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X-ray compositional microanalysis and X-ray diffraction of Haltern 70 amphorae sherds

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Abstract

About 100 sherds from Haltern 70 amphorae recovered from Castro do Vieito (NW Portugal) and from kiln sites located at Guadalquivir valley, Rio Tinto valley, bay of Cadix and Algarve coast, were analyzed by X-ray fluorescence spectroscopy (XRF) and X-ray diffraction (XRD). The study aimed mainly to verify the provenance of Castro do Vieito (CV) Haltern 70 amphorae. Principal components analysis (PCA) and cluster analysis (CA) were performed. A CV sherd with a potter's stamp "LH…" was studied among other CV sherds and it was found that they have the same origin, and probably a unique provenance. The most considered area of Haltern 70 type, Guadalquivir valley, is not likely to be the origin of CV Haltern 70 amphorae. Moreover, it is quite possible that these amphorae were produced in a region with Nb rich soils.

Keywords Roman amphorae · Provenance analysis · Archaeometric study · Castro do Vieito settlement · Kiln sites · Multivariate analysis · XRF · XRD

1 Introduction

Amphora is a portable jar manufactured on a large-scale during Antiquity to transport foodstuffs by ship [1]. This receptacle was frequently fired alongside different sorts of ceramics and bricks, with clay normally extracted at short distance from the kilns [2]. Producers and traders, operating close [3] or even sometimes far away from the potter's facilities [4], used such container to export wine, olive oil, fish sauces and more rarely other kinds of goods [5]. Arrived at the destination, the amphorae were recycled in several ways [1, 2], often to storage [3] or as a compound of mortar [6]. In some cases, they were just abandoned as it happened at the doors of Rome, forming an artificial hill locally known as the Monte Testaccio [7]. Due to their great size, this kind of piece is easy to break. However, after that, the fragments are almost indestructible. Their presence within the consumption contexts of the Roman period, allows to track, not only the commercial routes linking provinces [2], but also the supply network of the legions and auxiliary troops along all the Empire [8]. At this point of view the determination of the provenance of this kind of ceramics is a crucial step of any research program focusing on the ancient economy. Some parts of the amphorae, as the rim, the bottom and the handles have characteristics easy to identify, being used for decades by scholars to categorize the sherds by morphological types [5], which sometimes corresponds to a unique origin, but not always. One of these classes, called Haltern 70, was produced since the end of the Republic or, perhaps, only during the early imperial period, being not documented after the Flavian dynasty [9–12]. This kind of vessel has a height of approximately 0.95 m and a maximum diameter of about 0.35 m, with an irregular cylindrical body, a band rim, two handles with elliptical section and a pointed base filled

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with a ball of clay [13]. It had been founded in consumption contexts of several areas of the Western Empire. However, it is in the NW of the Iberian Peninsula where this class is better documented, representing close to 80% of the amphorae recovered in archaeological sites of the Roman period [14]. In 1980, Tchernia [15] was not sure if Haltern 70 type were from the Baetican province, i.e. the Spanish region of Andalusia, or Southern Lusitania, that is nowadays Algarve (Portugal). In the beginning of the next decade, Peacock and Williams [5] proposed to locate the manufacturing area in the Guadalquivir Valley. This assumption was based on the petrographic similarities observed between samples studied earlier by one of them (P.) with the Dressel 20, the most common amphora class of this area. Since then, Haltern 70's exemplars had been identified in other production centers of Baetica [11, 16–18]. However, this is almost always a residual amount recovered in kilns excavated until now [11, 17]. The presence of sherds of this category at the surface of the workshops is also rare [12], excepting a few ones situated in the Medium Guadalquivir as Orippo (Dos Hermanos, Seville) and Pinguele (Bonares, Huelva) in the Rio Tinto valley, close to Algarve. This is the reason why these two areas were pointed out before as being probably the most important production centers of the Haltern 70 type [11, 16]. Some scholars believe that this class of pottery had also been made somewhere in Western Lusitania (Centre and South of Portugal) too, possibly in the Sado or the Tage Valley, however this assumption is not consensual [19–22]. Imitations had probably been crafted in North Africa [12] being also attested in France [12, 18]. More recently, Spanish archaeologists identified a new production center at Emerita Augusta (Eastern Lusitania), i.e. the Spanish town of Mérida [23–25]. In fact, the provenance of this amphora's class found in consumption contexts from the NW of the Iberian Peninsula and other provinces of the Empire continue to be uncertain today, even if most scholars still consider the Guadalquivir Valley as the main supplier.

This paper presents the results of an archaeometric study of the largest assemblage of the Haltern 70 type. It was recovered in 2004/2005 at Castro do Vieito (CV), during an extensive excavation [11, 26, 27] (Fig. 1), directed by one of the authors (António J.M. Silva). This indigenous settlement located near the estuary of the Rio Lima (Alto Minho, NW of Portugal), was occupied during the early imperial period, more precisely from the reign of Augustus until the middle or third quarter of the 1st century AD [11]. The inhabitants were involved in the supply of Roman troops charged to control auriferous explorations down the river [11] (Fig. 2).

The study of the pottery from this excavation reveals the reuse of the Haltern 70 amphorae in several ways [26]. A macroscopic examination led to conclude that all the fragments of this type correspond to a unique paste (CV-A), sandy and reddish or ochre color, with small rolled

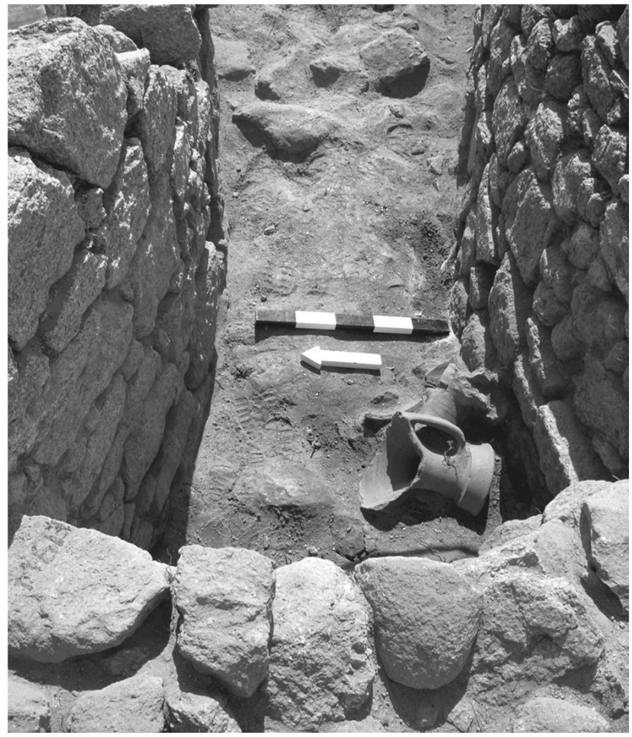

Fig. 1 Excavations site at CV (North-Western Portugal). We can see a large fragment of amphora Haltern 70 type in situ. (Author: A.J.M. Silva)

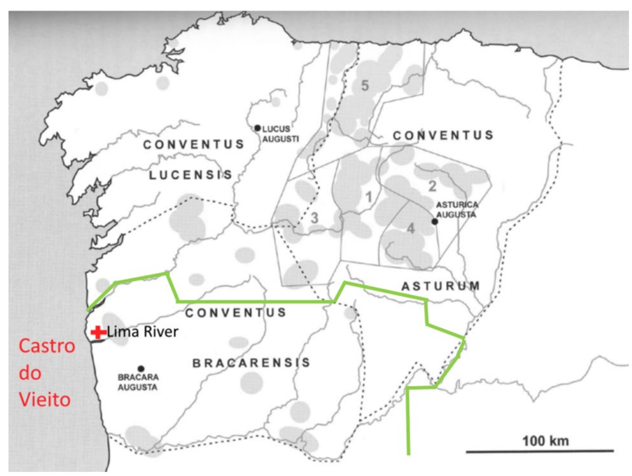

Fig. 2 Location of CV in the context of the NW Peninsular gold areas. This region is located in the northern part of todays Portugal, near Galiza. Adapted from [28]

gravels observed in a few cases [11]. The uniformity of the petrographic characteristics suggests that all exemplars of this amphora recovered during the intervention have the same origin, or in alternative, they came from different regions with clay deposits with a similar signature too. A potter mark (L. H …; Fig. 3) had been stamped in one of the analyzed handles collected from this site (sherd CV-A-4125 [11]).

This potter mark had been identified before in other Roman sites of the Iberian Peninsula, most of them in the Western Area, being associated by scholars with the Ovoid and Haltern 70 types. Whether the exact location of this workshop is still unknown, some authors believe that it can be somewhere in the Guadalquivir Basin, being related to the supply of the Roman army detached in the NW of the Iberian Peninsula [29], as besides the Haltern 70 in general [12, 18].

2 Materials and methods

In this work, we will be analyzing and comparing the results of samples from CV ($n = 60$) with others collected in the 2000s by one of the authors (António J.M. Silva) at the surface of production centers ($n_{Total} = 195$), where amphorae had been manufactured during the Roman period (Fig. 4) in:

1. the Upper Guadalquivir: Arva ($n = 5$) (Fig. 5);
2. the Medium Guadalquivir: Orippo (Torre de los Herberos) ($n = 24$);
3. the Lower Guadalquivir: Lebrija ($n = 4$);
4. the bay of Cadix: Puerto Real ($n = 31$);
5. the Rio Tinto valley: Pinguele ($n = 58$);
6. the Algarve coast: Marim ($n = 3$), Olhos de São Bartolomeu ($n = 5$), São Lourenço ($n = 5$).

The objective of this study is to confirm if the unique-origin hypothesis of the Haltern 70 sherds found at the CV is true (including the stamped handle). We also try to specify the provenance of this assemblage.

The total set of 195 samples used in this work consists of 60 samples recovered from CV in 2004 and 2005 [11, 26, 27] (Fig. 1), as well as 135 samples collected during the 2000s, from production centers in the Guadalquivir Basin, bay of Cadix, Rio Tinto valley and Algarve coast, which were active in the Roman period. Further details of each sample can be found in the supplementary material, Table S1. After gathering all these samples, a uniform analysis was performed using X-Ray Fluorescence (XRF) spectroscopy, as well as X-Ray Diffractometry (XRD). The results from these methods were collected, they were analyzed using Principal Component Analysis (PCA) and Cluster Analysis (CA) to determine any relationships and fundamental similarities between the samples. The results of these analyses will be shown in Sect. 3.

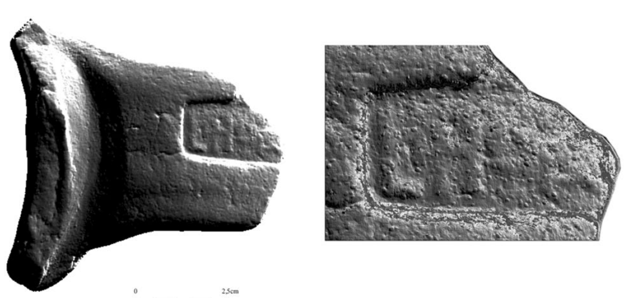

Fig. 3 Digital model of the handle CV-A-4125 with a detail of the stamp L.H…. (Author: A.J.M. Silva)

2.1 X-ray fluorescence

All X-ray fluorescence measurements were performed on a custom-made spectrometer, consisting of an Eclipse IV Amptek X-ray tube (45 kV; 50 mA) with a Rh anode.

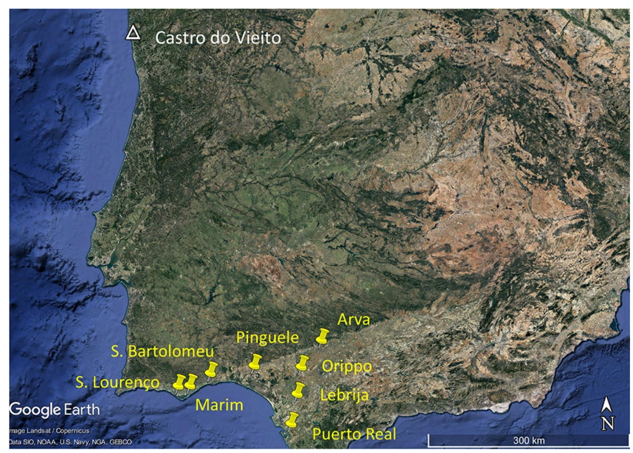

Fig. 4 Production centers from where sherds were collected in this study

Fig. 5 Kilns from the Roman city of Arva (Upper Guadalquivir, Alcolea del Río, Sevilla, Spain). (Author: Liliana Pereira)

Table 1 Average concentration of each quantified element in the samples, grouped by region in wt%

	Al	Si	P	S	Cl	K	Ca	Ti
Arva	7.56	29.7	0.23	0.08	BQL	7.93	11.76	0.41
Castro do Vieito	9.19	28.4	1.81	0.10	BQL	7.64	2.68	1.04
Lebrija	5.54	25.2	0.07	0.08	BQL	7.16	16.31	0.30
Marim	9.25	31.2	0.25	0.06	BQL	7.10	10.40	0.44
Olhos de S. Bartolomeu	12.47	55.3	0.37	0.06	BQL	10.07	0.85	0.86
Pinguele 1	7.87	30.0	0.26	0.06	BQL	7.71	10.41	0.50
Pinguele 2	7.76	29.3	0.16	0.08	BQL	8.26	11.06	0.48
Puerto Real	5.63	22.0	0.12	0.78	6.19	5.84	9.62	0.36
S. Lourenço	8.90	29.3	0.27	0.05	BQL	7.04	8.74	0.59
Torre de los Herberos	6.36	23.0	0.14	0.04	BQL	6.64	15.73	0.33
	Cr	**Mn**	**Fe**	**Ni**	**Cu**	**Zn**	**Ga**	**Se**
Arva	0.02	0.09	3.87	0.09	0.01	0.01	0.03	BQL
Castro do Vieito	0.05	0.52	8.11	0.15	0.02	0.02	0.06	BQL
Lebrija	0.01	0.07	2.46	0.05	0.01	0.01	0.02	BQL
Marim	0.02	0.12	4.30	0.09	0.01	0.01	0.03	BQL
Olhos de S. Bartolomeu	0.03	0.08	5.06	0.13	0.02	0.01	0.05	BQL
Pinguele 1	0.02	0.11	4.52	0.08	0.02	0.01	0.02	BQL
Pinguele 2	0.02	0.10	4.11	0.08	0.03	0.01	0.02	BQL
Puerto Real	0.01	0.11	3.20	0.08	0.01	0.01	0.02	BQL
S. Lourenço	0.02	0.12	5.50	0.10	0.01	0.01	0.03	BQL
Torre de los Herberos	0.01	0.08	3.09	0.06	0.01	0.01	0.02	BQL
	Br	**Rb**	**Sr**	**Y**	**Zr**	**Nb**	**Pb**	
Arva	0.09	0.03	0.02	0.29	0.01	0.00	0.01	
Castro do Vieito	0.44	0.04	0.01	0.42	0.02	0.11	0.02	
Lebrija	0.09	0.03	0.03	0.21	0.01	0.00	0.01	
Marim	0.09	0.03	0.02	0.23	0.01	0.00	0.01	
Olhos de S. Bartolomeu	0.15	0.05	0.01	0.40	0.03	0.00	0.01	
Pinguele 1	0.07	0.02	0.03	0.24	0.01	0.05	0.02	
Pinguele 2	0.08	0.03	0.02	0.27	0.01	0.06	0.02	
Puerto Real	0.19	0.03	0.02	0.25	0.01	0.01	0.01	
S. Lourenço	0.14	0.04	0.02	0.35	0.02	0.00	0.01	
Torre de los Herberos	0.07	0.02	0.02	0.20	0.01	0.02	0.01	

The absolute uncertainties are estimated to be 0.01% for all elements except Si whose uncertainty is estimated as 0.1%. BQL- Below Quantification Limit

This portable setup features a collimated beam of 5 mm in diameter, by using a tantalum collimator. The measuring spot position, 55 mm from the X-ray tube's window and 10 mm away from the detector's beryllium window, is calibrated using two laser pointers and a fluorescent target. The detector is an Amptek silicon drift detector (SDD) XR-100SDD with a 25 mm^2 detection area collimated down to 17 mm^2 and with a 500 μm thickness and a dead layer of 150 nm. The detector's beryllium window is 12.5 μm thick and it features an energy resolution of 125–140 eV at 5.9 keV. The spectrometer geometry consists of a 90° angle between the incident beam and the sample's fluorescence beam, with the sample surface being at ° from both. This geometry allows a partial suppression of scattered Compton radiation from the X-ray tube due to polarization, thus resulting in a higher signal to noise ratio [30, 31]. With this setup we can determine the amount of each element in the sample with atomic numbers higher than 13 (Al), with varying sensitivities. All the samples described in Table S1 were analysed by XRF. The samples were analysed directly on air and at room temperature, with an acquisition time of 300 s. All the spectra evaluations were performed using the PyMca software package [32].

The Nb elemental map of the CV sample with inscription was obtained with a μ-EDXRF system, M4

Table 2 Loadings of the first 3 principal components, describing the weights of each element

	Al	Si	P	S	Cl	K	Ca	Ti
PC1	0.1983	0.0823	0.2304	−0.0629	−0.0763	0.1058	−0.2776	0.2552
PC2	−0.2986	−0.3270	0.1523	0.3315	0.3932	−0.4423	−0.0919	0.0186
PC3	0.1239	−0.1196	0.1449	0.1652	0.1369	−0.0958	−0.0491	−0.1993
	Cr	Mn	Fe	Ni	Cu	Zn	Ga	Se
PC1	0.3127	0.0855	0.3535	0.2887	0.0940	0.1926	0.2508	−0.0092
PC2	0.0606	0.0348	0.0162	0.0530	−0.2241	−0.0531	0.0140	0.0719
PC3	−0.1490	0.1772	−0.0974	0.0969	0.0607	0.1864	0.0086	−0.0018
	Br	Rb	Sr	Y	Zr	Nb	Pb	
PC1	0.2818	0.2076	−0.2112	0.2691	0.2246	0.1098	0.1150	
PC2	0.3175	−0.1856	−0.3135	−0.0270	−0.0323	0.0781	−0.0635	
PC3	0.0827	0.1768	0.2462	0.2450	0.0997	−0.7564	0.0075	

Tornado—Bruker (Germany) [33]. The X-ray tube is a micro-focus side window Rh tube powered by a low-power HV generator and air cooled. A polycapillary lens allows a spot size of 29 µm for Rh-Kα. Detection of fluorescence radiation was performed by an energy dispersive silicondrift detector with a 30 mm^2 effective area and an energy resolution of 142 eV for Mn-Kα. The elemental map was obtained on the surface of a cut sample using a step size of 50 µm and a 1 ms/pixel time step.

2.2 X-ray powder diffraction

A few sets of sherds from each site, in a total of 30 (see Table S1), were investigated by X-ray powder diffractometry. The technique provides information about the presence of different minerals phases and of minerals newly formed during firing or burial. The samples were ground in a mortar. Powder X-ray diffraction (XRD) was performed at RT in 2θ range from 5° to 100° and a scanning step width 0.002°, using a Bruker D8 Advance diffractometer equipped with a Ni filter for CuK_α radiation (λ = 1.5406 Å) and discrimination against Fe fluorescence background. The XRD patterns were refined using Pawley method (computer program TOPAS [34]).

3 Results and discussion

We have determined and quantified a set of elements present in the collected samples by using the results from our XRF measurements. Through spectra analysis, the elements that we could measure in the samples are Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Se, Br, Rb, Sr, Y, Zr, Nb and Pb. Taking this set of elements and their concentrations for each sample (Table S2), we performed further analysis to establish similarities and relationships between the samples. Some noteworthy results from the average elemental compositions for each region can be seen in Table 1.

From this data we can observe clear distinctions between regions and the sherds elemental composition. For example, in terms of the Ca content we observe Ca-poor regions such as Castro do Vieito and Olhos de S. Bartolomeu, in contrast to Ca-rich regions such as Lebrija and Torre de los Herberos.

Using the elemental concentrations determined, we then proceeded to perform a PCA on the data. The PCA was performed using labeled data, i.e. each sample's composition was labeled by the region from which it was collected. For this analysis we determined the principal components until a 95% variance was achieved for the dataset, resulting in 12 principal components. A total variance of 74% for the first 3 components (PC1−56.47%; PC2−10.71%; PC3−6.81%) was observed. These 3 components were first used to visually explore the results, which can be seen in Figs. 6 and 7. The loadings for these 3 components are detailed in Table 2.

In this representation, we can clearly see the formation of several clusters. The clusters from samples which are geographically close to each other overlap almost completely, while the one from CV (dark green) shows good separation.

On the top of Fig. 6, it is noted that the CV sherd with the potter's stamp "LH..." fits well into the CV cluster. One more noteworthy detail from this representation is the presence of a secondary group of clustered data points in the CV cluster, which is separated by the third principal component. From the loadings of this component, which are present in Table 2 and represented in Figs. 6 and 7, it appears that there is a difference in the concentration of Nb. The separation of some clusters can be better observed in Fig. 7.

In addition to CV, both the Torre de los Herberos and Pinguele clusters show a similar separation of some data

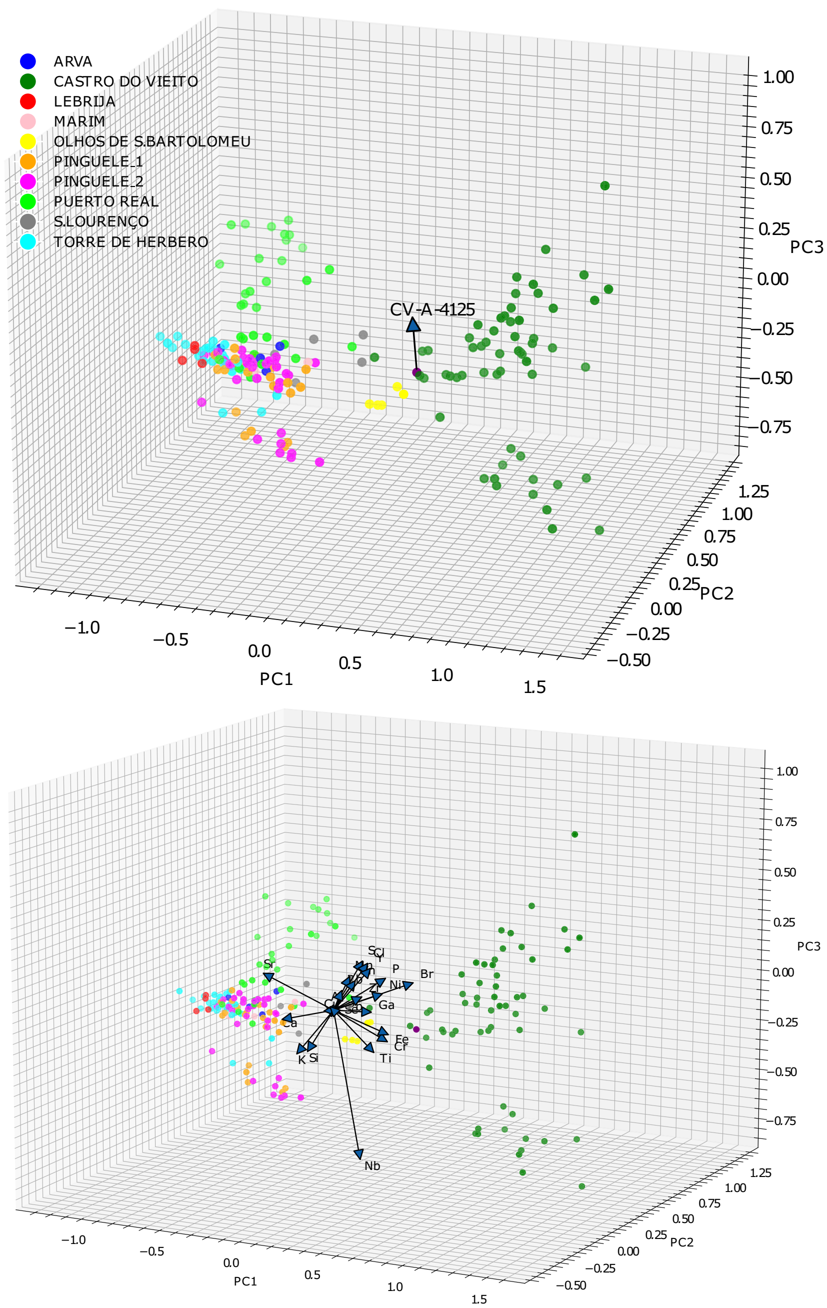

Fig. 6 Elemental analysis represented using the first 3 principal components obtained through PCA. On the top, the stamped sample is annotated. On the bottom the loadings from Table 2 are represented

points by the third principal component. In these regions, we no longer observe a difference in Nb concentration but rather a higher concentration of K and Si. These separated data points could indicate a secondary source for the amphorae in these regions.

Regarding the CV cluster, there is also a second possibility since CV is close to high Nb concentration zones (see Fig. 5 of reference [35]). For this sub-cluster we believe that it could indicate either a secondary source of raw material for the amphorae (north of Portugal and Galiza, the region of Spain near the frontier with Portugal (south of Merida), etc., or that the amphorae were buried in these zones, where Nb was incorporated into their composition over time. Concerning the first hypothesis, it should be noted that despite north of Portugal and Galicia being very well known archeological regions, no amphorae production is identified in those areas. A similar argument could be made for the sub-cluster in the other regions with higher concentration of K and Si, however we could not find data to support it. To test the hypothesis of Nb being present in the amphorae raw material or incorporated during the time they were buried, we measured a 2D

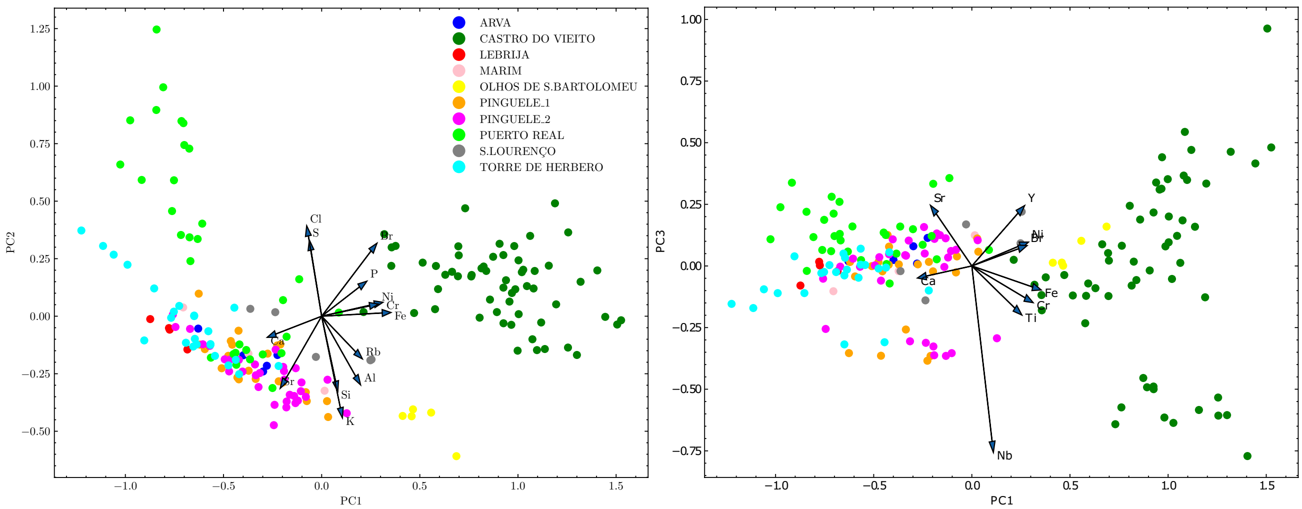

Fig. 7 2D projections of the elemental analysis represented in Fig. 6. PC1 clearly separates *Castro do Vieito* samples from the other sets while PC2 separates the small subset of *Olhos de São Bartolomeu* from the CV set. The loadings for the elements with larger contributions are also represented

elemental map of a cut CV sample where Nb was present. The measured sample was CV-A-4125, i.e. the handle with the LH... stamp.

From Fig. 8 we observe a homogeneous distribution of Nb, which would not be expected if this element was incorporated over time, as opposed to initially present in the raw material.

A more detailed study of the clusters observed in Fig. 6 was also performed using CA. In this analysis we included all 12 principal components and determined a dendrogram graph, containing the final clustered samples, which can be seen in Fig. 9. From this dendrogram we can observe how the samples are clustered, as well as some correlated sources. There is a clear separation between the samples from CV (green branches) and the sources from the Guadalquivir Basin (orange branches).

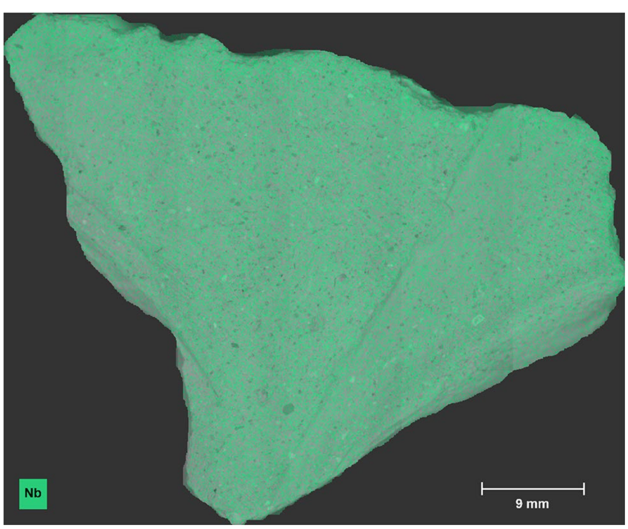

Fig. 8 2D elemental map of the CV-A-4125 sample cross section cut where Nb was present. The elemental map is overlaid with the sample's image

This archaeological site (Olhos de São Bartolomeu) is located in the estuary of the Rio Guadiana (commune of Castro Marim, Faro District). It was identified for the first time in the XIX century, being recorded the existence of a ceramic kiln. The beginning of the activity is from the 2nd half of the first century or maybe before, the production of amphora Dressel 14 type being documented by the finding of several complete exemplars. In the later phase, this workshop also produced amphorae of the Almagro 50 type. However, there is no archaeological evidence of having produced amphora Haltern 70 type.

Figure 10 shows a representation of CV and CV with inscription, as well as Ca-rich group (Lebrija) and Ca-poor group (Olhos de S.Bartolomeu) XRD patterns. The results are shown in Table 3. The Ca-rich sherds have a very common mineralogical composition, mainly represented by quartz and calcite. High temperature Ca-silicates like gehlenite, anorthite, diopside or wollastonite were also detected. These minerals suggest a firing temperature higher than 800 °C [36, 37]. The CV sherd with the LH… inscription has a mineralogical composition similar to other CV sherds. The sherds with low Ca-contents (Olhos de S. Bartolomeu) show a very different mineralogical composition, and do not contain the high temperature Ca-silicates, which is related to the absence of calcite in these sherds. We know from other studies that these amphorae must have been fired at a temperature of or above 900 °C [38]. Quartz is still the main component. Being the CV and Olhos XRD

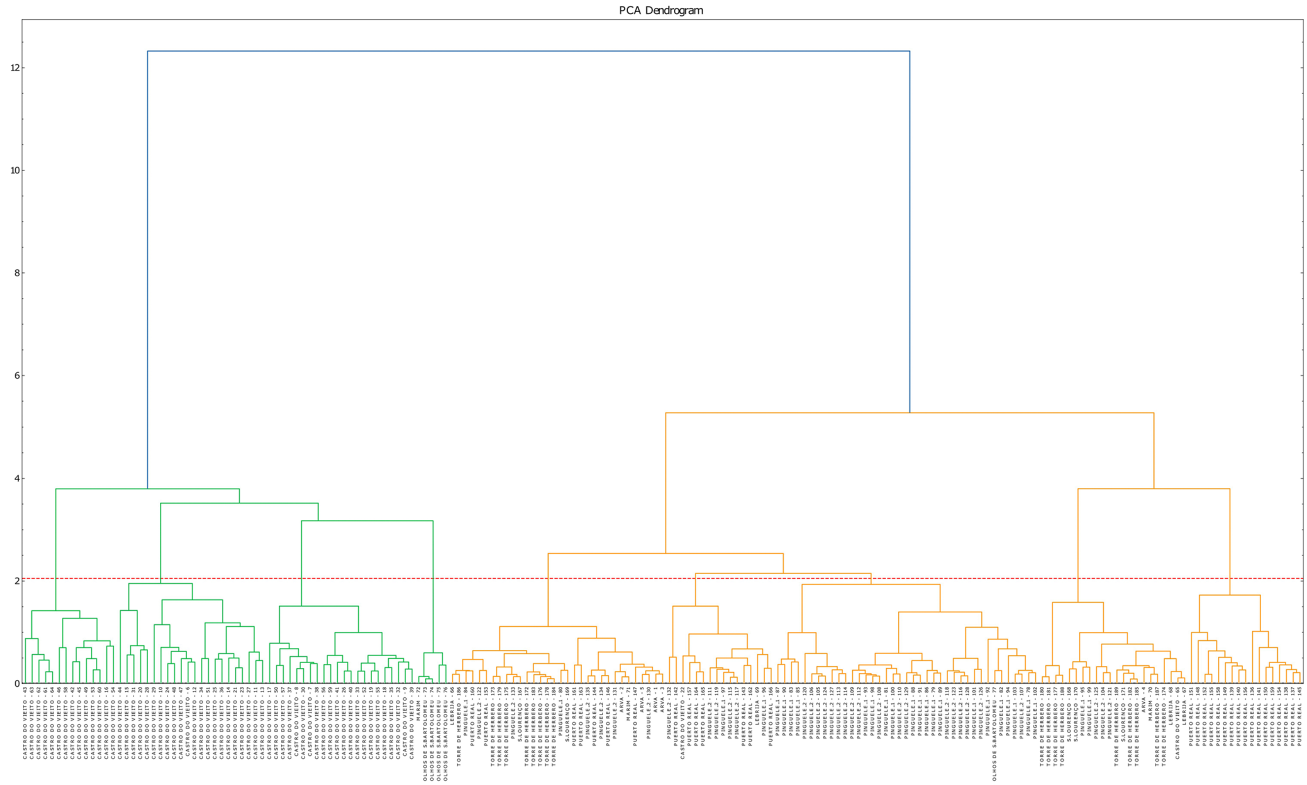

Fig. 9 Dendrogram graph constructed from the 12 principal components determined. A clear separation between CV samples (green branches) and Guadalquivir Basin samples (orange branches) is observed. The dashed red line represents a cutoff where 9 clusters (number of collected regions) are present

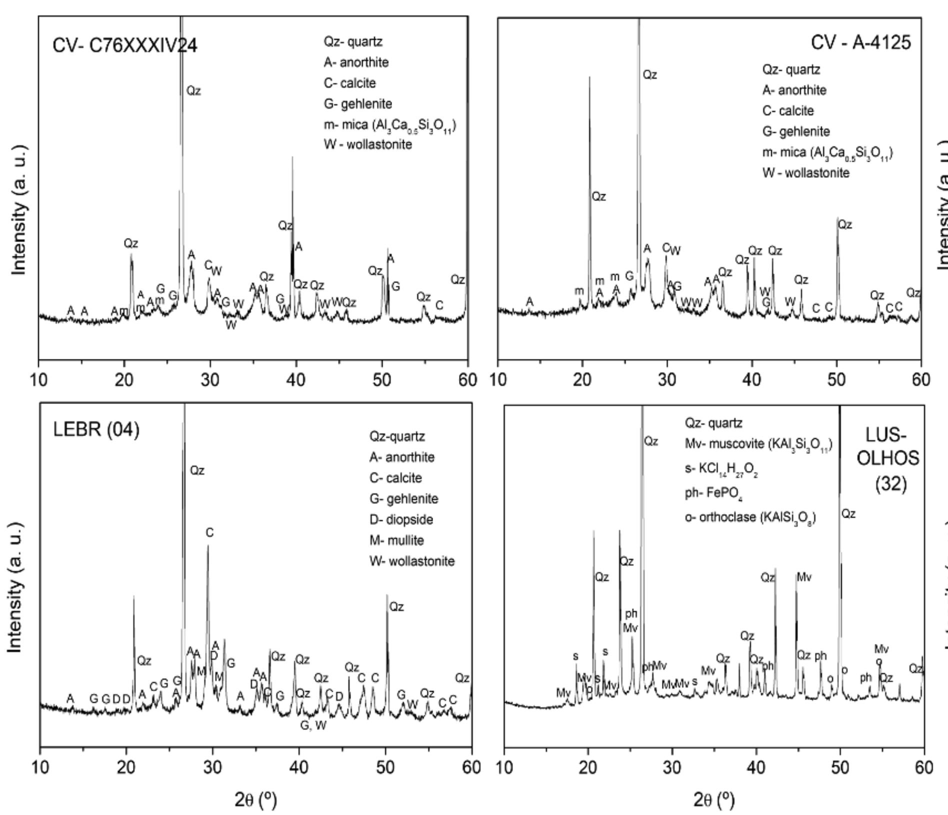

Fig. 10 XRD patterns of representative CV, CV with inscription, Lebrija (Ca-rich) and Olhos (Ca-poor) sherds

Table 3 Mineralogical phases identified by XRD analysis of sherds

	CV	CV-Insc	Olhos	Lebrija	PReal	Marim	TH	Ping	Arva	SLour
Quartz SiO_2	#	#	#	#	#	#	#	#	#	#
Anorthite $CaAl_2Si_2O_8$	#	#		#	#	#	#	#	#	#
Gehlenite $Ca_2Al_2SiO_7$	#	#		#	#	#	#	#	#	#
Calcite $CaCO_3$	#	#		#	#	#	#	#	#	#
Diopside $CaMg(SiO_3)_2$				#			#			
Mullite $Al_6Si_2O_{13}$				#			#			
Wollastonite $(Ca,Fe)SiO_3$	#	#		#						
CaAl Mica $Al_3Ca_{0.5}Si_3O_{11}$	#	#								#
Muscovite K mica			#		#	#		#	#	#
Albite $NaAlSi_3O_8$					#	#		#	#	
Sylvite $KCl_{14}H_{27}O_2$			#							
$FePO_4$			#							
Orthoclase $KAlSi_3O_8$			#							

patterns different, this also supports the hypothesis that the CV sherds were not produced in Olhos de S. Bartolomeu.

A Prompt Gamma Activation Analysis (PGAA) study on the same sherds discussed in this paper, supplemented with results from other production sites in ancient Lusitania (Sado and Tage valleys) and Baetica (Guadalquivir valley), will be published soon.

4 Conclusion

From the assemblage of 195 Haltern 70 type amphorae sherds, 189 were analyzed using XRF, which allowed us to quantify the set of elements detailed in Sect. 3 present in each sample. Through this quantification, we separated the sherds into groups using PCA and CA techniques. When comparing the clusters calculated from the compositions with the source regions, we found a good separation between CV and Guadalquivir Basin samples. With that established, we analyzed the overlaps between these clusters, where we can see that the sherds from geographically close sources present a large overlap. In addition, the cluster of samples from Castro do Vieito, shows almost no overlap with the remaining clusters. The presence of some sub-clusters also indicates a second source of amphorae. Although not conclusive, we have explored (Fig. 8) the hypothesis of CV amphorae being manufactured with a second source of raw, Nb rich, material.

Regarding the XRD measurements, it was observed that quartz is the main component. There is a clear distinction between the patterns of Ca-rich, Ca-poor (Olhos de São Bartolomeu) and CV sherds. These results reinforce the idea that amphorae are not from Olhos de S. Bartolomeu neither from Baetica province which include the Guadalquivir valley, despite being pointed as the main producing area of Haltern 70 in archaeological literature.

In summary, there are important conclusions that can be pointed out from the studies performed:

1. The Haltern 70 amphorae sherds found in Castro do Vieito, including the one with potter's stamp "LH..." seem to have a unique origin.
2. The production center of Haltern 70 amphorae found in Castro do Vieito is not likely to be located at the Guadalquivir Basin.
3. Some of the Castro do Vieito Haltern 70 amphorae contain a higher concentration of Nb, which, given its spatial distribution within the samples (Fig. 8), may indicate that these amphorae could have been produced in a region with Nb rich soils.

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Declarations

Conflict of interest The authors declare no conflict of interest

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