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Composition and microstructure of Roman metallic artefacts of Southwestern Iberian Peninsula

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Abstract The Roman invasion introduces new alloys and metallurgical practices in Iberian Peninsula. The southwestern end of this region has many evidences of connections with the Roman World, but there are no studies about the manufacture and use of copper-based artefacts during this period. Therefore, a set of about 20 ornaments, tools and small attachments recovered at the Roman sites of Monte Molião and Cidade das Rosas was studied by an analytical approach combining micro-EDXRF, optical microscopy, SEM–EDS and Vickers microhardness testing. The artefact composition shows a good correlation with function, namely pure copper for nails and rivets, low-tin bronze (2–6 wt% Sn) for basic tools, high-tin bronze (14 wt% Sn) for fibulae and high-lead bronze (19 wt% Pb) for a decorated jug handle. The manufacture also depends on function because most artefacts were subjected to thermomechanical processing, except the ornaments that would not benefit from post-casting work. Brass and gunmetal were only present in the site with a later chronology. A metallurgy visibly ruled by economical, aesthetical and technological concerns reinforces the evidences about the total integration of Southwestern Iberian Peninsula in the Roman World, but further studies will be essential to determine the evolution of copper-based alloys in Lusitania under Roman influence.

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1 Introduction

The arrival of Roman armies to Iberian Peninsula in 218 BC brings new materials and technologies that are differently absorbed by indigenous communities over time. In Hispania Ulterior, the farthest region of the Empire, some advances are recorded in the casting technique and in the use of brass as happened among the Vaccei [1], a Celtic people inhabiting the central Duero Basin. However, a few Roman ornaments recovered at Castanheiro do Vento, an archaeological site in northeastern Portugal, suggest a persisting selection of bronze for decorative items, although with different amounts of tin and lead due to technological and economic issues [2]. Another example of the alloy selection is the adoption of high-leaded bronze to cast statuettes, such as the Centaurus from Canas de Senhorim [3]. Additionally, an ongoing research on a collection of anthropomorphic situlae handles of Conimbriga (first–third century AD) has been identifying mostly copper, bronze and gunmetal, often with very high lead contents [4].

In the southwestern coast, the archaeological record contains numerous fine ware and amphorae revealing the integration in the Roman World throughout the last two centuries of the first millennium BC. Consequently, this region of Hispania Ulterior, later designated as Lusitania, seems to be more than just a point in the Atlantic route used to supply the Roman armies in the Iberian Peninsula and Britain [5]. In spite of those important contacts with the heart of the Roman World, there are no studies about the metallurgy under Roman influence in this southwestern end of Iberian Peninsula.

An integrated approach combining microanalytical techniques was used to study the composition and post-casting operations of Roman artefacts. A micro-EDXRF spectrometer and an optical microscope, specially designed for the analysis of cultural heritage materials, enabled the investigation of artefacts without damaging the cultural significance. The elemental and microstructural characterisation was complemented with SEM–EDS analyses and Vickers microhardness testing of selected artefacts. The archaeological collection comprises artefacts from Monte Molião, a Roman settlement located in the southern coast, which were compared with artefacts from Cidade das Rosas, a Roman inland villa in southern Portugal. The study includes the search for relations between manufacture, typology/function and composition of artefacts, to identify the choices made by ancient metallurgists in view of technological, aesthetical and economic issues.

2 Artefacts and archaeological contexts

The site of Monte Molião (Lagos) is located on a small hill that during the first millennium BC would be a peninsula facing the Atlantic Ocean (Fig. 1). Archaeological excavations held from 2006 to 2011 have exposed tens of thousands of materials that established the *floruit* of this non-military settlement from 175 BC to 150 AD [6, 7]. Cidade das Rosas (Serpa) was a Roman inland villa, located on the left bank of the Guadiana River, which connected the interior to the southern littoral region. The material culture, particularly the amphorae types for transporting olive oil, wine and fish products established a long occupation period comprising the end of the first century BC to the fifth century AD [8].

The collection from Monte Molião mostly belongs to an occupation from 175 to 50 BC and consists of artefacts that evidence the daily life of Roman inhabitants. Household items include a long handle (MM12863) from a simpulum or colander showing distinct sections connected by rivets (Fig. 1). A second handle (MM12862) with an anthropomorphic head with poor ornamental details belongs to the first–second century AD. This type of handle was used in jugs being exclusively table and kitchen ware [9]. There is also a semicircular rod (MM12896) that belongs to a snaffle bit used to drive a horse. Ornaments include a finger ring (MM13003), whose small diameter indicates that was worn by a child or a woman, and two annular fibulae with different working designs but similar shapes. The bow and spring of fibula MM12861 belong to the same piece, while fibula MM12895 worked with a separate hinged pin. The first design fits the most successful pre-Roman type utilised from the sixth to first century BC, while the hinge spring can be found in La Tène types from the fourth to first century BC [10]. The Monte Molião fibulae may belong to a pre-Roman occupation from 350 to 200 BC. The set is completed by simple attachments such as nails and one fragmented rod.

Metallic artefacts from Cidade das Rosas include of a pair of stylus (CR1 and CR2), a wick dipper snuffer (CR4) and two sheets (CR5 and CR6) (Fig. 1). There is also a fragmented awl (CR3) and a wire section (CR7). The wick dipper snuffer was used to control the light intensity of the Roman lamp (lucerna) and has an almost exact parallel in the collection from Conimbriga [11]. The sheets have riveting holes thus probably constitute repair plates from large objects such as vessels.

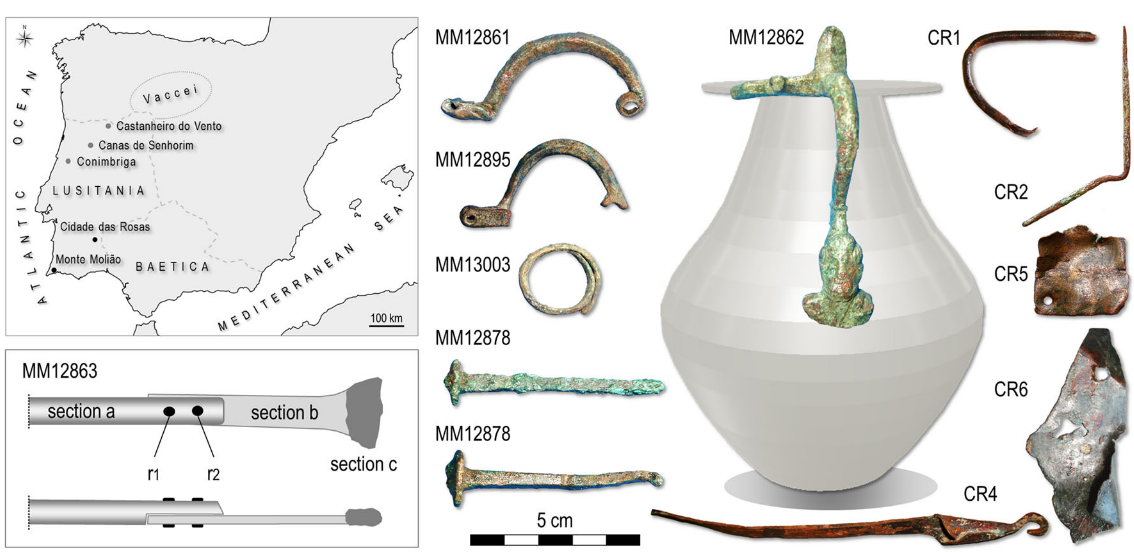

Fig. 1 Location of Vaccei culture and Roman sites in the Iberian Peninsula (Hispania Ulterior was divided into Lusitania and Baetica in 27 BC). Photographs of some of the artefacts recovered at Monte Molião and Cidade das Rosas (drawing of jug with ornamented handle MM12862)

3 Materials and methods

The analytical study has required the exposure of a minute area of metal on artefacts. The preparation comprised the corrosion layer removal by polishing a small area (3–5 mm diameter) with diamond pastes (15–1 μm). Optical microscopy observations were used to confirm a proper metallic surface for analysis. An alternative procedure was used in fragmented artefacts, as it was possible to cut a small section (1–2 mm) with a manual jeweller's saw. The section was mounted in epoxide resin, grinded with SiC papers (1000–4000 grit size) and polished with diamond pastes (3 and 1 μm). Vickers microhardness testing was also applied to mounted sections of artefacts. Finally, the affected areas of artefacts were protected with benzotriazol (3 % m/v in ethanol) and coated with Paraloid B-72 (3 % m/v in ethanol), while the colouration of the surrounding patina was replicated with a mixture of pigments dissolved in Paraloid-B72 solution (20 % m/v in ethanol).

Micro-EDXRF analyses involved an ArtTAX Pro spectrometer with a 30 W Mo X-ray tube, focusing polycapillary lens (<100 μm diameter of analysis area) and an electro-thermally cooled Si drift detector (FWHM of 160 eV at 5.9 keV) [12]. Samples were analysed in three spots with 40 kV, 600 μA and 100 s of live time. Quantifications were made with WinAxil software comprising calibration factors calculated with Phosphor Bronze 551 (British Chemical Standards), Leaded Bronze C50.01 (BNF Metals Technology Centre) or Leaded Gunmetal 183/3 (British Chemical Standards). The relative uncertainty is better than 10 %, while the detection limits (DL $= 3 \times$ background$^{1/2}$/sensitivity) of elements of interest are 0.02 wt% Fe, 0.02 wt% Ni, 0.03 wt% As, 0.03 wt% Pb, 0.06 wt% Zn and 0.15 wt% Sn (quantification limits reported are equal to 10/3*DL).

Microstructural features were observed in a Leica DMI 5000 M inverted optical microscope with automatic acquisition of digital images at different focus positions [13]. Surfaces were etched with aqueous ferric chloride solution. Selected artefacts were analysed with a Zeiss DSM 962 SEM equipped with a conventional tungsten filament and secondary electron (SE) and backscattered electron (BSE) imaging modes. SEM–EDS analyses involved an Oxford Instruments INCAx-sight spectrometer with an ultra-thin window for the detection of low Z elements. Samples were coated with a carbon conductive bridge to prevent charge accumulation and analysed with 25 mm of working distance, 20 kV of accelerating voltage, 3 A of filament current and an emission current of 70 μA.

Zwick-Roell Indentec equipment was utilised for Vickers microhardness testing of sections mounted in epoxy resin using a 0.20 kgf load for 10 s. The average hardness reported comprises at least three indentations having a relative standard deviation lower than 10 %.

4 Results and discussion

Micro-EDXRF analyses of Monte Molião collection have identified artefacts composed of copper, bronze and leaded bronze alloys with low amounts of impurities, such as Fe, Ni, Zn or As (Table 1). The iron is probably the most significant impurity, showing variable but relatively higher contents (0.27 ± 0.30 wt% Fe). The increased iron content of Roman

Table 1 Composition of Roman artefacts from Monte Molião

Type	Artefact	Reference	Cu	Sn	Zn	Pb	Fe	Ni	As
Ornaments	Fibula	MM12861	81.7	14.3	n.d.	3.6	0.09	n.d.	0.29
	Fibula	MM12895	79.4	13.6	<0.20	6.7	0.07	n.d.	n.d.
	Finger ring	MM13003	96.6	2.2	n.d.	n.d.	1.15	n.d.	n.d.
Tools	Handle (jug)	MM12862	74.7	6.0	<0.20	19.0	0.15	0.09	n.d.
	Handle (section a)	MM12863a	91.2	6.3	n.d.	1.9	0.40	<0.08	0.16
	Handle (section b)	MM12863b	92.6	5.0	n.d.	1.7	0.35	0.18	0.10
	Snaffle bit	MM12896	83.4	9.9	<0.20	6.0	0.35	0.10	<0.10
Attachments	Nail	MM12878	99.3	n.d.	<0.20	n.d.	0.65	n.d.	n.d.
	Nail	MM12908	99.9	n.d.	n.d.	n.d.	<0.05	n.d.	<0.10
	Nail	MM12901	99.6	n.d.	n.d.	0.24	0.08	<0.08	<0.10
	Nail	MM12924	99.7	n.d.	n.d.	0.17	0.09	<0.08	<0.10
	Nail	MM12925	99.8	n.d.	n.d.	n.d.	0.17	n.d.	n.d.
	Nail	MM13001	99.5	n.d.	<0.20	n.d.	0.08	n.d.	0.33
	Nail	MM13002	99.4	n.d.	n.d.	0.28	0.14	n.d.	0.11
	Rivet	MM12863r1	99.2	n.d.	n.d.	0.19	0.16	0.19	0.12
Unknown	Rod	MM12883	94.8	4.1	n.d.	0.83	0.07	n.d.	0.12

Values in wt%; *n.d.* not detected

Fig. 2 Optical microscopy images of fibulae MM12895 and MM12861 and finger ring MM13003 (bright field, etched: *pink* inclusions in MM12895 are redeposited copper, and *dark* inclusions in MM12861 are copper oxides)

metal indicates efficient smelting operations (lower pO_2 and higher temperature) which in Iberia appear to begin during the Iron Age with the influence of Phoenician technology [14]. Despite the absence of brasses at Monte Molião, the traces of zinc detected in some artefacts may well result from the use of scrap or crucibles previously utilised to melt brass alloys. In fact, several experimentations showed that a zinc-free bronze can reach up to about 0.5 wt% Zn by contamination from oxides in the melting crucible [15].

Bronze fibulae of Monte Molião (~14 wt% Sn) were probably used not only for fastening garments but also for aesthetical reasons because bronze alloys with higher tin amounts have more golden shades [16]. However, the brass alloy has an even more golden colour and a set of 25 BC–200 AD Aucissa fibulae recovered at Roman settlements in the Iberian Peninsula suggests that eventually brass became preferred over bronze for this type of ornaments [17]. Additionally, the Roman fibulae of Titelberg settlement (Luxembourg, first century BC–fourth century AD) show an earlier preference for brass than other typologies [18]. Therefore, all evidence seems to suggest an early chronology for the fibulae of Monte Molião, most certainly before the adoption of brass in the region.

The finger ring MM13003 was made with a low-tin bronze. A large collection of finger rings (Aquicum, Budapest, second–fourth century AD) was found to be composed of different alloys (Cu, Cu–Sn, Cu–Zn, Cu–Zn–Sn, with low and high lead amounts) without any relation with typology, suggesting the undifferentiated use of raw materials for this type of cheap jewellery [19]. A low-tin bronze might result from the use of scrap because tin is preferentially oxidised during melting; i.e. experimental trials have established that a few melting cycles reduce the tin content from 9.5 wt% to 3.1 % [20].

The pair of fibulae of Monte Molião shows different microstructural characteristics comprising small twinned grains (MM12861) or cored dendrites (MM12895) (Fig. 2). These features match the fibulae designs since the evidences of thermomechanical processing observed in the first might be related with the spring coiling (the bow and spring belong to the same segment), whereas for the latter the bow did not suffered post-casting work since it is separated from the spring. The fibula MM12895 also presents copper inclusions (pink in bright-field illumination) deriving from long-term preferential oxidation of tin (a dealloying corrosion process termed destannification that is accompanied by copper redeposition in regions with low oxygen concentration) [21]. The finger ring MM13003 shows well-recrystallized grains with annealing twins evidencing one or more cycles of forging and annealing (see the much larger size of these grains when compared to the ones of fibula MM12861, Fig. 2).

The lead content of those bronzes also varies significantly, and objects with complex forms (fibulae), larger size (snaffle bit) or refined decoration (jug handle with anthropomorphic figure) have higher amounts (3.6–19.0 wt% Pb). Lead is insoluble in copper–tin α phase, thus forming low-melting-point inclusions in the interdendritic regions (Fig. 3). Pb-rich inclusions improve the fluidity of molten bronze, thus enabling better castings for different types of Roman artefacts ranging from statuary to coins [22]. Moreover, the lead was much cheaper than bronze because of excess availability of Roman lead [23]. Regarding the post-casting works, the optical microscopy observations show that the ornamented jug handle was left as-cast (dendritic microstructure, Fig. 3), while the snaffle bit was subjected to forging plus annealing, and concluded with a strong forging evidenced by crossed slip bands (the grains boundaries and slip bands are seen enhanced by intragranular corrosion in Fig. 3).

Small attachments such as nails and rivets were made with highly pure copper (>99 wt%). The raw material was probably smelted ore, as melted scrap could introduce some unwanted elements that would weaken the mechanical properties. Nails display microstructures with distorted recrystallized grains with annealing twins revealing post-casting processing by forging and annealing (Fig. 4). Vickers microhardness testing on nails MM12901 and MM12924 show values (55 HV0.2 and 67 HV0.2, respectively) comparable to non-hardened copper, while the nail MM12925 has a higher hardness (112 HV0.2). The latter was measured on a section closer to the nail tip that was significantly elongated to make a sharp and tougher edge (see the lengthened grains in the microstructure MM12925, Fig. 4).

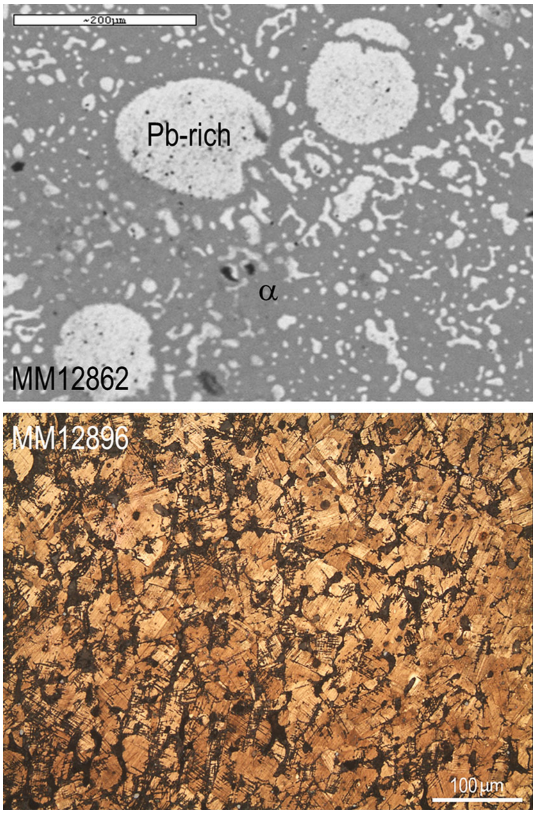

Fig. 3 SEM–BSE image of jug handle MM12862 (SEM–EDS results show 4.9 wt% *Sn* and 21.4 wt% *Pb*, and the small difference in micro-EDXRF results are related with the heterogeneous distribution of lead-rich inclusions in copper–tin α phase) and optical microscopy image of snaffle bit MM12896 (bright field, etched)

Micro-EDXRF analyses of handle MM12863 identified two bronze sections (a and b) connected by copper rivets (r1 and r2) and the vestiges of a third section (c) made of iron (see the scheme in Fig. 1). No attempt was made to remove the corrosion layer in this last segment due to its brittle nature. This peculiar handle comprising different metals and alloys is probably the result of a repair using whatever scrap materials were available for that task (note the similar composition of sections a and b: different parts of a broken handle, later connected by rivets?). Optical microscopy observations of both sections identified deformed twinned grains from forging plus annealing operations (Fig. 5), while the flattened section (b) also shows crossed slip bands, as a consequence of an intense final deformation.

Micro-EDXRF analyses of artefacts from the Roman villa of Cidade das Rosas evidence a more diversified copper-based metallurgy (Table 2). Besides the copper (snuffer, CR4) and bronze (awl CR3, stylus CR2 and wire CR7), there are two brass sheets (CR5 and CR6) and a second stylus (CR1) made of gunmetal. The relation between typology and composition is difficult to perceive. For instance, the pair of styluses is made of different alloys (bronze and gunmetal) and the brass sheets have different lead contents (0.43 and 4.4 wt% Pb). A high lead content is

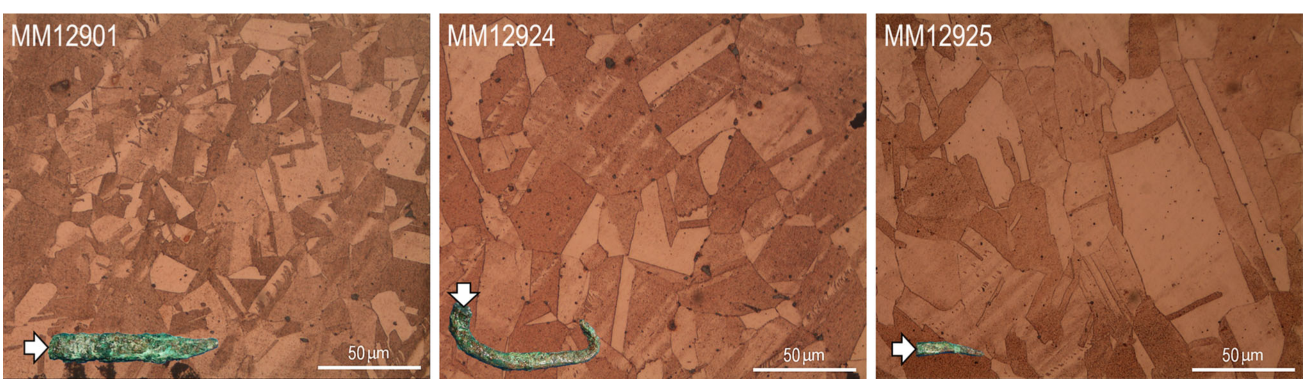

Fig. 4 Microstructures of nails MM12901, MM12924 and MM12925 (bright field, etched; *bottom left* observed sections of nails, the *left* nail has 3.1 cm length, and the remaining are on the same scale)

more likely to produce cracks on hammering due to the insolubility of lead in the Cu–Zn solid solution. In fact, Roman copper alloys from Northern Britain show an almost absence of sheet metal with more than 1 wt% lead [24].

The composition of Roman artefacts in the Lusitania province, namely from Monte Molião, Cidade das Rosas, Canas de Senhorim and Castanheiro dos Vento, was compared in Cu–Sn–Pb and Cu–Zn–Pb diagrams (Fig. 6). The most obvious difference is the higher use of zinc at the Roman villa of Cidade das Rosas, probably due to the later chronology of this site. However, rural sites in Northern Britain also have a higher proportion of brass than Roman forts and towns, which indicates the deliberate preference of those rural inhabitants for the high-status alloy [25]. On the contrary, evidence was found for the military control of brass technology in Palestine during the first century AD [26]. Apparently, the use of brass among the Romans depends not only on technological and chronological factors, but also on cultural and regional issues. For instance, locations in the periphery of the Empire like Thamusida (Morocco, first–third century AD) show a very low ratio of brasses (about one-tenth), suggesting that the alloy never really entered the local metalworking activities [27].

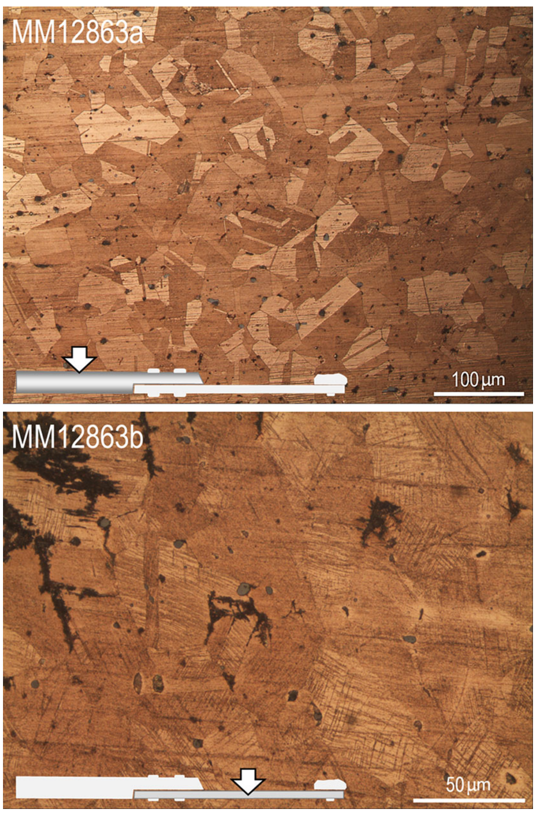

Fig. 5 Microstructures of segments from handle MM12863 (bright field, etched; *bottom left* observed sections of rod)

Another noteworthy implication of those diagrams concerns the good control of the lead content of Roman metal in Lusitania. Leaded artefacts have a shape or size requiring an alloy with good castability, even when presenting the same function, as evidenced by the two handles, i.e. ornamented jug handle (leaded bronze) and plain simpulum handle (binary bronze). A similar instance was found on a leaded bronze handle with a Centaurus from a ritual vase at Canas de Senhorim [3]. The brass sheet with high contents of lead and tin is an exception among Roman metal [24], probably resulting from the use of undifferentiated scrap.

The tin consumption is also properly contained because small attachments are composed of copper, simple typologies have low tin contents and prestigious fibulae show higher amounts of tin. This feature is shared by the Roman artefacts of Castanheiro do Vento, namely two high-tin bronzes (penannular fibula and decorated plaque) and a low-tin bronze common fibula of annular type [2]. At Monte Molião, the use of higher amounts of tin for superior status fibulae may have been established in an earlier period, considering that those examples can belong to a pre-Roman occupation. However, Romans really mastered the bronze metallurgy, as evidenced for instance by some bronze mirrors with a tin-rich reflective layer induced by a complex manufacture involving inverse segregation, thermal treatments and accelerated oxidation/corrosion processes [28].

Table 2 Composition of Roman artefacts from Cidade das Rosas

Type	Artefact	Reference	Cu	Sn	Zn	Pb	Fe	Ni	As
Tools	Awl	CR3	96.1	2.9	n.d.	0.90	0.05	n.d.	n.d.
	Stylus	CR1	88.1	4.2	6.8	0.38	0.39	n.d.	0.12
	Stylus	CR2	92.4	5.6	n.d.	1.8	0.16	n.d.	n.d.
	Wick dipper snuffer	CR4	98.8	0.51	n.d.	0.17	0.45	n.d.	n.d.
Unknown	Sheet	CR5	74.2	1.7	19.4	4.4	0.26	n.d.	n.d.
	Sheet	CR6	85.5	2.0	11.8	0.43	0.25	n.d.	n.d.
	Wire	CR7	89.3	9.5	n.d.	0.89	0.07	n.d.	0.20

Values in wt%; *n.d.* not detected

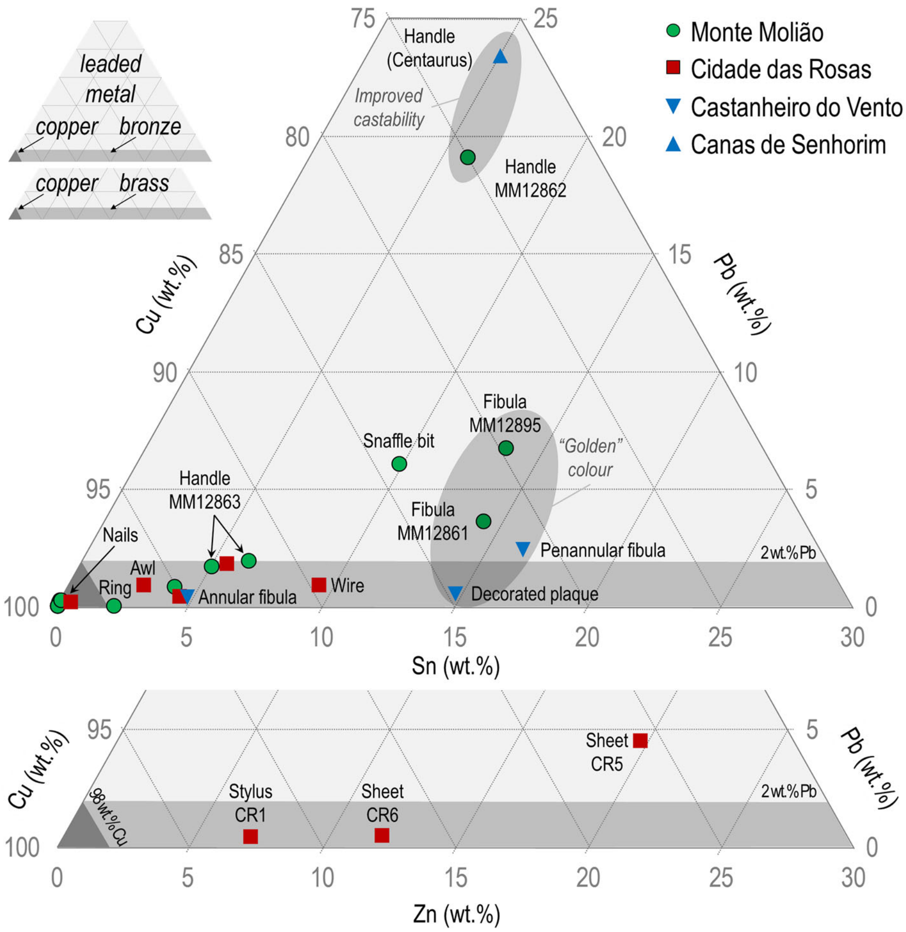

Fig. 6 Composition of artefacts from Monte Molião, Cidade das Rosas, Castanheiro do Vento and Canas de Senhorim (values considering $Cu + Sn + Pb = 100$ wt% or $Cu + Zn + Pb = 100$ wt%, respectively)

5 Conclusions

A technological survey of artefacts from a seashore town and an inland villa gives a preliminary appraisal on the Roman metallurgy in the southwestern end of Iberian Peninsula. The association of certain typologies with specific alloys indicates that the raw materials were carefully selected according to technological, aesthetical or economic concerns. There is a clear compositional distinction between what nowadays is defined as "wrought alloys" and "cast alloys", which seem to be worked accordingly; i.e. ornaments that not benefit from post-casting work remain as-cast, the tip of copper nails was hardened, and the majority of tools was subjected to thermomechanical processing.

In particular, copper was an inexpensive raw material used for attachments, while ornamented objects take advantage of the improved castability of leaded bronze alloys. Plain tools and simple adornments were made with low-tin bronzes, while the "golden" high-tin bronze alloy was reserved for more exclusive ornaments. The brass alloy seems to be absent from Monte Molião, probably due to the earlier chronology (175–50 BC) of most of those artefacts.

As a final conclusion, it may be said that the metallic artefacts recovered in those Roman sites, similarly to the fine ware and amphorae, reveal the full integration of the southwestern end of Iberian Peninsula in the Roman World since the last centuries of the first millennium BC. However, additional studies would be very important to better establish the Roman influence on the evolution of copper-based alloys, especially of brass, in the Lusitania Province.

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