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Mössbauer and X-Ray Fluorescence Studies of Haltern 70 Amphorae from Roman Hispania Provinces

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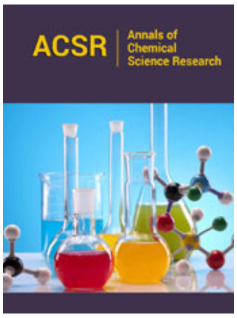

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Abstract

Haltern 70 amphora sherds from Castro do Vieito and from production sites in the Roman provinces Baetica and Lusitania were studied by Mössbauer spectroscopy and XRF. The amphorae were fired under reducing atmosphere and oxidized during cooling down. The firing conditions as well as the Ca content are essential for the colour and the state of iron of the amphorae.

Keywords: Haltern 70 amphorae; Mössbauer spectroscopy; X-ray fluorescence analysis; Firing conditions

Introduction

Halter 70 is the name of a type of amphorae that were produced in Hispania, a region of the Roman Empire during the second half of the first century BC and the first century AD. Morphologically, these amphorae are containers of about 0.90m height and a maximum diameter of about 0.35m. They have an irregular cylindrical body, a band rim, two handles with elliptical section and a pointed base filled with a ball of clay [1,2]. Amphorae were the standard vessels for transportation products like wine, vinegar, garum, oil, and other foodstuff in antiquity, from about 1500 BC to 700 AC. For this reason, the Roman provinces did not only produce agricultural products, but also a vast number of amphorae. In the NW of Iberia Haltern 70 amphorae are well documented, being more than 80% of the total number of amphorae found in archaeological sites [3]. Fifteen years ago, the excavation of the Castro do Vieito (NW of Portugal, Rio Lima estuary), where there was a settlement of Roman troops involved in the supply's network of the Roman army, provided the most extended collection of Haltern 70 amphorae of all the Roman world [1,4].

The origin of these amphorae is still under discussion, although their production sites are usually assigned to several places in Baetica or Lusitania, both provinces of Hispania. Aiming to find the origin of the Castro do Vieito amphorae, an archaeometric study has been started of Castro do Vieito sherds as well as of sherds from the first century AD from a number of production sites of the Roman provinces Baetica and Lusitania. The Baetica sites are Pinguele, Puerto Real, Lebrija, Arva and Orippo, while the Lusitania sites are Marim, São Lourenço and Olhos [1,5,6].

Results and Discussion

The Castro do Vieito sherds are reddish brown, no longer than 10cm and all exhibited a slight curvature. The specimens from the kiln sites are large fragments of amphorae like rims, handles and foot ends. They have colors ranging from reddish brown to pale cream. The sherds found in Castro do Vieito are soft and could easily be fractured. The most significant feature in all the samples is the sandy texture, sometimes with big inclusions of silicates. XRF results shown that the presence of Si is about 20-30wt% [5,7]. This confirms that sand was added to the raw clay, probably as a temper [8]. Amphorae sherds from Castro do Vieito are similar, and the same is verified for the amphorae from each of the individual sites, that are also quite similar in each group. From the kiln sites, only three typical cases will be described in the following, namely São Lourenço, Lebrija and Arva. The archaeological codes of the items are used in this paper.

The description of the kiln site specimens is as follows: The São Lourenço 1 sherd is the uniformly colored foot of a brick-red amphora; the Lebrija 2 sherd is a piece of an amphora wall with a thickness of about 11 mm of uniform buff-cream color ; the Arva 11 sherd is part of a handle which is red outside and grey in the core.

As mentioned before, the Castro do Vieito sherds are reddish. Table 1 presents element contents of the studied sherds. It is observed that Si is the main component in all the samples. The contents of Fe and Al are of the same order in all cases. The broadest range of concentrations is found for Ca, but there are also large differences in the Mg contents, which tend to be high when the Ca contents are high.

Table 1: XRF data for element contents [7].

Amphorae	Fe %	Ca %	Al %	Mg %	Si %
C Vieito 112	5.9	1.2	11.5	2.6	17.3
S Lourenço 1	4.1	6.4	13.3	6.2	30.5
Lebrija 2	2.4	13.4	10.0	10.6	23.4
Arva 11	3.4	10.4	10.6	6.6	28.0

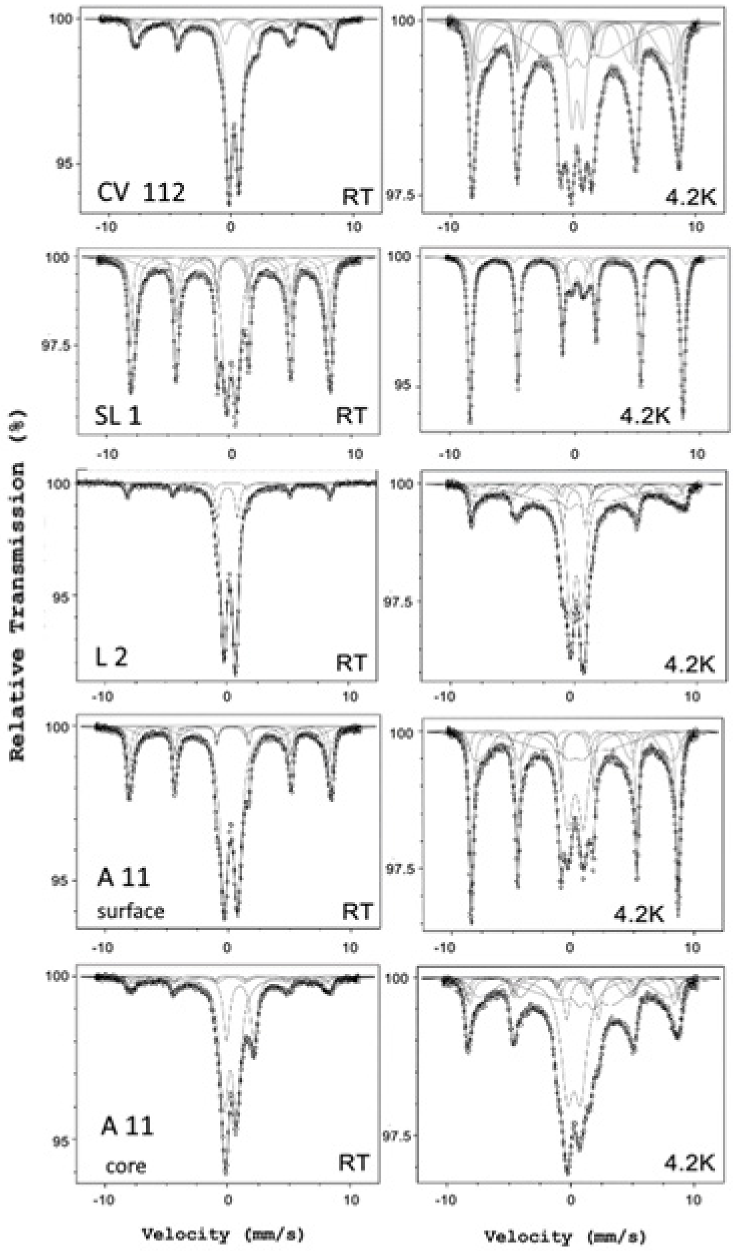

Figure 1: ^{57}Fe Mössbauer spectra of indicated sherds. RT spectra are shown on the left, 4.2K spectra on the right.

The Mössbauer spectra of the four samples are shown in Figure 1. The room temperature spectra exhibit a strong Fe^{3+} doublet with a quadrupole splitting of about 80-85mm/s, a weaker Fe^{2+} doublet and a magnetic contribution, mainly hematite. There may also be a minor broad magnetic contribution fitted with a Gaussian distribution of hyperfine fields, with a mean hyperfine field of about 40T, and attributed to nano-sized hematite or maghemite particles. The Fe^{2+} doublet found in some samples is always less than 10%. Firing under a reducing atmosphere would show a much higher fraction. The data obtained from RT spectra are incompatible with a purely oxidizing or a strongly reducing firing. The observations already suggest that the amphorae were fired in a changing atmosphere, perhaps under reducing conditions followed by oxidation during cooling down. This seems to be especially true for the sample São Lourenço 1 and explain the hematite percentage observed in the surface but not the core of Arva 11.

At 4.2K part of the broad magnetic pattern is resolved into hematite. The remaining broad distribution, with a mean hyperfine field between 45 and 50 T, is still from a vitreous phase that forms during reducing firing at or above 800 ºC [5,9]. The ferric doublets always decrease substantially when one cools the samples to 4.2K showing that at room temperature there is superparamagnetic hematite. Comparing the spectra obtained at 4.2K, we can observe that Lebrija sample and the sample taken from the core of Arva 11, which are not red in color, have the largest vitreous phase and smallest content of hematite. As described previously [5,9], a glassy phase is formed in a reducing atmosphere at 800 ºC or more. Iron is dissolved in the amorphous phase as Fe^{2+}. When the atmosphere becomes oxidizing at the end of the firing, the ferrous iron oxidizes. Fe^{3+} is less soluble in the glassy phase and therefore tends to form hematite. For this to occur, diffusion of the iron in the vitreous phase is required, which occurs the faster the higher the temperature is. When the cooling is too fast, oxidation may take place, but the formation of hematite may not occur because of sluggish diffusion. Lebrija and Arva samples have already less iron than the other samples. Moreover, they have more Ca that is proven to stablish the buff color of the fired amphorae [7]. Studies in which these sherds were refired at different temperatures and in different atmospheres [6] showed that the Ca content is essential for the color and state of Fe in the fired samples. Also, it was observed from those studies that a changing kiln atmosphere contribute to different colors in the inside and surface of the amphorae.

Conclusion

Haltern 70 amphora sherds from Castro do Vieito and from production sites in the Roman provinces of Baetica and Lusitania were studied by Mössbauer spectroscopy and XRF. Amphora sherds from Castro do Vieito are similar, and the same is verified for the amphorae from each of the individual sites, that are also quite similar in each group. Mössbauer spectroscopy revealed that the firing procedure was similar for all amphorae, involving a reducing firing around 800 ºC and oxidation during cooling. The firing conditions as well as the Ca content are essential for the color and the state of iron of the amphorae.

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