Mössbauer study of Haltern 70 amphora sherds from Castro do Vieito, North of Portugal

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Abstract. Haltern 70 amphora sherds obtained from Castro do Vieito were studied by Mössbauer spectroscopy, X-ray diffraction and X-ray fluorescence. In all our samples non magnetic Fe$^{3+}$ and haematite species were found. In some samples, also Fe$^{2+}$ was found. We conclude that the samples were fired under changing atmosphere, air being admitted at the end of the firing cycle following firing in a reducing atmosphere.

1. Introduction

In many areas of the world, sherds from broken pottery vessels are the most common artefacts found during the excavation of archaeological sites, and indeed sometimes the only evidence of past cultures.

Haltern 70 is the name of a particular type of amphora (a ceramic vase used in the Antiquity to transport commodities by the sea), that had been produced in the Hispania Baetica Roman province during the second half of the first century BC and the first century AC. A typical Haltern 70 amphora is shown in Figure 1. Recently, the excavation of the Castro do Vieito (Northwest of Portugal, Rio Lima estuary), an indigene settlement from the beginning of the Roman occupation of the region in the early empire, provided the most extended collection of Haltern 70 amphorae of all the roman world.

The signification of the massive presence of this type of artifact in the northwest of the Roman province of Hispania is actually the object of an intense debate. Traditionally, the presence of the amphorae was explained by the importance of the Atlantic coast of Hispania for the ancient commercial rotes in the beginning of the Roman Empire. Today, the most consensual theory explains this fact mostly by the role of the Haltern 70 amphorae in the supply system of the roman troops who controlled the region after its definitive conquest by the emperor Augustus [1].

Haltern 70 sherds were subjected to Mössbauer spectroscopy (MS) and X-ray diffraction (XRD) studies. The combination of XRD and MS has a considerable potential in the study of the chemical and physical transformations occurring in pottery clays during firing, as non iron-bearing minerals are

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only accessible by XRD, while iron-containing oxidic and amorphous phases may be difficult to detect by XRD due to poor crystallinity and small particle size, but can readily be detected by MS.

2. Experimental
Twelve Haltern 70 sherds obtained from the excavation of the Castro do Vieito were studied. The specimens were red in color, were no more than 10 cm long and all exhibited a slight curvature. The archeological codes of the items are used in this paper. Small quantities of powder were taken from the sherds and subjected to MS and XRD analysis.

XRD was performed at room temperature (RT) using Cu Kα radiation (λ = 0.154184 nm). Powder diffractograms were collected in a X-ray powder diffractometer equipped with a CPS120 curved position sensitive detector, from 0 to 120° 2θ, in Debye-Scherrer geometry. 57Fe Mössbauer spectra were recorded at RT in transmission geometry using a standard constant acceleration spectrometer. A 57Co source in Rh matrix with strength of ≈ 20 mCi was used. The least squares fitting of the spectra were carried out with a set of Lorentzian lines. The isomer shifts are given with respect to α-Fe at RT.

X-ray fluorescence (XRF) spectrometry has been used as a qualitative chemical elemental analysis method. A gas proportional scintillation counter filled with pure Xe at atmospheric pressure and with a mylar film window [2] was used to detect the X-ray lines emitted by the specimens under study, when excited with α-particles from a 244Cm source placed under vacuum. The spot area incident at the sherds had about 3 cm diameter. X-ray energy spectra were acquired for up to 15 min time.

3. Results and Discussion
Figure 2 shows only the XRF spectra obtained for one specific sherd because it is similar to all the other ones obtained for the different sherds. The elements found are Si, Mg and/or Al, Ca, Fe and small amounts of Ti or V. In our conditions it is not possible to distinguish clearly between Si, Mg and Al as all the peaks lie in the same energy range [2].

![Figure 1](image1.png)  
**Figure 1.** Characteristic form of Haltern 70 amphora [3].

![Figure 2](image2.png)  
**Figure 2.** Representative XRF spectrum and identification of elements.

Figure 3 shows some photographs of representative sherds. The most significant feature is the sandy texture, sometimes with big inclusions of silicates. In figure 4 we present some 57Fe RT Mössbauer spectra of Haltern 70 sherds. Solid lines are fits to the spectra. Mössbauer parameters obtained from representative spectra are shown in table 1.
The conclusions we can draw from Mössbauer spectra of clay-based ceramics depend on the chemical variability of iron, which may occur as Fe$^{2+}$ or Fe$^{3+}$ depending on the redox conditions in the kiln, and which may occur in a variety of silicate and oxide phases, also depending on the firing conditions.

We can derive the relative amounts of iron in individual phases from the fractional area of the respective pattern in the spectrum. Doing so, one often assumes that the Lamb-Mössbauer f-factors are the same for all components, which may not be strictly the case, but appears to be a reasonable guess for ceramic materials as long as one does not need to obtain a very high accuracy.

In raw clays (not heated) an intense Fe$^{3+}$ doublet with a small QS of about 0.70 mm/s, is characteristic of iron contained in the structure of the clay minerals. Oxidising firing between 400 and 600°C causes the splitting increases to 1.2 mm/s or even higher. It decreases again to below 0.8 mm/s firing above 800°C there is an increase of the splitting until about 0.80 mm/s [4]. The small quadrupole splitting of the Fe$^{3+}$ doublet thus indicates either a firing temperature above 800°C or a very low one of less than 600°C.

It is also known that haematite forms from iron present in the clay minerals when the layer structure collapses above 800°C and that another frequent source of haematite in fired clays are the iron oxyhydroxides, mainly goethite, that may be present in the clay and decompose to haematite between 200 and 400°C [4].

In all our samples non magnetic Fe$^{3+}$ and haematite species were found. Haematite was found in a small percentage, indicating that the iron in the clay matrix was not liberated during firing, which rules out firing above 800°C in an oxidising atmosphere.

In most of the samples also Fe$^{2+}$ was found. Firing under reducing conditions would show a fraction of Fe$^{2+}$ higher than that obtained. It is possible that the Fe$^{2+}$ oxide is FeAl$_2$O$_4$ as the Mössbauer parameters are close to this oxide [5].

The Mössbauer data for the Haltern 70 amphorae thus seem to be incompatible with a purely oxidising or a strongly reducing firing. They rather seem to have been fired under changing conditions, most probably being fired under reducing conditions and then oxidised towards the end of the firing cycle.

Recently it has been reported that similar parameters were obtained at RT for Celtic pottery. Mössbauer measurements at 4.2 K have been helpful to understand the firing conditions the sherds were subjected to [6].

XRD (figure not shown) identified SiO$_2$ (quartz) as the main crystalline phase common to all samples.

The photographs and respective amplification (5x) of 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).
This indicates that sand had been added to the clay [7], as also observed in photographs of Figure 3. Other less crystalline phases, changing slightly from sample to sample, are also present in small percentages, and are mostly identified as mineral silicates. Iron oxides were not found in crystalline form; however the shape of the background indicates the presence of amorphous phases.

| Table 1. RT $^{57}$Fe Mössbauer data for representative samples. |
|-----------------------------------|---|---|---|---|
| SC                               | QU | IS  | Γ  | B (T) | %  |
| Fe^{3+}                           | 0.98(1) | 0.41(2) | 0.79 | 1.42  | 51.2 | 33.2 |
| haematite                         | -0.20(1) | 0.32(2) | 1.42 | 51.2  | 33.2 |
| Fe^{3+}                           | 0.79(2) | 0.42(2) | 0.56 | -      | -    | 60.4 |
| C112                              | 2.41(1) | 0.97(2) | 0.76 | -      | -    | 16.0 |
| haematite                         | -0.21(1) | 0.42(2) | 0.95 | 51.5  | 23.7 |
| Fe^{3+}                           | 0.78(2) | 0.40(2) | 0.55 | -      | -    | 55.1 |
| C651                              | 2.42(1) | 1.00(1) | 0.72 | -      | -    | 27.0 |
| haematite                         | -0.18(1) | 0.37(1) | 0.93 | 50.5  | 17.9 |
| Fe^{3+}                           | 0.75(1) | 0.37(2) | 0.52 | -      | -    | 52.6 |
| C76                               | 2.28(1) | 1.03(1) | 0.78 | -      | -    | 33.8 |
| haematite                         | -0.20(1) | 0.36(1) | 0.67 | 51.0  | 13.6 |
| Fe^{3+}                           | 0.84(2) | 0.37(2) | 0.64 | -      | -    | 59.9 |
| C121                              | 1.14(1) | 2.36(1) | 0.60 | -      | -    | 7.1  |
| haematite                         | -0.19(1) | 0.40(1) | 0.81 | 50.5  | 33.0 |
| Fe^{3+}                           | 0.82(2) | 0.33(2) | 0.87 | -      | -    | 75.7 |
| C499                              | 2.17(1) | 1.07(2) | 0.50 | -      | -    | 7.0  |
| haematite                         | -0.18(2) | 0.40(1) | 0.83 | 51.0  | 17.3 |

Figure 4. RT Mössbauer spectra of some of the samples.

In conclusion, from the above observations it is inferred that the samples were fired under a changing atmosphere, air being admitted at the end of the firing cycle following the reducing firing, and that is the reason for red colour of the amphorae. In order to confirm this conclusion we intend to perform in the future Mössbauer measurements at 4.2K.

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