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Ancient fibulae and contemporary scientific riddles

Scanning Electronic Microscopy (SEM) and Energy Dispersive X-ray Analysis (EDAX) between archaeology and the physical chemistry of materials

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In memory of Romano

Abstract. Analysis by SEM and EDAX of the remains of two ancient fibulae, identical in material (bronze), design (leech-shaped), cut and size has revealed that, despite appearances to the contrary, they were not cast in the same mould, presenting substantial differences in the microstructure and composition of the alloy. Moreover, EDAX investigation has produced an unexpected result, as one of the two alloys has been found to present little less than 4% aluminium, despite having been buried for over 2000 years in a ground rich in halides, fairly acidic and constantly waterlogged.

Key words. SEM, EDAX, bronze, aluminium, microanalysis.

Premise

Sutor, ne ultra crepidam! (Cobbler, stick to the sandal!)

Many times I was rebuked by my senior colleagues at University who, by the use of this judicious Latin phrase, attempted to convince me to proceed with caution in my research. It must have been a waste of breath, otherwise I would not be here writing about antique *fibulae* – the use of the Latin word being justified by the fact that at least one of the brooches which are the subject of this paper is thought to be Roman.

On the other hand, what would scientific research be if one were always to "stick to the sandal"? In short, archaeologists need not worry, I do not mean to steal their thunder. I have stumbled upon the remains of these ancient clasps partly by chance and partly through my natural curiosity. Now the fairly extraordinary re-

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sults of the SEM and EDAX analyses are urging me to divulge them, in the hope that specialists of the field could help me solve this mystery.

The general picture. Ever since ancient times, brooches have not only been used to fasten clothes but also to ornate gowns (particularly women's), so from the early Bronze Age until today they have been produced in a great variety of shapes, sizes and materials.

The two brooches we are about to consider are both made of bronze and are apparently identical in design – a typical leech-shaped bow – size and carving technique (Figure 1). One would think they were produced by the same artisan but in actual fact they were found more than 1,400 nautical miles apart.

One of the two brooches (from now on called "fibula T") was concealed among the gravestones in the oldest part of the "tophet" (children's cemetery) of Tharros, once a Punic city-state in the gulf of Oristano in Sardinia (Figure 2). The other ("fibula A") had been buried in a field near Aquileia, a former Roman city at the northern end of the Adriatic Sea.

According to the archaeologist who has lent me the Tharros brooch,

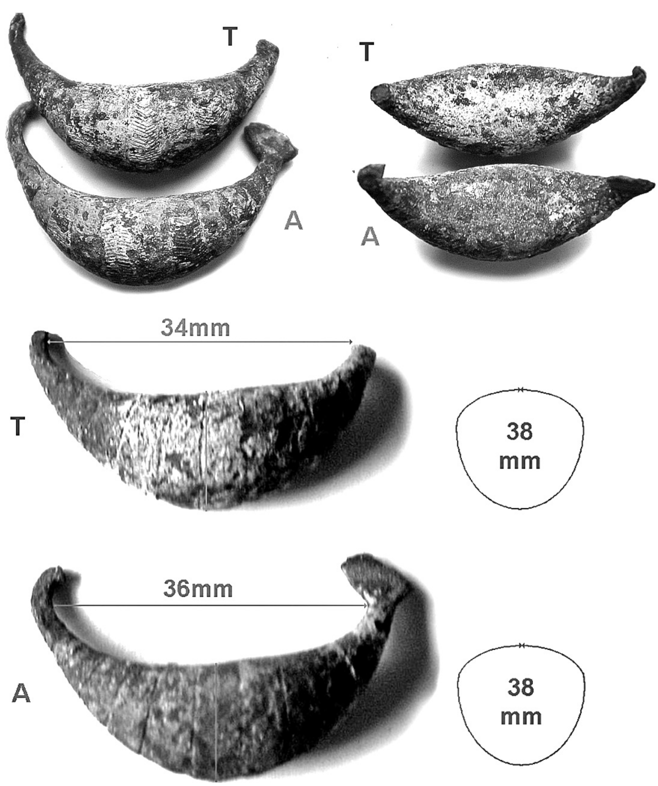


Figure 1. Fibula T found in Tharros children's cemetery and fibula A excavated from a field near Aquileia. On top the two fibulae before being cleaned, below having been cleaned and dried.

fibula T is probably Phoenician and might have been buried before the fifth century BC. This is disputed by Professor Giovanna Pisano, a world-famous expert on Phoenician and Punic antiquities, who is certain that the brooch is not Phoenician, as leech-shaped brooches were never produced by that particular culture. In her opinion, fibula T could be Etruscan or Italian or could be older than the Tharros "tophet" and have been brought there by merchants.

Fibula A, which was part of a small "treasure" also including Roman coins from the age of Sulla and older, was probably buried between 81 and 79 BC and, according to the archaeologist, is certainly Roman.

In my opinion, the fact of having been found in Aquileia together with Roman coins from the first century BC did not necessarily mean that fibula A was locally produced at that time. It could have been inherited or acquired by the person who buried the treasure, so it could be much older and have been produced abroad.

Also in my opinion, the fact of having been found under a gravestone in the oldest section of Tharros children's cemetery did not mean that fibula T was from the fifth century BC or older nor that it was produced locally or elsewhere in Italy. In fact, considering that the Romans had ruled over Tharros ever since the second century BC and had also excavated the cemetery, fibula T could be much more recent, could have been produced abroad and might not be Phoenician, Etruscan or Italian, but Roman.

Figure 2. Tharros "tophet" (children's cemetery).

Considering also that ancient merchants, in order to expand their trades, were sailing across the Mediterranean with even greater ease than today, I wondered if the two fibulae could have been produced by the same workshop and later scattered in different parts of the world.

Analysis, findings and discussion. In other to shed light on the origin of the brooches and verify if they really were twins cast in the same mould, I decided to analyse the microstructure and composition of the bronze alloys.

Naturally I did not have the permission to scrape the surface of the two fibulae, so I examined them by Scanning Electronic Microscope (SEM) to observe their microstructure and by Energy Dispersive X-ray Analysis (EDAX) to determine the chemical make-up of the outer strata.

Prior to being tested, the two brooches were cleaned by an ultrasound cleaner and distilled water in order to eliminate dust and encrusted dirt, then they were vacuum dried.

The analysis was carried out using

an *Assing Stereoscan 2000* microscope with a *Falcon* EDAX attachment. For the morphological analysis we employed an accelerating voltage of 25 keV, reaching 30 keV during the chemical analysis (EDAX). Naturally, we only examined the area which was free from encrustation.

The morphological analysis, even at a relatively low magnification (X 300 to 1000), showed that the bronze of fibula T had a uniform structure with a very fine grain size (2-6 μm) (Figure 3), while the bronze of fibula A was characterized by an uneven structure with a much coarser grain (Figures 4 to 6).

Moving to higher magnitudes (X 5000-20000) it appeared that, in the case of fibula T, grains presented an even structure without signs of deformation from mechanical stress; in the case of fibula A, its larger grains consistently displayed signs of deformation from mechanical stress (Figure 7).

Subsequently, detailed EDAX mapping was carried out to determine the chemical composition of the two bronze alloys.

It was discovered (Table 1) that: fibula T was made of high-quality binary bronze which was very homogeneous in composition (Cu 85,6%, Sn 14,4% ± 2,5%) (Figure 8), while fibula A was made of very poor-quality quinary bronze with a composition (average: Cu 82,1%, Sn 12,2%, Fe 2,2%, Pb 1,8%, Al 3,8%) that greatly varied from one area to the other (Figures 9 to 12).

In addition, while most microzones of fibula A were found to be made of quaternary (Cu-Sn-Fe-Pb) o quinary (Cu-Sn-Fe-Pb-Al) alloy, a few microzones were found where the alloy was only binary (Cu-Sn) and two zones were shown to be made of pure aluminium (!).

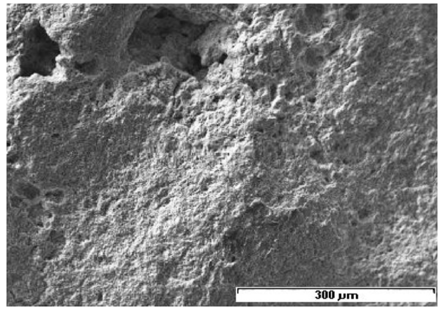


Figure 3. Microstructure with a very fine grain size typical of fibula T.

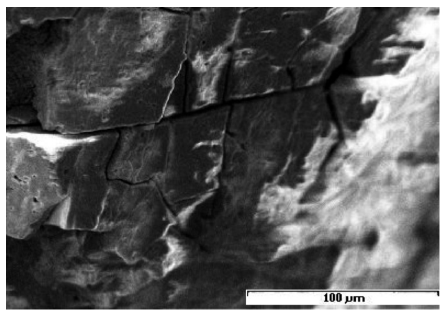


Figure 4. Microstructure of fibula A: coarse-grained areas.

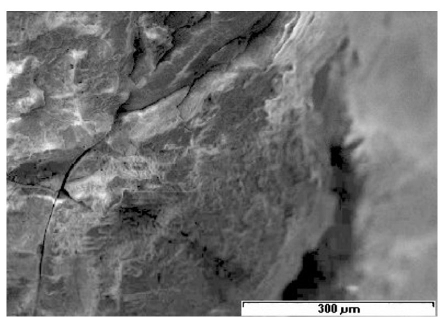


Figure 5. Microstructure of fibula A: very coarse-grained areas resulting from the mechanical welding of smaller grains.

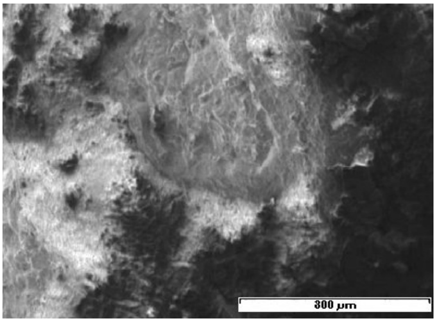


Figure 6. Microstructure of fibula A: fine-grained areas.

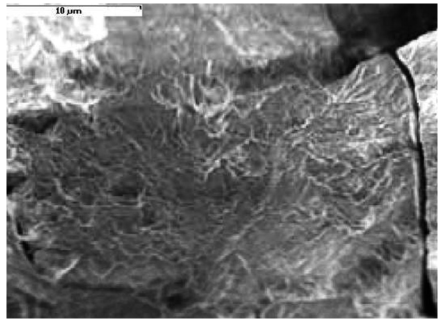


Figure 7. Signs of deformation from mechanical stress in the grain structure of fibula A.

So regardless of their similarities in design, size and carving style, the two brooches were not identical twins. SEM and EDAX investigation had shown substantial differences in their composition and microstructure; also their morphological discrepancy, as detected by SEM, indicated different production methods: gravity die casting with limited hand-finishing for fibula T and manual thermomechanical welding of metallic grains (considering the composition variations, possibly metal discarded from previous work) for fibula A.

atomic %	Sanguete Fibula						
	T		A				
	Cu	Sn	Cu	Sn	Fe	Pb	Al
90-100							
80-90							
70-80							
60-70							
50-60							
40-50							
30-40							
20-30							
10-20							
0-10							

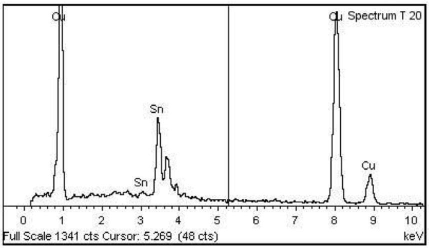
Table 1. Variations detected by EDAX in different parts of the fibulae with percentages of chemical components.

But can we be sure that the two brooches were not produced by the same workshop?

A friend of mine who is a goldsmith and an antiquarian, as well as an expert of antique crafts, tells me that in the absence of a mark one cannot be sure of anything. And even if there is a mark, you still cannot be sure because forgeries were common even in ancient times. Also according to him, the uneven composition of fibula A may indicate that it was a hastily-made copy replacing an original that had gone lost. A similar hypothesis has been put forward to me by Dr Maurizio Buora, curator of Udine Municipal Museums.

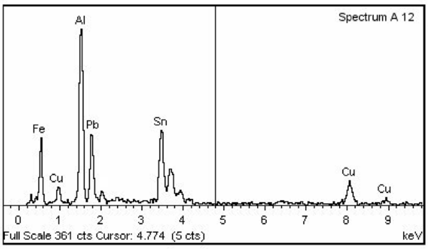
So it looks as if I must keep my doubts to myself.

However, if from an archaeological point of view the analysis has not produced any interesting outcome, from the point of view of the chemistry and physics of materials the re-



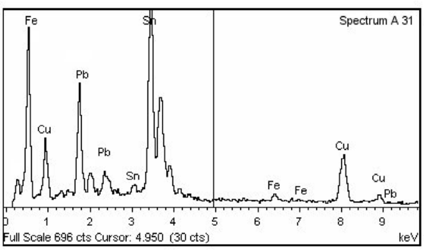
Element	Atomic %
Cu K	85,30
Sn L	14,70
Al K	00,00
Fe K	00,00
Pb M	00,00

Figure 8. EDAX spectrum typical of fibula T.



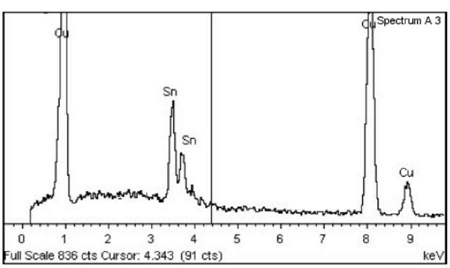
Element	Atomic %
Cu K	15,10
Sn L	24,70
Al K	36,20
Fe K	18,80
Pb M	05,20

Figure 9. EDAX spectrum of one of the many micro-zones of fibula A with quaternary composition.



Element	Atomic %
Cu K	28,00
Sn L	46,90
Al K	00,00
Fe K	19,20
Pb M	05,90

Figure 10. EDAX spectrum of one of the many microzones of fibula A with pentenary composition.

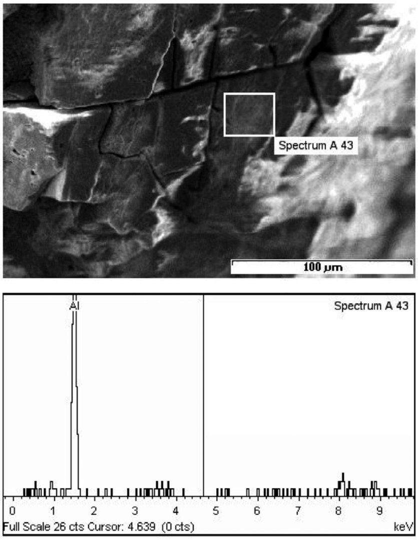


Element	Atomic %
Cu K	88,80
Sn L	11,20
Al K	00,00
Fe K	00,00
Pb M	00,00

Figure 11. EDAX spectrum of one of the few microzones of fibula A with binary composition.

sults have been exceptional, having shown the presence of pure aluminium in fibula A, certainly manufactured in the centuries BC.

Even though in 1958 Chinese archaeologists had found a clasp made of aluminium alloy (Al 85%, Cu 10% and Mn 5%) in the burial of general



Element		Atomic %
Cu	K	00,00
Sn	L	00,00
Al	K	100,00
Fe	K	00,00
Pb	M	00,00

Figure 12. One of the microzones of pure aluminium found in fibula A.

Chou Chu (265-316 AD, Tsin dynasty), it is still commonly believed that aluminium is a modern discovery, made by Sir Humphry Davy in 1807; that it was first extracted in its pure form by Hans Cristian Ørsted in 1825 and industrially produced for the first time by Henri St. Claire Deville in 1858.

Moreover, in 1845 Friedrich Wöhler demonstrated that aluminium cannot be found alone in nature because of its instability towards oxygen, acids, bases or salts. Also aluminium has a lower electronegativity value than copper and tin and a much lower one than bronze, so if combined with bronze it would behave as a dispensable anode corroding itself while providing cathodic protection to the alloy.

So how is it possible that aluminium was being used in Roman times? And even more incredibly, how could have it been buried for over 2,000 years, in combination with bronze, without reacting and consuming itself like a candle?

According to Professor Lorenzo Fedrizzi, a well-known expert on metal corrosion at our University, aluminium would be able to preserve itself only if it were buried in a ground similar to that of general Chou Chu – neuter, free from halogenures, dry and compact. But fibula A was found in a ground that was saline, fairly acidic, not compact enough and constantly waterlogged.

So is there anyone who could help me solve this riddle?

Or should I think that the time has come for us to rewrite, at least partially, the foundations of the chemistry and physics of materials?

Conclusions. SEM and EDAX investigation of the two ancient brooches has conclusively demonstrated that, despite their appearance, they were not cast in the same mould. EDAX mapping, however, by revealing the presence of little less than 4% aluminium in one of the two alloys, has produced an extraordinary result which may possibly call for a rewriting of the foundations of the chemistry and physics of materials.

Acknowledgements. I wish to thank Luca Paussa from the Department of Chemical Science and Technology, University of Udine, for his precious assistance during the SEM and EDAX analyses.