Archaeometric study of a broad collection of pre-Roman bronze fibulae from the center of the Iberian Peninsula

Suset Barroso Solares (1,2,3*), Elvira Rodríguez-Gutiérrez (1,2), Ana I. Quílez-Molina (1,3), Óscar Fadón (1,3), Carlos Sanz-Mínguez (1,2), Javier Pinto (1,2,3)

(1) Study, Preservation, and Recovery of Archaeological, Historical and Environmental Heritage (AHMAT) Research Group, Condensed Matter Physics, Crystallography, and Mineralogy Department, Faculty of Science, University of Valladolid (Spain), Paseo de Belen 7, 47011 Valladolid (Spain)
(2) Centro de Estudios Vacceos Federico Wattenberg, Faculty of Philosophy and Literature, University of Valladolid, Valladolid, Spain
(3) BioEcoUVA Research Institute on Bioeconomy, University of Valladolid (Spain)
* corresponding author: suset.barroso@uva.es

Palabras clave: Fluorescencia de rayos X, Composición elemental, Pintia, Vacceos. **Key Words:** X-ray fluorescence, Elemental composition, Pintia, Vacceos.

INTRODUCTION

This work summarizes the results of an archaeometric study of pre-Roman bronze fibulae found at the Pintia site (Padilla de Duero/Peñafiel, Valladolid, Spain), located in the center of the Northern plateau of the Iberian Peninsula. Pintia was a large Vaccean city that developed in the second Iron Age, from the 5th century BC. overcoming the change of era in the Romanization process, at which time it could house around 8 to 10 thousand people (Pinto *et al.*, 2021; Sanz Minguez, 1997). The archaeological research carried out on this site, over more than four decades, has provided important findings, among which it is worth highlighting the collection of fibulae with some 370 specimens, which places it in second place after Numancia (Soria) regarding the total number of this kind of finding (Rodriguez Gutierrez, 2024). This large set is also relevant both for the diversity of models and for the perfect state of conservation of many of the pieces, constituting a magnificent testimony of the metallurgical activity of the Vaccean people (Fig. 1). At the same time, there are a series of pieces that find their parallels among the finds of other bordering ethnic groups (Celtiberia, Vetonia and Autrigón world) and in more distant regions, such as Tras Os Montes, Gallaecia or even Central Europe (Rodriguez Gutierrez, 2024).

SAMPLES AND METHODS

With the aim of improving our knowledge about Vaccean metalwork, and trying to look for evidence of its political and commercial relationships with other cultures, a selection of sixty-three fibulae from the archaeological site of Pintia (Fig. 1.a) has been studied by X-ray Fluorescence. For the analysis, a portable Micro-FRX ELIO X-ray Fluorescence (XRF) spectrometer (Bruker) was used, equipped with a rhodium X-ray microfocus tube (10-50 kV, 5-200 μA, 4 W) and a 50 mm^2 SDD detector with CUBE technology. The spectrometer has a motor and control software to make elemental composition maps of up to 10 x 10 cm^2. The measurements were made in air at 40 kV, 80 μA and 60 seconds of data collection. At each point studied, two point measurements were made separated by 100 μm and the obtained signal was averaged. The qualitative and quantitative analysis of the results obtained was carried out using the ESPRIT Reveal software, being able to detect elements from Al to U.

Several parts of each fibula were studied, reaching a total number of three hundred and ninety points analyzed, to ensure the representativeness of the obtained results, as well as to identify differences between the pieces that make up the most complex specimens. Moreover, elemental composition maps were obtained for some representative or complex pieces (Fig. 1.b).

 ISSN 2659-9864

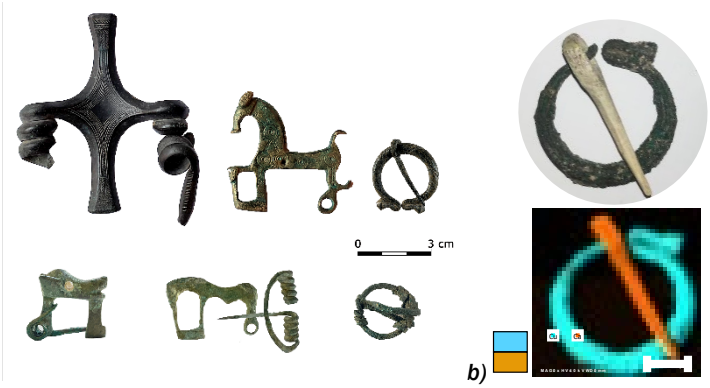

Fig 1. (a) Examples of bronze fibulae recovered at Pintia with diverse morphologies. (b) Example of an elemental composition map of a fibulae with bronze and bone parts.

RESULTS AND CONCLUSSIONS

The obtained results allow for the identification of the main composition of the bronze alloys, generally presenting very low amounts of lead (< 5 wt.%) and a broad range of tin (generally between 5 and 40 wt.%). However, a significant number of pieces with high lead contents (from 10 to 75 wt.%) are also found in this collection. In addition, it was possible to evaluate the effects of the patina on a representative selection of pieces that present polished areas, obtaining a good qualitative agreement between the results obtained from the patina and the polished surfaces (e.g., correlative order regarding tin content is generally preserved, although notable tin enrichment on the patina was detected, while measured lead contents are rather stable), in good agreement with previous results (Holakooei *et al.*, 2021). Finally, the hypotheses about a possible different provenance of some notable pieces have been reinforced by the detection of anomalous contents of some elements (e.g., silver, antimony, gold, etc.) (Figure 2).

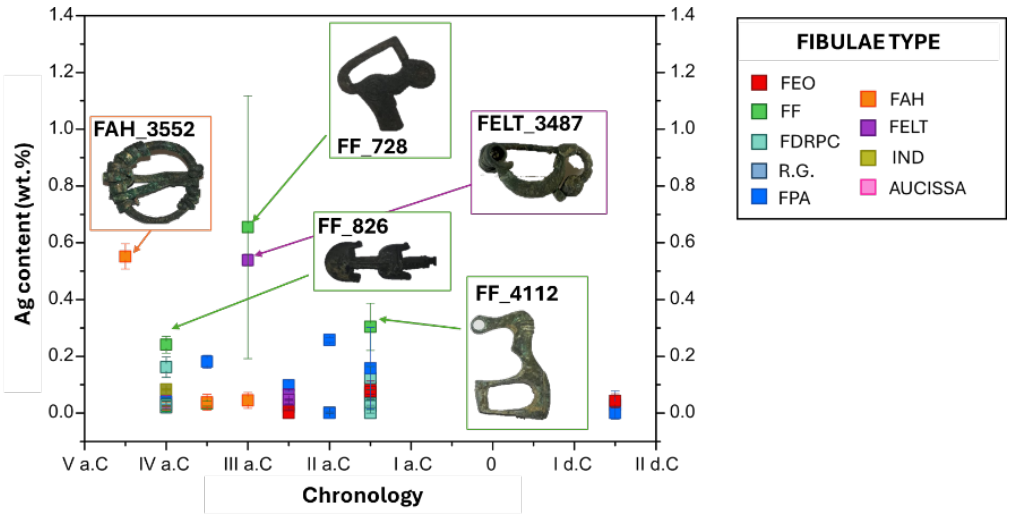

Fig 2. Ag content (weight %) of the studied fibulae from Pintia.

REFERENCES

Holakooei, P. Oudbashi, O. Mortazavi, M. Ferretti, M. (2021): On, under and beneath the patina: Evaluation of micro energy dispersive X-ray fluorescence quantitative data on the classification of archaeological copper alloys, Spectrochim. Acta B: At. Spectrosc., **178**, 106128, DOI: 10.1016/j.sab.2021.106128

Pinto, J. Prieto, A.C. Coria-Noguera, J.C. Sanz-Minguez, C. Souto, J. (2021): Investigating glass beads and the funerary rituals of ancient Vaccaei culture (S. IV-I BC) by Raman spectroscopy. J. Raman Spectrosc., **52**, 170–185. DOI: 10.1002/jrs.6049

Rodriguez Gutiérrez, E. (2024): Las fíbulas de la «Vacceia», siglos V al I a.C. Diversidad tipológica y composicional. Desperta Ferro, **55**, 1-6.

Sanz Mínguez, C. (1997): Los vacceos: cultura y ritos funerarios de un pueblo prerromano del valle medio del Duero. La necrópolis de Las Ruedas, Padilla de Duero (Valladolid), Arqueología en Castilla y León, Memorias 6, Valladolid, Junta de Castilla y León., Valladolid.