} showed two different CO_3 stretching signatures. A few samples showed the band at lower wavenumbers (about 1400 cm^{-1}) with a sharp peak, which has been attributed to unheated calcite.[42] Furthermore, all samples presented a broad brand centered at 1440 cm^{-1}. This band is assigned to recarbonated calcite, characterized by a lower degree of crystallinity.[42] The presence of this type of calcite in all pottery samples confirms the hypothesis that the firing was above the calcite decarbonization temperature but below

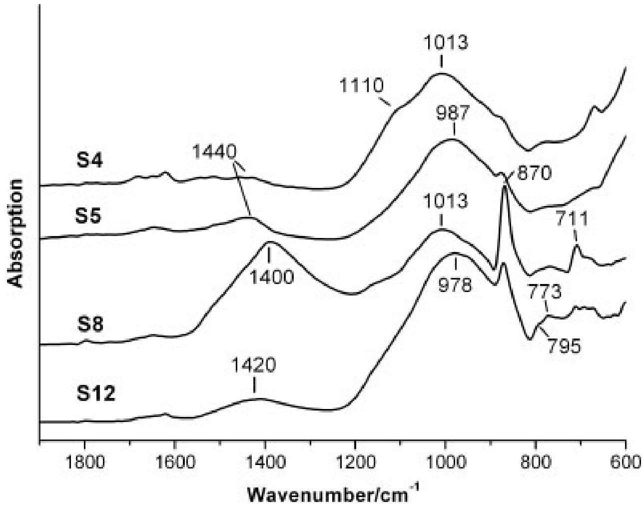

Figure 3. Typical ATR-FTIR spectra of some pottery samples.

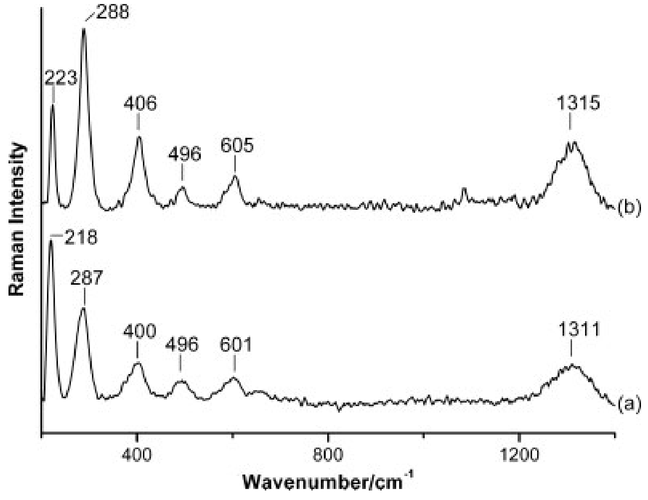

Figure 4. Raman spectra of different hematite samples in the (a) decoration and (b) ceramic body of sample S11.

the temperature that makes this process irreversible. Moreover, the presence of calcium silicate signatures in the FTIR spectrum cannot be completely disregarded, as firing minerals such as diopside, gehlenite, and wollastonite also give strong bands in the region 920–960 cm^{-1}.[41] The simultaneous presence of firing minerals and primary calcite suggests a firing temperature of about 850–900 °C.

In the ceramic body of four samples (S10, S11, S12, and S13), characteristic Raman bands of anatase (at 146, 395, 514, and 638 cm^{-1}) were detected (Fig. 2(c)). The presence of anatase (TiO_2) in this kind of samples must be attributed to mineralogical impurities in the clay body, suggesting the use of kaolinic clay.[43] However, no clear bands attributable to aluminosilicates could be detected, probably because those of anatase completely dominated the spectrum. The clear identification of this mineral in trace amounts is due to its exceptionally high Raman scattering cross section, in contrast to the weak signal produced by kaolinite.[44,45] It is frequent that stable and harder minerals, such as quartz and anatase among others, remain as residual phases in clays, which are essentially sedimentary. Such impurities as anatase, if identifiable, may be used as markers of the raw materials employed to make the pottery.[44] Furthermore, this phase of titanium oxide usually transforms into rutile between 800 and 1100 °C.[24] Thus, the fact that the high-temperature polymorph of TiO_2, i.e. rutile, was not detected in the Raman spectra of the fragments can be considered as a good marker of a firing temperature not exceeding 1100 °C.[36]

Raman spectra acquired on the ceramic body of all samples revealed the presence of hematite, one of the mineralogical phases most commonly found in reddish pottery. The red coloring of pastes is due to the presence of iron oxides, which always appear in the original earthen clays used in ceramic manufacturing.[36] In the decoration, hematite was also always identified as the main phase. This could point to the use of red ochre as a pigment in all the samples.[46] The presence of hematite (α-Fe_2O_3) is indicative of firing under oxidizing conditions. The hematite spectra recorded in the different samples showed differences in band positions and relative intensities, as can be seen in Fig. 4. The Raman spectrum of hematite is known to be very sensitive to different factors such as the size of the crystals and the imperfect stoichiometry of hematite due to lattice defects, for example, the presence of various metal ions replacing the iron atoms inside the oxide structure.[47–49]

In an attempt to clarify the origin of these differences, a principal component analysis was performed to investigate whether groupings or tendencies exist within the hematite spectra of the different samples. To do this, the exact position of the peaks at ~290, 410, 600, and 1330 cm^{-1}, as well as the relative intensity of the bands at 410, 600, and 1330 cm^{-1} with respect to the one at 290 cm^{-1}, was used as variables. A certain separation between the hematite present in the paste and the decoration was observed through the first principal component (54.24% of the variance). An exception occurred for the decoration of samples S2 and S15 whose spectral characteristics were more similar to those of the ceramic body. Leon *et al*.[50] have reported wavenumber upshifts and peak broadening for heated hematite. In our samples, the hematite bands in ceramic bodies are slightly shifted to higher wavenumbers in comparison to those of the pigments. Such differences in band position between body and decoration hematite could be related to different firing temperatures. An explanation would be a two-step firing process in which pottery was fired and then decorated and fired again at lower temperature. Other possible reasons, and may be more plausible for Iberian pottery, can be differences in the crystallinity of hematite present in the clay employed for the paste and that used for decorating, probably an enriched and purified material.

Furthermore, the spectra recorded in the decoration of some samples (S2, S5, S13, and S16) revealed two bands at 667 and 730 cm^{-1}, which can be attributed to maghemite (γ-Fe_2O_3). These samples were characterized by a dark red or brownish decoration. The presence of maghemite can be attributed to an atmosphere with low oxygen content, which prevented the development of hematite. However, the use of a long reducing atmosphere should result in a grey to blackish color in the ceramic, which is not the case. Thus, the presence of maghemite suggests the use of a reducing atmosphere during a short stage in the firing in the case of these samples.[51] Nevertheless, the attribution of the bands around 670 cm^{-1} is not completely clarified in the literature. For example, other authors propose that it can be associated with the recrystallization of hematite, which occurs when firing under oxidizing conditions above 750–850 °C depending on the nature of clay.[50]

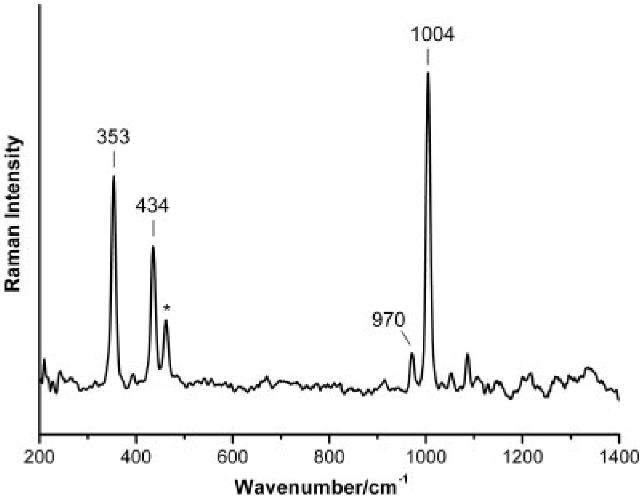

Figure 5. Raman spectra of zircon in sample S16. The asterisk indicates the characteristic band of quartz.

One of the samples (S16) showed a very different decoration pattern with grey stripes alternating with red ones. The red pigment was identified as hematite like in the rest of the samples. In the grey zone, it was difficult to obtain good quality spectra, although the characteristic band of quartz could be identified. Furthermore, narrow and intense Raman bands at 353, 434, 970, and 1004 cm^{-1} were recorded when focusing on the dark crystals (Fig. 5). These bands can be assigned to zircon ($ZrSiO_4$).[52] This is a common accessory mineral in all types of igneous rocks and detrital deposits derived from these rocks, which is especially frequent in the more silica-rich types of igneous rocks such as granite. As already mentioned for anatase, zircon is a strong Raman scatterer, and it can be easily identified despite being a minor component.

Finally, an attempt to classify different pottery groups considering several aspects such as ceramic typology, pictorial style, and results from the spectroscopic characterization was performed; in particular, we were interested in validating and clarifying archaeological hypothesis based on a simple visual examination of ceramic objects. Thus, we associated the samples examined within the frame of the reported study with different potteries. From the results of this association, samples with anatase in their pastes could have been produced using the same type of clay. Samples with maghemite in their decoration must have suffered a lack of oxygen during firing. Samples S15 and S16 are different from the rest, considering visual aspects of ceramic body and paste. Furthermore, S16 is unique, not only in its appearance but also in its chemical composition, being the only sample that contains zircon.

Conclusions

These spectroscopic analyses constitute the first attempt to characterize Iberian pottery from the *La Vispesa* Spanish archeological site. Raman microspectroscopy was demonstrated as a useful tool to investigate the pigments and crystalline inclusions of different minerals in the ceramic pastes. Information about the firing conditions was obtained through the identification of minerals such as calcite, anatase, and hematite. The presence of calcite and the absence of rutile in samples containing anatase suggest a milder firing temperature not higher than 900 °C. Furthermore, the widespread presence of hematite is indicative of an oxidizing atmosphere in most cases. Finally, some mineral impurities such as anatase or zircon can be used as provenance markers for the clays. Taking into account all these findings, samples were tentatively grouped in two different production potteries, three samples being particularly different from the rest.

Acknowledgements

The Supporting Research Program of the University of Jaen is acknowledged for the use of instrumentation of the CICT. Research group FQM363 supported this work through the Project Campus of International Excellence in Cultural and Natural Heritage. Research Group OAAP (248-52 DGA-Zaragoza) is also acknowledged. Archaeological materials, which are actually deposited in the Provincial Museum of Huesca, have been provided by the Department of Antiquity Sciences, University of Zaragoza.

Supporting information

Supporting information may be found in the online version of this article.

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