# Study of imperial brass Chinese coins and archaeological Portuguese Cu-based artefacts by X-Ray diffraction

*Rui M. S. Martins [1,2], Norbert Schell [3], Maria J. Furtado [1,4], Filipa Pereira [1,4], and Rui J.C. Silva [4]*

[1]*Instituto Tecnológico e Nuclear, EN10, 2696-953 Sacavém, Portugal*

[2]*Centro de Física Nuclear da Universidade de Lisboa, Av. Prof. Gama Pinto 2, 1649-003 Lisboa, Portugal*

[3]*Helmholtz-Zentrum Geesthacht, Max-Planck-Str. 1, 21502 Geesthacht, Germany*

[4]*Faculdade de Ciências e Tecnologia, FCT, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal*

Chinese coins were usually manufactured from leaded bronze until the 16th century. Brass coinage was introduced in the beginning of the 16th century [1]. The brass Chinese coins selected for this study are part of the Macau Scientific and Cultural Centre's Museum (CCCM) coin collection and they all belong to the Qing dynasty. It is very important to study this material for a better understanding of the metallurgical cash production in China and predict the corrosion phenomena for conservation purposes.

Furtado *et al*. [2] studied twenty brass Chinese coins of the CCCM collection. Results obtained by energy-dispersive micro X-ray fluorescence spectrometry showed that these brass alloys (Cu-Zn) frequently contain up to 3% Sn, have highly variable Pb content (from n.d. up to 14%) and Fe, Sb, and As as minor elements. The coins present typical as-cast microstructures although very fine-grained, which are supported by binary (Cu-Zn) and ternary (Cu-Zn-Sn) equilibrium phase diagrams that explain microstructural differences due to the presence of Sn in these brasses, namely a Sn-rich phase similar to the gamma phase in brasses. Other systems, like the binary As-Fe helped to explain the Fe and As rich-phases in some coins; and the presence of a Sb-rich phase microstructurally similar to the Sn-rich phase cited above is being studied.

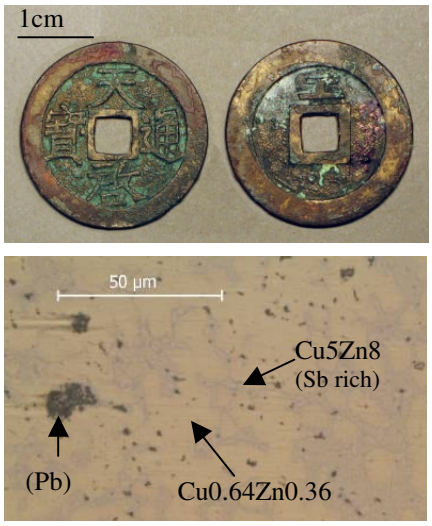


**Figure 1:** Chinese coin (#2642 [2]): obverse and reverse of the coin and detail view of polished area at rim. ⇒

The Castro de Vila Nova de São Pedro is a Chalcolithic fortified settlement located at Vila Nova de São Pedro (Azambuja, Portugal). Its material richness is of great value to the understanding of relevant aspects of pre-historic societies. Alongside agriculture and grazing, some evidence of other practices such as hunting, fishing and gathering were found. Research involving metallic artefacts is needed to answer essential questions related to the ancient metallurgy of this region and intercultural relationships with other Iberian prehistoric societies.

F. Pereira Master's thesis [3] presents a significant archaeometallurgical study of artefacts from Castro de Vila Nova de São Pedro. The collection selected for the preparation of this Master thesis was composed of 275 metallic artefacts or fragments of metallic artefacts, all recovered from Afonso do Paço's archaeological excavations. Most of the artefacts could be classified according to different typologies: awls, wires, chisels, axes, blades, arrowheads, saws, daggers and a socket. The work increases the knowledge of this important Portuguese archaeological site not only by evaluating the arsenic content of copper-based artefacts and correlating it with artefact typologies and functions, but also in the determination of the manufacturing operations involved such as forging and annealing, their evolution and their contribution to the production of harder or stronger metallic material.


⇐ **Figure 2:** Fragment of an axe blade VNSP148D [3] with sampling area and a cross section view of the sample mounted in resin.

Micro X-ray diffraction studies at a laboratory source have been carried out to investigate fine structural details. However, complementary experiments with a synchrotron radiation source were required to increase resolution and to obtain enough signal in the small gauge volumes. The HEMS beamline at PETRA III offers excellent research possibilities (high flux in parallel beam). X-ray diffraction experiments on two brass Chinese coins (Fig. 1) and on a piece of the cutting edge of an axe (Fig. 2) were carried out at HEMS. XRD data were acquired in transmission mode (image plate MAR345) using a beam with energy of 87 keV. For the study of the coins the spot size was fixed to 500×500 $\mu m^2$ and the acquisition time was 2 s. In the case of the piece of the axe, a spot of 500 µm in horizontal and 100 µm in vertical was selected and the acquisition time was 60 s. The image plate detector allowed us to record the respective Debye-Scherrer rings. The data were evaluated and the intensity of the diffracted beam represented as a function of the angle of diffraction (scaled to Cu radiation: $\lambda$ = 1.5406 Å).

The phases identified in the analyzed Chinese coins were the $Cu_{0.64}Zn_{0.36}$ phase (matrix - α brass phase), the eutectic $Cu_5Zn_8$ (γ brass phase), which SEM-EDS analysis found to be Sb-rich, and the (Pb) phase as Pb-rich globules scattered across the microstructure (see Fig. 1).

Figure 3 presents XRD data obtained for the piece of the blade of the axe VNSP148D [3] recovered from Castro de Vila Nova de São Pedro. Some authors refer that the solubility of arsenic in copper falls markedly at low temperature and that As-rich (γ) phase ($Cu_3As$) can precipitate from solid solution at ambient temperatures over archaeological times [4]. Therefore, the As-rich (γ) phase can precipitate along grain boundaries by natural aging (slow evolution to a more stable condition) during the thousands years in burial context. The XRD results confirm the presence of domeykite ($Cu_3As$ – cubic and hexagonal phases), besides cuprite ($Cu_2O$) and arsenic copper ($As_7Cu_{93}$).

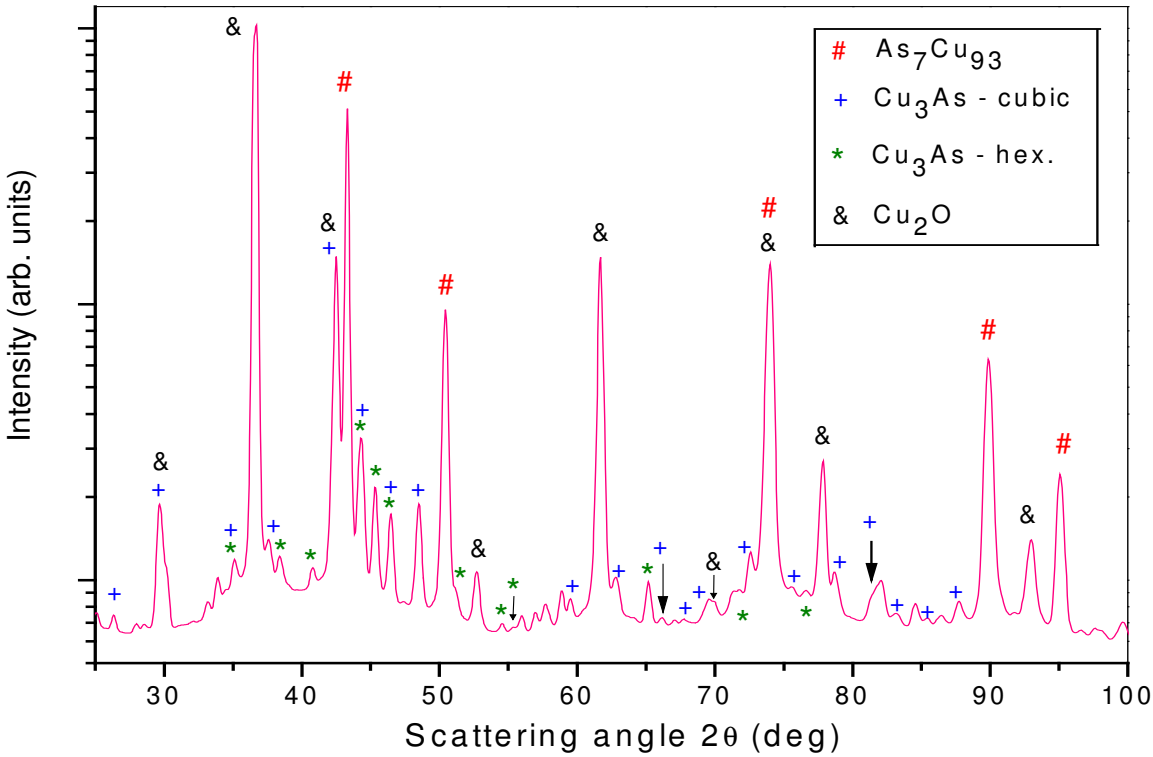


**Figure 3:** XRD data obtained for a piece of the blade of an axe (VNSP148D – Fig. 2).

## References


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