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CHEMICAL CHARACTERIZATION VIA PXRF OF EARLY IRON AGE POTTERY FROM SW IBERIA

ABSTRACT
The main aim of this paper is to present the results of archaeometric analyses of Tartessian pottery recently undertaken in the Lower Guadalquivir region (western Andalusia, Spain). A non-invasive portable X-ray fluorescence spectrometer (pXRF) has been used to determine the chemical composition of pottery from seven archeological sites dated to the Early Iron Age. The purpose of this research was to create a database of Tartessian pottery in order to establish the provenance of the ceramics. The method adopted to categorize pottery based on differences in its chemical composition was the potassium-titanium test and principal component analysis. It was possible to establish three groups of wheel-made pottery according to their provenance.

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INTRODUCTION

Our current knowledge about the chemical characteristics of pottery in the south-western part of the Iberian Peninsula at the beginning of the Iron Age is unsatisfactory. Most research in this field has been piecemeal, using a variety of different methods and scientific equipment. This is a clear consequence of the recent and rapid development of archaeometric techniques in pottery studies, aimed at recording microstructural and compositional information (Hunt & Speakman, 2015).

Still, this type of evidence is crucial for interpreting the technological process in pottery production, and also for establishing the provenance of the analysed artefacts. There is no doubt that by helping to distinguish local products from imported ceramics, and by pinpointing different production centres in the region, archaeometric studies can further our understanding of the cultural process conventionally referred to as “Orientalization” in the western Mediterranean.

This paper presents results from recent research conducted on ceramic material from the Los Alcores plateau (Fig. 1). The pottery is dated to the Early Iron Age and was excavated mainly by George Bonsor at the beginning of the 20th century. Unfortunately most of it is lacking detailed and reliable information about the precise archeological context. However, in many cases, this is the only archeological material available for study, as no other excavations were undertaken in the 20th or 21st centuries at the relevant sites. Pottery from excavations carried out in the ’70s and ’80s of the 20th century in Setefilla and in Campo de las Canteras is also included in this study. Remains of pottery kilns or misfired ceramics with which to compare the results and identify local production were not available for analysis. The sampled material was carefully selected, based on its typological features and its representativeness for Tartessian material culture. Analyses were conducted using a handheld XRF, with the aim of characterizing the chemical composition of the pottery and helping to identify their place of production. The main reference site with which to compare the results from the Los Alcores sites is Setefilla, located on the right bank of the Guadalquivir river, about 20 km to the NE of the northern part of the Los Alcores plateau. It is the closest site to Los Alcores from which results of chemical and petrographic pottery analyses are available for comparison (Bartkowiak and Krueger, 2015).
MATERIAL AND METHODS

At the recording stage in the museums of Andalusia, the proper selection of ceramic material from Tartessian sites in some instances proved problematic, as the material was fragmented and not always representative of the beginnings of the Early Iron Age. Sixty-three artefacts were selected from ten archaeological sites: El Campo de las Canteras (13 samples), La Cruz del Negro (19 samples), Setefilla (12 samples), Ranilla (2 samples), Túmulo de los Vientos (1 sample), Cristo de la Sedia (3 samples), Entremalo (3 samples), Gandul (3 samples), Bencarrón (1 sample) El Alcaudete (2 samples) and Huerta Cabello (3 samples). El Campo de las Canteras and La Cruz del Negro are two different archaeological sites, but both cemeteries relate to the Tartessian settlement under the urban centre of modern-day Carmona, in whose suburbs they are located. Eight of the aforementioned sites have contributed no more than three samples each to the present study, which is why the analytical data from these samples cannot necessarily be considered representative for the relevant sites. However, the data published in this study constitutes the first attempt to determine the chemical composition of ceramic artefacts from the Los Alcores plateau and from Setefilla, an important Tartessian centre on the right bank of the Guadalquivir river.

Mainly undiagnostic potsherds were analysed (the clear exception were the amphorae from La Cruz del Negro with complete profile). However, in some cases it was possible to recognize the form of a vessel.

The sampling strategy aimed at choosing technologically diverse ceramic material. The results of the previous study (Bartkowiak and Krueger, 2015) showed a significant correlation between techniques of manufacture and chemical results. For this reason wheel-made and hand-made pottery were studied separately.

The chemical composition of all samples was studied by means of a portable X-ray fluorescence spectrometer Bruker Tracer III SD. Measurement conditions were 15 kV and 25 µA, and acquisition time was 15 s per analysis. The measurements were done with the help of a vacuum pump and their accuracy was verified by means of comparison with a test piece of known chemical composition. The sampling strategy consisted in taking measurements from both the external and internal surface. Where possible, pXRF readings were also taken on a broken edge. However, for the present study only external measurements have been selected: normally two readings were taken at different points of a flat surface of the sherd. The surface of the artefact was cleaned prior to analysis, so the surfaces were free of any visible dirt. The distance between detector and sample was equal for all readings. MajMudRock calibration, provided by the manufacturer of the device, was used during the analyses. With the results obtained from these measurements, it was possible to detect 15 elements: Mg, Al, Si, P, K, Ca, Ti, V, Cr, Mn, Fe, Co, Cu, Zn, Ba. Two values of each chemical element were averaged and their intensity was estimated. Previous experimental research showed that the lowest statistical measurement uncertainties are achieved for: Al, Si, P, K, Ca, Ti, V, Cr, Fe, Ba. For the statistical treatment of the data, P and Ba were excluded, as they are known to be affected by post-depositional processes (Goren et al., 2011). In consequence, the final set of chemical elements included eight data-points: Al, Si, K, Ca, Ti, V, Cr, Fe. Two different statistical procedures were used in order to group the chemical results in a comprehensive scheme: the potassium-titanium test and principal component analysis. The first method is well established among scholars specialized in provenance studies (Goren et al., 2011) and is especially useful for an initial classification of the artefacts. The use of the potassium-titanium test is justified by the geological background of the region. The area around Setefilla is geologically complex and comprises four different geological formations:
Schists, molasses, intrusive rocks and marls (Drain et al., 1971). The landscape is dominated by soils of reddish colour. Local pottery from this area contains ferruginous rock fragments and iron oxide concretions that are rich in titanium. Intrusions of igneous rocks such as gabbro are also likely to occur. In contrast, the Los Alcores plateau is composed mainly of calcarenite sedimentary rocks.

The pXRF chemical data were also treated by means of principal component analysis. The PAST software package (Hammer et al., 2001) was our statistical tool to prepare the graphs.

**RESULTS**

Two-dimensional graphs were plotted to verify whether the potassium-titanium combination can group the samples according to their chemical similarities. With the results obtained from the K-Ti test (Fig. 2), it was possible to observe that the wheel-made samples from La Cruz del Negro and Setefilla form clear clusters. The samples from La Cruz del Negro are characterized by low concentrations of potassium and titanium. What is striking is that in the case of the wheel-made samples there is no correlation between those from El Campo de las Canteras and La Cruz del Negro, despite the fact that these two archaeological sites are located in close vicinity. In the case of El Campo de las Canteras average and high concentrations of titanium can be observed.

As shown in Fig. 3 samples from Setefilla (low concentration of potassium and average to high concentration of titanium) are forming a clear cluster among the hand-made pottery analysed. Samples from El Gandul are forming a distinct group as well (low to average concentrations of potassium and average concentrations of titanium). It should be highlighted that also in the case of scarce numbers of samples from other sites, some patterns can be observed: hand-made samples from Cristo de la Sedia, Entremalo and Túmulo de los Vientos are characterized by a high concentration of potassium and a low to average concentration of titanium.

Principal component analysis offers a more accurate evaluation of the samples from different sites, using the eight elements mentioned above. Especially significant is the clustering of wheel-made samples visible in Fig. 4. The samples are divided in three groups according to their chemical composition: 1) Setefilla, 2) El Campo de las Canteras, 3) La Cruz del Negro. To the second group we can also ascribe samples from Huerta Cabello and Ranilla. This is not a coincidence, as these three sites (to be precise: cemeteries), are located in close vicinity and depended on the Early Iron Age settlement at Carmona. The third group, defined mainly by samples from La Cruz del Negro (the other large necropolis at Carmona) also includes samples from Cristo de la Sedia and Bencarrón, Entremalo, as well as one sample from El Alcaudete.
The difference already demonstrated between the hand-made samples from Setefilla and from other sites is also reflected in the relevant PCA plot (Fig. 5). No other pattern can be observed. We interpret the dispersion of samples from the majority of archaeological sites on the graph as indicative of a common practice of mixing clays from different locations on the Los Alcores plateau.

**Fig. 3:** K-Ti test of the hand-made samples. Data plotted as percentages. Description of symbols: black circle – El Campo de las Canteras; plus – La Cruz del Negro; white triangle – Setefilla; star – Ranilla; cross – Túmulo de los Vientos; black bar – Cristo de la Sedia; white diamond – Entremalo; white square – El Gandul.

**Fig. 4:** Principal component analysis (PCA) of the wheel-made samples using the eight significant elements: Al, Si, K, Ca, Ti, V, Cr, Fe. Description of symbols: black circle – El Campo de las Canteras; plus – La Cruz del Negro; white triangle – Setefilla; star – Ranilla; black bar – Cristo de la Sedia; white diamond – Entremalo; black triangle – Bencarrón; black square – El Alcaudete; white circle – Huerta Cabello.

**Fig. 5:** Principal component analysis (PCA) of the hand-made samples using the eight significant elements: Al, Si, K, Ca, Ti, V, Cr, Fe. Description of symbols: black circle – El Campo de las Canteras, plus – La Cruz del Negro, triangle – Setefilla, star – Ranilla, X – Túmulo de los Vientos, bar – Cristo de la Sedia, diamond – Entremalo, white square – El Gandul.
CONCLUSIONS
The two statistical tests have produced results that are consistent with each other. It is not possible to determine the geographic provenance of the wheel-made pottery, as no Early Iron Age pottery kilns have been identified in the studied area. Nevertheless, previous studies suggest the local origin of the ceramic products from the region (Bartkowiak and Krueger, 2015). The chemometric results indicate that in important Tartessian centres like Setefilla and Carmona (represented here by the samples from El Campo de las Canteras and from La Cruz del Negro) at the beginning of the Early Iron Age, pottery of clearly different chemical composition was produced. The Carmona group shows differences between wheel-made samples from El Campo de las Canteras and La Cruz del Negro, to which samples from other Tartessian sites are chemically related. This grouping is significant enough to hypothesize the existence of at least two clearly different clay sources for the production of wheel-made ceramic products from the cemeteries near Carmona.

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BIBLIOGRAPHY