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Mössbauer Studies of Haltern 70 Amphorae from Castro do Vieito, Northwest of Portugal

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Abstract: Haltern 70 amphorae sherds from Castro do Vieito, a Roman settlement from the NW of Portugal occupied during the early imperial period, were studied by Mössbauer spectroscopy at room temperature and 4.2 K, XRD, and XRF, aiming to understand the firing conditions of their production. Firing in air at 750 and 800 °C were performed in a sherd that was carefully studied. Also, a handle with part of the neck attached and with the potter's stamp "LH . . ." was studied. In general, it can be deduced that the amphorae were fired under reducing conditions between 800 and 950 °C, having been subjected to an oxidation process only when already cooling. It was also inferred that the provenance of all the Haltern 70 amphorae found in Castro do Vieito is probably the same and that the stamped amphora also seems to come from the same locality.

Keywords: Haltern 70 amphorae; Castro do Vieito excavations; Mössbauer spectroscopy; X-ray diffraction; X-ray fluorescence

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1. Introduction

Generally, during archaeological excavations, the most frequently found artifacts are fragments of ceramic vessels, and these are often the only references to past cultures [1–3].

There is a particular type of ceramic vessel, the Haltern 70 amphora, which was used in ancient times mainly to transport wine and other goods across seas and rivers [4–6]. It is believed that most of the Haltern 70 amphorae have been produced in Baetica, the Southern Roman province of Hispania (nowadays Spain) since the end of the Republic or, perhaps, only during the early imperial period, being not documented after the Flavian dynasty [7–11].

From a morphological point of view, these amphorae are vessels of about 0.90 m in height and a maximum diameter of about 0.35 m. Their body is an irregular cylinder, and they have a banded rim, two handles with an elliptical section, and a pointed base filled with a ball of clay [9,12,13] (see Figure 1 for illustration [14]).

The importance of this type of artifact is found massively in the northwest of Hispania (currently northwestern Portugal and the Spanish province of Galicia), which has been the subject of discussion. The presence of these amphorae used to be explained by the importance they had in ancient trade routes along the Atlantic coast of Hispania during the beginning of the Roman Empire [15]. Nowadays, the most common explanation is that the Haltern 70 amphorae played a very important role in supplying the Roman troops who controlled the region after its final conquest by the emperor Augustus [9,16]. Until a few

years ago, the presence of the Imperial army was poorly documented in the NW of Portugal. However, recent research using the LIDAR technology allowed for the identification of several military establishments, some of them with a significant contingent, located in this area [17].

We have been reporting an ongoing archaeometric study of Haltern 70 amphorae sherds from Castro do Vieito [13,18]. In those papers, we only presented room temperature Mössbauer measurements in the amphorae sherds from the Castro do Vieito settlement. This paper presents the results of an archaeometric study of the same collection, which is the largest assemblage of the Haltern 70 type of the Roman world [11]. It was recovered in 2004/2005 during an extensive dig [19,20] directed by one of us (AJMS). This indigenous settlement, located near the estuary of the Rio Lima (Alto Minho, NW of Portugal), was occupied during the early imperial period [11]. All the Haltern 70 sherds collected were first subject to a macroscopic examination. This preliminary analysis led to the conclusion that all the fragments of this type correspond to a unique paste (CV-A), sandy with low calcium content and reddish or ochre color, with small, rolled 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 alternatively, they came from different regions with clay deposits with a similar signature.

The study is now focused on the analysis of not only room temperature Mössbauer spectra but also of 4.2 K measurements, which are necessary to understand the firing conditions of the amphorae in their production. Also, re-firing experiments are presented on a given sherd, providing a better insight into the firing conditions. With this study, we aim to obtain valuable information for the research of the amphorae's production techniques and distribution routes when comparing the results with others from ceramics produced in kiln sites. Additionally, a piece of an amphora handle to which part of the neck of the amphora is still attached, with the potter's stamp "LH . . ." ([11], Figure 2) was also studied by Mössbauer spectroscopy at room temperature and 4.2 K. This sherd (CV-A-4125) was recovered in the square XXX-23, located in the southeastern sector of the site, belonging to the stratigraphic unit C0499, dated from the Tiberian/Claudian period [11]. This potter's stamp 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. Where the exact location of this workshop is remains unknown; some authors believe that it could be somewhere in the Guadalquivir Bassin, being related to the supply of the Roman army detached in the NW of the Iberian Peninsula [21], besides the Haltern 70 in general [9,16].

Figure 1. Morphology of a Haltern 70 amphora [14].

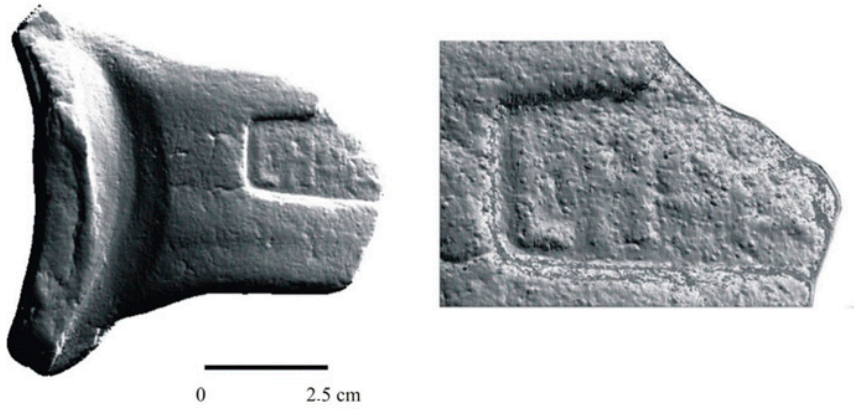

Figure 2. Piece of the handle, with part of the neck attached, of an amphora with a potter's stamp (archaeological code Haltern CV-A-4125) and detail of the potter's stamp beginning with "LH . . ." stamped into the handle [11].

2. Materials and Methods

This is a study of Haltern 70 amphorae recovered in 2004/2005 during an extensive excavation in Castro do Vieito, a Roman settlement located near the estuary of Rio Lima (NW of Portugal) occupied during the early period of the imperial period. All the sherds have similar petrographic characteristics, so they probably came from the same production area. A piece of an amphora handle with the potter's stamp "LH . . .", found in the same assemblage, was also studied. Those are the largest assemblage of these kinds of amphorae of the Roman world, and they have good chances to be from the same production area of Haltern 70 imported to the other settlements from the NW of the Iberian Peninsula during the imperial period. Twelve of those sherds were studied. Table 1 depicts the sample description of the sherds for which Mössbauer spectra are shown, as an example, in this study. The archaeological codes of the samples are used in this paper.

Table 1. Description of the sample sherds. All handle sherds had an oval section with a longitudinal linear groove on the external side, while the body sherd had a curved surface.

Sample	Description
C76	Handle
C112	Body
C499	Handle
C651	Handle
C665	Handle
CV-A-4125	Handle-with potter's stamp

The aim of the study was to find out the firing conditions of the clays when amphorae were produced inside the kilns. These studies were carried out mainly by Mössbauer spectroscopy at RT and at 4.2 K.

The sherds were ground in a mortar, and Mössbauer samples of about 150 to 200 mg/cm^2 thickness in perspex holders were prepared, which means 10 to 20 mg/cm^2 of iron. ^{57}Fe Mössbauer spectra were recorded in transmission geometry using a standard FAST Comtech (Munich, Germany) spectrometer with a sinusoidal velocity waveform (differential nonlinearity of the velocity scale below 0.4%). Measurements at 4.2 K were carried out in a liquid He bath cryostat. The source, of about 25 mCi of ^{57}Co in a Rh matrix, was always at the same temperature as the absorber. The spectra were fitted using a least-squares procedure with appropriate superpositions of Lorentzian lines. Some spectra were analyzed with a distribution of hyperfine magnetic fields using Gaussian lines. The

acquisition time was 4 to 6 days, being higher in the case of low-temperature measurements. However, the stability of the spectrometer was always good. The isomer shifts are given with respect to α-Fe at room temperature (RT). The XRD patterns were recorded using a Philips PW1070 diffractometer (PANalytical, Almelo, The Netherlands) equipped with a graphite monochromator (PANalytical) and a Co-radiation source (λ = 1.7903 Å). Random powder samples were measured from 5 to 60° 2θ in steps of 0.02° 2θ with a counting time of 5 s for each step. Natural quartz inside the sample was used as an internal standard to correct the 2θ position of each peak. X-ray fluorescence (XRF) was performed at RT using a portable NITON XL3t-980He spectrometer (Thermo Fisher Scientific, Waltham, MA, USA).

3. Results and Discussion

Twelve Haltern 70 sherds from Castro do Vieito were studied, including the stamped sherd. They are reddish-brown, no longer than 10 cm, and all exhibit a slight curvature. They are soft and can easily be fractured. It is easily verified, in all samples, a sandy texture, sometimes with big inclusions of silicates (Figure 3). The XRF spectrometer we used gives great uncertainty, mainly relative to light matrices. Even so, we can have an idea of the elemental composition of the amphorae. The presence of Si is about 20–30 wt%, confirming that sand was added to the raw clay, probably as a temper [22]. The sherds have about 1 wt% Ca, despite not being tough. Also, Al concentration is about 9 wt%.

Figure 3. Photographs and respective amplification (5×) of Vieito sherds C121 (**top**) and C112 (**bottom**). The most obvious feature is the sandy texture, sometimes fine (**bottom**) but in other cases with rather large inclusions (**top**) [13].

All the twelve samples were studied by Mössbauer spectroscopy, and the recorded spectra are quite similar. Typical spectra are shown in Figure 4, and the refined parameters are depicted in Table 2. The RT spectra were fitted with a strong ferric doublet (area (A) 50–60%; isomer shift (IS): 0.39–0.43 mm/s; quadrupole splitting (QS): 0.76–0.90 mm/s), a weak ferrous doublet (A: nearly 0–30%; IS: 0.95–1.07 mm/s; QS: 2.37–2.51 mm/s); minor sextets of maghemite and hematite, roughly in equal amounts (3–11% each), and a broad magnetic Gaussian distribution (8–21%). At 4.2 K, the spectra exhibit a broad magnetic pattern that has been fitted by distributions of hyperfine fields of 28 to 50% of the spectral

area. Fe^{3+} and Fe^{2+} are present in amounts of 14–25% and 1–8%, respectively, and the sextets of maghemite and hematite represent 11–22% and 5–11% of the total area, respectively.

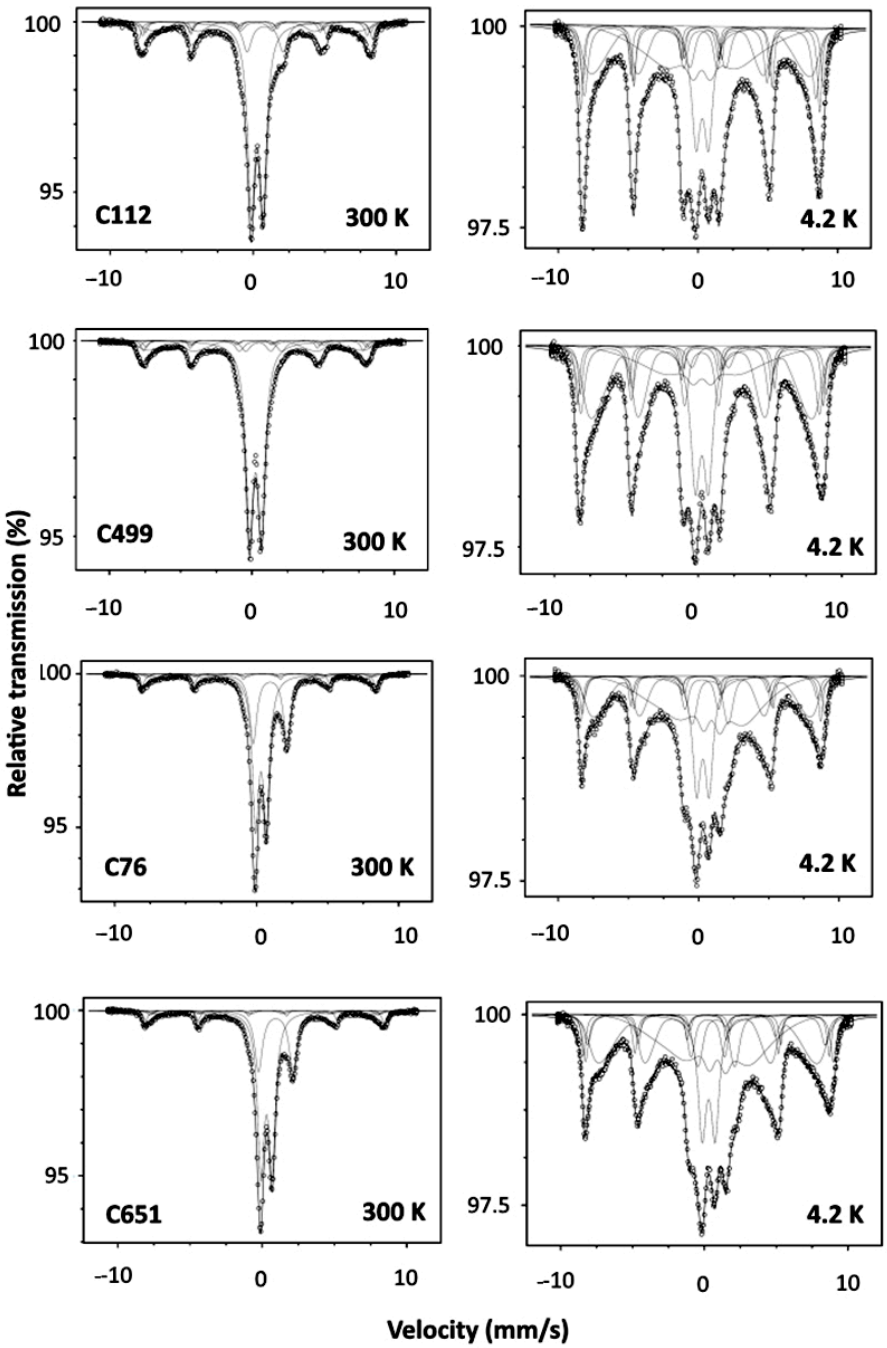

Figure 4. Mössbauer results, obtained at RT and 4.2 K, of different sherds of Castro do Vieito. These are typical results of all the sherds.

The broad magnetic component at RT might be a slow relaxation of Fe^{3+} in the glassy phase that becomes visible at 4.2 K. Such a broad distribution might also derive from super-paramagnetic relaxation of crystallites having a relatively heterogeneous size distribution [23,24], in line with the massive ordering observed at 4.2 K. At this temperature, maghemite and hematite increase, maybe because some are super-paramagnetic at RT, being present as very small oxide particles.

Table 2. Mössbauer parameters obtained from the fitting to the spectra shown in Figure 4. The isomer shifts are given relative to α-Fe measured at RT. The values in brackets (<>) are mean values for the distribution of HF used to fit the broad sub-spectra.

Sample	Temperature	IS (mm/s)	2ε/QS (mm/s)	H (T)	FWHM (mm/s)	A (%)	Site
C112	RT	0.39 (1)	0.83 (1)	-	0.63 (1)	55	Fe^{3+}
		0.94 (1)	2.51 (1)	-	0.75 (1)	11	Fe^{2+}
		<0.33 (1)>	0.00 (1)	<43.0 (1)>	0.50 (1)	16	Dist H
		0.30 (1)	−0.02 (1)	48.8 (1)	0.52 (1)	11	Maghm
		0.38 (1)	−0.21 (1)	50.8 (1)	0.33 (1)	7	Hematite
	4.2 K	0.55 (1)	0.89 (1)	-	0.75 (1)	14	Fe^{3+}
		0.94 (1)	2.56 (1)	-	0.50 (1)	5	Fe^{2+}
		<0.42 (1)>	0.00 (1)	<46.0 (1)>	0.50 (1)	24	Dist H
		<0.50 (1)>	0.00 (1)	<22.3 (1)>	0.50 (1)	24	Dist H
		0.50 (1)	−0.21 (1)	53.0 (1)	0.30 (1)	5	Hem n-Morin
		0.50 (1)	0.40 (1)	53.7 (1)	0.30 (1)	6	Hem Morin
		0.401)	0.01 (1)	52.0 (1)	0.37 (1)	22	Maghm
C499 Inner side	RT	0.39 (1)	0.90 (1)	-	0.60 (1)	58	Fe^{3+}
		0.95 (1)	2.51 (1)	-	0.75 (2)	10	Fe^{2+}
		<0.41 (1)>	0.00 (1)	<50.5 (1)>	0.50 (1)	19	Dist H
		0.40 (1)	−0.02 (1)	48.5 (1)	0.52 (1)	10	Maghm
		0.39 (1)	−0.21 (1)	50.7 (1)	0.33 (1)	3	Hematite
	4.2 K	0.50 (1)	0.90 (1)	-	0.70 (2)	17	Fe^{3+}
		1.07 (1)	2.56 (1)	-	0.63 (1)	3	Fe^{2+}
		<0.48 (1)>	0.00 (1)	<49.0 (1)>	0.50 (1)	33	Dist H
		<0.50 (1)>	0.00 (1)	<22.6 (1)>	0.50 (1)	18	Dist H
		0.50 (1)	−0.21 (1)	53.0 (1)	0.40 (1)	3	Hem n-Morin
		0.50 (1)	0.35 (1)	53.2 (1)	0.38 (1)	4	Hem Morin
		0.40 (1)	0.01 (1)	52.0 (1)	0.34 (1)	22	Maghm
C76	RT	0.42 (1)	0.76 (1)	-	0.51 (1)	53	Fe^{3+}
		1.07 (1)	2.37 (1)	-	0.60 (2)	28	Fe^{2+}
		<0.51 (1)>	0.00 (1)	<44.1 (1)>	0.50 (1)	8	Dist H
		0.30 (1)	−0.01 (1)	48.6 (1)	0.50 (1)	3	Maghm
		0.39 (1)	−0.21 (1)	51.2 (1)	0.33 (1)	8	Hematite
	4.2 K	0.55 (2)	0.89 (1)	-	0.70 (2)	17	Fe^{3+}
		1.07 (2)	2.56 (19	-	0.50 (1)	8	Fe^{2+}
		<0.47 (1)>	0.00 (1)	<48.9 (1)>	0.50 (1)	24	Dist H
		<0.97 (1)>	0.00 (1)	<20.9 (1)>	0.49 (1)	32	Dist H
		0.50 (1)	−0.21 (1)	53.0 (1)	0.26 (1)	3	Hem n-Morin
		0.50 (1)	0.30 (1)	53.8 (1)	0.30 (1)	4	Hem Morin
		0.40 (1)	0.04 (1)	52.0 (1)	0.27 (1)	12	Maghm
C651 Concave side	RT	0.42 (1)	0.78 (1)	-	0.55 (1)	55	Fe^{3+}
		1.07 (1)	2.38 (1)	-	0.65 (2)	25	Fe^{2+}
		<0.44 (2)>	0.00 (1)	<44.0 (1)>	0.50 (1)	8	Dist H
		0.30 (1)	−0.01 (1)	48.9 (1)	0.34 (1)	5	Maghm
		0.39 (1)	−0.21 (1)	51.4 (1)	0.33 (1)	7	Hematite
	4.2 K	0.54 (2)	0.90 (1)	-	0.55 (1)	15	Fe^{3+}
		1.07 (2)	2.56 (1)	-	0.50 (1)	7	Fe^{2+}
		<0.48 (2)>	0.00 (1)	<48.4 (1)>	0.50 (1)	28	Dist H
		<0.99 (2)>	0.00 (1)	<20.4 (1)>	0.50 (1)	28	Dist H
		0.50 (1)	−0.21 (1)	53.0 (3)	0.27 (1)	2	Hem n-Morin
		0.50 (1)	0.35 (1)	53.3 (1)	0.28 (1)	4	Hem Morin
		0.40 (1)	0.02 (1)	52.0 (2)	0.27 (1)	16	Maghm

As broad magnetic patterns imply a glassy phase in which the iron is inhomogeneously distributed, the presence of a super-paramagnetic/spin glass pattern is consistent with a reduction in firing followed by oxidation at the end of the firing cycle, as also seen in studies of Haltern 70 amphorae produced in a kiln of Lusitania [18], and of Celtic pottery from Bopfingen [25].

The sherd C665 was studied in more detail as an example. Mössbauer spectra were recorded on this sherd at several temperatures. Figure 5 shows the spectra recorded at RT, 80 K, 30 K, and 4.2 K. The parameters that resulted from the fitting procedure are given in Table 3.

As mentioned before, at RT, a ferric doublet is dominant, and the ferrous doublet has, in this case, a relative area of practically zero. The magnetic sextet at RT contains both hematite and maghemite in roughly equal amounts, though it is difficult to separate them reliably.

At 4.2 K, a broad magnetic pattern that has been fitted by distributions of hyperfine fields amounts to more than 50% of the spectral area. These broad patterns develop only below about 25 K. It appears to be due to super-paramagnetic nanoparticles of oxidic iron that become super-paramagnetic at temperatures between RT and 25 K. It is probable that these are oxidation products of hercynite ($FeAl_2O_4$), which yield a broad magnetic Mössbauer pattern below around 25 K. Hercynite forms between about 800 and 950 °C under reducing firing conditions [26].

The explanation for this behavior could be that the amphorae were fired reducingly and re-oxidized only during the cooling phase at the end of the firing cycle. Reducing firing at or above 800 °C would give rise to the formation of hercynite and a vitreous phase that contains much of the iron as Fe^{2+}. When re-oxidized, the hercynite could convert to maghemite or hematite, while the iron that remains in the vitreous phase also oxidizes and, at least to some extent, forms the super-paramagnetic clusters.

Re-firing experiments were performed on this sherd (C665) at 750 °C and 800 °C for 1 h in air. Figure 6 shows the Mössbauer spectra that were recorded after re-firing the C665 sherd. Table 4 gives the values of hyperfine parameters obtained from the fitting procedure. The main feature observed is that maghemite decomposes to hematite largely between 750 and 800 °C. This means that the re-oxidation must have occurred below 750 °C. Another change caused by re-firing is that the quadrupole splitting of the ferric doublet in the RT spectra increases from 0.93 mm/s in the original sample to 1.30 mm/s after re-firing at 750 °C, with a similar change at 4.2 K (1.05 and 1.43 mm/s). This increase of the quadrupole splitting might be due to a re-arrangement of the environment of the Fe^{3+} atoms during re-firing.

These results suggest, in agreement with what was observed before in amphorae sherds produced in kilns of Lusitania [18], that the amphora was fired under reducing conditions, having been subjected to an oxidation process only when already cooling. With this procedure, in regions furthest from the surface, more Fe^{2+} is found. Regarding the spectra obtained at 4.2 K, it appears that approximately half of the spectral area consists of a broad magnetic background fitted with a distribution of magnetic hyperfine fields. This might be attributed to nanoparticles of oxidic iron precipitated on oxidation in a vitreous phase formed during the first reducing firing. Meanwhile, the magnetic phases with narrow linewidths, in most samples, both hematite and maghemite, are observed already at room temperature. Those areas vary from sample to sample but are usually around 30%, with about half of them attributed to maghemite. Supposedly these oxides were formed from iron Fe^{2+} during the oxidation process in the furnace cooling, which implies that the oxidation temperature must have been lower than around 750 °C since, at higher temperatures, maghemite is unstable and turns into hematite [27,28].

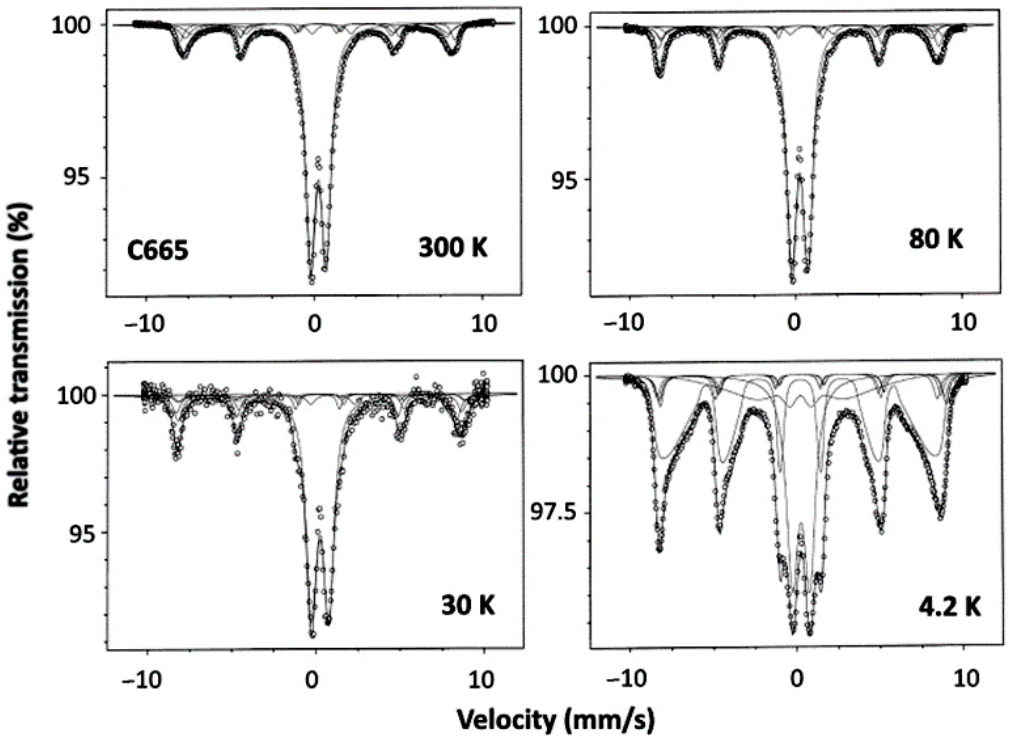

Figure 5. Mössbauer spectra of the C665 sherd recorded at different temperatures.

Table 3. Mössbauer parameters obtained from the fitting to the spectra shown in Figure 5 for the sherd C665. The isomer shifts are given relative to α-Fe measured at RT.

Temperature	IS (mm/s)	2ε/QS (mm/s)	H (T)	FWHM (mm/s)	A (%)	Site
RT	0.38 (1)	0.93 (1)	-	0.65 (2)	70	Fe^{3+}
	1.17 (1)	2.33 (1)	-	0.58 (1)	3	Fe^{2+}
	0.30 (1)	−0.02 (1)	48.2 (1)	0.40 (1)	19	Maghm
	0.38 (1)	−0.15 (1)	50.6 (1)	0.38 (1)	8	Hematite
80 K	0.38 (1)	0.98 (1)	-	0.60 (1)	68	Fe^{3+}
	1.13 (1)	2.60 (1)	-	0.63 (1)	2	Fe^{2+}
	0.30 (1)	−0.02 (1)	50.8 (1)	0.39 (1)	12	Maghm
	0.38 (1)	−0.15 (1)	52.5 (1)	0.38 (1)	12	Hem n-Mor
	0.38 (1)	0.30 (1)	52.9 (1)	0.38 (1)	6	Hem Morin
30 K	0.38 (1)	1.04 (1)	-	0.68 (1)	66	Fe^{3+}
	1.13 (1)	2.60 (1)	-	0.63 (2)	3	Fe^{2+}
	0.30 (1)	−0.02 (1)	51.7 (1)	0.39 (1)	18	Maghm
	0.38 (1)	−0.15 (1)	52.6 (1)	0.38 (1)	9	Hem n-Mor
	0.38 (1)	0.30 (1)	52.7 (1)	0.38 (1)	4	Hem Morin
4.2 K	0.50 (1)	1.05 (1)	-	0.75 (1)	27	Fe^{3+}
	<0.44 (1)>	−0.08 (1)	<50.3 (1)>	0.30 (1)	42	Dist H
	<0.50 (1)>	0.00 (1)	<24.0 (1)>	0.30 (1)	15	Dist H
	0.40 (1)	0.01 (1)	52.6 (1)	0.35 (1)	8	Maghm
	0.50 (1)	−0.21 (1)	52.8 (1)	0.38 (1)	3	Hem n-M
	0.50 (1)	0.30 (1)	53.2 (1)	0.39 (1)	5	Hem Morin

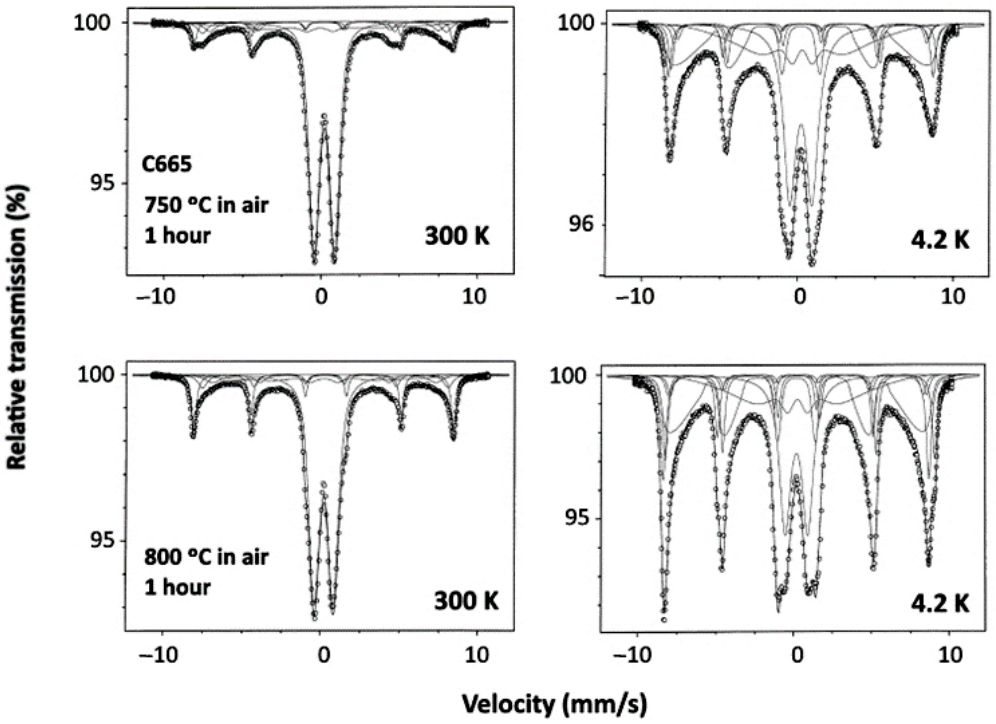

Figure 6. Mössbauer spectra recorded at RT and 4.2 K on the C665 sherd re-fired at 750 °C (**top**) and 800 °C (**bottom**).

Table 4. Mössbauer parameters deduced from the fitting to the spectra shown in Figure 6. The isomer shifts are given relative to α-Fe measured at RT. The values in brackets (<>) are mean values for the distribution of HF used to fit the broad sub-spectra.

Sample	Temperature	IS (mm/s)	2ε/QS (mm/s)	H (T)	FWHM (mm/s)	A (%)	Site
C665	RT	0.36 (1)	1.31 (1)	-	0.45 (1)	64	Fe^{3+}
750 °C/1 h		0.50 (1)	0.60 (1)	32.6 (1)	1.35 (1)	16	sext
		0.37 (1)	−0.02 (1)	47.4 (1)	0.53 (1)	14	Maghm
		0.38 (1)	−0.15 (1)	51.2 (1)	0.30 (1)	6	Hematite
	4.2 K	0.45 (1)	1.44 (1)	-	0.95 (1)	32	Fe^{3+}
		<0.41 (1)>	0.00 (1)	<52.8 (1)>	0.30 (1)	26	Dist H
		<0.50 (1)>	0.00 (1)	<24.0 (1)>	0.30 (1)	21	Dist H
		0.40 (1)	0.01 (1)	50.2 (1)	0.35 (1)	6	Maghm
		0.50 (1)	−0.21 (1)	52.8 (1)	0.33 (1)	8	Hem n-M
		0.50 (1)	0.30 (1)	53.3 (1)	0.33 (1)	7	Hem M
C665	RT	0.35 (1)	1.22 (1)	-	0.56 (1)	59	Fe^{3+}
800 °C/1 h		0.56 (1)	0.12 (1)	34.0 (1)	1.30 (1)	11	sext
		0.38 (1)	−0.02 (1)	45.2 (1)	0.64 (1)	14	Maghm
		0.38 (1)	−0.15 (1)	51.3 (1)	0.30 (1)	16	Hematite
	4.2 K	0.44 (1)	1.43 (1)	-	0.88 (2)	23	Fe^{3+}
		<0.42 (1)>	−0.02 (1)	<52.5 (1)>	0.30 (1)	29	Dist H
		<0.50 (1)>	0.00 (1)	<24.0 (1)>	0.30 (1)	17	Dist H
		0.40 (1)	0.01 (1)	50.9 (1)	0.34 (1)	6	Maghm
		0.50 (1)	−0.21 (1)	52.9 (1)	0.33 (1)	14	Hem n-M
		0.50 (1)	0.30 (1)	53.6 (1)	0.33 (1)	11	Hem M

Figure 7 shows X-ray patterns of the C665 sherd before and after re-firing at 800 °C for 1 h in air. It is observed that initially, hematite is present only very weakly but has been formed on firing at 800 °C for 1 h. This confirms the Mössbauer results about the conversion of maghemite to hematite.

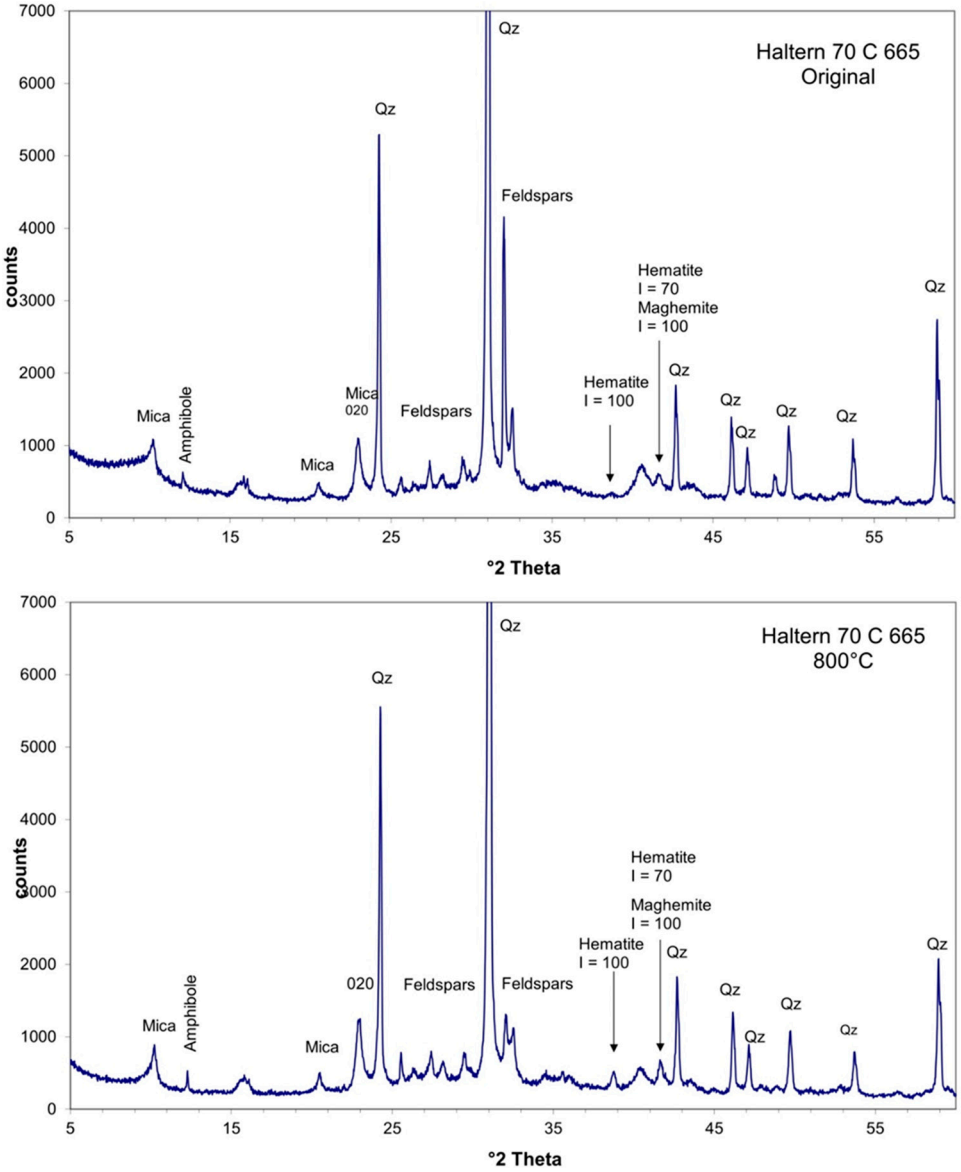

Figure 7. X-ray powder patterns of original C665 sherd (**top**) and re-fired at 800 °C for 1 h in air (**bottom**).

It is also interesting to note that mica is still present in the samples. Since mica decomposes at about 950 °C, the amphora to which this sherd belongs cannot have reached higher temperatures during firing in antiquity.

Summing up, we can say that the amphorae were fired in a reducing atmosphere between 800 and 950 °C and re-oxidized below 750 °C. This kind of firing signature is in accordance with the results of previous archeometric studies of Roman amphora from Hispania. A comparative analysis of sherds from several kilns of the Guadalquivir valley suggests that amphora Dressel 23 type was usually fired at between 850 and 950 °C under reducing–oxidizing atmospheres [29].

We now present Mössbauer spectroscopy results on a stamped Castro do Vieito sherd. The piece is the upper part of a handle with part of the neck, and its photograph is shown in Figure 8.

Figure 8. Stamped Haltern CV-A-4125 sherd.

A part of the amphora handle, in the side of the neck, was cut away to lay the interior open for sample taking. On the cut face, slightly different colorations could be distinguished. Samples were taken from the outer surface, the surface inside the neck, a reddish layer below the surface, and the core of the handle, as shown in Figure 9. Mössbauer spectra of these samples are shown in Figure 10, and the hyperfine parameters are given in Table 5.

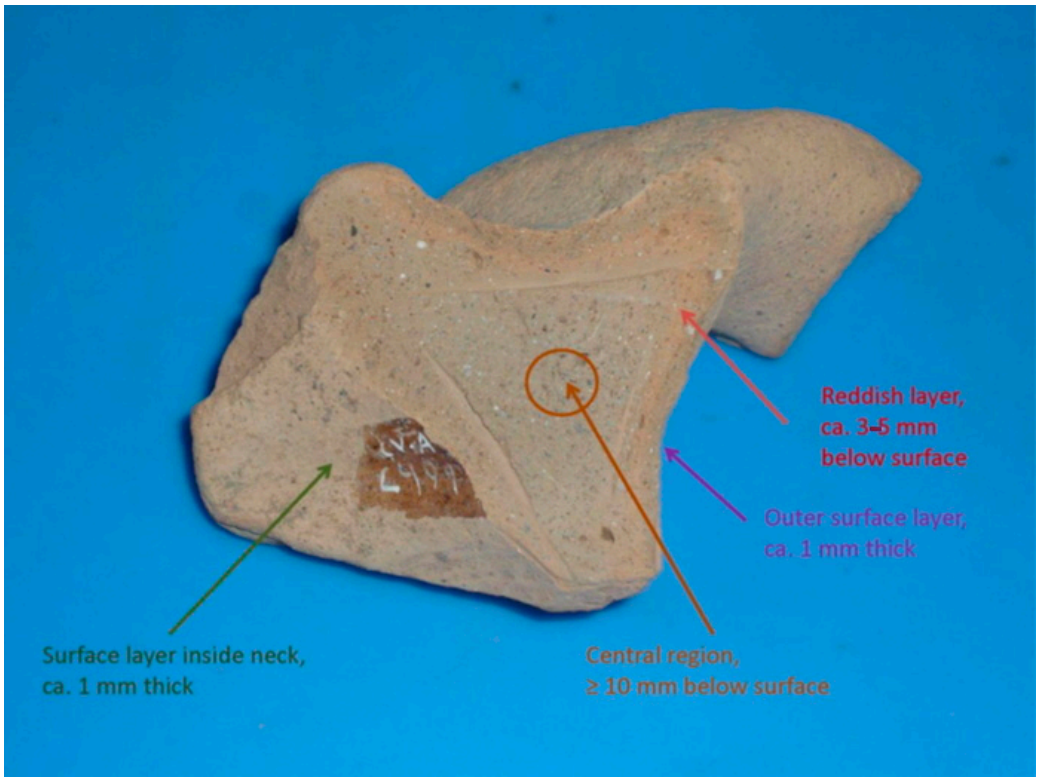

Figure 9. Cut made obliquely through the handle and body of the stamped CV-A-4125 sherd.

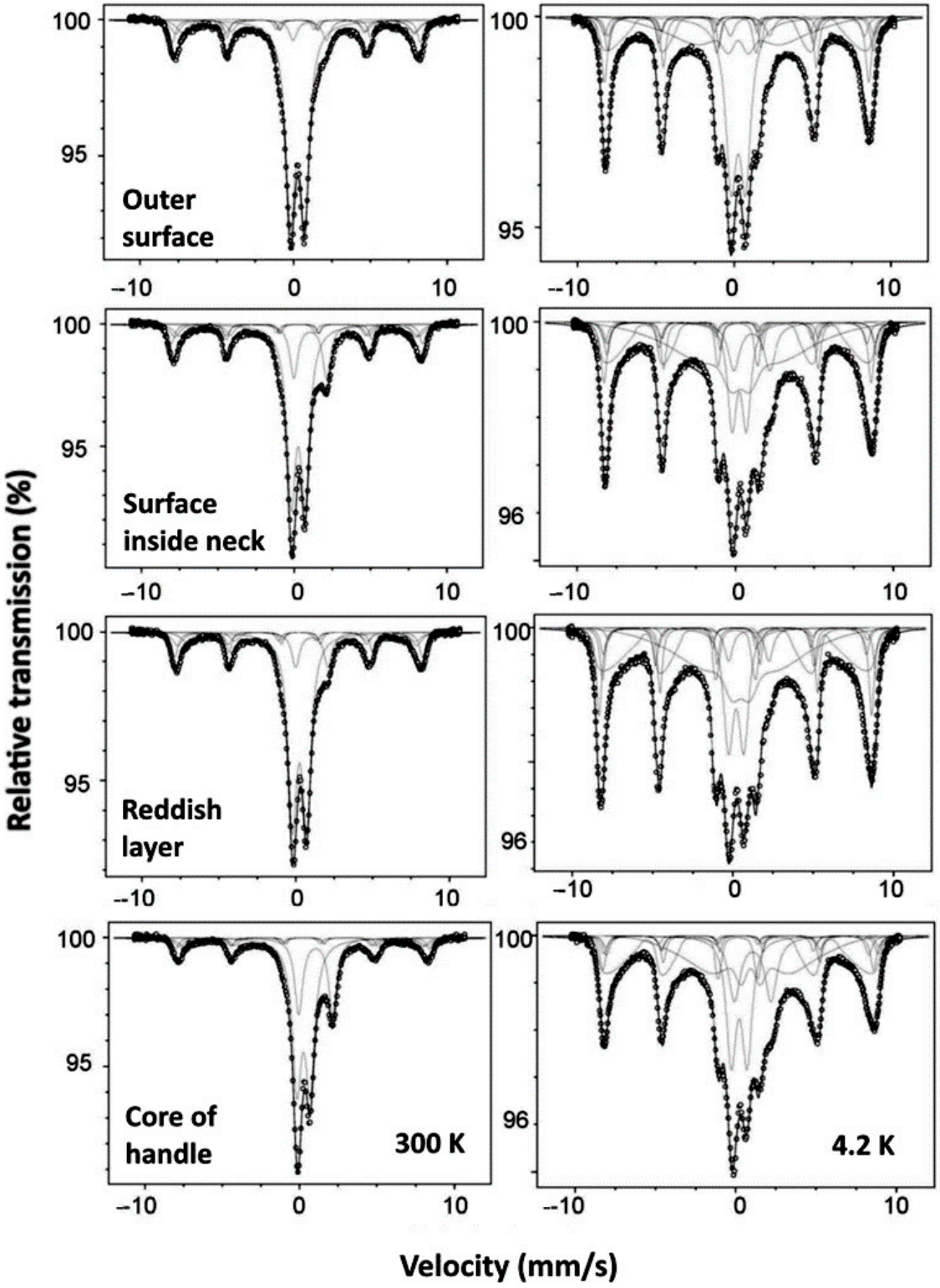

Figure 10. Mössbauer spectra recorded at RT (**left**) and 4.2 K (**right**) on different layers of the cut surface of stamped CV-A-4125 sherd.

Table 5. Mössbauer parameters deduced from the fitting to the spectra shown in Figure 10. The isomer shifts are given relative to α-Fe measured at RT. The values in brackets (<>) are mean values for the distribution of HF used to fit the broad sub-spectra.

Sample	Temperature	IS (mm/s)	2ε/QS (mm/s)	H (T)	FWHM (mm/s)	A (%)	Site
Outer Surface	RT	0.38 (1)	0.91 (1)	-	0.70 (2)	55	Fe^{3+}
		1.16 (1)	2.29 (2)	-	0.56 (1)	8	Fe^{2+}
		0.36 (1)	−0.21 (1)	49.7 (1)	0.59 (1)	13	Hematite
		0.35 (1)	0.04 (1)	45.6 (1)	<0.70 (2)>	24	Maghm
	4.2 K	0.38 (1)	0.95 (1)	-	0.74 (1)	24	Fe^{3+}
		1.29 (1)	2.22 (1)	-	0.63 (1)	3	Fe^{2+}
		<0.52 (1)>	<-0.20 (1)>	<52.5 (1)>	0.30 (1)	12	Dist H
		<0.50 (1)>	0.00 (1)	<22.5 (1)>	0.30 (1)	26	Dist H
		0.50 (1)	−0.21 (1)	53.0 (1)	0.25 (1)	4	Hem n-Morin
		0.50 (1)	0.35 (1)	53.2 (1)	0.25 (1)	6	Hem Morin
		0.37 (1)	0.05 (1)	52.1 (1)	0.30 (1)	25	Maghm
Surface inside neck	RT	0.39 (1)	0.88 (1)	-	0.65 (1)	48	Fe^{3+}
		1.17 (1)	2.19 (1)	-	0.75 (1)	16	Fe^{2+}
		0.32 (1)	0.09 (1)	50.0 (1)	0.60 (1)	22	Maghm
		0.47 (1)	−0.23 (1)	44.6 (1)	<0.60 (1)>	14	Hematite
	4.2 K	0.46 (1)	0.90 (1)	-	0.63 (1)	14	Fe^{3+}
		1.17 (1)	2.26 (1)	-	0.63 (1)	5	Fe^{2+}
		<0.52 (1)>	<−0.13 (2)>	<51.7 (1)>	0.30 (1)	20	Dist H
		<0.75 (1)>	0.00 (1)	<16.8 (1)>	0.30 (1)	27	Dist H
		0.50 (1)	−0.21 (1)	53.0 (1)	0.28 (1)	4	Hem n-Morin
		0.50 (1)	0.30 (1)	53.4 (1)	0.27 (1)	6	Hem Morin
		0.38 (1)	0.03 (1)	51.5 (1)	0.31 (1)	24	Maghm
Reddish layer near surface	RT	0.37 (1)	0.91 (1)	-	0.70 (1)	54	Fe^{3+}
		1.17 (1)	2.13 (1)	-	0.63 (1)	9	Fe^{2+}
		0.32 (1)	0.04 (1)	49.1 (1)	0.62 (1)	22	Maghm
		0.45 (1)	−0.21 (1)	44.5 (1)	<0.69 (1)>	15	Hematite
	4.2 K	0.48 (1)	0.95 (1)	-	0.65 (1)	16	Fe^{3+}
		1.29 (1)	2.20 (1)	-	0.60 (1)	4	Fe^{2+}
		<0.52 (1)>	<−0.10 (1)>	<51.5 (1)>	0.30 (1)	26	Dist H
		<0.75 (1)>	0.00 (1)	<16.1 (1)>	0.30 (1)	21	Dist H
		0.50 (1)	−0.21 (1)	53.0 (1)	0.25 (1)	4	Hem n-Morin
		0.50 (1)	0.33 (1)	53.1 (1)	0.25 (1)	7	Hem Morin
		0.38 (1)	0.07 (1)	52.1 (1)	0.35 (1)	22	Maghm
Core	RT	0.38 (1)	0.85 (1)	-	0.65 (1)	45	Fe^{3+}
		1.17 (1)	2.20 (1)	-	0.73 (1)	25	Fe^{2+}
		0.33 (1)	0.08 (1)	50.0 (1)	0.65 (1)	18	Maghm
		0.52 (1)	−0.17 (1)	42.6 (1)	<0.70 (1)>	12	Hematite
	4.2 K	0.49 (1)	0.93 (1)	-	0.75 (1)	20	Fe^{3+}
		1.29 (1)	2.38 (1)	-	0.63 (1)	8	Fe^{2+}
		<0.53 (1)>	<−0.08 (1)>	<51.5 (1)>	0.30 (1)	20	Dist H
		<1.24 (1)>	0.00 (1)	<20.1 (1)>	0.30 (1)	82	Dist H
		0.50 (1)	−0.21 (1)	53.0 (1)	0.28 (1)	3	Hem n-Morin
		0.50 (1)	0.31 (1)	53.2 (1)	0.28 (1)	5	Hem Morin
		0.35 (1)	0.12 (1)	51.2 (1)	0.33 (1)	16	Maghm

First of all, one can observe that the spectra are similar to those taken for the other Castro do Vieito samples, which could indicate the same provenance (stamped sherd and other Castro do Vieito sherds). The Mössbauer spectra of the four samples taken are quite similar, but they do show differences that give indications on the firing procedure:

- The amount of Fe^{2+} increases from the surface to the center. This is in agreement with the notion that the amphora was first fired under reducing conditions [30] and then

re-oxidized; by the time the oxidizing atmosphere reached the center, the temperature had already become too low for (nearly) complete oxidation.

- The Fe^{2+} content of the core in the RT spectrum is considerably higher (25%) than that in the 4.2 K spectrum. The most probable explanation for this is that much of the Fe^{2+} splits magnetically at 4.2 K. This is supported by the fact that the background at around +3 mm/s is noticeably higher than it is at −3 mm/s, supposedly because of the unresolved magnetically split Fe^{2+} pattern. As referred to before, this is probably a result of oxidation products of hercynite, which yields a broad magnetic Mössbauer pattern below about 20 K.
- The buff outer surface contains less Fe^{2+} than the buff surface inside the neck. Apparently, re-oxidation was less perfect inside the neck. This is not totally surprising since when the amphora was intact, the oxidizing atmosphere may have taken some time to penetrate the amphora. Perhaps the neck was even obstructed, and hence, the oxidizing atmosphere reached the interior only after the temperature had fallen too much for (nearly) complete oxidation. This can be explained by the way the amphorae were stacked in the kiln, i.e., upside down, with the neck towards the base of the kiln.
- The iron oxide that splits magnetically already at RT is certainly not pure hematite. Most probably, it is a mixture of hematite and maghemite. Maghemite seems to form below about 700 °C (it is unstable at higher temperatures) [27,28] when reduced ceramics are oxidized.
- The summed content of hematite plus maghemite (and including the broad component that may be any type of oxidic phase) is highest (37% at 4.2 K) in the reddish layer near the surface as well as in the buff surface layer (37% at RT). In the center, it is lower (29% at RT). The explanation may be that in the outer layers, the temperature of re-oxidation was still high enough for the formation of oxide phases, while the oxidation front reached the center only when the temperature was already a bit too low for iron oxide formation.

It is worth mentioning that the characteristics of the spectra belonging to different layers of the neck of this stamped sherd are similar to the ones obtained from re-firing experiences on the C665 sherd and discussed before.

4. Conclusions

The results obtained in this study, using Mössbauer spectroscopy at RT and 4.2 K, indicate that the Haltern 70 amphorae, whose sherds were recovered in the excavations of the Castro do Vieito settlement, probably have the same provenance. In agreement with the previously obtained results for amphorae from kilns at Olhos, in the Lusitania Roman province, the present study suggests that the amphora was fired under reducing conditions between 800 and 950 °C and having been subjected to an oxidation process only when already cooling. With this procedure, in regions furthest from the surface, more Fe^{2+} is found. Regarding the spectra obtained at 4.2 K, it appears that approximately half of the spectral area consists of a broad magnetic background fitted with a distribution of magnetic hyperfine fields. This might be attributed to nanoparticles of oxidic iron precipitated on oxidation in a vitreous phase formed during the first reducing firing. Meanwhile, the magnetic phases with narrow linewidths, in most samples, both hematite and maghemite, are observed already at room temperature. Those areas vary from sample to sample but are usually around 30%, with about half of them attributed to maghemite. Supposedly, these oxides were formed from iron Fe^{2+} during the oxidation process in the furnace cooling, which implies that the oxidation temperature must have been lower than around 750 °C since, at higher temperatures, maghemite is unstable and turns into hematite.

A Haltern 70 stamped sherd, with potter's stamp LH . . . (handle with part of neck attached), was carefully studied. The results obtained are similar to the ones obtained for other Castro do Vieito sherds, indicating a probable same provenance. The samples taken from the stamped sherd were from the neck part of the amphora, and it was observed that more Fe^{2+} was kept in the inside surface of the neck, so the oxidizing kiln atmosphere also

seems to have had only limited access to the interior of the neck, presumably due to the manner in which the amphorae were stacked in the kiln. A probable scenario is that the amphorae were stacked upside down, keeping the interior isolated from the overall kiln atmosphere during firing.

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